MERCURY AS A GLOBAL POLLUTANT

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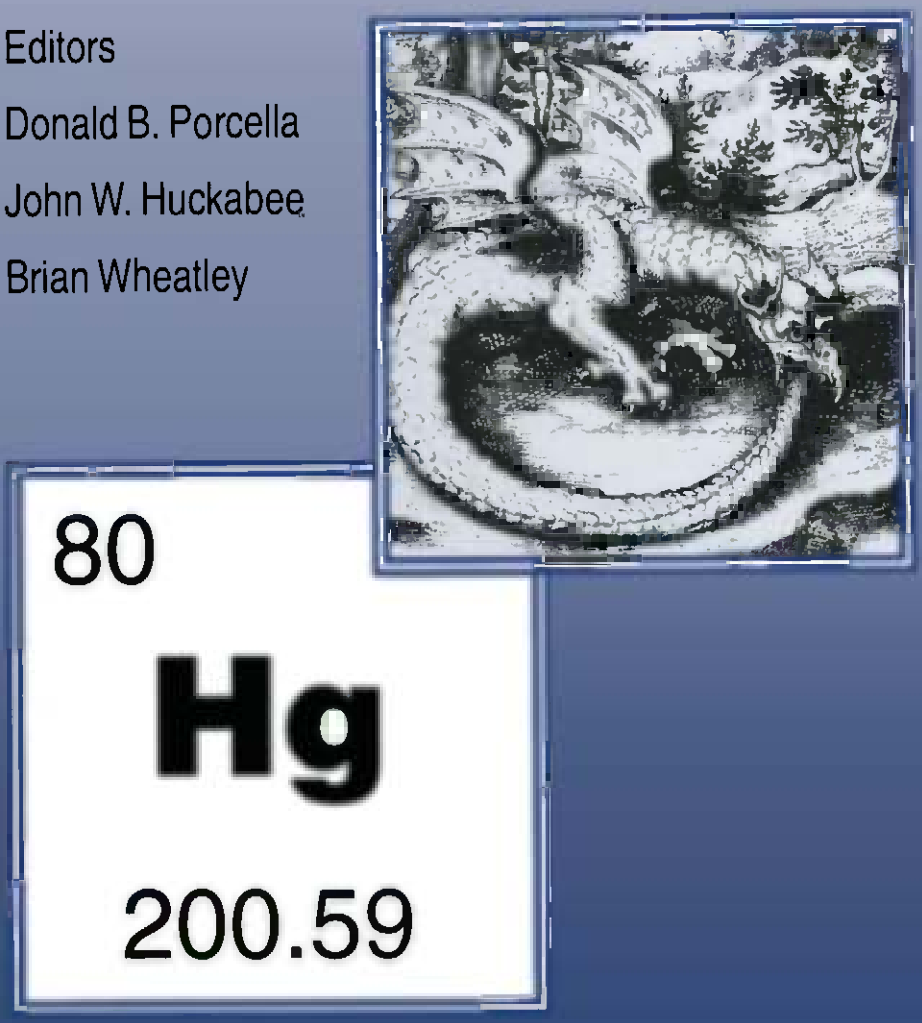

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MERCURY AS A GLOBAL POLLUTANT

Mercury as a Global Pollutant

Proceedings of the Third International Conference held in Whistler, British Columbia, July 10–14, 1994

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PREFACE

The Third International Conference on Mercury as a Global Pollutant was convened in Whistler, British Columbia, Canada, in July 1994. The 151 papers in this volume are the proceedings of that conference.

The apparent general increase of mercury in the global environment has highlighted the potential importance of anthropogenic mercury emissions. Environmental cycling of mercury leads to its bioaccumulation in the human food chain. The amount and toxicity of mercury in human foods is controlled by complex ecological and biogeochemical processes.

The Conference objectives were to integrate and synthesize current knowledge and to identify the information needs for the development of assessment frameworks. To these ends, the state of the science, integration of ecological and health studies, and the research - policy interface were explored in technical presentations on human health, ecological effects, emissions, biogeochemistry, analytical chemistry, and modeling.

The Whistler Conference was the third in a *de facto* series of recent international conferences on the problems of mercury in the environment. The growing interest in the topic is reflected in the numbers of attendees: 200 in Gavle, Sweden, in 1990, 300 in Monterey, California, USA in 1992, and 400 in Whistler in 1994.

The reader will see that knowledge of the behavior of mercury in the environment is rapidly building, and that assessment tools will soon be in hand. Further advances in our understanding will be reported at a fourth international mercury conference, being planned for 1996, in Hamburg, Germany.

Guest Editors:

John W. Huckabee	Brian Wheatley	Donald B. Porcella
Conference Cochairman	Conference Cochairman	

ACKNOWLEDGMENTS

We are indebted to the authors who prepared papers for this volume and to the reviewers, many of whom reviewed several papers. We especially thank the sponsors of the conference : the Electric Power Research Institute; Environment Canada: Atmospheric Environment Service; Frontier Geosciences; Health Canada; Ontario Hydro; State of Florida, Department of Environmental Protection; Wisconsin Department of Natural Resources; and the US Food and Drug Administration. The Conference Technical Advisory Team evaluated more than 300 abstracts, organizing them into a coherent program. We thank the members of this Team: Tom Atkeson, George Becking, Nicolas Bloom, Alain Boudou, Tom Clarkson, Charles Dumont, William Fitzgerald, Christine Gillette-Welling, Robert Hecky, Hans Hultberg, Tom Hutchinson, Ake Iverfeldt, Steve Lindberg, Oliver Lindqvist, Don Porcella, David Rodgers, John Rudd, William Schroeder, Hugh Tilson, Matti Verta, Carl Watras, and Ron Wyzga. The quality and success of the Conference is largely due to them. Conference Coordinator Pam Turner, assisted by Ellen Lanum, ably handled a mass of detail - planning, administrative, and logistical - that is encountered in a meeting of this size and complexity. Their contribution to the success of the Conference cannot be over-estimated. Sujata Pamidi helped in the onerous tasks of organizing the program.

Billy McCormac, Editor of *Water, Air, and Soil Pollution*, Joe Wisniewski, special editor, and Dee McCormac, copy editor, orchestrated an efficient and effective review and production process, which resulted in the very quick publication of this volume.

Guest Editors:

John W. Huckabee
Conference Cochairman

Brian Wheatley
Conference Cochairman

Donald B. Porcella

PART I

MERCURY AND HUMAN HEALTH

EXPOSURE OF CANADIAN ABORIGINAL PEOPLES TO METHYLMERCURY

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Abstract Aboriginal peoples living a traditional lifestyle are potentially exposed to contaminants, such as methylmercury (MeHg), which bioaccumulate in aquatic ecosystems. A preliminary analysis of testing of Canadian indigenous people for MeHg from 1970 to 1992 is outlined. By December 1992, 71,842 tests of 38,571 individuals had been carried out in 514 native communities across Canada. Of these, 8,847 individuals (23%) had blood, or blood equivalent, MeHg levels greater than 20 μg/l and 608 (1.6%) had levels over 100 μg/l. Clinical examinations were offered to all with levels greater than 100 μg/l in blood, but were unable to produce a definitive diagnosis. In an attempt to ascertain fetal exposure, 2,405 umbilical cord blood samples were taken. In about half of these cases the samples were paired with maternal levels. Of the cord samples 523 (21.8%) were found to have levels greater than 20 μg/l, and the highest level was 224 μg/l. The highest maternal level found was 86 μg/l. A discussion of the assessment of risk from exposure to MeHg in this population is presented as are the initial results of the 20 year retrospective analysis including seasonal exposure patterns and trends in exposure levels. Probable future intiatives based on this analysis are noted.

1. Introduction

In Canada, a significant number of the indigenous people continue, at least in part, to follow a traditional lifestyle, close to the land and using natural resources, such as fish from lakes and streams (Wheatley, 1979; Berkes, 1990), game from the forests, and in the north, sea mammals such as seals and whales (Wheatley and Wheatley, 1981)). All are essential parts of the traditional diet. Native people are therefore potentially much more exposed than the general Canadian population to environmental contaminants, especially those in aquatic eco-systems. This exposure is particularly significant for contaminants such as MeHg which can bio-accumulate up the food chain.

This potential for high exposure and significant risk to health was first noted in the early 1970's in two northern Ontario Ojibwa communities, Grassy Narrows and Whitedog. Both communities are on the English-Wabigoon river system into which effluent was being poured by a chlor-alkali plant up-stream in Dryden (Rudd *et al.*, 1983). The effluent contained Hg which was then methylated in the aquatic eco-system and bio-accumulated to significant levels (up to 24 μg/g) in the fish eaten by the people living at Grassy Narrows and Whitedog (Bishop and Neary, 1976). As a result of eating these fish, many residents of the two communities developed high blood Hg levels, including one individual who attained a level of 660 ppb (μg/l) in blood (Wheatley, 1979). Residents in the two communities were exposed through subsistence fishing and also because a number of them acted as fishing guides for visiting sports fishermen. On a regular basis these guides prepared and ate shore lunches using the fish which had been caught by the group that morning.

At approximately the same time, in northwest Quebec, levels of Hg in fish in excess of 4 ppm (μg/g) were being found. In this case the source of the Hg was less immediately obvious, although it was believed to be at least partially industrial. The Cree people in this area were still living a relatively traditional existence, very much dependent on consumption of fish and wildlife. Also, the first major damming of rivers under the James Bay hydro-electric development project was under way. The significance of this project became evident

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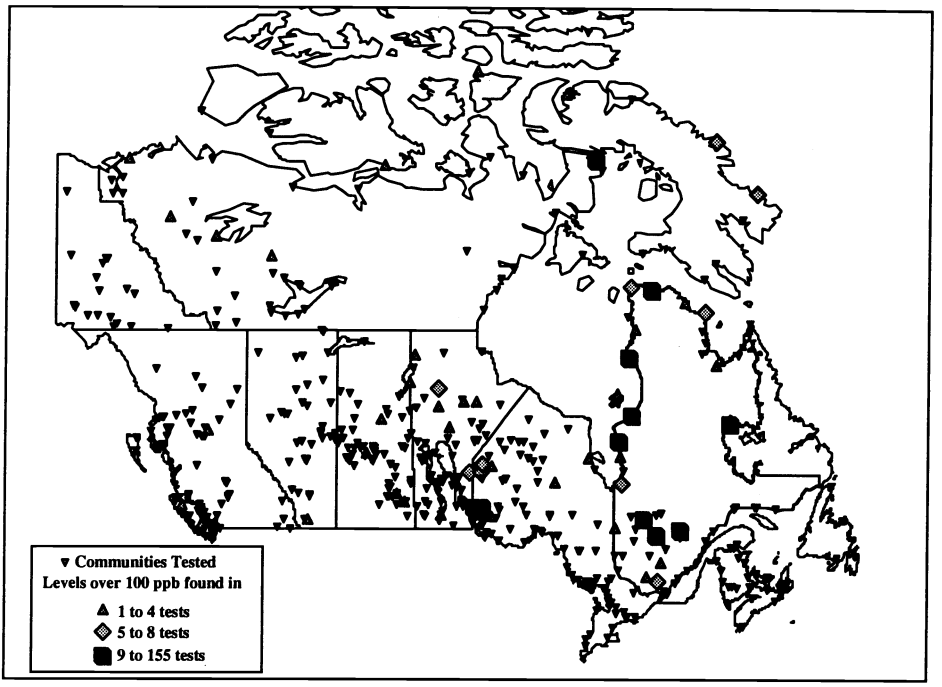

Fig. 1 Methylmercury in Canadian Native Communities

later when it was recognized that immersion of vegetation by flooding releases Hg into the aquatic eco-system, where it then follows the normal process of methylation and bio-accumulation through the food chain (Bodaly *et al.*, 1984). From the point of view of health authorities at that time, we were simply conscious of the fact that significant levels of blood Hg were being found among the Cree people. A decision was made to develop an extensive program for assessing Hg levels in native people across Canada, beginning with Grassy Narrows and Whitedog in Ontario and the James Bay Cree communities in Quebec and then extending across the country (Wheatley, 1979). The program activity peaked in the late 1970's and early 1980's, with a second peak in the mid-1980's in northern Manitoba where again there was extensive flooding being produced by hydro-electric damming activities (Figure 1).

The program is presently continuing at a somewhat lower level and is concentrating on communities with significant exposure. The program in Quebec among the Crees has been continued since the mid 1980's by the Cree Board of Health and Social Services. This paper presents some of the initial results from the 20 year retrospective analysis of the data and notes likely future initiatives based on this analysis.

2. Methodology

The program began, not as a research project but, rather, as a means of assessing exposure of native people to MeHg and the levels of risk produced by this exposure (Wheatley, 1979). We therefore initially concentrated on individuals most likely to be at risk because of their lifestyle, such as guides, heavy fish eaters and those living a traditional lifestyle, including Inuit exposed to MeHg through eating sea mammals. We rapidly realized that blood samples gave us only a very limited amount of information, and might well reflect simply what the individual had eaten at the most recent meal. We changed to using hair samples as our biological indicator, made the assumption that hair grows at approximately 1 cm per month (WHO, 1976) and developed the technique of cutting the hair into 1 cm long samples which were then analyzed using the cold vapor atomic absorption method (Farant *et al.*, 1981). This approach provided a temporal view of exposure going back as many months as the hair sample was centimetres long. This analysis gave us an estimate of the highest exposure during that period and also the length of significant exposure. However, for the sake of reporting consistency, we converted hair levels to blood equivalents using a factor of 300, derived from Canadian data, for conversion (Phelps *et al.*, 1980). We also noted at a very early stage, that there was considerable confusion in the native communities and in the national media over the variety of units being used to report Hg levels. Therefore, again for clarity and consistency, we decided to report hair levels in parts per million (ppm) and blood levels in parts per billion (ppb). Based on then current WHO environmental health criteria (WHO, 1976), the decision was made to refer to blood levels below 20 ppb (or 6 ppm in hair) as being in the acceptable range and levels greater than 100 ppb in blood (30 ppm in hair) as "at risk". We offered clinical neurological examinations to all individuals considered to be in the "at risk" group. The program was carried out through the national network of nursing stations and health centres through which the Federal Government provides health care services to native people in Canada. Links were also made to local health authorities and in key areas, such as Grassy Narrows and Whitedog, where the program was very intensive, community residents were hired and trained to carry out the program and to report the findings to the individuals concerned.

3. Results and Discussion

Up to December 1992, 71,842 blood or hair tests (368,000 analyses) were carried out in 514 native communities across Canada. The extent of the program is shown graphically in Figure 1. The overall findings are shown in Table I. This represents testing on 38,571 individuals. Of these individuals, 8,239, or 21.4%, had levels between 20 to 99 ppb in blood; 541, or 1.4%, had levels between 100 to 199 ppb; and 67, or 0.2%, had levels greater than 200 ppb in blood. The highest level found was 660 ppb in blood, in a fishing guide from Grassy Narrows. The highest numbers with levels greater than 100 ppb were found in Quebec, followed by Ontario, Northwest Territories and Manitoba. With the exception of the Northwest Territories, where exposure was largely through consumption of sea mammals, these are fish eating populations. As mentioned earlier, all individuals with levels greater than 100 ppb were offered full neurological examinations. Not all accepted, but, of 99

Region	No. of Communities	Total Tests	< 20	20-99	100-199	200-299	300-399	400-499	500-599	600-699	Highest result	Year
					ppb							
Atlantic	23	710	695 (97.89)	15 (2.11)	-	-	-	-	-	-	99	1978
Quebec	52	23621	14556 (61.62)	8376 (35.46)	609 (2.58)	57 (0.24)	13 (0.06)	5 (0.02)	4 (0.02)	1 (0.00)	649	1975
Ontario	106	20296	16296 (80.29)	3714 (18.30)	239 (1.18)	32 (0.16)	8 (0.04)	5 (0.02)	-	2 (0.01)	660	1971
Manitoba	69	13897	11565 (83.22)	2296 (16.52)	34 (0.24)	2 (0.01)	-	-	-	-	262	1989
Saskatchewan	74	2505	2248 (89.74)	252 (10.06)	5 (0.20)	-	-	-	-	-	124	1978
Alberta	38	1505	1451 (96.41)	52 (3.46)	2 (0.13)	-	-	-	-	-	105	1977
British Columbia	88	4620	4302 (93.12)	315 (6.82)	3 (0.06)	-	-	-	-	-	146	1978
Northwest Territories	59	3826	2273 (59.41)	1514 (39.57)	33 (0.86)	3 (0.08)	3 (0.08)	-	-	-	363	1971
Yukon	18	862	855 (99.19)	7 (0.81)	-	-	-	-	-	-	67	1977
Total	514	71842	54241 (75.50)	16541 (23.02)	925 (1.29)	94 (0.13)	24 (0.03)	10 (0.01)	4 (0.01)	3 (0.00)		

Table I. Exposure of Canadian Aboriginal Peoples to Methylmercury, Cumulative Results 1970-1992, by Region and level, % of total tests in brackets

individuals clinically examined, 61 had no significant abnormalities, 27 were found to have some abnormalities not attributable to MeHg, and 11 had neurological findings possibly attributable to MeHg. No definitive diagnosis of MeHg poisoning was made.

In an attempt to ascertain fetal exposure, 2,405 umbilical cord blood samples were taken. In about half of these cases the samples were paired with maternal levels. The highest cord blood level found was 224 ppb and 523 samples (21.8%) were found to have levels greater than 20 ppb. The highest maternal level found was 86 ppb. Neurological examinations performed on the children showed no findings that could be attributed to MeHg. We are presently starting a follow-up study of this group of children to try to assess development and educational attainment.

An earlier study funded by Health Canada in 1979 was carried out by McGill University, among the Crees of James Bay in northern Quebec. In that study, although an association was noted between findings on examination of tone and reflexes in Cree boys and the concentration of MeHg in their mothers' hair during pregnancy, the abnormalities were very mild and in most children it was difficult to be certain that they represented abnormal function (McKeown-Eyssen *et al.*, 1983).

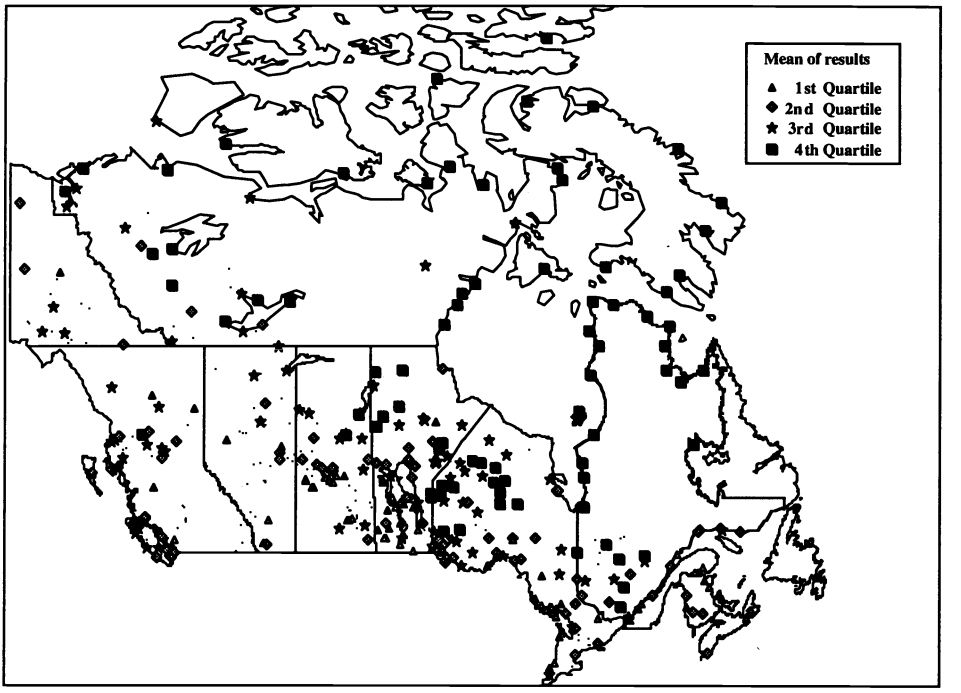

Fig. 2 Native Communities Mean Methylmercury levels from 1972-1992 results

We are now in the process of analyzing the data obtained over the past 20 years. Some details may change as we proceed. However, we believe that the general thrust and conclusions will remain valid.

One of our first steps in the review was to ascertain in which communities, over time, we had found the highest mean blood (or hair equivalent) Hg levels. Figure 2 illustrates our findings. In general terms the fourth (upper) quartile (10.5 to 49.5 ppb) communities, except for a few in Quebec, are northern. The common link is almost certainly the traditional native lifestyle and the consumption of fish and sea mammals in these communities. Superimposed on this, however, has been local industrial activity such as, in the past, chlor-alkali plants associated with the pulp and paper industry and currently hydro-electric dams, and the general increase in Hg in the global environment.

Seasonal exposure of native peoples has continued to cause concern over the years. At the individual level we have a record of almost twenty years of seasonal exposure in a guide from Grassy Narrows (Figure 3). The reason the peak levels fell in recent years was not because of the advice we gave but because of a lack of sports fishermen. At the community level, Figure 4 shows the mean blood Hg levels in individuals with levels over 20 ppb (i.e. presumed fish eaters) in First Nations communities with ten or more sampling years, by month through the year. The seasonal pattern is very obvious. We still do not know whether potential effects from these seasonal peaks are cumulative.

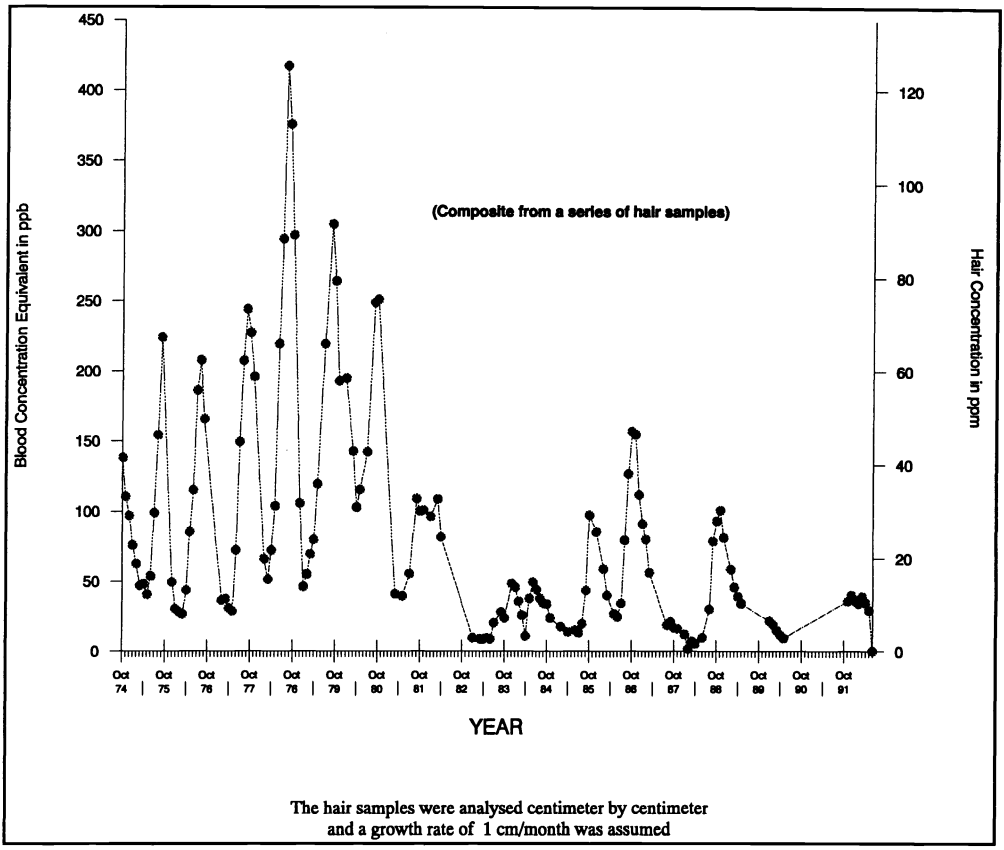

Fig. 3 Seasonal variation of methylmercury levels in a fishing guide from Grassy Narrows Reserve, Ontario

There is, of course, considerable interest in trends in Hg levels in community residents over the 20 year period. Figure 5, which again concentrates on individuals with over 20 ppb Hg in blood, or hair equivalent, and communities with at least ten sampling years, does show a general downward trend. Whether this is because of falling Hg levels in fish or because less fish is being eaten by the people has yet to be determined.

One special concern relates to how to achieve a balanced assessment of risk as it applies to the aboriginal peoples of Canada. There are a number of factors linked to this assessment which need to be considered. Fish and wildlife are a vital component of the diet of many native people. They are also an integral part of the culture, lifestyle and socio-economic well being of these people. A decision to advise them not to eat the fish or wildlife because of the levels of MeHg and perceived risk cannot, therefore, be made lightly. The impact can be catastrophic, as can be the way the media may use partial information to run sensational stories which frighten people. In 1979, for example, we noted relatively high (up to 267 ppb) blood Hg levels being reported from the small Inuit community of Sugluk on the Hudson Strait in northern Quebec. These levels were difficult to explain on the basis of

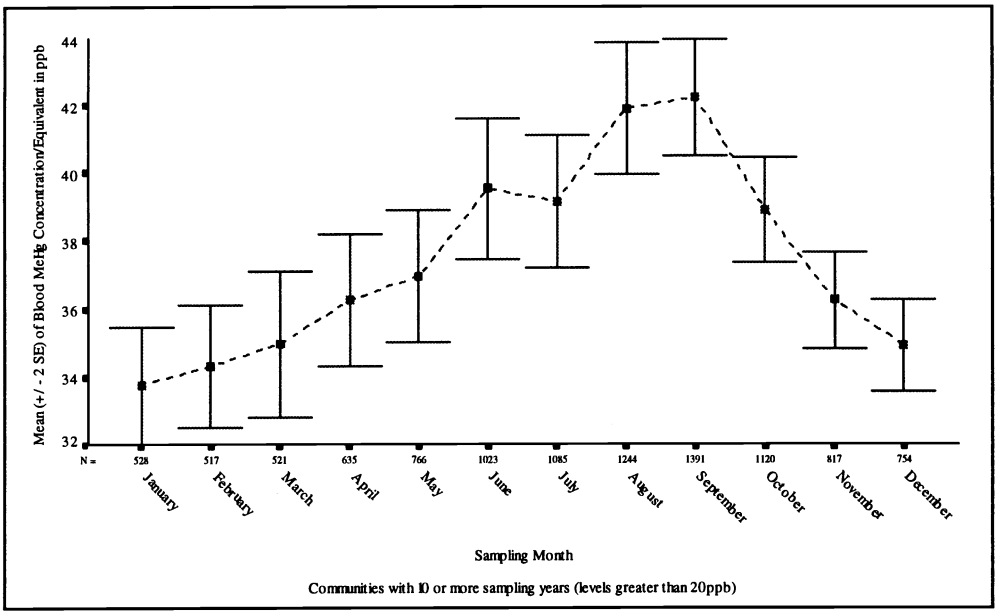

Fig. 4 Annual pattern of exposure to methylmercury in Canadian First Nations Communities

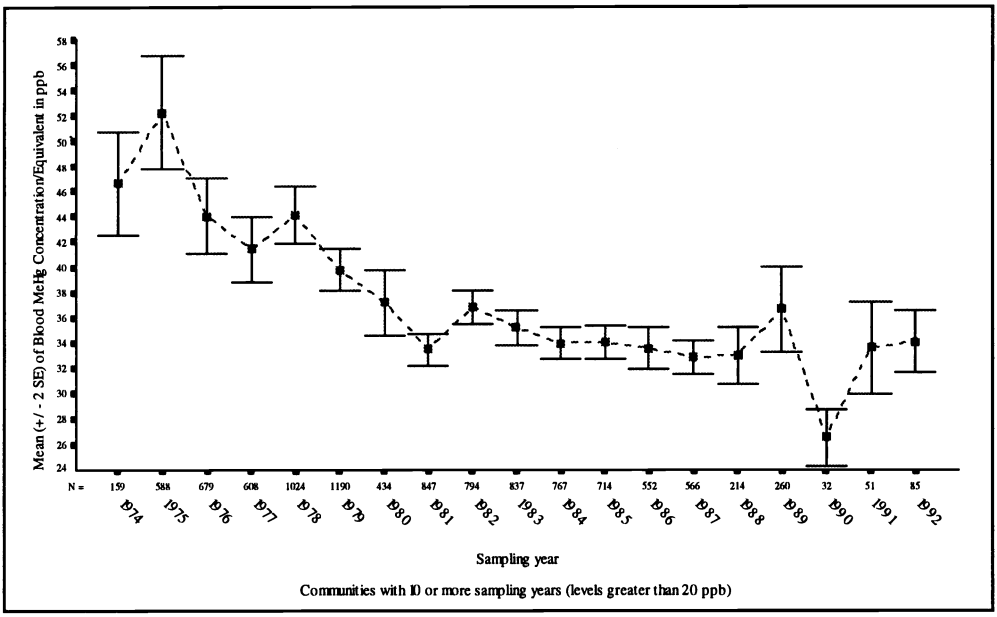

Fig 5. Trend in First Nations mean Methylmercury levels 1974-1992

known Hg levels in sea mammals in the area. A visit to the community was therefore planned but CBC Radio produced a sensational story referring to "Minamata" disease. The people stopped eating their traditional diet and, as there was no available, affordable, acceptable food alternative, a crisis situation resulted. An emergency visit to the community resolved the situation which was found to have been caused by the eating of an unusual combination of Beluga Whale and Lake Trout (Wheatley and Wheatley, 1981). We were able to advise the people that there was no reason to change their diet, although women of child bearing age should take care with certain combinations of food. The greatest problem in Sugluk was the fear produced by lack of understanding of risk levels of MeHg.

In true risk situations such as Grassy Narrows and Whitedog there was no alternative but to advise no consumption of locally caught fish. The result was social and cultural disruption, destruction of a lifestyle, change of diet and severe socio-economic damage, the consequences of which are still affecting those communities. Despite the concerns we had regarding the levels of MeHg we were finding in some native people, as mentioned earlier, we were unable to prove direct, clinical effects despite the best efforts of a number of people (Wheatley *et al.*, 1979). We were therefore open to criticism that despite the devastating indirect effects, there was no basis to our anxiety about risk to human health, at least so far as Canadian native people were concerned. We disagreed. There have also been challenges relating to the origin of MeHg in the Arctic - whether it is of natural or industrial origin (Wheatley and Wheatley, 1988). This now appears to have been resolved with the recognition of both sources.

Very current is the ongoing debate regarding the relative sensitivity of the fetus compared to the adult. In Environmental Health Criteria 101, Methylmercury (WHO, 1990), the WHO expert committee notes that a 5% risk may be associated with a peak Hg level of 10 to 20 μg/g (ppm) in maternal hair. In our work with Canadian native people we found 1,404 women in the 15 to 45 years age group (13.1% of the women in this group who were examined) with levels greater than 10 ppm in hair. In simplistic terms, therefore, based on the 1990 WHO criteria, a risk statistically exists, or may have existed, for the fetuses of some 70 native women in Canada, dependent on coincidence of time, exposure and pregnancy. But what does this really mean, especially when lifestyle and diet factors, mentioned earlier, are taken into account? Is risk greater if this exposure occurs or if the lifestyle, culture and eating patterns are disrupted? What is the level at which the risk from the potential effects of MeHg on the fetus outweigh the negative effects of socio-cultural and dietary disruption? There is no doubt that it will remain a judgement call for some time to come, but hopefully ongoing discussions will help to shed more light on this need to take a broad approach to our assessment of risk (Wheatley, 1993).

4. Conclusion

The data base on the exposure of Canadian indigenous people to MeHg now covers a 20 year period, up to December 1992 (Table I). It is geographically spread over most of the native communities in Canada (Figure 1). It includes information on human levels of Hg, by age, sex and location. We have started a 20 year follow-up analysis of the data, and we have indicated some of the initial findings. There is a great deal of analysis still to be done, including further assessment of temporal trends by community and individuals, relationships

between maternal and fetal levels of MeHg, and, if possible, a re-assessment of potential risk, concentrating especially on the communities where the highest human MeHg levels have been found.

Acknowledgements

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EXPOSURE OF JAMES BAY CREE TO METHYLMERCURY DURING PREGNANCY FOR THE YEARS 1983-91

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Abstract: Since 1982 the Cree Board of Health and Social Services of James Bay (Quebec, Canada) has taken samples of hair from Cree men and women in the course of the methylmercury (MeHg) surveillance program. As a measure of foetal exposure, samples of hair of the mother are taken at the beginning of pregnancy and shortly after birth (to determine exposure at birth) and a blood sample is taken from the umbilical cord blood of the newborn. Of the 2360 births between 1983 and 1991, 25% had all three samples taken, but there was not a single sample for 25% of the births. From 1983-1991, the concentrations of mercury (Hg) at the time of conception, at the time of birth and in the umbilical cord have decreased progressively. There is no relationship between Hg in the umbilical cord blood and the weight of the newborn. As is to be expected there is a relationship between the maternal hair concentration at birth and umbilical cord blood Hg concentration at birth. The relationship is the following: Hg cord blood = 8.53+.88xHg maternal blood equivalent {r=0.623, 95% CI(r) [0.770, 0.769] p<.001}.

1. Introduction

Methylmercury is a known teratogenic compound. Babies born from mothers exposed to MeHg have a number of neurological abnormalities *(Tsubaki, 1977; Amin-Zaki, 1979).* Methylmercury crosses the placenta *(Sager, 1986).* Methylmercury exposure of the foetus is therefore generally estimated from maternal exposure *(Marsh, 1987; Kjellström, 1986).* Increased risk to the foetus starts with maternal exposure at a range between 10 and 20 mg/kg as measured by maternal hair concentration *(Mckeown-Eyssen, 1983).* Some have suggested that it may start at even lower exposure in some cases *(Kjellström, 1986).*

The Cree Indians of Quebec are a group of about 10,000 persons living in nine communities in Northern Quebec (Figure 1). They live along the coast of James Bay and inland close to northern mining communities. Fish is traditionally a very important part of their diet *(Weinstein, 1987).* In recent years however children and young adults rely more and more on store-bought foods. Fish found in natural lakes and in hydro-electric reservoirs of the area are contaminated by MeHg *(Penn, 1978; Verdon, 1992).* The sources of Hg and the factors affecting its transformation to MeHg in Northern Quebec are controversial. The presence of Hg in natural lakes of the area has been attributed to natural and anthropogenic sources *(Verdon, 1992).* The relative importance of those two factors is still the subject of debate. The increase of MeHg in fish from hydro-electric reservoirs has been extensively followed by Hydro-Quebec *(Verdon, 1992).*

Fish is very important in the diet of the Crees *(Weinstein, 1987).* We should not be surprised then that high hair Hg results were observed among the Crees in the 1970's *(NHWC,1984).* Because of this, MeHg exposure has been a cause for worry among the Cree

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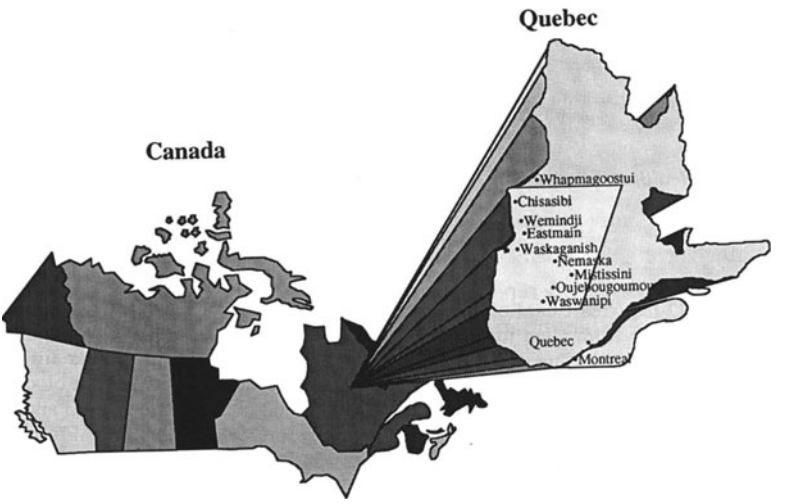

Fig. 1. Cree Territories in Northwestern Quebec

communities. The foetus is known to be much more sensitive than the adult to the ill-effects of Hg *(Amin-Zaki, 1979; Marsh ,1987; Mckeown-Eyssen, 1983)*. There is therefore even greater concern for exposure during pregnancy. Because of this concern, the Cree Board of Health and Social Services of James Bay (CBH) has implemented since 1982, a MeHg monitoring program *(Dumont, 1989)*. The CBH is an institution responsible for health care among the Cree Indian communities of James Bay in Northern Quebec. Part of the mercury program consists of measuring Hg in blood of umbilical cord at birth and in maternal hair at the first prenatal visit and during the month following delivery.

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Maternal and foetal exposure during the years 1983 to 1991 will be described. Changes in exposure according to community of residence and year of sampling will also be described. Maternal exposure at birth was determined by maternal hair Hg concentration in the segment of hair corresponding to the time of birth. The correlation between maternal exposure and Hg concentration in umbilical cord blood taken at birth will be described.

2. Methods

A strand of hair the size of a pencil is taken at the occipital area (*Noël, 1989*). This strand of hair is sent to the laboratory where it is divided in one centimeter strands for Hg analysis. Hair and blood Hg concentrations were determined by a modified method of Magos at the *Laboratoire de Santé Publique du Québec* , Ste. Anne de Bellevue, Québec (*Magos, 1971*). The method for hair collection and for Hg analysis remained the same throughout the years (*Farran, 1981*). Methylmercury represents 93% of total Hg (range 88%-97%).

All the results of Hg concentrations from 1983 to 1991 were recorded in a central data bank managed by the CBH. The data had to be checked because of errors in spelling, date of birth, etc. This validation process consisted of checking with the data on the SP-1 forms (notification of live birth), with the personel of the clinic in each community, with official population lists such as the population lists maintained by the Band Council and the list of the beneficiaries of the James Bay and Northern Quebec Agreement (this list is maintained by the Ministry of Health and Social Services of Quebec).

When there were two samples of the same type for the same pregnancy, one of the results was discarded. In the case of the prenatal sample, the sample farther from the date of conception was discarded (5 discarded). In the case of the post-natal sample, the sample taken farther from the date of delivery was discarded (3 discarded). When there were two umbilical blood samples for the same birth, the result with the highest value was kept. (4 discarded; the difference between the two samples values were ≤ 0.1 µg/L).

Comparisons were done with Statview 4.0 (Abacus Concepts), Systat 5.2 (SPSS Inc.) and Excel 4.0 (Microsoft) software for the Macintosh. Non-parametric methods were used generally because the distribution of the data was highly skewed towards lower values, whether in the original form or after the log-transformation. Ps derived from Student t-tests comparisons should therefore be interpolated with caution.

3. Results

3.1. SAMPLING RATES

From 1983-1991 there were 2,360 births among the Crees. Out of these births, 626 had both maternal hair sampled shortly after birth and umbilical cord blood taken at birth for Hg measurement. From these 112 had maternal hair Hg concentrations above detection limits (2.5 mg/kg). Twenty percent had the three types of samples taken, that is, early on in pregnancy, at the end of pregnancy and from the umbilical cord at birth. There was not a single sample for 25% of the births.

In 1986 the James Bay Mercury Agreement was signed between the Crees, Hydro-Quebec and the Government of Quebec. This agreement provided for additional funding to implement the Hg exposure monitoring program. This program received a new impetus in 1986 with the signature of this agreement. It was thus relevant to determine if these increased

resources changed the sampling rates. Before the Agreement 41% of individuals did not have any sample whatsoever compared to 12% after the Agreement. Before the Agreement only 12% had the three types of samples taken compared to 26% after the Agreement.

Rates of sampling varied between communities. Sampling rates for the coastal communities are higher than for the inland communities. Of all the deliveries, there were 1242 samples corresponding to the time of conception and 991 samples corresponding to time of delivery.

3.2. HG CONCENTRATIONS

Maternal hair Hg concentrations decreased slightly during pregnancy between the time of conception and the time of birth, p=0.028 (Figure 2).

Over the years, the number of mothers with high hair Hg concentrations has decreased considerably. There were 21% of the sample at the time of conception over 6mg/kg in 1983 compared to 2% in 1991 (Table I). Similarly, there were 33% of the sample at the time of delivery over 6mg/kg in 1983 compared to 1% in 1991 (Table II). This decrease could not be explained by differences in time of sampling during the year or by differences in the proportion of samples from the various villages between the two periods.

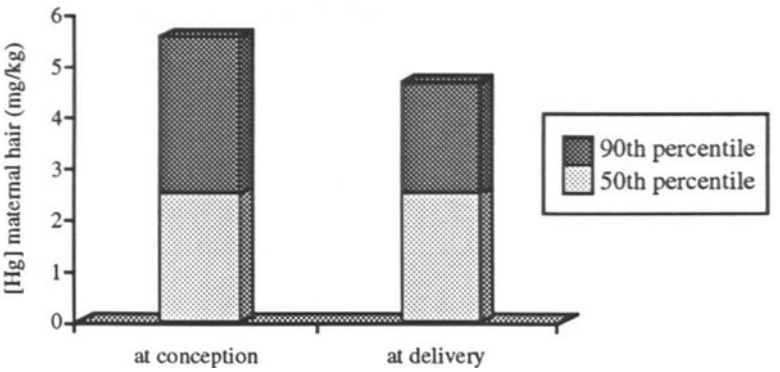

Fig. 2. Evolution of Hg during pregnancy

Mercury concentrations were generally slightly higher before the signature of the Agreement than after the Agreement (p for 1242 samples corresponding to the time of conception: ≤0.001, p for 991 samples corresponding to the time of delivery: ≤0.001).

There was no relationship between the weight of the newborn and maternal hair Hg at birth (p=0.638).

There was no difference in umbilical cord blood Hg concentrations between boys and girls (p=0.505).

TABLE I

Percentage of mothers having high hair results at the time of conception, 1983-91

Year	Number of persons sampled	%≥6mg/kg	%≥9mg/kg	%≥15mg/kg	%≥30mg/kg
1983	42	21	10	2	0
1984	58	26	14	10	2
1985	86	9	6	1	0
1986	145	7	2	1	0
1987	166	2	0	0	0
1988	157	6	2	1	0
1989	192	4	1	0	0
1990	207	3	0	0	0
1991	189	2	1	0	0

TABLE II

Percentage of mothers having high hair results at the time of delivery, 1983-91

Year	Number of persons sampled	%≥6mg/kg	%≥9mg/kg	%≥15mg/kg	%≥30mg/kg
1983	43	33	12	5	0
1984	54	11	6	2	2
1985	54	11	7	0	0
1986	80	3	1	0	0
1987	94	4	1	0	0
1988	116	3	1	0	0
1989	155	1	0	0	0
1990	206	1	0	0	0
1991	189	1	1	0	0

3.3. MATERNAL HAIR [HG] AND UMBILICAL CORD BLOOD [HG] RELATIONSHIP

For purposes of analysis only maternal-child pairs when the mother's Hg concentrations were above detection limits *(2.5 mg/kg for hair, 5.0 µg/L for blood)* were retained *(n=112)*. The regression equation obtained is the following: *newborn umbilical cord blood Hg in µg/L = 2.9 maternal hair Hg concentration in mg/kg + 8.5.* The correlation coefficient was: 0.6. Transforming values to log did not improve the correlation.

It has been shown that hair concentration is 300 times that of blood concentration *(Kershaw, 1980)*. Maternal blood concentrations in µg/L were estimated by dividing maternal hair concentrations in mg/kg by 300. So as to compare our results with those of Ong *(Ong, 1993)* we transformed our maternal hair concentrations in maternal blood concentration

equivalent in µg/L. This gives the following equation: *cord blood mercury (Hg) = 0.88 x maternal blood Hg + 8.53*. This is not very much different from Ong who obtains cord blood Hg concentration = 0.69 x maternal blood concentration + 7.18. We had 112 cases, Ong had 28 cases (Figure 3).

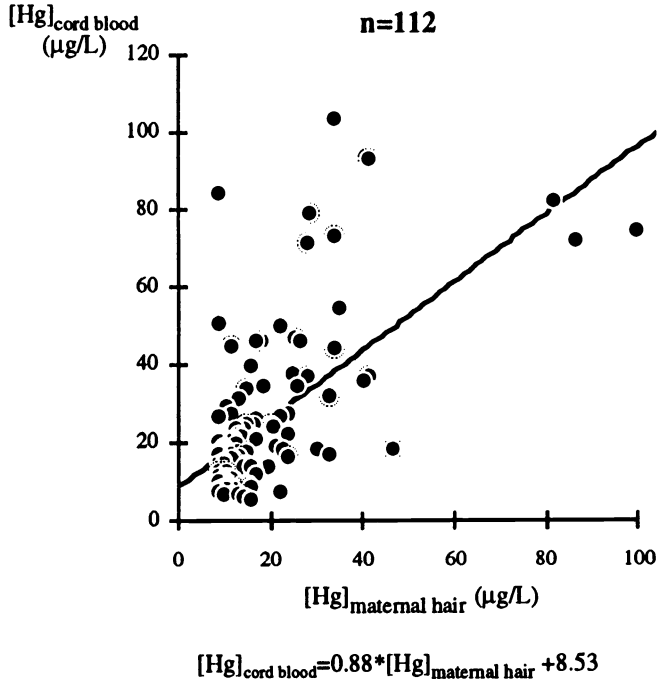

Fig. 3. Maternal hair Hg concentration (µg/L) vs umbilical cord blood Hg concentration

4. Conclusion

We described our results from a program for monitoring foetal Hg exposure among the James Bay Crees of Northern Quebec by measuring umbilical cord blood Hg concentration at birth and maternal hair Hg concentration during pregnancy. Over the years the proportion of mothers with high Hg concentrations has decreased considerably to the point that Hg exposure in that population is of much lesser concern at the present time. There is no difference in Hg exposure between boys and girls. There is no relationship between birth weight and maternal hair Hg concentration. After the Mercury Agreement, participation to the program improved markedly. The relationship between mother and child is estimated by the following equation: umbilical cord blood Hg concentration = 2.925 x maternal hair Hg concentration + 8.532.

Aknowledgements

This study was founded by the Ministry of Health and Social Services from funds available through the Mercury Agreement (1986). The authors owe special thanks to Louisa Saganash without whose extensive knowledge of the Cree communities it would have been impossible to validate the data, the Community Health Representatives in each community who took the hair samples, Francine Noël who coordinated their activities and Stephen Lapierre from the Laboratoire de Santé Publique du Québec who did the mercury analysis.

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EXPOSURE TO MERCURY IN CANADA: A MULTIMEDIA ANALYSIS

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Abstract. A thorough assessment of Canadian exposure to mercury (Hg) has not been undertaken since 1970. A multimedia approach was used to update estimates of Hg exposure to members of the general population in Canada, based on currently available information. Adult Canadians have an estimated intake of all Hg species via all routes of 7.7 μg/day (0.11 μg/kg body weight/day), which equated to an absorbed dose of 5.3 μg/day (0.076 μg/kg bw/day). Fish consumption accounts for much of this exposure (27% of intake, 40% of absorbed dose), in the form of methylmercury. However, dental amalgam appears to account for a greater proportion of total Hg exposure than fish consumption. Exposure from amalgam was estimated for intake and absorbed doses (of Hg^0) at 2.81 and 2.25 μg/day, respectively. This represents 36% of total Hg intake and 42% of absorbed dose. Hg^{2+} arises principally from foods other than fish. Intake of Hg^{2+} by adults was determined to be 1.82 μg/day and absorbed dose only 0.18 μg/day. Exposures for four other age groups of the population were also evaluated.

1. Introduction

An assessment of dietary exposure of the general Canadian population to Hg has not been undertaken since 1970 (Kirkpatrick and Coffin, 1974). The elapsed time since this last assessment (24 years), and the recent debate over exposure to Hg from dental amalgam (Eley and Cox, 1993) indicated that a revised total exposure assessment in Canada was required.

The purpose of this paper is to present current exposure estimates for infants, toddlers, school-aged children, adolescents and adults to Hg in Canada. Exposures are presented both as delivered dose (not accounting for differential absorption of each Hg species), and as absorbed dose. The sources of data and information are reviewed and discussed and estimated exposures are compared to recent assessments for other countries.

2. Methods

A detailed search for published and unpublished data and information on Hg concentrations in environmental media in Canada was performed. If possible, data from 1980 onward, were sought due to problems with analytical methods and possible sample contamination in earlier analyses (Fitzgerald and Watras, 1989). Where possible, weighted mean values derived from all relevant data sets were employed. However, it was necessary in some cases to select the single most representative study as a basis for exposure estimation. Canadian data for some media were surprisingly sporadic or virtually non-existent (Hg levels in indoor and outdoor air, and foods other than fish, for example). Where no suitable Canadian data were available, relevant American or other international data were used.

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This assessment was prepared assuming an urban setting because 77% of the Canadian population reside in urban and suburban areas (Statistics Canada, 1993). Body weights and standard intakes of air, water, and soil employed routinely by Health Canada for risk assessment purposes are presented in Table I. Intakes of 112 food categories were based on the Nutrition Canada Survey (HWC, 1977) as reorganized by Conacher *et al.* (1989). Other assumptions used in this exposure assessment were: (1) Hg in fish was 100% methylmercury (meHg) (Bloom, 1992); (2) Hg from all other commercial foods was inorganic (Hg^{2+}) (WHO, 1991); (3) Hg in drinking water was 25% meHg and 75% Hg^{2+} (Schintu *et al.*, 1989); (4) Hg in ambient air was 75% elemental (Hg^0) in vapor phase, 20% organic in vapor phase, and 5% Hg^{2+} bound to particulates (Schroeder and Jackson, 1987), with the particulate phase assumed to be fully respirable; (5) Hg in indoor air is 100% Hg^0 (Beusterien *et al.*, 1991); (6) Hg in soil was 100% Hg^{2+}, because it is the non-humic, fine particle fraction of soil to which we are generally exposed through unintentional ingestion; (7) an indoor:outdoor time ratio of 20 hours:4 hours was used for air and soil/dust intakes.

Regarding absorption of the various Hg species, the following assumptions were made: (1) 100% of ingested meHg was absorbed (WHO, 1990); (2) 10% of ingested Hg^{2+} was absorbed by adults (WHO, 1991), whereas infants and toddlers were assumed to absorb 100%; (3) 80% absorption of all Hg forms when inhaled (WHO, 1991).

Exposure to Hg^0 results from dental amalgam, with estimates of exposure ranging from 1.24 μg/person/day to 27 μg/person/day (summarized by Vimy and Lorcheider, 1990). However, the precise quantification of this exposure has not been resolved. These estimates of exposure relate varyingly to individuals with $\geq$14 amalgams, $\leq$4 amalgams or 1 to 16 amalgams, etc. As with other approaches to Hg exposure estimation related to amalgam, our approach has not been validated, but no other approach offered a ready determination of dose per filling per day, as required here. Our approach was as follows:

a) The average number of filled teeth per age group was determined from literature sources (see Table I). Assuming one filling per filled tooth, the regression presented by Skerfving (1991) was used to determine the corresponding urine Hg concentration (infants: 0 μg Hg/g creatinine; toddlers: 0 μg Hg/g creatinine; school-aged children: 0.53 μg Hg/g creatinine; adolescents: 0.68 μg Hg/g creatinine; adults:0.88 μg Hg/g creatinine).

b) Roels *et al.* (1987) reported a strong linear association between workroom air and urine Hg in workers. This regression model was redefined with a Y-intercept of 0.45 μg Hg/g creatinine (after Skerfving, 1991), on the assumption that non-occupationally exposed individuals would have a much lower, but not zero, background urine Hg concentration, but the dose-response relationship (i.e. the slope) would not change. Finally, assuming an inhalation rate for workers of 6.6 m^3 per 8 hour work shift (U.S. EPA, 1989) and 80% absorption of Hg^0 (WHO, 1991), the corresponding air concentration was converted to dose for each age group. These exposure estimates are summarized in Table II.

The following text describes remaining data sources from which concentrations of Hg in various media were derived.

2.1 AMBIENT AND INDOOR AIR

The level of Hg in ambient air was based on the results of Schroeder and Jackson (1987) who reported concentrations of several Hg species in the air in and around Toronto, Ontario during the fall of 1981. This was the only recent study identified where Hg levels in the ambient air of a Canadian city were collected. The weighted average concentration for two urban sites (10.1 ng Hg/m^3, total n=25) was selected for this exposure assessment.

No published or unpublished data could be located on Hg levels in indoor air of Canadian homes. Agocs *et al.* (1990) and Beusterien *et al.* (1991) reported indoor air Hg data for 10 homes in Michigan (1989) and 16 homes in Ohio (1990), respectively, where no Hg-containing paint had been applied within the preceding 18 months. In both studies, the median Hg levels were non-detected when measured by atomic absorption spectro-photometry (reported detection limit (DL)=0.5 $nmol/m^3$). Analysis of 4 homes by cryogenic gas chromatography with atomic fluorescence detection (reported DL = 3 ng/m^3) measured Hg at a median level of 0.052 $\mu g/m^3$ (range: 0.036-0.107 $\mu g/m^3$) (Beusterien *et al.*, 1991). An indoor air concentration of 0.05 $\mu g/m^3$ was therefore assumed here.

2.2 DRINKING WATER

The Ontario Ministry of Environment and Energy (OMOEE) analyzed 1,355 samples of treated drinking water from 134 sites in 1991/92 (OMOEE, 1993) and all but 8 had total Hg levels below the limit of detection (0.02 $\mu g/L$). For this assessment a value of 0.01 $\mu g/L$ (½DL) was employed as the best estimate of Hg levels in drinking water, particularly since 82% of urban dwelling Canadians (63% of total population) receive treated drinking water (Tate and Lacelle, 1992). Other provinces routinely report non-detected Hg levels in drinking water but use methods with a higher DL than that employed by OMOEE and it was believed that incorporation of these other data with non-detected samples equal to one half of the DL would inappropriately bias the results.

2.3 SOIL AND DUST

Limited recent data on total Hg levels in Canadian soils were located. 310 samples from Alberta, mostly of cultivated soils, had a mean Hg concentration of 0.05 $\mu g/g$ (G. Lutwick, Alberta Environment, pers. com.). In Ontario, 4 samples from allotment gardens had a mean concentration of 0.07 $\mu g/g$ (McLaughlin, 1989), and 22 samples from residential properties near industrial facilities in Cornwall had a mean value of 0.074 $\mu g/g$ (Rinne, 1988). Between 1980 and 1990, the Geological Survey of Canada collected 1,684 soil samples, with a geometric mean concentration of 0.060 μg Hg/g (range: 0.002-1.53), from Ontario and western Quebec, consisting mostly of glacially-deposited tills (Kettles and Shilts, 1983; Kettles 1988a,b, 1990). OMOEE (1994) reported a mean concentration of 0.08 $\mu g/g$ for 60 samples collected from old urban parkland

Table I

Reference Values for the Canadian General Population[1]

Age class	Body weight (kg)	Air intake (m^3/d)	Water intake[2] (L/d)	Soil ingestion[3] (mg/d)	No. of filled teeth (n)
"infants" (birth-6 mo.)	7	2	breast-fed: 0 (0.75)	20	0[4]
"toddlers" (7 mo.- 4 yrs)	13	5	0.2 (0.8)	80	0[4]
"children" (5 - 11 yrs)	27	12	0.3 (0.9)	20	1.7[5]
"adolescents" (12 - 19 yrs)	57	21	0.5 (1.3)	20	4.4[6]
"adults" (20+ yrs)	70	23	0.4 (1.5)	20	7.0[7]

[1] Reference values for average body weights, and air and water intakes as employed by the Environmental Health Directorate, Health Canada. [2] Water intake values in brackets include water consumed in tap water-based beverages such as tea and coffee; those not in parentheses exclude tea, coffee, etc. [3] soil ingestion rates as employed by the Air and Waste Section, Health Canada. [4] Assumed that dental care involving repair of dental caries using Hg amalgam is uncommon in preschool-aged children. [5] Unweighted average based on Lizaire *et al.* (1987), Johnston *et al.* (1986), Hann *et al.* (1984), and Stamm (1980). [6] The median value between the average reported number of fillings for school-aged children and adults in the U.S. (see footnote 7); average for 13 to 15 year olds was 3.9 filled teeth, based on Payette *et al.* (1988), Lizaire *et al.* (1987), Johnston *et al.* (1986), and Hann *et al.* (1984). However, this value does not include ages 16 through 19 for this age group. [7] Unweighted average based on Graves and Stamm (1985) for the adult U.S. population; assumed to be representative of Canada.

sites. For this assessment, a weighted mean value based on these studies was determined to be 0.059 μg/g. This is slightly higher than the average background value of 0.05 μg/g (range: 0.001-0.77 μg/g) reported by McKeague *et al.* (1979) for Hg in 253 undisturbed surface soils from across Canada.

No reliable published or unpublished data on Hg levels in the dust of Canadian or American homes were located. Therefore, it was assumed that the Hg in house dust would be equivalent to that for soil (i.e. 0.059 μg/g).

2.4 COMMERCIAL FOODS OTHER THAN FISH

No systematic or routine Hg monitoring has been conducted on the Canadian food supply since 1970/71 except for fish and fish products destined for commercial sale (B. Huston, Foods Directorate, Health Canada, pers. com.). Therefore, more recent (1982 to 1986) American total diet surveys of Hg levels in food stuffs (Gunderson, 1987) were used, for all foods other than fish and shellfish. For 10 composite food groups, recalculated (non-detected samples = ½ limit of quantitation) and re-grouped (for Canadian composites) unweighted average concentrations of Hg were: dairy, 0.0009 μg/g (11 commodities);

Table II

Estimates of exposure to Hg^0 via amalgam fillings

Age class	No. of filled teeth (n)	Estimated urine [Hg][1] (μg/g cr.)[2]	Estimated daily absorbed dose (μg/d)	Dose estimate after Vimy and Lorscheider (1990)[3] (μg/d)	Dose estimate after Mackert (1987)[3] (μg/d)
"infants" (birth-6 mo.)	0	0	0	0	0
"toddlers" (7 mo.- 4 yrs)	0	0	0	0	0
"children" (5 - 11 yrs)	1.7	0.53	0.42	1.7-2.1	0.22-0.26
"adolescents" (12 - 19 yrs)	4.4	0.68	1.21	4.4-5.3	0.56-0.67
"adults" (20+ yrs)	7.0	0.88	2.25	7.0-8.4	0.90-1.10

[1] after Skerfving (1991). [2] μg/g cr. = μg Hg/g creatinine. [3] assumes 1 amalgam filling per tooth and equal contribution from all filled teeth.

meat/poultry/eggs, 0.0017 μg/g (13 commodities); grains/cereals, 0.0068 μg/g (16 commodities); vegetables, 0.0020 μg/g (25 vegetables and related products); fruit and fruit products, 0.00086 μg/g (19 commodities); oils and fats, 0.0008 μg/g (3 commodities); sugar and adjuncts, 0.0009 μg/g (8 commodities); mixed dishes, 0.0008 μg/g (8 commodities); beverages, 0.57 μg/L (excludes tapwater but includes tapwater-based beverages such as tea and coffee). Actual intakes of Hg from foods by the Canadian population were calculated on the basis of Hg concentrations in the 112 individual food commodities, combined with the specific rates of consumption of these items by the Canadian population.

2.5 BREAST MILK

No survey of Hg levels in breast milk of the general Canadian population was located. Hg may be excreted in breast milk at concentrations of 3 to 8% of the maternal blood concentration (Wheatley, 1979). The U.K. Ministry of Agriculture, Fisheries and Food (1987) reported that each of 39 samples of human breast milk contained less than 3 μg total Hg/kg. Data for Sweden, Japan, Alaska and the Faroe Islands, populations with relatively high fish consumption (Grandjean *et al.*, 1994) and for Germany (Schramel *et al.*, 1988) indicate a mean concentration of Hg in breast milk of 4 μg/L (range: 2-7.6 μg/L). The only available North American study was that of Pitkin *et al.* (1976). For 32 subjects the mean concentration of Hg in breast milk was 0.93 μg/L (recalculated with non-detected samples = ½DL). This latter value was employed in this assessment.

2.6 COMMERCIAL FISH

Gervais (Fisheries and Oceans Canada, pers. com.) provided results from unpublished fish monitoring data from Fisheries and Oceans Canada. Average total Hg levels in canned tuna imported between 1980 and 1988 were 0.195 μg/g (range: <0.01-0.97) for 885 samples. For all other types of commercial fish (fresh and frozen, etc.) the average Hg level was 0.137 μg/g (range: 0.02-1.4) based on 53 marine fish samples analyzed between 1988 and 1991. For shellfish, a mean value of 0.024 μg/g (range: <0.01-1.4) was determined for 60 samples analyzed between 1990 and 1991.

2.7 NON-COMMERCIAL FISH

Data on the total Hg concentration in a sample of dorsal muscle from 9,596 specimens of lake trout, northern pike and walleye collected in 1980 or later from across Ontario were provided by the OMOEE and the Ontario Ministry of Natural Resources (unpublished data). These data gave a geometric mean total Hg concentration of 0.38 μg/g (range: 0.01-13.0). This value was employed for quantification of the dose of Hg arising from the consumption of non-commercial fish by the general Canadian population. This mean and range agrees well with data collected from eastern Canada by Kelso *et al.* (1986), Muir *et al.* (1992), among others.

3. Results and Discussion

The total daily estimated Hg intake (as delivered and absorbed doses) from all major sources for the Canadian general population are presented in Table III. Food consumption appears to be the most significant route of exposure to both meHg and Hg^{2+}, with fish and shellfish being the single greatest contributor of meHg. Dental amalgam would appear to be the most significant source of exposure to total Hg, contributing 17 to 42% of total Hg absorbed for age groups $\geq$5 years of age (Table III). Amalgam is estimated to contribute more to total Hg exposure in adults than does fish for average rates of fish consumption as used here. Estimates of 'average' Hg exposure from amalgam based on Vimy and Lorscheider (1990) and Mackert (1987) are presented along with our estimates in Table II. Our estimates are approximately double those based on Mackert (1987) but are only about one fourth of those based on Vimy and Lorcheider (1990). Regardless of the actual dose of Hg received from amalgam, levels observed in urine and other tissues of the body likely associated with an average number of filled teeth would not approach those associated with known toxic effects (reviewed by WHO, 1991). However, work should be undertaken to accurately establish the dose received from this source on a per filling basis.

It is commonly assumed that the species of Hg in foods other than fish is Hg^{2+} (WHO, 1991). However, no data exist to substantiate this. Therefore, our use of this assumption introduces some uncertainty in the estimates of absorbed dose from food. Regardless, delivered doses for all age groups are well below the WHO guideline.

For the general adult Canadian population, exposure (as delivered dose) to meHg is well below the WHO/FAO (WHO, 1989) recommended permissible tolerable weekly intake of 200 μg (28.6 μg/day or 0.41 μg/kg body weight/day). Dietary exposure to Hg in Canada also compares favourably with reported exposure in other countries. Galal-Gorchev (1993) summarized information on the dietary intake of Hg in 14 countries. The estimates cited for adults ranged from 4.9 μg/person/day (assuming 70 kg body weight) for the U.K., Australia, U.S.A., Finland and Sweden to over 24 μg/person/day in Germany. Estimates of adult dietary Hg exposure in other countries include: U.S.A., 3.4 μg/day (Gunderson, 1988); Belgium, 13 μg/day (Fouassin and Fondu, 1978; Buchet *et al*, 1983); the Netherlands, <2 μg/day (Ellen *et al.*, 1990); U.K., 2-3 μg/day (U.K. MAFF, 1987); Italy, 10 μg/day (Mariani *et al.*, 1980); Spain, 4 μg/day (Moreiras *et al.*, 1992); Czechoslovakia, 14 μg/day (Palusova *et al.*, 1991). It is likely that the assumed rates of consumption of different food items, particularly fish, as well as data treatment results in much of the variation between these reports.

Our estimates for general adult dietary Hg exposure (3.93 μg/d ingested) are lower than previous Canadian reports. Earlier Canadian assessments of dietary Hg exposure ranged from 10 (Meranger and Smith, 1972) to 16 μg/day (Kirkpatrick and Coffin, 1974). This apparent reduction in Hg exposure can not be attributed solely to a decline in Hg contamination over time, although this is likely partially responsible. Meranger and Smith (1972) assumed non-detected samples had an Hg concentration equal to the detection limit (0.01 ppm). Also, assumptions concerning the rates of consumption of fish were likely higher. Both of these studies included fish in a composite of fish/meat/poultry, with a total consumption rate of 276.4 g/day. The rate of fish consumption alone could not be determined from available information.

In this assessment we employed U.S. Total Diet Study (1982 to 1986) (Gunderson, 1987), as more recent Canadian data were lacking. Based on the 1982-84 data, the average adult American dietary intake of Hg was 3.4 μg/day (Gunderson, 1988). Our estimate was different for two reasons. First, adjusting food intakes to Canadian preferences resulted in an estimated dietary intake of 2.7 μg Hg/day. Secondly, assuming that all samples with non-detected Hg had a concentration equal to half the quantitation limit (0.001 μg/g), instead of 0.0 μg/g as per Gunderson (1988), lead to an estimated adult dietary intake (not adjusted for absorption) of 3.93 μg Hg/day (see Table III).

Exposure via inhalation of indoor air may be substantial (see Table III) and represents a source of exposure requiring further study. Etzel and Agocs (1990) reported that levels of Hg in indoor air could remain significantly elevated for more than 33 months after Hg-containing paints were applied. In Canada, about 42 months has elapsed since Hg was voluntarily withdrawn as an additive to interior latex paints in January 1991 (B. Tom, Health Canada, pers. com.). However, this voluntary action was not accompanied by the recall of Hg-containing paints already distributed to the marketplace. Therefore, many homes will have been painted with Hg-containing paint well after January 1991. Also, Hg was often added to interior latex paints in excess of recommended U.S. EPA limits (Agocs *et al.*, 1990), and the same was likely true in Canada. Therefore, it is apparent that reliable data on Hg levels in the indoor air for a representative sample of Canadian homes should be collected.

Table III

Estimated average delivered and absorbed doses (μg Hg/person/day) of Hg for various age groups of the Canadian general population. Delivered dose = total Hg inhaled or ingested; absorbed dose = delivered dose X absorption.

Medium	0 - 6mo.		7mo. - 4yrs		5 - 11yrs		12 - 19yrs		20yrs+	
	del. dose	absorb. dose	del. dose	absorb. dose	del. dose	absorb. dose	del. dose	absorb. dose	del. dose	absorb. dose
dairy/breast milk	0.705	0.705	0.407	0.407	0.382	0.038	0.368	0.037	0.201	0.020
meat/poultry/eggs	--	--	0.139	0.139	0.164	0.016	0.217	0.022	0.247	0.025
fish/shellfish	--	--	0.713	0.713	1.394	1.394	1.818	1.818	2.113	2.113
cereal/grains	--	--	0.160	0.160	0.267	0.027	0.290	0.029	0.234	0.023
pasta/soups/mixed	--	--	0.079	0.079	0.109	0.011	0.126	0.013	0.120	0.012
vegetables	--	--	0.114	0.114	0.187	0.019	0.270	0.027	0.257	0.026
fruit	--	--	0.148	0.148	0.151	0.015	0.124	0.012	0.144	0.014
fats & oils	--	--	0.006	0.006	0.012	0.001	0.015	0.002	0.011	0.001
sugar & sweets	--	--	0.039	0.039	0.048	0.005	0.056	0.006	0.046	0.005
beverages	--	--	0.067	0.067	0.133	0.013	0.246	0.025	0.553	0.055
water	--	--	0.002	0.002	0.003	0.0008	0.005	0.0016	0.004	0.0013
soil	0.0012	0.0012	0.0047	0.0047	0.0012	0.0001	0.0012	0.0001	0.0012	0.0001
indoor air	0.083	0.066	0.208	0.166	0.500	0.400	0.875	0.700	0.958	0.767
outdoor air	0.0033	0.0027	0.0083	0.0066	0.020	0.016	0.035	0.028	0.038	0.031
amalgam	--	--	--	--	0.52	0.42	1.52	1.21	2.81	2.25
Grand total	0.783	0.775	2.095	2.051	3.891	2.376	5.966	3.931	7.737	5.343

4. Conclusions

It would appear that exposure to Hg in Canada it not excessive, compared to reports for other countries. Fish remains the single greatest source of exposure to meHg, whereas other food commodities provide our primary exposure to Hg^{2+}. For Hg^0, dental amalgam predominates as a source of exposure, although indoor air may be more important than previously thought. Current efforts to monitor fish for the commercial market should continue, to ensure that dietary intake of meHg remains low. Research is required to accurately establish the dose of Hg^0 received from dental amalgam. Also, a survey of indoor air levels should be conducted to confirm that the voluntary removal of Hg as an additive to interior latex paint by the Canadian paint industry in January 1991 (B. Tom, Health Canada, pers. com.) has had the expected effect on indoor air quality and human Hg exposure.

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HUMAN EXPOSURE TO MERCURY MAY DECREASE AS ACIDIC DEPOSITION INCREASES

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Abstract. It has been hypothesized that human mercury (Hg) exposure via fish consumption will increase with increasing acidic deposition. Specifically, acidic deposition leads to reduced lake pH and alkalinity, and increased sulphate ion concentration ($[SO_4^{2-}]$), which in turn should cause increased Hg levels in fish, ultimately resulting in increased human Hg exposure via fish consumption. Our empirical test of this hypothesis found it to be false. We specifically examined Hg levels in the hair of Ontario Amerindians, who are known consumers of fish from lakes across the province, and observed a weak negative association with increasing sulphate deposition. An examination of Hg levels in lake trout, northern pike and walleye, three freshwater fish species commonly consumed by Ontario Amerindians, found a similar weak negative association with increasing sulphate deposition. Further analysis of these fish data found that fish [Hg] was most significantly (positively) associated with lake water concentrations of dissolved organic carbon (DOC), not pH, alkalinity or $[SO_4^{2-}]$. Lake DOC levels are lower in regions of greater acidic deposition. We propose an alternate hypothesis whereby human Hg exposure declines with increasing acidic deposition. In particular, we propose that increasing sulphate deposition leads to reduced lake DOC levels, which in turn leads to lower Hg in fish, ultimately reducing human Hg exposure via fish consumption.

1. Introduction

It has been hypothesized that exposure to mercury (Hg) by persons who consume freshwater fish increases due to acidic deposition (Goyer *et al.*, 1985; Gilmour and Henry, 1991). However, this hypothesis has never been tested. This association has been inferred from two independent observations. First, sulphate deposition leads to lake acidification, most notably to reduced pH and alkalinity (Neary and Dillon, 1988), and increased sulphate ion concentration ($[SO_4^{2-}]$) (Sullivan *et al.*, 1988). Secondly, reduced lake pH and alkalinity have been associated with increased Hg contamination in fish (Scheider *et al.*, 1979; Wiener *et al.*, 1990), and increased sulphate ion concentration has been linked to increased Hg biomethylation (Gilmour *et al.*, 1992) which should also lead to increased Hg in fish. These Hg-contaminated fish would thereby pose an increased health risk to persons who consumed them.

In the present study, we examine three hypotheses: first that Hg in the hair of Amerindians from Ontario, Canada is higher in regions of higher acidic deposition; second that the Hg contamination in fish species commonly consumed by these Amerindians is higher in regions of higher acidic deposition; and third, that lake water pH, alkalinity and/or $[SO_4^{2-}]$ are the most significant correlates of [Hg] in the fish species being investigated. We will show that all three of these hypotheses are false.

2. Methods

We examined the first hypothesis using Hg exposure data for 3,187 Amerindians, aged 10 to 90 years, residing in 55 reserves located across Ontario (Figure 1). MeHg

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exposure in this population results primarily from consumption of freshwater fish (Clarkson, 1990; WHO, 1990). Data were excluded for individuals on reserves located on rivers or lakes impacted by industrial Hg contamination, and on reserves adjacent to urban centers where fish is commonly purchased from commercial sources. Reserves were ascribed sulphate deposition rates according to their location within sulphate deposition zones of Ontario, as described by Neary *et al.* (1990).

Data relating to total Hg concentrations in hair ($\mu g/g$) (which is directly related to Hg ingestion (WHO, 1990)), date of sample collection, date of birth, and reserve of residence for 1,840 female and 1,347 male Amerindians were obtained from the Medical Services Branch of Health Canada (Wheatley, 1979; Tupper, 1984). Samples were collected and analysed between 1976 and 1990. Total [Hg] is strongly correlated ($r > 0.99$) with MeHg in these data (Richardson and Currie, 1993). Since many more observations of total Hg were available, we analyzed these total Hg data.

Hg analyses were performed on several 1 cm long segments of hair, of known distance from the scalp, from a tuft of several hundred hairs collected from each individual. Hair grows at a rate of 1 cm per month (Pelifini *et al.*, 1969) and, therefore, the month of Hg exposure could be deduced from the available data. Hg exposure, and thereby fish consumption rate, is greatest during the summer months (Richardson and Currie, 1993). Therefore, the average concentration of Hg ($\log_e$-transformed) in those segments of hair relating to Hg exposure during June through October were averaged and this mean summer hair [Hg] was used for further analysis (geometric mean [Hg] = 2.95 $\mu g/g$ for females and 2.94 $\mu g/g$). These data had no relationship to year of sampling ($r=0.00$, $p>0.3$, $n=3,187$). Details of hair sample collection and Hg analytical methods are described elsewhere (HWC, 1987; Farant *et al.*, 1981).

Acidic deposition will influence human Hg exposure indirectly, through its influence on fish [Hg] levels. Human Hg exposure is a function of both fish [Hg] and fish consumption rate (Richardson and Currie, 1993). Therefore, it was necessary to eliminate the confounding influence of fish consumption rate to detect the association between sulphate deposition and human [Hg]. No direct data were available on the rate of fish consumption by Amerindians. However, the influence of fish consumption rate can be controlled indirectly, as a function of each individual's age, sex, and the degree of isolation from urban centres (Richardson and Currie, 1993), where increasing isolation leads to greater reliance on subsistence fishing for nutrition.

To test the second hypothesis, that fish Hg contamination is higher in regions of higher sulphate deposition, we obtained unpublished data from the Ontario Ministries of Natural Resources (OMNR) and Environment and Energy (OMOEE) on total fish length and the concentration of Hg in 7,337 walleye (*Stizostedion vitreum vitreum*) from 375 lakes, 5,914 northern pike (*Esox lucius*) from 396 lakes, and 4,125 lake trout (*Salvelinus namaycush*) from 235 lakes (see Figure 2). These species are those most commonly used as food by Amerindians across Ontario (Coad, 1993; Hopper and Power, 1991; Lawn, 1989). Fish were collected between 1970 and 1989, matching well with the hair [Hg] data. Fish collection and Hg analysis methods are described elsewhere (McMurtry *et al.*, 1989; Wren *et al.*, 1991). Again, lakes were ascribed sulphate deposition rates according to their location within sulphate deposition zones of Ontario, as described by Neary *et al.* (1990).

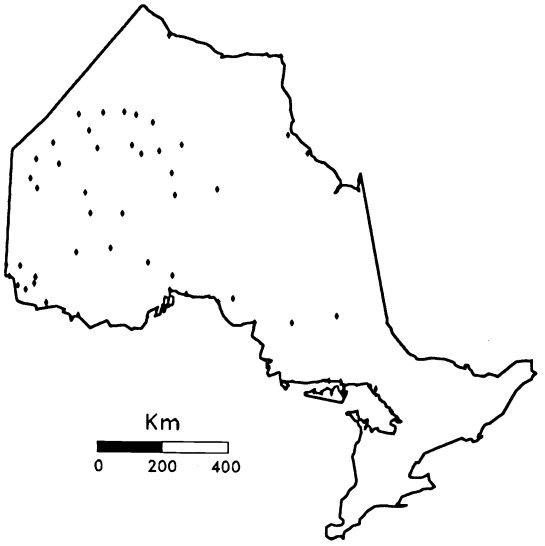

Fig. 1. Location of Amerindian reserves across Ontario from which residents supplied hair samples for Hg analysis.

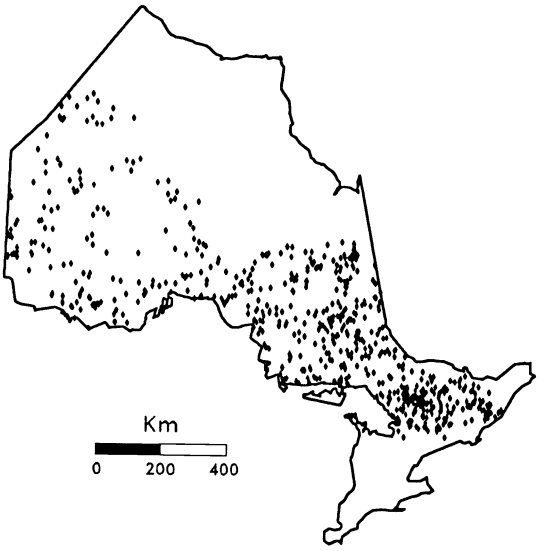

Fig. 2. Location of lakes across Ontario from which fish (lake trout and/or walleye and/or northern pike) were collected.

Fish [Hg] is influenced by a variety of factors which will confound the association between fish [Hg] and acidic deposition. Firstly, [Hg] in fish increases with fish length (Huckabee *et al.*, 1979). Lake and watershed morphometry will also confound this analysis (Bodaly *et al.*, 1993). In particular: total watershed area represents the total surface area available to receive incident precipitation; the ratio of the terrestrial drainage basin area to lake surface area is an index of the relative loading rates from terrestrial runoff *vs* direct aerial deposition; lake volume determines the degree to which acids entering the lake will be diluted. Therefore, these factors must be controlled to detect the influence of sulphate deposition on fish [Hg], independent of confounding by these variables. Finally, watershed buffering capacity (H^+ exchange capacity or acid neutralizing capacity) has a direct influence on a lake's susceptibility to acidification (NRCC, 1981), and thereby on any influence that acidic deposition may have on fish [Hg]. Data on lake surface area and lake volume were also provided by OMNR. Data on total watershed area (lake surface + drainage basin) were determined from 1:50,000 scale topographic maps. Lake buffering capacity was determined following the scheme of Cowell and Lucas (1986).

For the third hypothesis, unpublished water chemistry data (pH, alkalinity, $[SO_4^{2-}]$ and dissolved organic carbon concentration (DOC)) for these lakes were obtained from OMOEE. Sampling and analytical methods are described elsewhere (Neary *et al.*, 1990).

3. Results and Discussion

After statistically controlling Amerindian hair[Hg] data for the influences of age, isolation and sex ($R^2=0.366, p<0.0005, n=3187$), residual variation in these data were grouped by regions of sulphate deposition. Residual hair [Hg] represents an increase (>0) or decrease (<0) from the expected ($=0$) degree of contamination predicted from age, sex and degree of isolation. Although differences between regions were not significant by MANCOVA (or ANCOVA of residual [Hg]), a significant negative correlation was observed between mean residuals and the median sulphate deposition rate for each zone (Figure 3).

Fish being the source of Amerindian exposure to Hg, then fish [Hg] should also demonstrate a similar negative association with sulphate deposition. Fish [Hg] data were statistically controlled for the influences of fish length, total watershed area, the ratio of drainage basin area to lake surface area, lake volume and also watershed buffering capacity. All these variables were significant for each species of fish, explaining 15.5%, 16.1% and 41.5% of the total variation in [Hg] among individual fish for walleye, pike and lake trout, respectively. The residuals after controlling for these variables were then grouped by regions of sulphate deposition in Ontario. Residual [Hg] in all three fish species represents an increase (>0) or decrease (<0) from the expected ($=0$) degree of contamination predicted from fish length, lake morphometry and watershed buffering capacity. This residual [Hg] was significantly different among both buffering capacity and sulphate deposition zones by MANCOVA, and mean residual fish [Hg] was negatively related to sulphate deposition, although the correlation was significant only for walleye (Figure 4a,b,c). The non-significant negative relationships may or may not be consistent with the hypothesis that fish Hg is lower in regions with higher sulphate

deposition (statistical power was low, since n=6); they are unequivocally inconsistent with the hypothesis that fish Hg increases with sulphate deposition.

Neither fish [Hg] controlled only for fish length, nor residual fish [Hg], which was controlled for fish length, watershed morphometry and buffering capacity, were strongly correlated with lake pH, alkalinity or [SO_4^{2-}] (Table I). The most significant correlate of fish [Hg] was lake water DOC for all three species of fish. For walleye and lake trout, neither pH, alkalinity nor [SO_4^{2-}] demonstrated any significant association at all with fish [Hg]. For northern pike, residual [Hg] was significantly associated with pH, but less so than with DOC. These observations are consistent with several other reported analyses of Hg in these species (McMurtry *et al.*, 1989; Wren *et al.*, 1991; Sorensen *et al.*, 1990; Heiskary and Helwig, 1986).

The observed decrease in fish [Hg] at higher sulphate deposition rates is consistent with predictions made in a recent review of the literature (Richardson *et al.*, in press). The concentration of DOC is positively pH-dependent (Thurman, 1985), lake water DOC has been shown to decline with increasing lake acidification (Richardson and Currie in prep.; Schindler *et al.*, 1992; Neary *et al.*, 1990), and it is expected that watershed acidification will reduce the transport of DOC from the watershed to lakes via terrestrial runoff (Schindler *et al.*, 1992; de Haan, 1992). DOC plays a predominant role in transporting both inorganic and MeHg to, and binding them in, Ontario lakes (Lee and Iverfeldt, 1991; Mierle and Graham, 1991). Reduced lake water DOC due to acidic deposition would also lead to reduced Hg availability for methylation, and/or bioaccumulation by biota. Therefore, fish [Hg] is lower in regions with greater sulphate deposition, likely due to reduced bioavailability of Hg through loss of DOC-complexed Hg in the water column of these lakes.

4. Conclusions

We have tested three hypotheses related to the inferred increase in human Hg exposure with increasing acidic deposition and have found them to be false, based on available empirical evidence from Ontario Canada. An alternate hypothesis that human Hg exposure declines with increasing acidic deposition appears plausible. In this alternate hypothesis, sulphate deposition results in reduced lake water levels of DOC. This in turn leads to a decline in lake water [Hg] (methyl and inorganic), either by reduced transport to the lake or loss from the water column as DOC-complexed Hg precipitates with increasing acidification. The reduced bioavailability of Hg for methylation and/or bioaccumulation leads to reduced concentrations in fish, and reduced human Hg exposure via fish consumption.

The empirical support for this alternate hypothesis is weak, and requires further testing. However, experimental and empirical evidence exist to support the purported mechanisms which underlie it. At the very least, it appears evident that Hg exposure in fish consumers, and Hg levels in the fish themselves, are not higher in regions of Ontario with greater sulphate deposition.

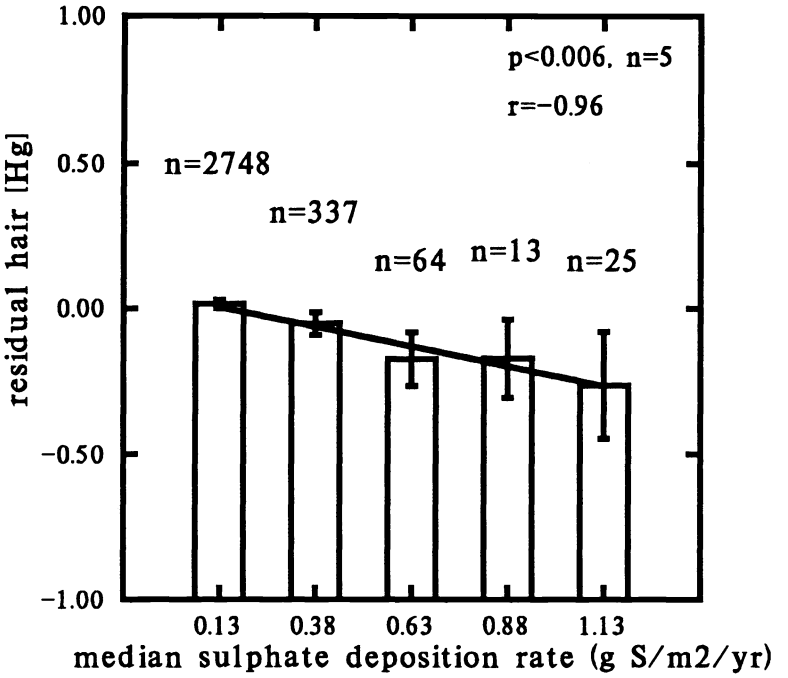

Fig. 3. Hair Hg concentration (controlled for age,sex, and degree of isolation) as a function of sulphate deposition across Ontario. Correlation results are for the association between mean residual hair [Hg] for all individuals within each sulphate deposition zone, and the median sulphate deposition rate for those zones (after Neary *et al.*, 1990). Differences between sulphate deposition zones were not significant by ANCOVA.

Table I

Pearson correlation coefficients for associations between mean ln(fish [Hg]) (controlled for fish length only) and residual fish [Hg] (also controlled for watershed morphometry and buffering capacity) and lake water chemistry parameters. Fish [Hg] was averaged by lake. Only those lakes with data for all four chemistry variables were considered. *=$p<0.01$; **=$p<0.0001$; †=$p>0.05$.

	ln[DOC]	ln[Alk+1]	$\ln[SO_4^{2-}]$	pH
[Hg] controlled for length only				
lake trout (n=108)	+0.55**	+0.16†	-0.11†	0.10†
walleye (n=172)	+0.43**	0.00†	-0.09†	0.00†
pike (n=148)	+0.33**	-0.13†	0.00†	-0.24*
[Hg] also controlled for morphometry and buffering capacity				
lake trout (n=108)	+0.45**	+0.09†	0.00†	0.00†
walleye (n=172)	+0.42**	0.00†	-0.09†	0.00†
northern pike (n=148)	+0.32**	-0.10†	0.00†	-0.21*

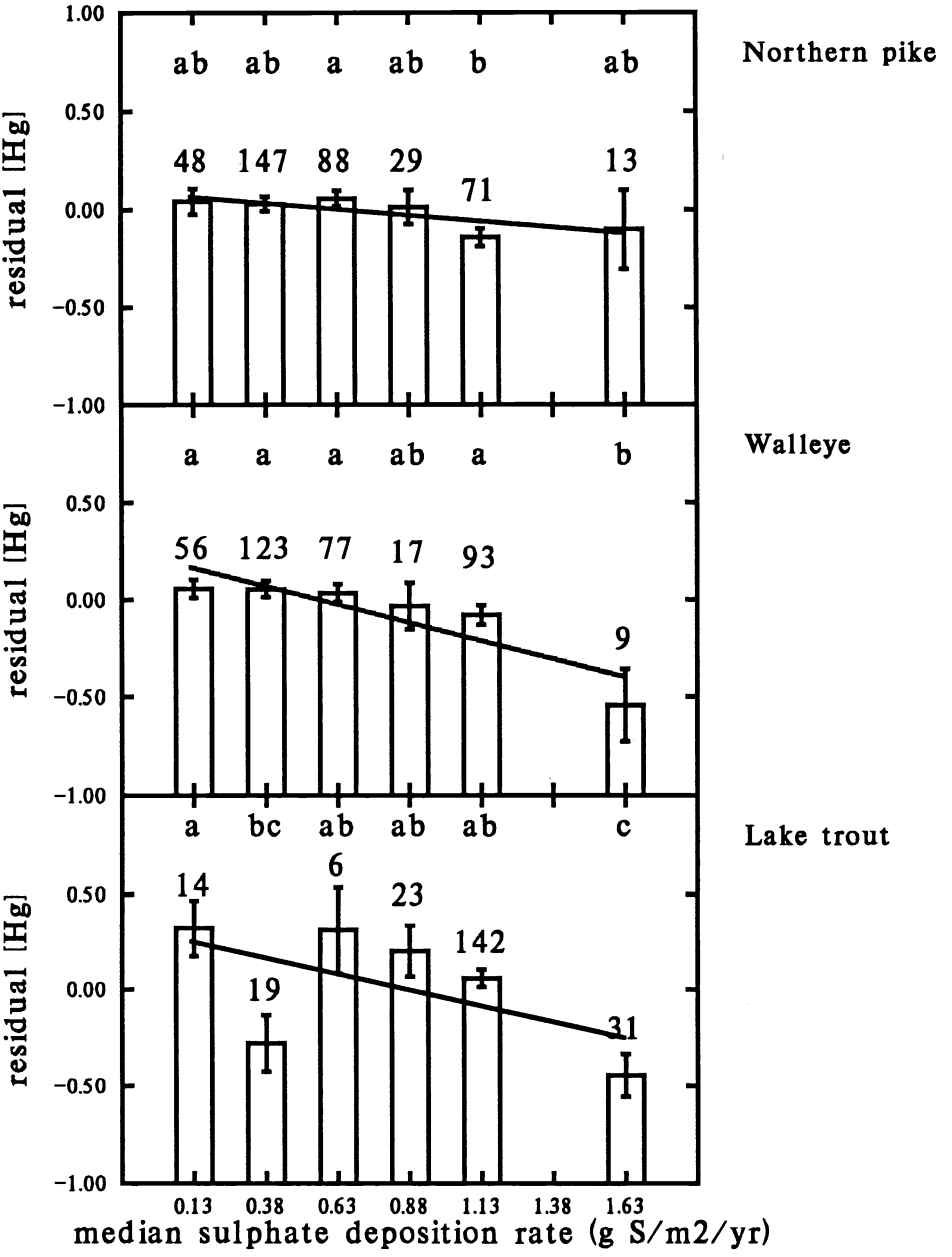

Fig. 4. Fish Hg concentration (controlled for fish length, lake and watershed morphometry and watershed buffering capacity) as a function of sulphate deposition across Ontario. Sample sizes are the number of lakes in each deposition zone. Lines drawn to illustrate general downward trend in residual fish [Hg] with increasing median sulphate deposition rate. Only for walleye was this downward trend statistically significant ($p < 0.02$). There were no data from lakes in the area receiving 1.38 g S/m^2/yr. Number of lakes varies due to availability of data.

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Mercury Exposure in Humans Through Food Consumption from the Everglades of Florida

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ABSTRACT. In March 1989, The Florida Department of Health and Rehabilitative Services (HRS) issued a Health Advisory recommending the limited consumption of several fish species caught from the Everglades region of South Florida due to elevated methylmercury (MeHg) levels (average 2-3 ppm in fish meat). There were no reports of clinical MeHg poisoning in humans in Florida, although deaths of Florida panthers were attributed to mercury (Hg) poisoning. This study evaluated the extent of MeHg exposure in persons eating contaminated fish in the Everglades region.

Populations at risk were identified including sport fishermen, Everglades Residents and subsistence fishermen. Over 1700 individuals were approached; those who had eaten fish or wildlife from the contaminated areas at least once/month for the prior three months were asked to participate. Three hundred and fifty (350) participants completed a brief questionnaire and provided a hair sample for Hg analysis. In 119 (36%) of individuals with levels above the limits of detection, the mean total Hg in hair was 3.62 $\pm$ 3.0 μg/g [$\pm$ standard deviation] with a range of 1.28 - 15.57. The most at risk populations identified with respect to Hg levels were Blacks and men.

Although the majority of the participants had fished in the Everglades for many years (>15 years), they reported relatively low intake of fish and had low hair Hg levels compared with similar populations in prior studies of other populations at risk. Although 71% of participants knew of the State Health Advisories concerning ingestion of Hg contaminated fish from the Everglades, this did not change their consumption habits. In addition, Blacks, individuals of lower income and of lower education levels were less likely to know about the Health Advisories. Given recent studies of neurologic effects from relatively low in utero MeHg exposure, the continuation of the Mercury Health Advisories and wildlife monitoring in the Everglades are warranted, especially for women of childbearing age and children. However, public education must be targeted for the populations at risk identified in this study in order to reach these populations more effectively.

1. Introduction

In March 1989, the Florida Department of Health and Rehabilitative Services (HRS) and the Game and Fresh Water Fish Commission (GFC) jointly issued a Health Advisory urging limitation of consumption of several fish species caught from the Everglades region of South Florida. This Advisory followed the finding of elevated MeHg levels (2.0-3.0 ppm) in largemouth bass, other freshwater fish, and subsequently other animals in the Everglades. The Health Advisory recommended that non-pregnant adults over the age of 15 years limit the consumption of the high Hg fish to one half pound per week, and that women of childbearing age and children less than 15 years limit consumption to one half pound per month.

An investigation of the causes and extent of the MeHg contamination was initiated by the State of Florida, assisted by Federal agencies, environmental groups and local industries. The death of at least one Florida Panther, the top carnivore in the Everglades, has been attributed to Hg poisoning. No cases of MeHg poisoning in humans in Florida were reported.

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However, MeHg poisoning is difficult to diagnose in humans, and no official reporting mechanism exists in the State of Florida (Clarkson, 1992, Galli and Restani, 1993).

The first objective of this study was to describe the human populations at risk for Hg exposure through their consumption of fish and other contaminated animals in the Everglades. The second objective was to evaluate the extent of Hg exposure in those persons consuming contaminated food, and their compliance with the voluntary Health Advisory.

2. Methods

After discussions with HRS and GFC personnel, as well as local environmental groups, several populations were identified as being at risk for Hg exposure as a result of consumption of Hg contaminated foods from the Everglades. These populations included traditional Native Americans, Bass and sport Fishermen, Everglades residents and subsistence fishermen.

Of these target groups, subsistence fishermen have the greatest risk of exposure due to their eating the fish and other wildlife from the Everglades. The Bass and sport fishermen predominantly catch and then release the fish with minimal consumption of contaminated fish and wildlife. The local Native American population performed their own study in collaboration with the Centers for Disease Control (CDC)(CDC, 1993).

Over the period of one year, individuals from the populations at risk were recruited by special targeted screenings, mailings, postings and multi-media advertisements of the study throughout the region, as well as face-to-face canvassing of people fishing along the canals and waterways in the contaminated area. Direct contact was the most effective recruitment method; it was performed throughout the daylight hours of all days of the week regularly for over 9 months. In addition, the investigators followed up on inquiries from concerned individuals, as well as making formal presentations at local fishing and airboat clubs.

Anyone, regardless of age, who had eaten fish or other animals from the Everglades at least once a month for the past three months was invited to participate by signing a Consent Form (approved by the University of Miami Human Subjects Committee). Participants answered a short administered questionnaire concerning demographic information, fishing and eating habits, and some possible confounding variables. A sample of hair from the nape of the neck was taken for Hg analysis. Each participant received a copy of the Mercury Health Advisories with explanations in English and Spanish, and $10.00 worth of food coupons. These persons were subsequently mailed a detailed letter explaining their individual hair Hg results and current information on known sources of Hg, as well as a new copy of the Health Advisories.

All hair samples were analyzed by atomic absorption analysis using established methodologies of Giovanoli-Jakubczak et al (1974) for hair. Ten percent duplicates were performed and reported, as well as external controls (with less than one standard deviation difference overall reported for either). The detection limit (DL) for total Hg in hair was 1.26 $\mu g/g$.

Hair sampling was used because of its ease of storage and transport, and increased acceptance by study participants. The relationship between hair and blood MeHg levels has been well established (Galli and Restani, 1993; WHO, 1990, 1976; Phelps *et al.*, 1980); blood MeHg levels provide recent exposure indices (several weeks) while hair MeHg levels reflect

historic exposures relative to the length of the hair (ie. months to years). A substantial number of hair samples in this study had elevated inorganic Hg levels (should be less than 10% of the total Hg in hair), which was felt to be due to contamination since no other confounding sources were identified. Therefore, total hair Hg levels were used in the statistical analysis because the total Hg levels are determined directly, independent from the determination of the inorganic Hg levels (Giovanoli-Jakubczak *et al.*, 1974; T. Clarkson verbal communication, 1994).

No Hg measurements were made of any food specimens from the individual participants for economic considerations and numerous prior measurements by the Florida GFC had established the fish and wildlife from the Everglades having elevated Hg.

A problem in analyzing the data concerned the treatment of the values of total Hg below the DL. Usually this problem is resolved by either eliminating the values below DL or substituting the value of zero. Slymen *et al.* (1994) suggest a different approach whereby the values below DL are considered to be left-censored data and then regression models that allow for left-censoring are fitted. This is the approach taken in this paper, using the value of 1.26 μg/g as the DL for total Hg in hair. LIFEREG, available in the 6.07 SAS statistical package, was used for regression analyses in which total Hg levels in hair were the dependent variable. Since the values of Hg were not normally distributed, a log normal transformation was used. In addition, chi-square testing was performed on categorical variables, as well as logistic regression in the analyses of knowledge of the Health Advisories.

3. Results

Of a total of 1794 individuals contacted, 405 individuals had eaten fish and/or wildlife from the Everglades at least once per month for the past three months. Of these 405 individuals, 55 persons refused to participate, leaving 350 participants. Of the 55 refusals, the most common reason was lack of interest because participation interfered with their fishing. No demographic or consumption data were collected from the group which refused, so they may differ from the group that responded. The majority of the eligible participants (>93%) were subsistence fishermen and/or Everglades residents.

In addition, an individual was excluded from further analysis if there was an inadequate hair sample (n=15) or if any person did not eat wildlife from the Hg contaminated areas (n=5). Thus, statistical analyses of the data were performed on 330 persons.

These 330 fish consumers ranged in age from 2-81 years (mean 38.64 $\pm$ 18.81) (Table I). The group was mostly male (62%), with a slight preponderance of Black individuals: 43% white, 46% Black Non Hispanic and 11% White Hispanic. Ninety-two percent reported English as their primary language and approximately 50% reported completing High School. The majority of the participants reported a low income of 0 to $15,000 per family per year before taxes. Of the 143 individuals who reported drinking ethanol, the intake ranged from 0 to 168 glasses and/or cans per week (mean 19.23 $\pm$ 28.9).

Fifty-six (17%) subjects were 18 years or less. The majority were employed in blue collar occupations. The Hg levels of all persons reporting jobs with possible exposures to inorganic Hg were individually examined, but none of them had elevated total and/or inorganic Hg levels in hair. Therefore, occupational sources of Hg did not appear to be a serious confounder.

Table I
Means and standard deviations of selected characteristics by subgroups of the population

Variables	Population	Hg Greater than the detection limit	Hg Less than the detection limit
N	330	119	211
Age (years)	38.6 ± 18.8 (2 - 81)	42.0 ± 17.6 (3 - 80)	36.7 ± 19.3 (2 - 81)
Sex			
Female	38%	28%	43%
Male	62%	72%	57%
Race-Ethnic			
Black	46%	58%	37%
White	43%	34%	48%
Hispanic	11%	8%	13%
Number of Years fished	15.8 ± 15.8 (0 - 70)	16.3 ± 15.1 (0 - 61)	1.7 ± 2.4 (0.1 - 70)
Number per week fished in last 6 months	1.8 ± 2.5 (0 - 20)	1.7 ± 2.6 (0 - 20)	1.8 ± 2.4 (0 - 20)
Number per week fished in last month	1.5 ± 1.4 (0 - 12)	1.4 ± 1.3 (0 - 7)	1.4 ± 1.5 (0 - 12)
Know Health Advisories	71%	72%	71%

(± Standard Deviation)

Seventy-one percent (n=232) reported knowing about the Mercury Health Advisories. Of these, 74% stated that this knowledge had not changed their fish eating habits. Of the 26% who did report a change in their fish eating habits, the majority (n=58) stated that they had lowered their Everglades fish intake. However, there was no significant difference between the mean total Hg level in hair of those persons who knew about the warnings and those who did not (see below).

One hundred and fifty-three persons reported catching and/or eating other species, including alligator (27%), turtles (20%), and other species of fish and fowl.

The range of years fished along the canals was 0 to 70 years (mean 15.8 ± 15.8). The fish consumers reported eating fish over the past 6 months a range of 0-20 times per week (mean 1.79 ± 2.46) and over the past month, 0-12 times per week (mean 1.45 ± 1.41). The mean total Hg levels in hair was 1.31 ± 2.53 μg/g (0 to 15.57 μg/g) if the detection limit was assumed to be zero; due to the high proportion (64%) of persons with Hg levels less than the detection limit, using the maximum likelihood method of Slymen *et al.* (1994) produced a negative estimate of Hg level.

Examining the variables one at a time revealed age, sex and Black race were significantly associated with total hair Hg levels (Table II). Neither the number of years fishing along the canal, nor the number of times fished/eaten over the past six months or over

Table II
Regression models for total Hg found in hair, assuming a log normal distribution

Variables	Regression coefficient	Standard error	X^2	p-value
		Univariate Models		
Age	0.011	0.004	6.51	0.011
Race			9.57	0.002
Black	0.481	0.155	9.57	0.002
Sex			6.00	0.014
Male	0.404	0.165	6.00	0.014
		Multivariate Model		
Age	0.006	0.004	2.38	0.123
Race	-0.462	0.161	8.22	0.004
Sex	-0.445	0.164	7.39	0.007

the past month, nor the type of fish eaten were associated with total hair Hg level. The other demographic variables such as education level, income level and ethanol intake were not associated with Hg level. Knowledge of the Health Advisory was not associated with the total Hg level in hair; this was also true whether or not the knowledge of the warnings had changed their consumption behavior. Models including the variables age, sex and race along with the interactions of these variables were fitted. None of the interactions were significant so that the final model included only the three variables. Black race and male sex were related to total Hg in hair; age was not. Table II presents the summary of this multivariate analysis.

Univariate logistic analyses of knowledge of the Health Advisories showed significant associations with age, race, number of years fished, income and education levels. Sex, the number of times fished/eaten over the past six months or over the past month, and total Hg level in hair were not associated with knowledge of the Health Advisories. Stepwise logistic regression modeling indicated that black race, fewer years fished, lower education and lower income levels were significantly associated with lack of knowledge of the Health Advisories, whereas age was not related (Table III).

Hg Levels Above and Below the Limits of Detection:
Out of the 330 fish consumers, there were 119 people (36%) with hair Hg levels above the limits of detection (Table I); their mean total Hg level in hair was 3.48 $\pm$ 3.01 μg/g (1.26 to 15.57 μg/g). Their demographics were similar to the total group of fish consumers although they were slightly older (42 $\pm$ 18.8), had a greater percentage of Blacks (58%) and fewer women (29%).

4. Discussion

Although the study participants had fished in the Everglades on the average almost 16 years, they reported relatively low intake of fish (mean 1.79 times per week over the past 6 months) compared with other populations sampled in prior studies of populations exposed to MeHg through fish consumption. The total Hg levels in hair for these fish consumers were

Table III
Final logistic regression model for knowledge of Health Advisories

Variables	Regression coefficient	Standard error	X^2	p-value
Race	0.703	0.307	5.24	0.022
Years Fished	-0.054	0.013	18.79	0.001
Years Education	-0.712	0.264	7.26	0.007
Income	-0.449	0.213	4.43	0.035

correspondingly low (mean 1.31 $\pm$ 0.53 μg/g using zero as the detection limit). Even those individuals who had detectable total Hg levels in hair reported a similar relatively low intake of fish and relatively low total Hg levels in hair (mean 3.48 $\pm$ 3.0) compared to other fish consuming populations (Kyle and Ghana, 1982; Skerfving, 1974; Birke *et al.*, 1972; Turner *et al.*, 1980; Marsh *et al.*, 1974; Suzuki *et al.*, 1988; Valciukas *et al.*, 1986; Clarkson, 1992).

To place these levels of intake and Hg in context (Table IV), in a study by Kyle and Ghana (1982) in Papua (New Guinea), "low fish eaters" with low Hg exposure were persons who ate less than one fish meal per day and had MeHg mercury levels in hair of 2.4 $\pm$ 1.8 μg/g while the "high fish eaters" with high Hg exposure were persons who ate fish two to three times per day and their MeHg levels in hair were 15.5 $\pm$ 6.9 μg/g. The WHO "normal" level of Me Hg in hair are less than 2 μg/g, although a true normal level would be non detectable since Hg serves no known physiologic purpose.

Increasing age was associated univariately with an increased risk of relatively elevated total Hg levels in hair which may be due to decreased clearance of Hg from the body with age and/or to increased consumption of contaminated fish and other animals by adults compared with children. Race and sex were individual significant predictors of total Hg level in hair; persons who were Blacks and males were more likely to have relatively higher total Hg levels.

The detectable total Hg levels in hair were not associated with consumption within the past month nor within the past 6 months nor even with the number of years fishing along the canal. This result may be an effect of decreased fishing due to Hurricane Andrew in August of 1992 and its aftermath. The preponderance of male participants who tended to have shorter hair may also have contributed to this result. However, female participants with longer hair (and thus longer measurable Hg exposure) did not have increased Hg levels compared to male participants as would be expected if either factor were an issue.

Of the populations targeted, only the Subsistence Fishermen, especially the Blacks and men, appeared to be at risk for increased Hg; the Sport Fishermen predominantly practice catch and release. The Florida HRS Mercury Health Advisories recommend that non-pregnant adults over the age of 15 years, limit the consumption of the high Hg fish to one half pound per week and that pregnant or nursing women, or children less than 15 years limit consumption to one half pound per month. This study showed that a substantial number of at risk persons are aware of these Health Advisories. Although these persons are following the recommended intake guidelines, when asked if the Health Advisories had changed their intake patterns, 70% denied any effect. Finally, those who may be at greatest risk, ie. Blacks and individuals with less education or lower socio-economic level, were less likely to know about the Health Advisories.

Table IV
Number of fish meals per day and mean and standard deviation of Hg in hair for different geographical locations

Location	N	Fish intake	Fish meals/day	Hair Hg level (μg/g)
Papua (New Guinea)				
High Hg Exposure	114	high	2-3	15.5 ± 7 (3.2 - 50.5)
Low Hg Exposure	51	high	2-3	6.4 ± 4.6 (0.6 - 25.7)
Low Hg Exposure	45	low	<1	2.4 ± 1.8 (0.3 - 9.0)
Peru				
A	190	high	0.233kg/d	16.1 (2.6 - 53)
B	52	low	0.042kg/d	1.93 (0.78 - 4.8)
Samoa				
High Hg Exposure	88	high	10.4oz/d	17 (3.3 - 47.8)
Everglades (FL)	330	low	0.1 (0-1)	1.3 ± 2.5 (0 - 15.6)

(Adapted from Kyle and Ghana, 1982, with citations from: Skerfving, 1974; Birke *et al.*, 1972; Turner *et al.*, 1980; Marsh *et al.*, 1974; Suzuki *et al.*, 1988)

Both this study and the CDC Native American study (CDC, 1993) found less fish consumption than originally thought, and relatively low human Hg levels. Nevertheless, recent studies in animals and humans of low level MeHg exposure in utero suggest that maternal hair levels above even 10 μg/g may cause neurologic effects (Stern, 1993; WHO, 1990; Clarkson, 1992; Burbacker *et al.*, 1990; Galli and Restani., 1993). Therefore, the continuation of the mercury Health Advisories with fish and wildlife monitoring, especially for pregnant/nursing mothers and children, is warranted. However, public education must be targeted for the populations at risk identified in this study in order to reach these populations more effectively.

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Pharmacokinetic Dose Estimates of Mercury in Children and Dose-Response Curves of Performance Tests in a Large Epidemiological Study

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Abstract. An analysis was performed of a large epidemiological study conducted in New Zealand to evaluate the neurological effects of prenatal methylmercury (MeHg) exposure in children. In the epidemiological study, 6-year-old children, whose mothers had been exposed to MeHg through the consumption of fish, were administered performance tests to ascertain academic attainment, language development, fine and gross motor coordination, intelligence and social adjustment. These responses were correlated with estimates of prenatal exposure based on average maternal hair concentrations during pregnancy. The Benchmark Dose analysis performed in the current study suggests that the NOAEL for the most sensitive indicator of developmental effects (Test of Language Development — grammar understanding) occurs at approximately 17 ppm Hg in maternal hair. A physiologically based pharmacokinetic (PBPK) model for MeHg was developed which coherently described MeHg pharmacokinetics in the adult rat, monkey and man, and predicts fetal levels of MeHg from *in utero* exposure. The model includes a description of enterohepatic recirculation of MeHg, conversion to inorganic mercury in tissues and intestinal flora, slowly reversible incorporation of mercury in tissues, and excretion of both organic and inorganic mercury into urine, feces, and hair. Analysis with the PBPK model indicates that fetal brain concentrations of MeHg at the NOAEL are on the order of 50 ppb (μg/L), and are associated with maternal dietary intakes of MeHg ranging from 0.8 to 2.5 μg/kg/day. Since this analysis is based on the most sensitive endpoint in a large, general human population, no uncertainty factor should be necessary using the standard USEPA approach for setting RfDs. Therefore, the RfD suggested by this analysis would be a factor of from 3 to 8 above the current USEPA RfD of 0.3 μg/kg/day.

1. Introduction

One of the principal health concerns regarding environmental mercury (Hg) is neurotoxicity resulting from methylmercury (MeHg) ingestion (Clarkson, 1990). The current reference dose (RfD) for MeHg is 0.3 μg/kg/day, based primarily on effects observed in a population of Iraqis who accidentally ate seed grains treated with MeHg compounds (Clarkson *et al.*, 1976). However, considerable uncertainty remains concerning the dose-response for the neurological effects of MeHg, particularly regarding the potential for developmental effects in children exposed prenatally due to ingestion of methylmercury by the mother (Choi, 1989; Burbacher *et al.*, 1990). A dose-response analysis of the exposed Iraqi population concluded that a threshold for developmental effects occurs at maternal hair concentrations of about 10 ppm (Cox *et al.*, 1989). Stern (1993) used a one-compartment kinetic model to determine that a daily intake of 0.7 μg/kg/day of MeHg was associated with this hair level. He considered the calculated effect-threshold to constitute a lowest-observed-adverse-effect-level (LOAEL) requiring a ten-fold safety factor; therefore, he proposed an RfD for MeHg of 0.07 μg/kg/day. However, the precision of the Iraqi analysis was limited by several factors, including (1) the difficulty of retrospective exposure assessment resulting from the acute nature of the exposure, (2) the rough measures of developmental effects available from this study (such as maternal recollection of "late walking"), and (3) the relatively simplistic pharmacokinetic and statistical dose-response analysis. The purpose of the present study was to employ more sophisticated pharmacokinetic and statistical dose-response analyses

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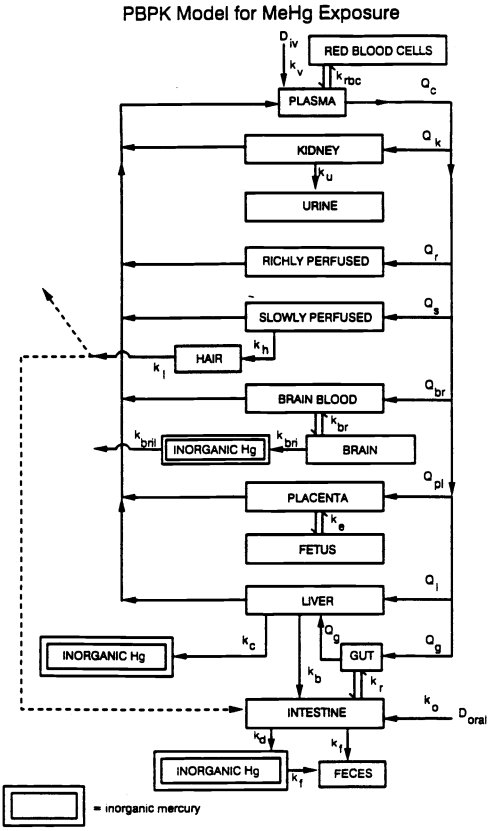
to a well-controlled epidemiological study in a large population in New Zealand which featured relatively constant chronic exposure to MeHg in fish (Kjelstrom *et al.*, 1989).

2. Model Development

The PBPK model for MeHg was fashioned after the rat model of Farris *et al.* (1993), except for changes designed to facilitate interspecies extrapolation. The overall goal of this modeling effort was to create a multispecies model that would be amenable to simulating the kinetics of MeHg by simply changing the species-specific parameters. In particular, separate RBC and plasma compartments were used, whereas the Farris model featured only a total blood compartment. The use of separate RBC and plasma compartments made it possible to predict changes in the kinetics of MeHg across species due to differences in the RBC/plasma ratio. The use of both RBC and plasma compartments was also important for validation of the model with data from the literature where only RBC or plasma data were available. This modification also obviated the need for the use of empirical transport parameters as in the Farris model; with the addition of separate RBC and plasma compartments, the actual measured blood flows from the physiological literature for each species could be used directly.

The PBPK model for MeHg developed in this study consists of an adult model having eleven compartments representing both organ-specific and lumped tissues (Figure 1a). The twelve compartments of the adult model include eight compartments for which transport of MeHg is characterized as flow limited, and four for which transport is diffusion limited. The flow-limited compartments are the plasma, kidney, richly perfused, slowly perfused, brain-blood, placenta, liver and gut compartments. Although MeHg binds to protein and non-protein sulfhydryls with high affinity, its kinetics are consistent with relatively efficient transport across membranes. This behavior has been accounted for by the suggestion that non-protein sulfhydryls (e.g., cysteine, glutathione) act as carriers for MeHg (Aschner and Aschner, 1990; Aschner and Clarkson, 1988; Ballatori and Clarkson, 1983; 1985). In particular, the physical resemblance of MeHgCysteine to an essential amino acid has been suggested as the basis for its relatively rapid transport across the blood-brain barrier, and both glutathione and cysteine conjugates of MeHg have been identified in the bile. The concentration of MeHg in each of the flow-limited tissue compartments is then simply a result of the arterial plasma concentration flowing to the compartment, the tissue/plasma partition coefficient of MeHg for that compartment, and the loss of MeHg from the compartment via the venous plasma, excretion, or metabolism to inorganic mercury (InHg). Transport to the other three compartments of the adult model — RBC, brain, and fetus — is described as being diffusion limited. There are also four other compartments in the model which are involved in MeHg uptake or elimination: MeHg in the urine, and MeHg and inorganic mercury (InHg) in the hair, feces, and the intestinal lumen. Enterohepatic recirculation of MeHg is described by the excretion of MeHg in the bile and its subsequent reabsorbtion into the gut tissue. The movement of MeHg and InHg in these sections of the model is described by first order processes. The most important excretion mechanism for mercury is the conversion of MeHg to InHg by the gut flora, with subsequent excretion of InHg in the feces. Some MeHg is also excreted in the feces, but most is reabsorbed. Incorporation in the hair is also a significant route of excretion. For the purpose of the modeling, all demethylation of MeHg in the tissues (except in the brain)

is described as taking place in the liver, and the resulting InHg is assumed to accumulate in the kidney. In the brain, both demethylation and slowly-reversible incorporation into tissue (not shown in Figure) are described.



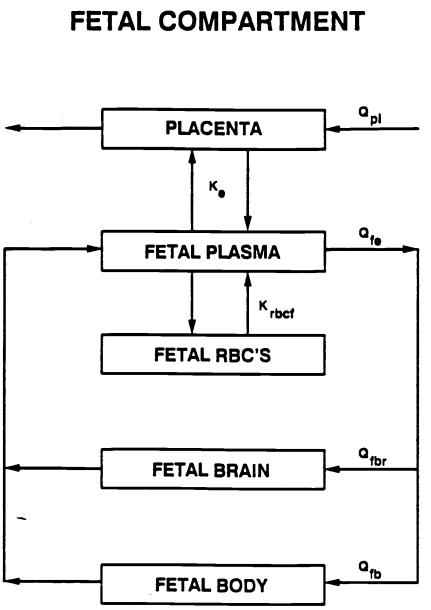


Figure 1a. Diagram of the multispecies, PBPK model for MeHg. Parameters are defined in the text and tables.

Figure 1b. Diagram of the fetal sub-model.

The fetal sub-model for MeHg (Figure 1b) consists of four compartments which grow during the time of gestation. These compartments are the fetal plasma, RBCs, brain and the remaining fetal body. Fetal plasma flows to the brain and body, while the RBC compartment communicates with the plasma compartment in the same fashion as in the adult model, with a diffusion parameter and RBC/plasma partition coefficient. The assumptions accounting for changes in the body compartments of the mother and fetus during pregnancy are that the overall increase of body weight by the mother is predominately due to the addition of a growing fetus and placenta, and the increase in blood volume of the mother. There is certainly an increase of fat storage compartments during pregnancy; however, due to the low affinity of MeHg for fat, it was decided that the exclusion of changes in this compartment during pregnancy would have limited effects on the kinetics of MeHg in the mother and fetus.

2.1. Physiological Parameters and Partition Coefficients

The pharmacokinetic parameters involving tissue volumes and flows were predominately taken from ICRP (1975), Hytten and Leitch (1971), and Gerlowski and Jain (1983) for the human values. The parameter values for the monkey were taken from Forsyth *et al.* (1968), Bourne (1975), and Gerlowski and Jain (1983). Where the parameter values for the two species were of very similar value, a common value was used for both species. The tissue/blood partition coefficients for both humans and monkeys were based on monkey pharmacokinetic studies of Evans *et al.* (1977), Rice (1989), and Kawasaki *et al.* (1986). The partition coefficients for some tissues were adjusted if there was evidence that a high level of InHg accumulation, as in the case of the kidney, could have caused an overestimate of the amount of MeHg which partitioned into the tissue of interest. The RBC/plasma ratio for humans was taken from Birke *et al.* (1972), and represents an average value of what is seen in the literature. The RBC/plasma ratio for monkeys was taken from Kawasaki *et al.* (1986).

2.2. Model Validation

The ability of the model to provide a coherent description of MeHg kinetics for a variety of dosing scenarios in both monkeys and humans is demonstrated in Figures 2 through 5. Figure 2 illustrates the kinetics of MeHg in the blood of monkeys exposed chronically to MeHg in their diet, while Figure 3 shows the MeHg concentrations in the hair of monkeys exposed to MeHg in their diet for both long and short durations. The model is able to describe both the approach to steady state and the clearance of MeHg following the termination of the exposure. Figure 4 displays the kinetics of MeHg in the blood of humans during and after exposure to constant levels of MeHg in their diet, while Figures 5a to 5c show the ability of the model to simulate the kinetics of MeHg in the plasma, red cells, and hair of human volunteers under similar conditions.

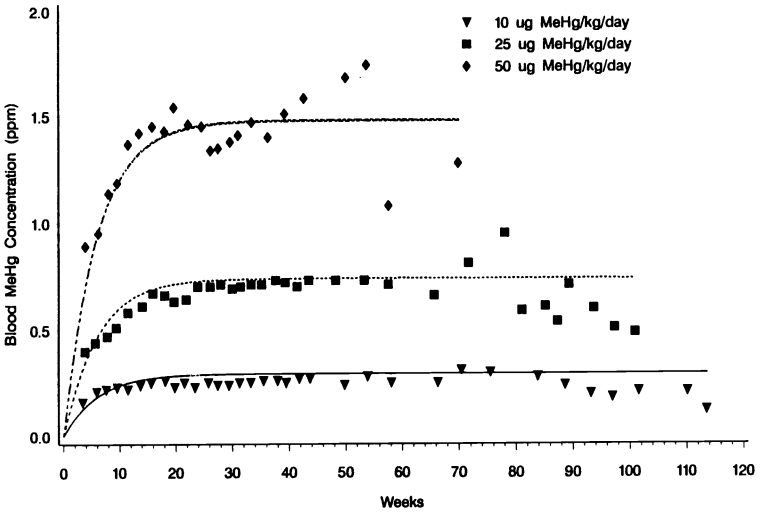


Figure 2. Time course of MeHg concentration (ppm) in the whole blood of female monkeys (*Macaca fascicularis*) after three oral doses per week of MeHg (23.3, 58.3, or 116.7 μg/kg/day) in apple juice for times varying from 35 to 100 weeks. Each datum represents the mean of five monkeys at each dose level (data from Rice *et al.*, 1989). The curves depict the computer simulation for each dose using the PBPK model.

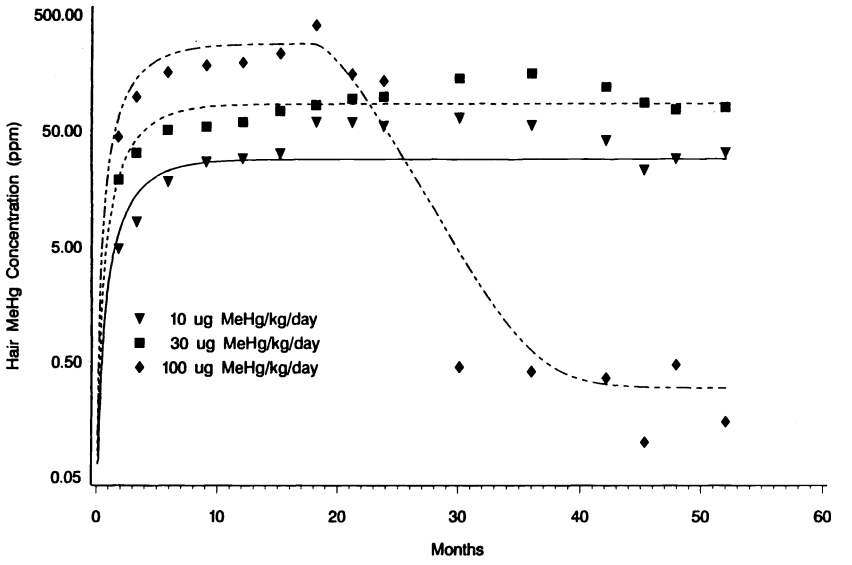


Figure 3. Time course of MeHg concentration (ppm) in the hair from monkeys (*Macaca fascicularis*) after daily oral doses of MeHg (10, 30, or 100 μg/kg/day) in monkey chow for times varying from 18 to 54 months. Each datum represents the mean of five monkeys at each dose level (highest dose n = 1 animal, data from Kawasaki *et al.*, 1986). The curves depict the computer simulation for each dosing scenario using the PBPK model.

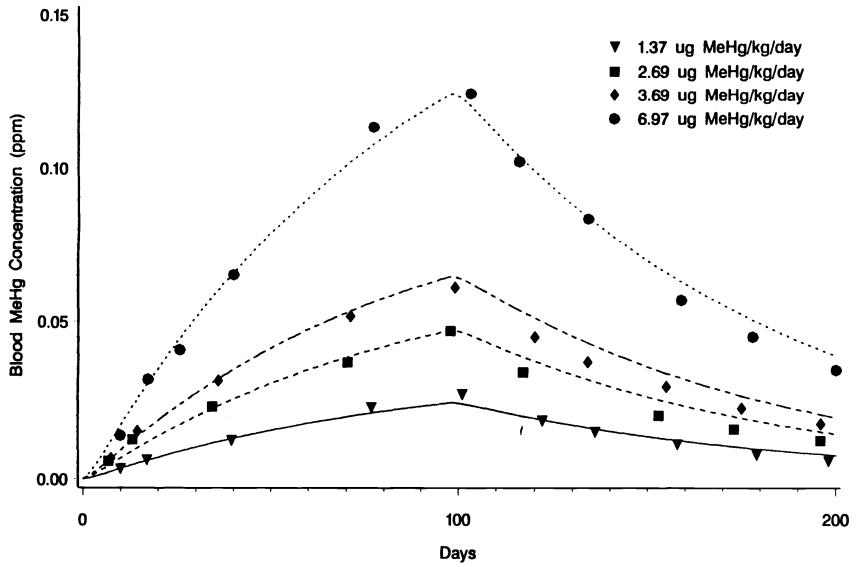


Figure 4. Time course of MeHg in whole blood from human subjects in a controlled study of chronic ingestion of MeHg in fish at a dose ranging from 40 to 230 μg/day for approximately 3 months (data from Sherlock *et al.*, 1984); the average number of subjects at each dose was five. The curves depict the computer simulation at each dose.

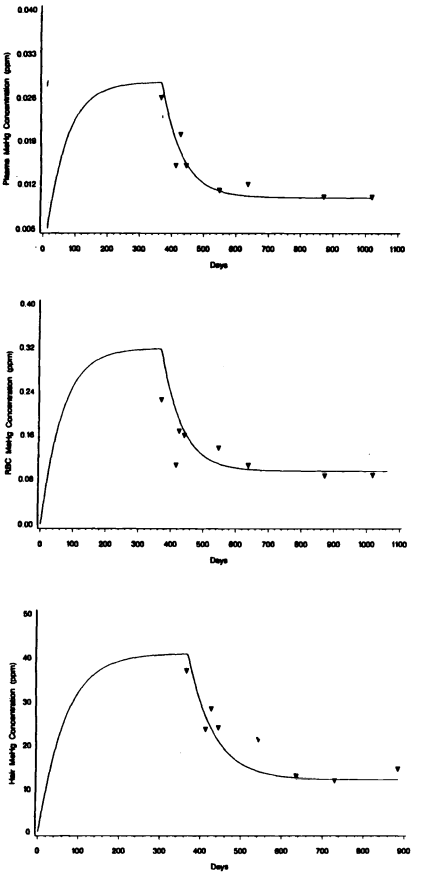


Figure 5a. Time course of MeHg in the plasma of an individual on a diet of fish for at least 4–6 years containing MeHg at a concentration 2.14 μg MeHg/kg/day (data from Birke *et al.*, 1972). The data points represent the change of MeHg levels after a change in diet from contaminated fish to less contaminated food stuffs. The curve depicts the computer simulation using the PBPK model.

Figure 5b. Time course of MeHg in the red blood cells of an individual on a diet of fish for at least 4–6 years containing MeHg at a concentration 2.14 μg MeHg/kg/day (data from Birke *et al.*, 1972). The data points represent the change of MeHg levels after a change in diet from contaminated fish to less contaminated food stuffs. The curve depicts the computer simulation using the PBPK model.

Figure 5c. Time course of MeHg in the hair of an individual on a diet of fish for at least 4–6 years containing MeHg at a concentration 2.14 μg MeHg/kg/day (data from Birke *et al.*, 1972). The data points represent the change of MeHg levels after a change in diet from contaminated fish to less contaminated food stuffs. The curve depicts the computer simulation using the PBPK model.

3. Benchmark Dose Analysis

The object of the dose-response assessment in this effort was an epidemiological study (Kjelstrom *et al.*, 1989) conducted in New Zealand on a large population exposed to high

levels of MeHg in fish. In this study, a battery of psychological, behavioral, and scholastic tests was administered to 6-year old children, and the performance of children exposed prenatally to MeHg was compared to unexposed controls. Prenatal exposure was characterized by average maternal hair levels of Hg during pregnancy. This study possesses several advantages over the Iraqi study, which is the basis of the current RfD. First, the exposures in the New Zealand study were chronic and reasonably constant, permitting more accurate estimates of exposure than in the Iraqi study, where the acute nature of the exposure, and the retrospective nature of the study made the exposure assessment more problematic. Second, several potential confounders (e.g., mother's smoking, ethnicity, and age) were recorded in the New Zealand study but not in the Iraqi study. Third, the battery of tests used in the New Zealand study, which included such endpoints as academic attainment, language development, fine and gross motor coordination, intelligence, and social adjustment, provide a potentially more sensitive and reproducible evaluation than the coarser measures used in the Iraqi study (maternal recollection of "late walking" or "late talking" and a neurological test).

The method chosen to perform a dose-response analysis on the results of the New Zealand study was the Benchmark Dose (BMD) methodology (Crump, 1984). The BMD is the dose (or exposure) predicted to result in a specified amount of increased risk (called the "benchmark risk"). The BMD is calculated using a statistical dose-response model applied to either experimental toxicological or epidemiological data. A statistical lower bound on the BMD (BMD lower bound or BMDL) has been proposed as a replacement for the traditional NOAEL, which must be selected from one of the actual experimental dosing levels, in the setting of acceptable exposure limits (USEPA, 1990; Kimmel and Gaylor, 1988; Gaylor and Slikker, 1990).

In the traditional approach for estimating a NOAEL from animal data, the response at each of the experimental doses is compared statistically with that in the controls, and the NOAEL is defined as the lowest dose showing no statistical difference. In the case of human epidemiological data, it is necessary to group the observations into arbitrary categories by exposure in order to perform this analysis. The benchmark approach has several advantages over the traditional NOAEL approach: (1) the benchmark approach makes better use of the dose-response information inherent in the data, (2) the BMD appropriately reflects the sample size of a study (Smaller studies tend to result in smaller BMDs, whereas the opposite is true for traditionally derived NOAELs), (3) the benchmark approach does not require arbitrary categorization of the data in epidemiological studies, (4) the benchmark approach does not involve difficult and argumentative "all or nothing" decisions, such as determining whether or not a NOAEL was observed in a particular experimental dose or exposure category, and (5) a BMD estimate of the NOAEL can be determined even when effects are observed in the lowest experimental dose group or exposure category. The USEPA is currently giving serious consideration to utilization of the benchmark approach for setting reference concentrations (RfCs) and RfDs. In its "Interim Methods for Development of Inhalation Reference Concentrations" (USEPA, 1990), the USEPA stated "This novel method utilizes more of the available data than the current methodology ... It also addresses to some degree several of the criticisms of the current approach, such as the use of dose-response slopes and the number of animals tested in defining NOELs."

A study recently conducted for the USEPA (Faustman *et al.*, 1994) compared BMDs with traditionally-derived NOAELs for 424 sets of animal data. This study found

(Table 1) that BMDs based on an additional risk of 0.1 ($BMDL_{0.1}$) were smaller than the corresponding traditional NOAEL for more than 75% of the data sets and were less than the traditional NOAEL by an average factor of 2.9; BMDs based on an additional risk of 0.05 ($BMDL_{0.05}$) were smaller than the corresponding NOAEL for between 90% and 95% of the data sets and were less than the NOAEL by an average factor of 5.9; BMDs based on an additional risk of 0.01 ($BMDL_{0.01}$) were smaller than the corresponding NOAEL for more than 95% of the data sets and were less than the NOAEL by an

Table 1

Ratios of NOAEL to BMDL[a]

BR	Mean Ratio (± SD)	Percentiles of Ratios						
		5th	10th	25th	50th	75th	90th	95th
0.1	**2.9** (±3.9)	0.49	0.66	**1.1**	2.0	3.8	5.2	7.2
0.05	**5.9** (±8.4)	0.87	**1.1**	1.7	4.0	7.8	11	15
0.01	29 (±44)	2.2	2.9	6.6	19	40	56	80

[a] 95% lower statistical confidence bounds on lifetime dose corresponding to given level of additional risk (BR). Source: Faustman *et al.* (1994).

average factor of 29. Based on this analysis, use of 0.1 additional risk appears to provide a BMDL that corresponds more closely to a traditional NOAEL than use of 0.05 or 0.01. BMDs corresponding to an additional risk of 0.1 also have the advantage that they are likely to be less dependent upon the dose-response model than BMDs corresponding to additional risk of 0.01 or 0.05 (Crump, 1984). The analyses summarized in Table 1 suggest that use of a 0.1 additional risk would increase the conservatism in the determination of RfCs and RfDs by a factor of about 2 to 3 (i.e., would decrease RfCs and RfDs by a factor of 2 to 3 on average) as compared to the traditional NOAEL approach. In this analysis, benchmark risks (BR) of both 0.05 and 0.1 were calculated to evaluate the sensitivity of the predicted NOAEL to the selection of benchmark risk.

An additional consideration in the application of the BMD methodology to continuous data, such as the test scores in the New Zealand study, is the estimation of P_0, the proportion of persons in the control group assumed to be deficient (Crump, 1994). The most commonly used value of P_0 is 0.05 (5% of controls deficient). In this analysis, both 0.05 and 0.01 (1% of controls deficient) were used as values for P_0 to evaluate the sensitivity of the predicted NOAEL to the selection of P_0. The dose-response model used in this analysis was: $\mu(d) = \mu_0 + \beta d^k$ where $\mu(d)$ is the mean of the responses associated with a specific dose, d, μ_0 is the mean of the responses for the controls, and β and k are the estimated parameters. The responses modelled were either the test scores or the logarithm of the scores, depending upon whether the scores were better described by a normal or lognormal distribution. In either case the responses were assumed to be normally distributed with standard deviation σ (independent of dose). Using this model, a P_0 of 0.01 and a BR of 0.1 is equivalent to defining the BMD as the dose that results in a 10% change in the mean response relative to the standard deviation (i.e., as the dose that satisfies $| \mu(d) - \mu_0 | / \sigma = 0.1$).

The BMD analysis was performed on all of the tests included in the New Zealand study (Kjelstrom *et al.*, 1989): clay diagnostic survey, Burt word recognition test, key math diagnostic arithmetic test; test of language development [(TOLD), grammar understanding, oral vocabulary, picture vocabulary, sentence imitation, spoken language quotient]; Peabody picture vocabulary test (1981 version); McCarthy scales of children's abilities (verbal, perceptual, quantitative, general cognitive, memory, motoric); McCarthy scales of children's abilities; Wechsler intelligence scale for children [(WISC-R, revised) (verbal, performance)]; and Everts behavior rating scale.

4. Results and Discussion

The results of the analysis are shown in Table 2. In this table, the range of BMDs and BMDLs obtained across the various tests used in the epidemiological study are shown for four different combinations of the model parameters P_0 and BR. Depending on the values selected for P_0 and BR, the BMD analysis suggests that the NOAEL for the most sensitive indicator of developmental effects occurs at approximately 10–31 ppm Hg in maternal hair, with a preferred estimate (for BR = 0.1 and P_0 = 0.05) of 17 ppm. The most sensitive indicator of effects (i.e., the test producing the lowest BMDLs) was the TOLD grammar understanding test, while the least sensitive was the Peabody picture vocabulary test. Analysis with the PBPK model described above indicates that fetal brain concentrations of MeHg associated with the above NOAEL are on the order of 50 ppb (μg/L), and result from a maternal dietary intake of MeHg in the range of 0.8 to 2.5 μg/kg/day. The range of the intakes corresponding to hair concentration reflects the high degree of variability of hair-to-intake ratios seen in human studies. The NOAEL derived from the New Zealand study is somewhat higher than that previously derived from the Iraqi study, particularly since the maternal hair level derived from the New Zealand study is representative of a NOAEL, rather than a LOAEL, as was assumed for the Iraqi analysis (Stern, 1993). However, given the superior features of the New Zealand study compared to the Iraqi study, these results should provide a more accurate estimate of an RfD for chronic exposure to MeHg in the diet. In particular, these results do not support the suggestion which has been previously made (Stern, 1993) that the current USEPA RfD for MeHg of 0.3 μg/kg/day needs to be reduced to be adequately protective against developmental effects.

Future efforts will focus on the use of the PBPK model to compare candidate measures of fetal exposure (e.g., concentration, area-under-the-curve, total incorporated Hg) with developmental effects across species and exposure durations. The PBPK model will also be used to examine animal and human fetal effects data for evidence of nonlinearities in dose-response. In particular, we will formally compare the Iraqi and New Zealand studies using the PBPK model and the BMD analysis. Another area of interest is to determine the extent of variation of key parameters (hair-to-blood ratio, enteric demethylation) due to racial, ethnic, and cultural differences. The PBPK model can then be used to determine the impact of racial, ethnic and cultural differences on the risk of developmental effects. The Benchmark analysis will also be expanded to incorporate covariates such as maternal age, smoking status, and ethnicity.

Table 2

Results of Benchmark Analysis

P0 Fraction of Unexposed Population Effected	BR Benchmark Risk Level	BMD Maximum Likelihood Estimate (range[a], ppm in maternal hair)	BMDL 95% Lower Bound (range[a], ppm in maternal hair)
0.01	0.10	61 - 379	31 - 90
0.01	0.05	43 - 347	22 - 64
0.05	0.10	34 - 7221	17 - 50
0.05	0.05	20 - 4364	10 - 30

[a] Range of values obtained over the various tests used in the epidemiological study.

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MASS BALANCE AND SYSTEMIC UPTAKE OF MERCURY RELEASED FROM DENTAL AMALGAM FILLINGS

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Abstract. The release of mercury (Hg) from dental amalgam fillings has been verified by several authors. In this study, the emission rate of Hg°-vapor from the oral cavity (O-Hg) and the urinary Hg-excretion rate (U-Hg) have been studied with 34 healthy individuals. In ten cases, the urinary excretions of silver (U-Ag) and the fecal excretions of Hg and Ag (F-Hg, F-Ag) were also monitored. All variables, except U-Ag, were significantly related to the load of amalgam. According to this study, an individual with a moderate load of amalgam, i.e. 30 restored surfaces, is predicted to exhibit the following emission rates: O-Hg=22, U-Hg=3, F-Hg=60 and F-Ag=27 μg/d (d=24 hours), consistent with a gross mass balance for Hg of approximately 60 μg/d. The corresponding systemic uptake of Hg was estimated to 12 μg/d based on external data relating air Hg°-exposures to urinary Hg-excretions. The worst case individual showed a gross mass balance of 200 μg Hg/d connected to a systemic uptake of 70 μg Hg/d. These values were compared to the average intake of total-Hg by a Swedish diet (2 μg/d) and to the WHO's tolerable value for intake of total-Hg by food (45 μg/d). Upscaled to the entire Swedish population (8 mill.), the data suggests a fecal/urinary emission to the environment of 100 kg Hg yearly originating from a population load of amalgam fillings containing 90,000 kg of Hg.

1. Introduction

Before the beginning of the 1980's, the stability of dental amalgam with respect to the release of mercury (Hg) was generally not very much questioned. The release of Hg from amalgam has, however, since then been described and verified by several authors (Aronsson, 1989; Berglund, 1988, 1990; Björkman, 1992; Brune, 1985; Frykholm, 1957; Jokstad, 1992; Patterson, 1985; Pleva, 1992; Skare, 1994; Svare, 1981; WHO, 1991; Vimy, 1985a, 1985b).

For individuals with a moderate load of amalgam, i.e. approximately 30 restored surfaces, a basic release rate of elemental Hg° from the oral cavity of 20 μg/d (d=24 hours) is normally averaged, reaching about 100 μg Hg°/d for such individuals most heavily loaded. By chewing and by drinking hot beverages the Hg°-emission may temporarily be increased by three to tenfold.

One part of the released elemental Hg° is exhaled, and one part is retained in the saliva and swallowed together with amalgam particles and corrosion products, giving a gastrointestinal inorganic-Hg flow from which, however, only a smaller fraction is supposed to be systemically absorbed (WHO, 1991).

The remaining part of the released Hg° should be systemically absorbed through the lungs or by resorption through the oral mucosa. Being uncharged and monoatomic, elemental Hg° is a highly mobile species capable of entering most of the body compartments. The systemic uptake of Hg is, in addition to the present number of amalgam fillings, also influenced by the mean ratio of the oral-to-nasal breathing and to the actual chewing pattern.

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For risk assessment of a long-term inorganic-Hg exposure, biological monitoring of the urinary Hg-excretion is normally applied. Several authors have significantly related elevated urinary Hg-levels to the load of amalgam (Aronsson, 1989; Berglund, 1990; Jokstad, 1992; Langworth, 1991; Olstad, 1987; Skare, 1990, 1994; WHO, 1991; Åkesson, 1991).

Other common biological monitoring indices used are the total-Hg plasma concentration and the level of inorganic-Hg in whole blood - designed for minimizing the confounding influence from MeHg present in the blood. Some authors have used the blood matrix when studying the Hg-exposure from amalgam (Jokstad, 1992; Langworth, 1991; Snapp, 1989; Svare, 1981; Åkesson, 1991).- Only few studies have been published where the monitoring of fecal Hg-excretion is attentioned (Frykholm, 1957; Stock, 1934).

In the present study, *the gross mass flow balance of Hg* and *the systemic uptake of Hg* have been estimated for individuals with different load of amalgam fillings, based on data from the monitoring of oral air Hg-emissions and excretion rates of Hg/Ag by urine and feces. In addition, the Hg-excretion data has been upscaled to represent the entire Swedish population, thus obtaining an estimate of the Hg-emission from amalgam fillings to the sewage systems and to the environment.

2. Subjects and methods

2.1. TEST SUBJECTS AND MEASUREMENTS

Basic monitoring of the emissions of oral air Hg and urinary Hg were performed with 34 healthy adult individuals of both sexes, occupationally unexposed to Hg or Ag. In ten cases, the urinary excretions of silver (U-Ag) and the fecal excretions of Hg and Ag (F-Hg, F-Ag) were also monitored. The individuals were selected to represent a broad range in amalgam loading. None of them normally eat fish from lakes and none was a present smoker. The number of restored amalgam surfaces (N) was examined by a dentist.

2.2. ANALYTICAL METHODS

2.2.1. Elemental Mercury Vapor Emission into the Oral Cavity

As amalgam surfaces are very easily influenced by all kinds of mechanical and chemical actions, the oral environment should be properly normalized prior sampling. Two different methods for monitoring of the emisssion of oral air Hg° have been used in the study (Skare, 1994).

By one method, a well-defined flow of oral air (1.5 l/min) was continously sampled through a mouth-piece and passed into a gas cell of a UV-instrument until a steady-state reading was established, from which the oral emission rate of Hg° was calculated. The lowest quantifiable Hg° vapor concentration in the cell, i.e. 1 μg Hg°/m^3, corresponds to a oral Hg° emission rate of approximately 2 μg/d (d=24 hours).

The other oral air Hg°-method was based on the covering of all amalgam surfaces with a 25-ml portion of water for a fixed period of time (2.0 min) by that collecting all Hg°-vapor emitted into the aqueous phase. The content of total-Hg in the aqueous sample was determined, after a wet-digestion step at room temperature with an acidified potasssium permanganate ($KMnO_4$) solution, by using a standard cold AAS-technique (D.L.≈ 0.2 ng Hg/ml) implying a releasing step to Hg°-vapor by Sn[II]-reduction (Skare, 1972).

The detection limits, equal for the two oral air Hg°-methods, correspond to a Hg°-rate expected from 2-3 restored amalgam surfaces, i.e. 1-2 μg O-Hg/d.

2.2.2. Total Mercury and Silver Excretions by Urine

The individuals were requested to collect all their urine voided during a 24-hour period. Sub-samples were wet-digested at room temperature by the addition of an acidified $KMnO_4$-solution.

The total content of U-Hg was determined by using the standard cold AAS- technique. The detection limit, expressed as excretion rate, was on the average 0.2 μg U-Hg/d.

The total content of U-Ag was determined using a graphite furnace AAS- technique. The detection limit, expressed as excretion rate, was on the average 0.6 μg U-Ag/d.

2.2.3. Total Mercury and Silver Excretions by Feces

The individuals were requested to deliver two consequtive fecal voidings while recording the duration intervals. The contents of Hg and Ag in the samples were, after digestion with warm concentrated HNO_3, determined by using an ICP-technique (external laboratory). After relating the results to the sampling times, the results were converted to excretion rates for Hg and Ag (Skare, 1994).

The lowest quantifiable excretion rates were approximately 3 μg F-Hg/d and 0.8 μg F-Ag/d, respectively.

2.3. MASS BALANCE CALCULATIONS ON MERCURY

In estimating the total exposure from Hg, i.e. the gross balance of Hg passsing the body, for individuals occupationally unexposed to Hg, the following Hg-containing sources should initially be considered: air, food and water supply, and amalgam fillings.

Urban air may contain 5 ng $Hg°/m^3$. If the mean breathing rate during the day is limited to 15 l/min and an uptake efficiency of 80% is assumed, then, the contribution to the systemic Hg-uptake by breathing environmental air may not exceed 0.1 μg Hg/d.

The mean contribution of total-Hg from a Swedish dietary (for normal fish consumers) has recently been determined to approximately 2 μg Hg/d, about 2/3 of which are present as MeHg species (Becker, 1991). The systemic uptake of Hg from the intestines is considered to be 90% for MeHg and 5 to10% for inorganic Hg-species (WHO, 1991).

The purpose of monitoring the fecal Ag-excretion was the possibility to make an indirect estimation of the fraction of Hg contained in the released and swallowed particles and corrosion species. At time of insertion, amalgam restorations contain Hg and Ag in a ratio of approximately 1:0.7 by weight. If the composition of the surface layers is

assumed to be constant for years, a rough estimate of Hg contained in particles and corrosion products can be calculated from the F-Ag rate after correction for food-Ag in feces (obtained from the F-Ag excretion with the amalgam-free individual).

The estimation of the systemic uptake of Hg is a more elusive task. However, since the systemic input and output of Hg, at equilibrium, by definition is the same, the systemic uptake of Hg should be more adequately estimated by using urinary excretion data than by using data related to intake patterns.

After entering the blood, most of the body-burden of Hg (90%) is stored in the kidneys, the Hg-content of which is reflected by the U-Hg excretions. A minor part part of the systemic-Hg is expected to be stored in other tissues exhibiting very long halftimes for Hg-clearance (i.e. years), where the equilibrium is very slowly attained. This latter fraction is, however, not predictable from urinary data (WHO, 1991).

In equilibrium with a long-term inorganic Hg-exposure, the daily urinary Hg-excretion has been shown to be rather constant (Skare, 1994). By mathematical integration of the kidney-clearance decay curve to infinity, assuming $t_{1/2}$ = 45 days, a first order of kinetics and by using the monitored U-Hg rate as input data, the kidney-burden can be estimated by the equation:

$$\text{Kidney-burden } (\mu g \text{ Hg}) = \text{U-Hg}(\mu g/d) * 45(d) / \ln 2.$$

For example, an individual with a moderate load of amalgam, exhibiting at equilibrium a daily urinary excretion of 3 μg Hg should have a kidney-burden of approximately 200 μg Hg. Individuals, very heavily loaded with amalgam, may in extreme cases show urinary Hg-excretions (and kidney-burdens), which are tenfold higher.

The body-clearance of Hg is not accomplished only by urine but also by feces, sweat, exhalation and by storage in hair and nails. However, only the excretions by urine and feces are large enough to be considered. The fecal excretions contain Hg-species (maybe biotransformed), which partly have been swallowed and partly originate from Hg systemically absorbed and excreted through the bile.

To estimate the excretion rate of Hg through the bile, again, U-Hg excretion rate data might be helpful. Referring to the report by WHO 1991, an occupational air concentration of 25 μg Hg°/m^3 is, on group level, consistent with a urinary excretion of 45 μg U-Hg/d (≈30 μg U-Hg/g creatinine). As a daily 8-h Hg°-exposure is consistent with a systemic uptake of 175 μg Hg/d [calculation: 25(μg/m^3) * 18(l/min (worker)) * 8(h) * 60(min/d) * * 80%(retention efficiency)], the difference between this total-Hg uptake rate and the U-Hg rate (45 μg/d) should be the averaged bile-Hg rate.

If this relationship between the urinary and the bile Hg-excretion is also valid at lower levels of exposure, then an equation can be made up for estimating the total systemic uptake of Hg for individuals loaded with amalgam:

$$\Sigma \text{ Hg}_{\text{uptake}} (\mu g/d) = 4 * \text{U-Hg } (\mu g/d)$$

This formula is not inconsistent with results from human Hg°-exposure studies reported by Cherian, 1978.

3. Results and discussion

3.1. BIOLOGICAL MONITORING OF MERCURY AND SILVER

The results obtained from the ten individuals concerning oral air Hg°-emissions and urinary and fecal excretions of Hg and Ag are summarized in Table I.

As seen from Table I, the flow rates of Hg/Ag for the amalgam-free individual were, with one exception, i.e. U-Ag, very low compared to the corresponding rates for the nine amalgam loaded individuals. In spite of this group of nine individuals, on average, was somewhat heavier loaded with amalgam (mean: N=40 surfaces) than is normally expected from a Swedish middle-age group (i.e. N=30), the results still clearly indicate that man's exposures to total Hg and Ag predominatly originate from the presence of dental amalgam fillings.

TABLE I

Emission and excretion rates of Hg and Ag from individuals loaded with amalgam fillings (Data from ten individuals; Hg = mercury, Ag = silver and d = 24 hours)

Variable	Symbol	Amalgam loaded individuals		Control individual
		Md-value	Range	
Number of amalgam surfaces	N	40	18 - 82	0
Oral air Hg° emission	O-Hg	29 µg/d	20 - 124 µg/d	0 µg/d
Urinary Hg excretion	U-Hg	4.5 µg/d	1.8 - 19 µg/d	0.4 µg/d
Urinary Ag excretion	U-Ag	1.7 µg/d	1.4 - 6.0 µg/d	1.3 µg/d
Fecal Hg excretion	F-Hg	64 µg/d	27 - 190 µg/d	1 µg/d *
Fecal Ag excretion	F-Ag	33 µg/d	11 - 97 µg/d	4 µg/d *

* Mean value based on a homogenized sample from ten consecutive days

In this study, the emission rate of Hg°-vapor from the oral cavity has been determined by using two entirely different methods. The close accordance in the results by the two methods gives support for assuming the averaged O-Hg rates to be reliable. The method, in which only a simple water trap is used for sampling, might, because of simplicity, be the method choice for out-of-laboratory purposes. This does not say that the determination of the unstimulated O-Hg rate should be the most appropriate way in assessing an amalgam Hg-exposure.

According to several studies, urinary excretions do not often exceed 1 μg Hg/d for amalgam-free individuals occupationally unexposed to Hg. Our control individual did apply to this prediction. Urinary excretions, due to amalgam, exceeding 15 μg Hg/d are also rare. Our worst case individual, having 82 restored amalgam surfaces, many of which in a bad condition, showed a urinary excretion of 19 μg Hg/d.

The content of Hg in feces was about twice the content of Ag in feces. The extremely high coefficient of correlation for F-Hg *vs* F-Ag (Table II) should be a strong evidence for the fecal Hg-excretions being connected to the bearing of dental silver-amalgam. For individuals with a moderate load of amalgam (N=30 surfaces), their fecal Hg-excretion rate was predicted to be about 20 times the urinary Hg-excretion rate and about 30 times the total-Hg intake by food (2 μg Hg/d) consuming an average Swedish diet. This food-Hg value, reported by Becker and Kumpulainen 1991, was consistent with the fecal Hg-excretion value exhibited by the amalgam-free control individual.

TABLE II

Correlation coefficients (Pearson, r) among N, O-Hg, U-Hg, U-Ag, F-Hg and F-Ag
See Table I for explanation of symbols. The number of observations (n) used and the adherent statistical p-values are also displayed

	N	O-Hg	U-Hg	U-Ag	F-Hg	F-Ag
O-Hg	r= 0.82 p< 0.0001 n = 34	--				
U-Hg	r= 0.80 p < 0.0001 n = 34	r= 0.91 p < 0.0001 n = 34	--			
U-Ag	r= - 0.20 p = 0.59 n = 10	r= - 0.23 p = 0.53 n = 10	r= - 0.23 p = 0.53 n = 10	--		
F-Hg	r= 0.67 p = 0.033 n = 10	r= 0.85 p = 0.001 n = 10	r= 0.81 p = 0.003 n = 10	r= 0.12 p = 0.75 n = 10	--	
F-Ag	r= 0.74 p = 0.02 n = 9	r= 0.93 p< 0.0001 n = 9	r= 0.90 p = 0.0003 n = 9	r= 0.16 p = 0.69 n = 9	r= 0.97 p < 0.0001 n = 9	--

Referring to Table II, significant levels of interplay were, excl. U-Ag, seen among all the emission/excretion variables and the number of amalgam surfaces. The deviating behavior of the U-Ag variable, e.g. no significant correlation to N, indicates that Ag from amalgam is not, or only to a very low extent, systemically absorbed.

The following linear regression line equations have been calculated:

O-Hg = 0.1 + 0.73 * **N**; (based on 34 observations)
U-Hg = 0.4 + 0.08 * **N**; (based on 34 observations)
F-Hg = 15 + 1.45 * **N**; (based on 10 observations)
F-Ag = 4 + 0.77 * **N**; (based on 9 observations)

3.2. MASS BALANCE CALCULATIONS ON MERCURY

3.2.1. Gross mass balance of Hg

After a long-term Hg-exposure, the input and output flows of Hg should, at equilibrium equalize. The two main pathways for man's excretion of inorganic Hg are through urine and feces. Thus, a satisfactory estimate of the mean daily input of total-Hg should be the sum of the daily U-Hg and the F-Hg excretion rates. With a load of amalgam scored to be 30 restored surfaces, i.e. the average load of amalgam for middle-age people in Sweden, the predicted excretion rates (see regression equations above) should make up a gross mass balance being approximately 60 μg Hg/d.

In Figure 1, the intake, uptake and excretion flows of Hg for this average individual are outlined. As seen from Figure 1, the intake of amalgam-Hg is the most dominant origin to the Hg-exposure.

The elimination of all amalgam fillings should result in a very rapid decay of the F-Hg rate level. The U-Hg rate and some part of the bile-Hg rate, both reflecting the body-burden of Hg, should decline more slowly, i.e. during months.

The fecal Hg-excretions may consist of Hg-species as amalgam particles, corrosion products (oxidized Hg), bile-Hg (probably Hg connected to SH-groups in low-molecular weight proteins), biotransformed MeHg from food (mineralized by bacterial action) and species originating from the swallowing of elemental Hg°-vapor with the saliva. Some of these Hg-species may have passed the gastro-intestinal tract without any interactions at all, whereas other Hg-species have had a systemic past.

Upscaled to the entire Swedish population (8.5 mill.), the fecal-urinary excretions contain about 100 kg Hg/year originating from a population load of dental amalgam restorations containing approximately 90,000 kg of Hg.

3.2.2. Systemic uptake of Hg

The systemic uptake for an individual moderate loaded with amalgam (N=30 surfaces) has here been calculated to 12 μg Hg/d based on urinary excretion data and assumptions concerning the relationship between air-Hg° exposure and U-Hg data (see 2.3). This amalgam Hg-exposure should be equivalent to a daily 8-hour occupational Hg°-exposure of 2 μg Hg°/m^3, and corresponds to a total body-burden of 200 to 250 μg Hg.

Our worst case individual was suggested to exhibit a systemic uptake of 70 μg Hg/d, which value might be compared to a food standard by WHO stating the daily "tolerable" intake of total-Hg and MeHg should not exceed 45 and 30 μg Hg/d, respectively (WHO, 1972). The "acceptable" intake should be *none* according to the same report.

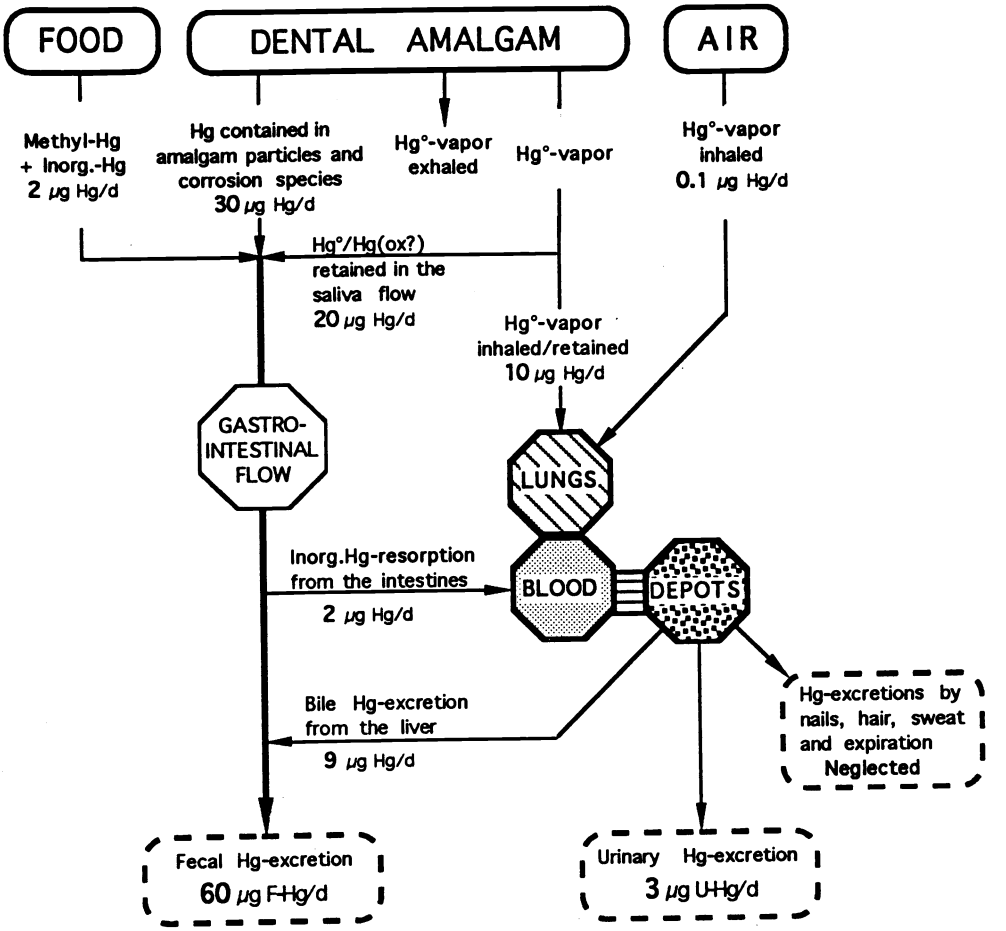

Figure 1. Flow chart exhibiting the intake, uptake and excretions of Hg originating from environmental air, food and dental amalgam.. Applicable to individuals with a moderate load of amalgam , i.e. 30 surfaces.

(For lucidity, the enterohepatic recirculation of MeHg is not outlined)

4. Conclusions

The study has confirmed that human emissions of oral air Hg° and excretions of urinary Hg are significantly related to the present load of dental amalgam fillings. In addition, even the fecal excretions of Hg and Ag were shown to exhibit a significant relationship to the number of amalgam fillings.

For an individual with a moderate load of amalgam, the predominating part of the gross mass balance of Hg originates from the fillings. At comparison, a normal contribution to the Hg-exposure from air, water and food should be neglectable.

The daily systemic absorption of Hg was, for individuals heavily loaded with amalgam, predicted to be close to or even exceeding the WHO´s recommendation for "tolerable" intake of total-Hg by food.

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MERCURY CONTAMINATION OF FISH IN THE OJIBWA DIET: I. WALLEYE FILLETS AND SKIN-ON VERSUS SKIN-OFF SAMPLING

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Abstract. During the past two years, walleye (Stizostedion vitreum) have been collected and prepared into skin-off fillets and submitted for total mercury analysis. The survey included 105 fish from 18 lakes in 10 counties in northern Wisconsin and the upper peninsula of Michigan. Fourteen lakes yielded walleye fillets with greater than 0.5 ppm mercury, and six lakes yielded samples in excess of 1.0 ppm mercury. Fourteen fish were collected in the spring and prepared as fillets ground up as either skin-on or skin-off samples. The difference in Hg was significant (T_M=-3.26,p=0.006) with skin-on fillets, resulting in an approximately 10% decrease in mercury concentrations. Results of this study suggest that by leaving the skin on the sample, mercury concentrations will be reported 10% lower than if the skin is removed. Obviously, consumption advisories based on skin-off samples could provide more protection for Ojibwa people eating the spring harvest of walleye. In the fall, the difference in Hg samples between skin-on versus skin-off, was less and not statistically significant. However, removal of the skin would be expected to underestimate lipophilic organochlorine burdens and may not be appropriate for fish species where PCBs, DDT, and chlordanes are the major concern. Fall data for 67 fish from 26 lakes in 9 counties are also reported.

1. Introduction

The Lake Superior region Ojibwa tribes of Wisconsin in the United States have a long history of utilizing walleye taken with spears during the spring as a major part of their diets. During the past four years, walleye (Stizostedion vitreum) have been collected and prepared into fillets and submitted for total mercury analysis. Eighty-three fish from 11 counties (with 5 counties resurveyed herein) were collected during the 1990 and 1991 spear fishing seasons, and the results were reported earlier (Gerstenberger et al., 1993). Nearly half of the walleye samples from the lakes exceeded the fish consumption advisory of 0.5 ppm set by the Wisconsin Department of Natural Resources (WDNR, 1993). Therefore, we concluded that precautions should be taken when consuming fish on a regular basis, and extra caution taken for pregnant women and children as mercury is particularly toxic to the developing fetus and nursing infants.

Mercury (Hg) occurs naturally, and anthropogenic activities increase the environmental loading. Anthropogenic activities include: burning fossil fuels, municipal incineration, industrial activities, and the agricultural use of mercuric compounds. Once the mercury is in the environment, alkylation results in the conversion of inorganic mercury to the more toxic organic forms of mercury such as methylmercury (Huckabee et al., 1978). Methylmercury bioaccumulates in the fish and the predatory fish such as walleye biomagnify methylmercury to significant concentrations. The mercury contaminated fish constitute the most significant route of exposure to environmental mercury for humans (Inskip et al., 1985). Numerous tribal, state, and federal agencies collect fish for contaminant analyses and risk assessments, but rarely have those results been published in the open literature. This paper provides some of the data for scientists to use.

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Furthermore, some questions have surfaced regarding using fillet samples ground up with the skin on versus those with the skin off for contaminant analysis. Many lipophilic environmental contaminants are known to bioaccumulate in the subcutaneous adipose tissue. Therefore, typically most agencies prefer to analyze skin-on fillets to not underestimate the lipophilic contaminants such as the organochlorine pesticides. Fish consumption health advisories routinely advise anglers to trim away skin and adipose tissue to minimize contaminant exposures. However, mercury accumulates in the muscle and trimming skin and fat do not significantly lessen exposures (WDNR, 1993). Testing skin-on walleye fillets that are usually consumed by tribal members as skin-off fillets may therefore underestimate the actual risks associated with consuming those fish.

The present survey expands the reported mercury contaminant data base to a total of 188 fish from 20 lakes in 15 counties in northern Wisconsin and the upper peninsula of Michigan. Furthermore, this paper provides a comparison of the Hg concentrations in skin-on and skin-off walleye fillets. The skin-on versus skin-off sampling may vary from season to season. In this survey, samples were taken from the same lakes in both the spring and the fall. Traditionally, tribal members harvest spawning walleye over a 3-4 week period in the spring using spear fishing techniques. The season for sport anglers begins the first week in May, and fish are caught throughout the open water months. Sample preparation and season of collection may be important factors when developing risk management decisions for tribal versus non-tribal walleye fishing. The purpose of this paper is to consider the risks for tribal members catching fish in the spring spear fishing season.

2. Materials and Methods

During 1992 and 1993, 105 walleye samples were collected during the spring spear fishing season and submitted by Great Lakes Indian Fish and Wildlife Commission (GLIFWC) personnel for total mercury analyses. During the 1993 season, GLIFWC and the U.S. Fish and Wildlife Service (USFWS) collected the majority of the samples using electrofishing. Fourteen of the electroshocked fish were split into skin-on versus skin-off fillets samples. All samples were frozen at -20^{0}C, until analyzed for total mercury. During the fall of 1993, 18 additional fish were taken from the same four lakes and split into skin-on versus skin-off fillets. Fish length, weight, and collection locations were recorded by the GLIFWC staff.

Fillets were cut into small samples and then ground using a commercial meat grinder. The grinder attachment was washed with soap and water, rinsed with tap water, rinsed with dilute (0.1M) hydrochloric acid, and rinsed with deionized water before use and between samples. The first few grams of each sample were discarded as waste, and the rest of the ground sample was collected in an acid-washed beaker. The sample was passed through the grinder a second time, collected in an acid washed beaker, and then thoroughly mixed with a stainless steel spatula. This homogeneous walleye sample was placed in an acid-washed glass bottle and returned to the freezer for subsequent analysis. To insure that the grinding process was not contributing Hg to the samples, a grinder blank was also analyzed using commercially purchased ground beef as described in Gerstenberger et al. (1993).

The sample preparation and mercury analysis was completed according to the cold vapor atomic absorption method of Hatch and Ott (1968) and the specific steps described

earlier (Gerstenberger, et al. 1993). Briefly, each sample was digested (heated at 80-90°C) using concentrated nitric and sulfuric acids, potassium permanganate, and potassium persulfate as oxidants. Mercury vapor was volatilized following the addition of hydroxylamine hydrochloride and stannous chloride to the sample solution. Nitrogen gas was used to carry the mercury vapor through the atomic absorption detector (253.7 nm), and the peak absorbance was measured to determine the ug of Hg per gram (ug/g) of fish tissue (part per million (ppm) wet weight). A mercury analysis quality assurance program with the government of Canada provided an opportunity for 27 labs to analyze samples for Hg and compare their data. As a participator our laboratory consistently provided data within two standard deviations of the target values and met their performance standards.

Statistical analysis was performed with SAS Institute programs on a personal computer. The hypotheses tested were: skin-on versus skin-off (paired T-test), spring versus fall (ANOVA), and the length versus mercury concentrations by lake (multiple regression). Length and location were considered as main factors, and Type I sums of squares correcting for these effects were used prior to testing for the skin-on versus skin-off effect with a $p<0.05$ being used to indicate statistical significance.

3. Results and Discussion

The 105 fish ranged in length from 12.4 to 27.0 inches (mean 18.1 inches) [31.5 to 68.6 cm (mean 46.0 cm)] and in mercury concentrations from 0.14 to 1.97 ug/g (mean 0.59). This sample of 105 fish may not be representative of speared fish, because the average length recorded by GLIFWC in 1992 and 1993 was much less (15.1 and 15.2, respectively). During the 1993 spring season, the number of harvested fish expected to produce Hg concentrations greater than 0.5 ug/g were determined by GLIFWC for 108 of the 130 speared lakes. Based on this analysis, 8% (1,398 of 17,938 fish) would have been over 0.5 ug/g.

Fish length, lake of origin, and the interaction between length of fish and lake concentrations were tested in the General Linear Model ANOVA for predicting mercury concentrations. The interaction between length of fish and lake was not significant ($F_{(17,104)}=1.38;p<0.17$) indicating that sizes of fish collected at different lakes was *not* a significant factor. Using the Type I sums of squares to first account for fish length ($F_{(1,104)}=98.86;p<.0001$) and then examine lake of origin ($F_{(17,104)}=20.81;p<.0001$), both effects *are necessary* to predict mercury concentrations with an R^2 of 87% ($F_{(35,104)}=13.60;p<.0001$)).

These effects can be depicted graphically by plotting length versus mercury concentrations (Figure 1). Most officials base risk management calculations on a linear relationship between fish length and mercury concentrations, and the multiple regression model above used general linear models to test for length. However, a quadratic or second order curved line would be expected to fit the data more closely. Figure 1 graphically depicts a second order regression for length versus mercury concentrations for all lakes and data. All 105 data points are listed without reference to location, and obviously, many of the data points are not near the regression line *even with the second order curve*. Therefore, the length of fish alone cannot be used to predict the mercury concentrations in the fillets. The geographical information (lake) is important for predicting mercury concentrations, and a spearer must consider the lake as well as the length of fish in order to avoid excessive dietary mercury. In addition, the mercury accumulation in fish will also depend upon other chemical parameters of each particular lake.

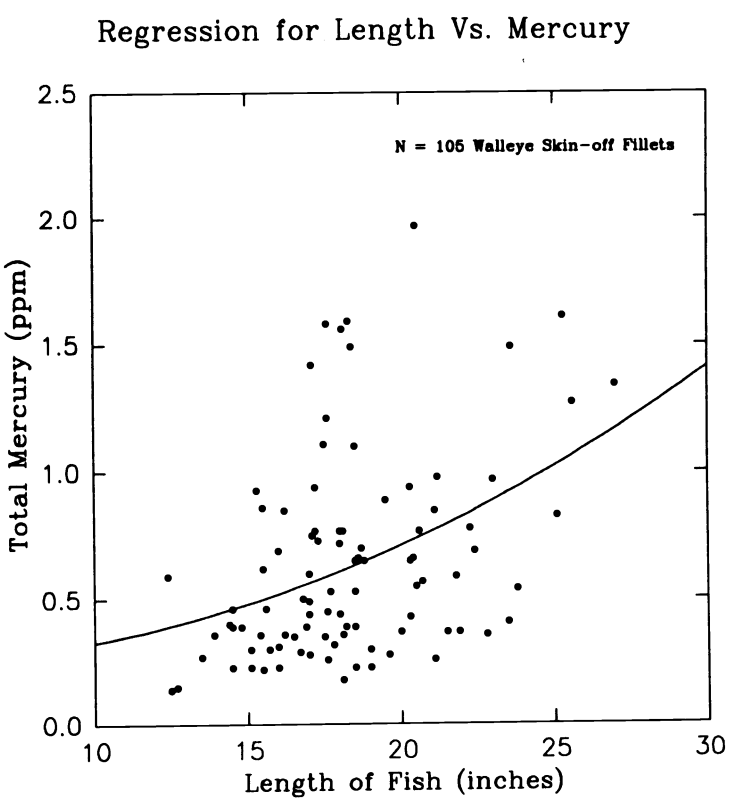

Fig. 1. Quadratic regression using length of fish to predict total mercury.

Table I provides the average lengths, mercury concentrations (skin-off samples only) for the spring data during the 1992 and 1993 by lake and county. Table I also provides the incidence of the number of fish in health advisory categories (less than 0.5 ppm, greater than 1.0 ppm, etc.) for Wisconsin (WDNR, 1993). This table can be used to obtain a general idea of the relative mercury contamination by lake. For example, looking only at those lakes with an average sample of approximately 18 inches (45.7 cm), some differences are obvious. Lac Courte Oreilles (LCO) lake in Sawyer County had an average concentration of 0.27 ug/g whereas Kentuck lake in Vilas County was 0.63 ug/g. However, there is even a more dramatic difference depicted by comparing LCO to Lake Minnesuing in Douglas County which with an average length of 17.9 inches (45.5 cm) had a mean mercury concentration of 1.48 ug/g. Obviously, tribal members have a lower relative risk when harvesting fish from LCO rather than Lake Minnesuing.

Table I
Incidence and mercury concentrations in skin-off walleye sampled by GLIFWC during spring of 1992 and 1993

County	Lake	Area (Acres)	Sample Size	Average Length (Inches)	Average Hg (ug/g)	Incidence/Group*: 1	2	3	4
Bayfield	Namekagon L	3227	7	18.0	0.49	4	2	1	
Douglas	L Minnesuing	432	6	17.9	1.48				6
Forest	Butternut L	1292	5	16.6	0.29	5			
Gogebic	Cisco L	506	7	19.3	0.48	5	1		1
Gogebic	Thousand Island L	1020	7	18.5	0.68	2	2	2	1
Marinette	High Falls Reservoir	1498	5	19.2	1.28			2	3
Oneida	Indian L	397	7	19.9	0.34	7			
Oneida	Squirrel L	1317	3	20.7	0.66	1		2	
Polk	Pipe L	270	3	17.3	0.93		1	1	1
Sawyer	Lac Courte Oreilles	5039	7	18.4	0.27	7			
Sawyer	Nelson L	2503	7	18.0	0.50	5	1	1	
Sawyer	Sissabagama L	719	7	16.0	0.31	6	1		
Vilas	Big St Germain L	1617	3	16.8	0.23	3			
Vilas	Harris L	507	8	18.2	0.62	4	3		1
Vilas	Kentuck L	957	7	18.0	0.63	1	5	1	
Vilas	Squaw L	785	5	16.3	0.77		2	3	
Vilas	Tenderfoot L	437	5	18.2	0.53	3		2	
Washburn	L Nancy	772	6	18.4	0.53	3	2	1	
		Total:	105			56	20	16	13
		Average:	6	18.1	0.61	4	2	2	2

*Group 1. Number of fish with total mercury less than 0.50 ppm (ug/g).
*Group 2. Number of fish with total mercury 0.50 - 0.74.
*Group 3. Number of fish with total mercury 0.75 - 0.99.
*Group 4. Number of fish with total mercury >= 1.00.

Fourteen fish were prepared as skin-on versus skin-off fillets following the spring 1993 harvest (Figure 2.a.). The difference was significant (T_{14}=-3.26,p=0.006) with skin-on fillets resulting in an approximately 10% decrease in mercury concentrations. Therefore, the results of this study suggests that by leaving the skin-on the sample, mercury concentrations will be reported 10% lower than if the skin is removed. Obviously, using skin-off fillets may be preferable for mercury determinations aimed at protection the health of the Ojibwa eating the spring walleye. In the fall, 18 fish were sampled from the same lakes, and the difference between skin-on versus skin-off was not statistically significant (Figure 2.b.). The lesser difference between skin-on and skin-off fillets in the fall may be a function of the decreased ratio of muscle to body mass as the fish accumulate adipose tissue over the summer. This portion of the study should be repeated including lipid analyses of the fillets.

On the other hand, state officials may wish to continue assessments in the late summer and fall, when non-tribal sport anglers also catch walleye, and the effect of leaving the skin on or removing it may not be significant. Also, it is important to remember that the removal of the skin would be expected to underestimate lipophilic organochlorine burdens and may not be appropriate for fish species and health advisories when polychlorinated biphenyls or other organochlorines are the major concern.

Table II provides fall assessment data for 26 lakes in 9 counties. These data are provided for comparison purposes. If there is a seasonal difference, Table II data are more valuable to the non-tribal anglers. These are not necessarily the same lakes that were surveyed in the spring, and therefore, direct comparisons are difficult.

Table II
Incidence and mercury concentrations in skin-off walleye sampled by GLIFWC during fall of 1992 and 1993

County	Lake	Area (Acres)	Sample Size	Average Length (Inches)	Average Hg (ug/g)	Incidence/Group*: 1	2	3	4
Burnett	Big Mckenzie L	1185	3	20.3	0.38	2	1		
Florence	Keyes L	202	1	15.4	0.13	1			
Florence	Patten L	255	2	18.1	0.41	2			
Forest	Butternut L	1292	4	15.9	0.16	4			
Oneida	Big Stone L	548	1	17.3	0.77			1	
Oneida	Booth L	207	3	20.0	0.44	2	1		
Oneida	Buckskin L	634	3	19.6	0.54	1	2		
Oneida	Julia L	401	3	20.8	1.07		1		2
Oneida	Laurel L	232	2	18.9	0.64		2		
Oneida	Planting Ground L	1012	2	19.8	0.67	1		1	
Oneida	Squirrel L	1317	6	16.1	0.24	6			
Polk	Big Butternut L	378	1	16.7	0.12	1			
Polk	Pipe L	270	2	17.4	0.58		2		
Sawyer	Whitefish L	786	3	19.9	0.56	1	2		
St Croix	Cedar L	1107	2	18.2	0.13	2			
Vilas	Big St Germain L	1617	3	16.4	0.31	2	1		
Vilas	Eagle L	572	2	18.4	0.44	1	1		
Vilas	Fawn L	74	2	17.8	0.39	1	1		
Vilas	Harris L	507	3	19.8	0.57	1	1	1	
Vilas	Kentuck L	957	3	17.1	0.42	2	1		
Vilas	Little Star L	244	2	17.1	0.30	2			
Vilas	Spider L	272	2	18.0	0.42	1	1		
Vilas	Squaw L	785	5	14.2	0.53	1	4		
Vilas	Tenderfoot L	437	3	20.4	0.37	2	1		
Washburn	L Nancy	772	2	18.1	0.60	1		1	
Washburn	Middle Mckenzie L	530	2	17.4	0.24	2			
		Total:	67			39	22	4	2
		Average:	3	18.0	0.44	2	1	1	2

*Group 1. Number of fish with total mercury less than 0.50 ppm (ug/g).
*Group 2. Number of fish with total mercury 0.50 - 0.74.
*Group 3. Number of fish with total mercury 0.75 - 0.99.
*Group 4. Number of fish with total mercury >= 1.00.

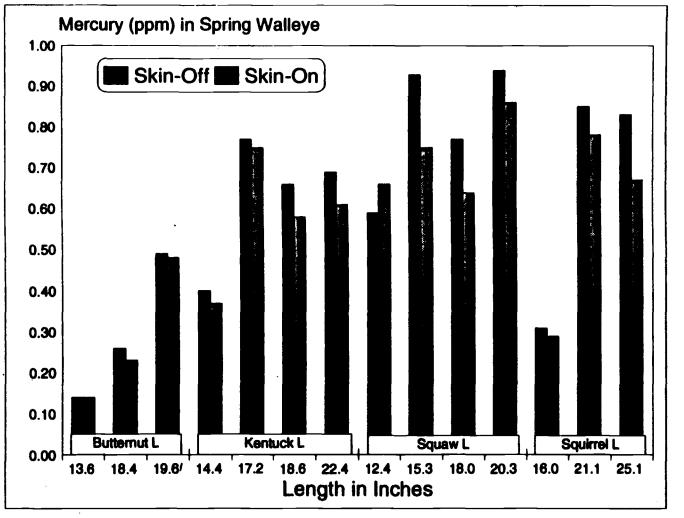

Fig. 2.a. Mercury concentrations versus length comparing skin-on to skin-off fillets (Spring).

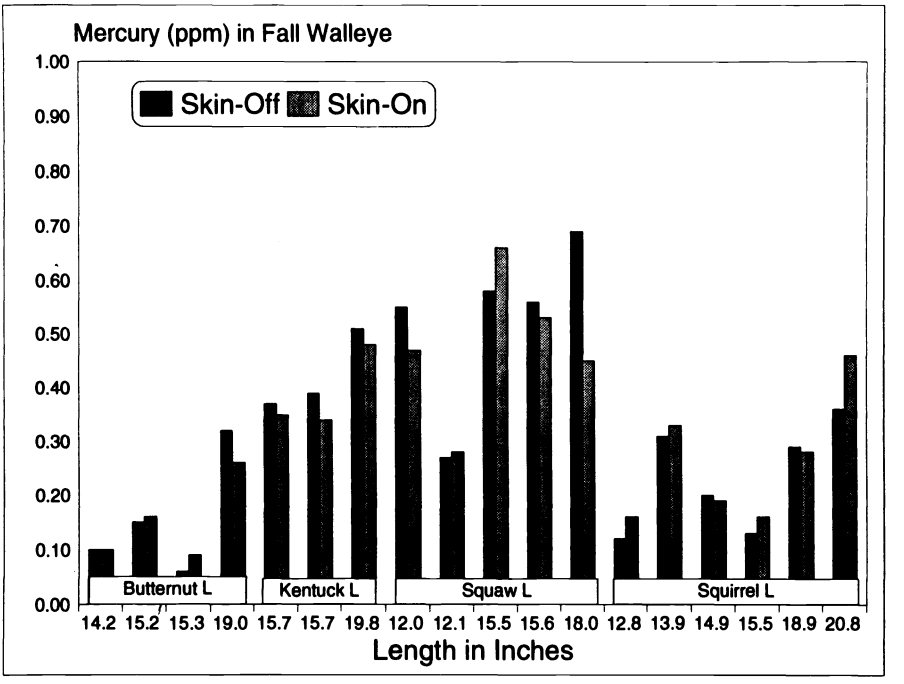

Fig. 2.b. Mercury concentrations versus length comparing skin-on to skin-off fillets (Fall).

4. Conclusion

Many lakes in northern Wisconsin and the upper peninsula of Michigan contain walleye contaminated with mercury at concentrations above the 0.5 ppm Wisconsin advisory action level (WDNR, 1993). Therefore, Ojibwa harvesting walleye in the spring should consult the appropriate health advisories, but they should realize that the advisories may not be strict enough.

Tribal members should realize that during the spear fishing season the spring walleye may have higher mercury concentrations than the state data suggests. Furthermore, the health advisory and mercury data used to construct that advisory are based upon skin-on walleye fillets, and since the skin is not normally consumed by the tribal members, results of this study suggests that their intake of mercury from fillets may be 10% higher than the assumptions used to construct the advisories.

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MERCURY CONTAMINATION OF FISH IN THE OJIBWA DIET: II. SENSORY EVOKED RESPONSES IN RATS FED WALLEYE

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Abstract. The Ojibwa people of the upper Great Lakes in the United States have a long history of utilizing walleye caught by spear fishing as a major part of their diets. Walleye (Stizostedion vitreum) have been collected and prepared into fillets using traditional methods, submitted for total mercury (Hg) analysis, and fed to laboratory rats in standard neurotoxicity protocols to determine the human health risks associated with consuming these fish. Wisconsin officials recommend avoiding the consumption of fish containing more than 0.5 ppm Hg. Laboratory rodent neurotoxicity bioassays included blending composite fish samples of 0.8, 0.4, and 0.2 ppm total mercury and feeding it to 48 young adult female Long Evans rats for 90 days. Standard behavioral assessments included: clinical neurologic observations, motor activity, and accelerating rotarod. Twelve of the 48 rats were surgically implanted for electrodiagnostic evaluations using sensory evoked potentials with auditory and visual stimuli. Auditory (clicks) responses were relatively stable and unaffected by Hg laden diets. However, visual evoked responses at low flash intensities demonstrated a dose related slowing of brain visual processing activity. Methylmercury contamination is known to affect visual systems, and visual evoked brain potentials are apparently sensitive indicators of dietary Hg.

1. Introduction

The Native American Ojibwa people of the Great Lakes in the United States have been dependent upon fish for food and as a commodity for many generations. Due to this dependence they are at a high risk for exposure to toxic chemicals especially methylmercury (MeHg) and polychlorinated biphenyls (PCBs) which are common environmental contaminants of the Great Lakes. The inland lakes are annually harvested by the Ojibwa people using spear fishing techniques. The fish in these lakes are predominantly contaminated with mercury (Hg) (Gerstenberger et al., 1993).

Both MeHg and PCBs are known neurobehavioral toxicants to laboratory animals and humans (Evans et al., 1975; Flint and Vena, 1991). Neurobehavioral effects have been observed in rodents fed a diet of Lake Ontario salmon contaminated with PCB's. Effects included reduced activity and decreased rearing and nose-poke behavior in comparison with controls (Hertzler, 1990). In the presence of a mildly negative stimuli, rats fed salmon from Lake Ontario displayed greater reactions to the events than controls (Daly, 1992). These studies demonstrated the usefulness of the rodent model for fish contaminant feeding studies.

Methylmercury is a classic developmental neurotoxicant, and recently Burbacher et al. (1990) reviewed the literature and concluded that the effects of MeHg are relatively consistent across species, including humans, and that specific sensory deficits, primarily visual, are well documented. Methylmercury is the neurotoxic form of Hg that bioaccumulates in fish and biomagnifies in aquatic food chains, and nearly all of the total Hg in fish tissues is in the form of MeHg. Recently, Grandjean et al. (1994) studied human milk as a source of MeHg exposure to infants in the fishing communities of the Faroe Islands, and they concluded that the breast-fed island infants may be at increased risk of developing MeHg toxicity. The Ojibwa people eat relatively large amounts of fish and are also a population at risk.

Water, Air, and Soil Pollution **80**: 77–83, 1995.

Mercury contaminated walleye diets from Lake Superior (Red Cliff fish in Table I), fed to adult rats for 90 days and perinatally to dams in a developmental protocol, resulted in behavioral alterations that, similar to Daly's observations, could be classified as adverse reactions to negative stimuli (GLPF, 1993). By measuring performance (time) on an accelerating rotating rod, we found that perinatally exposed offspring worked much harder to avoid the mild shock. Furthermore, the adult walleye-fed rats were poorer accelerod performers and more affected by a d-amphetamine pharmacologic challenge (GLPF, 1993). The diets of these rats were also contaminated with significant amounts of PCBs (Table I).

TABLE I
Composite Walleye samples

Lake(s) Sampled	Total Mercury (ppm)	Polychlorinated Biphenyls (ppb)	Other Organochlorines (ppb)	Comments
Siskiwit/ Lyman	0.79	9.2	4.8	"0.8"
Big Fork/ Namekagon	0.42	16.1	21.1	"0.4"
Nipigon	0.19	--	--	"0.2"
Red Cliff	0.58	193.3	42.0	GLPF, 1993
Bad River	0.46	64.7	38.6	WADRC, 1993

Because sensory deficits result from MeHg exposures, we sought methods to quantify those deficits in the visual system. One can record the specific responses over the brain cortex corresponding to flashes of light to identify very specific peaks in the electrical activity of the brain. As proposed by Mattsson et al. (1992), these sensory evoked potentials (SEPs) have recently become an accepted method in neurotoxicology for evaluating the safety of chemicals. The evoked responses or SEPs provide very stable electrodiagnostic indicators of the integrity of the nervous system being tested. The SEPs can provide some indication of the locus of damage, but the signals should not be interpreted as being direct recordings from specific brain sites. SEPs can be elicited using somatosensory, auditory, or visual stimulation. SEPs have been widely used in human neurology and laboratory animal studies (Dyer, 1985), and now they are becoming more accepted for use in toxicology.

Therefore, the present study examines inland lake (non-Great Lakes) walleye which are predominantly MeHg contaminated ("0.8" and "0.4" composite samples in Table I) to determine if the earlier behavioral effects could be explained on the basis of MeHg contamination. Next, to look for specific sensory deficits in the walleye-fed rats, we used auditory and visual SEPs to further investigate any neurotoxic consequences of MeHg contamination in the adult rat diet.

2. Materials and Methods

Walleye were collected during the Wisconsin 1993 spear fishing season by Ojibwa tribal members. These fish were then fed to 48 young adult Hooded Long Evans (HLE) female rats for 90 days as 30% of their diet. Behavioral measures were collected throughout the 90 day feeding schedule, then afterwards each rat received a d-amphetamine challenge (2.5 mg/kg,s.c.). At six months post-feeding, twelve of the rats were implanted with epidural electrodes for SEP recordings.

The fish samples that were collected during the spear fishing season were ground into a composite, tested for total Hg (Gerstenberger et al., 1993), PCBs and other organochlorines (Table I) at the Lake Superior Research Institute, University of Wisconsin in Superior, WI. The composite samples were mixed with Purina certified ground rat chow in a 30% fish to 70% chow ratio to make a homogeneous mixture. Similar to the methods used by Daly (1992) for Lake Ontario fish, the HLE rats were fed one of four diets for 90 days: rat chow (labeled "0.1 ppm" on Figures) or one of the rat chow/fish mixtures with total Hg levels at approximately 0.8, 0.4, or 0.2 ppm (Table I). Total Hg in fish is known to be predominantly MeHg. The "0.2 ppm" group was from the Canadian Lake Nipigon and purchased commercially. The rat feeding and behavioral assessments were completed at the Department of Behavioral Sciences, University of Minnesota at Duluth, MN.

Behavioral measures included a modified Functional Observational Battery similar to Moser et al. (1988), motor activity using Figure 8 mazes, accelerating rotarod performance, startle responses, grip strength, and landing foot splay. All behavioral tests except motor activity were conducted prior to dosing, and on days 1, 7, 14, 55, and 85 of dosing. Motor activity was assessed prior to dosing, and on days 30, 60, and 90 of dosing. Testing at and beyond 30 days was allowed +/- 2 days.

Upon completion of the standard behavioral assessments, the rats were shipped to the Medical College of Wisconsin in Milwaukee, WI. Twelve of the rats were surgically implanted with epidural electrodes (three per diet group). To perform this procedure, each animal was sedated by an im injection of 10 mg zylazine per kg and 87 mg ketamine per kg body weight.

Stereotaxic placement of four electrodes were made relative to the Bregma as follows: Reference electrode 0.7 cm anterior, just off center to the left; Somatosensory 0.15 cm posterior, 0.3 cm laterally left; Auditory/Visual (A_2) electrode 0.68 cm posterior 0.3 cm laterally right; Cerebellar (O_z) 1.2 cm posterior, 0.0 laterally (Mattsson, personal communication).

After a two week recovery period, the animals were ready for evoked potential recording. Two types of evoked potentials were recorded. Visual evoked recordings were completed using the A_2 and O_z electrodes. The N1, N2 and N3 peaks were recorded on a Nicolet Pathfinder Electrodiagnostic system. Normal latencies are approximately 35, 75, and 180 ms respectively. (N1 - N3 peaks were inverted for ease of visual interpretation.) Mattsson et al. (1992) reported

that alterations in N1 are indicative of changes either peripheral to the first cortical or at the first cortical neuron itself. Altered N2 or N3 components are indicative of subcortical or cortical changes.

Auditory evoked potentials were based on a click induced brain stem response which occurs during the first 10 ms of the auditory response, and these were also recorded using the Nicolet Pathfinder system. Mattsson et al. (1992) reported that the neural generators of peaks I through VII represent the acoustic nerve (I), lower brain stem (I-III), and upper brain stem (IV-VII). Typical latencies are recorded for peaks I (1.2 ms), III (3.0 ms), V (4.5 ms) with a speaker 17 cm from the ear.

Testing sessions required about 60 min per animal with test sessions repeated twice over a four week time period to insure peak integrity. The resulting graphs and statistical analyses are based upon the first recording session with the second session used only to confirm peaks. Statistical analysis was performed with SAS Institute programs on a personal computer. General linear models analysis of variance was used to test all the dependent variables. When appropriate, repeated measures were used to test for trends, and co-variance models were used to control body weight effects on strength and reflex measures. A $p<0.05$ was considered appropriate for rejecting the null hypotheses of all statistical tests, and multivariate analysis included corrections for multiple dependent variables. For the multiple regression testing of the SEP latencies, the rat chow diet was assumed to be less than 0.1 ppm MeHg, and a value of "0.1 ppm" was assigned to that group.

3. Results and Discussion

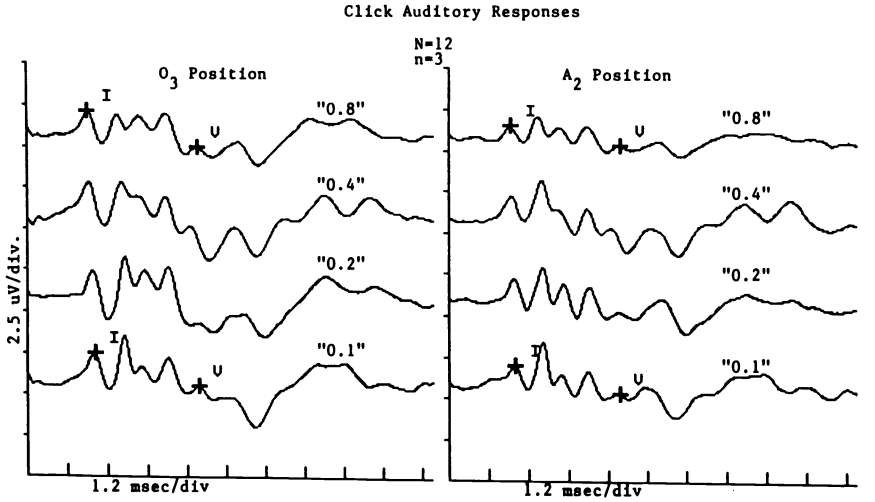
There were no consistent nor significant behavioral alterations noted during the first portion of the study. However, there was a significant increase in body weight due almost entirely to the "0.8 ppm" group gaining approximately 9 g or 3% more weight than the rat chow only ("0.1 ppm") group ($F_{(3,4)}=9.62;p<.027$).

During the pharmacologic challenge with d-amphetamine, there were noticeable trends that appeared to be dose-related in motor activity and startle responses, but none of the trends were statistically significant. Thus the behavioral effects that were noted in the Red Cliff study may have been due to the combination of Hg with other contaminants (PCBs and other organochlorines). The organochlorine contaminants in the fish groups used herein were considerably less than those measured in the Red Cliff study (Table I).

Using the SEPs to more clearly define any alterations in sensory function appears to have been effective (Figures 1 and 2). The auditory (click) responses were relatively stable and did not have significant mercury dose related alterations ($F_{(2,21)}=0.487$; $p<.952$). This was expected as MeHg is known to affect primarily the visual cortex. The visual (flash) evoked responses did have a dose-related increase in the latency between the N1 and N3 peaks. The low flash SEPs depicted a slowing between N1 and N3 of approximately 11 ms for the log dose increase in mercury ($F_{(2,21)}=7.549;p<.003$). The high intensity flash was not expected to be as sensitive, and it was not ($F_{(2,21)}=2.992;p<.071$). Clearly the low intensity flash evoked responses provide the best dose related measure of possible Hg effects.

The multiple regression model using 12 rats was sufficient to demonstrate a linear relationship between increasing MeHg contaminants and increased visual processing time. However, the number of rats and the study design did not allow for testing contrasts between

dietary groups or other dietary factors (i.e. lipids or organochlorines). The known cause effect relationship between methylmercury and adverse visual effects leads one to conclude that MeHg in the fish leads to increased flash SEP latencies in the rat model.



OZ

Peak	msec
I (0.1)	1.968
V (0.1)	5.088
I (0.8)	1.752
V (0.8)	5.040

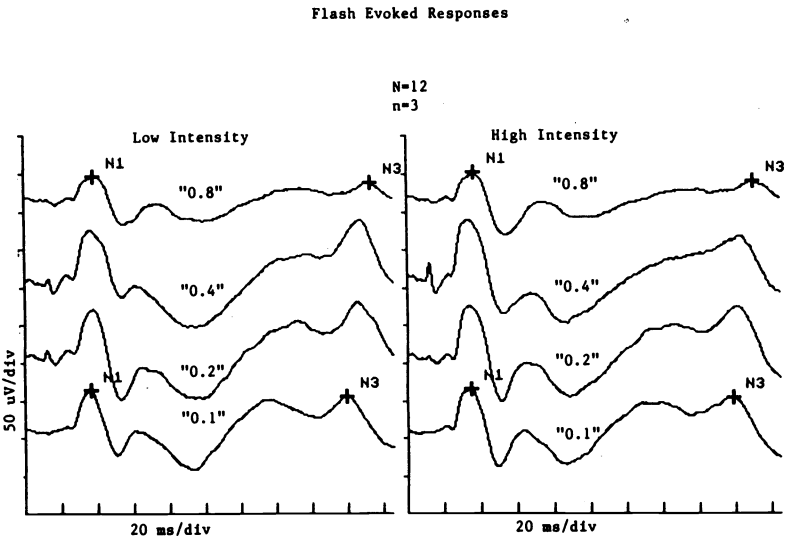
Interval	msec
I-V (0.1)	3.120
I-V (0.8)	3.288

A2

Peak	msec
I (0.1)	1.920
V (0.1)	5.064
I (0.8)	1.776
V (0.8)	5.088

Interval	msec
I-V (0.1)	3.144
I-V (0.8)	3.312

Fig. 1. Auditory responses to a click from 12 one year-old HLE rats fed mercury contaminated walleye (0.1-0.8 ppm).



LOW

Peak	msec
N1 (0.1)	35.2
N3 (0.1)	178.8
N1 (0.8)	37.2
N3 (0.8)	192.4

Interval	msec
N1-N3 (0.1)	143.6
N1-N3 (0.8)	155.2

HIGH

Peak	msec
N1 (0.1)	33.2
N3 (0.1)	177.2
N1 (0.8)	35.2
N3 (0.8)	188.8

Interval	msec
N1-N3 (0.1)	144.0
N1-N3 (0.8)	153.6

Fig. 2. Visual evoked responses to low and high flashes from one year-old HLE rats fed mercury contaminated walleye (0.1-0.8 ppm).

4. Conclusions

The Hg-related behavioral effects were minor and not significant at the feeding levels used herein. However, our earlier work indicated that similar Hg levels in combination with other environmental contaminants in Great Lakes walleye can lead to behavioral decrements (GLPF, 1993). Furthermore, this study did not examine developmental neurotoxicity resulting from perinatal exposures with inland walleye. Sensory evoked potentials may provide a sensitive measure of the neurotoxic potential of Hg contaminated fish. However, the increase in body weight by the high dose rats could be a contributing factor to the increased latency in flash evoked responses. The cause-effect relationship between Hg contaminated fish diets and SEPs could be confirmed using the simultaneous administration of a chelating agent to bind with the Hg and block the effect.

The official fish consumption health advisory for the State of Wisconsin cautions against consuming fish with greater than 0.5 ppm mercury (WDNR, 1993). Michigan, Minnesota and Canadian officials have similar advisories but in some cases at lower action levels. The SEP data reported herein provides additional evidence that Ojibwa tribal members need to heed the appropriate advisories, and more research may be needed to clearly establish no observable effect levels for Hg in dietary fish.

Acknowledgements

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HUMAN EXPOSURE TO MERCURY DUE TO GOLDMINING IN THE TAPAJOS RIVER BASIN, AMAZON, BRAZIL: SPECIATION OF MERCURY IN HUMAN HAIR, BLOOD AND URINE

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Abstract. To obtain the basic information on human exposure to mercury (Hg) due to gold mining activities in Amazon, total mercury (T-Hg) and methylmercury (MeHg) were determined for human hair, blood and/or urine samples collected from populations living in gold mining area and fishing villages upstream of the Tapajos River basin. Abnormally high levels of T-Hg were observed in hair and blood from all fishing villages investigated and more than 90% of T-Hg was in the form of MeHg in both samples, whereas in goldmining area the value were much lower and the %MeHg values varied widely (20-100%) with individuals even in blood samples. Urine from gold shop workers contained Hg mostly in inorganic form at 165 μg/g creatinine on the average, with the range of 20 to 450 μg/g creatinine. A good correlation between Hg in hair and blood was found in fishing villages and the ratios of hair Hg to blood Hg were very close to 250, generally established for MeHg. T-Hg and inorganic Hg levels in urine from gold shop workers were also significantly correlated with inorganic Hg in blood.

1.Introduction

Environmental mercury (Hg) pollution due to gold mining in the Amazonian region has become a matter of worldwide concern in recent years. In the goldmining processes an enormous amount of metallic Hg has been used and released in an abusive way into local ecosystems over the last 20 years. It is estimated that around 100 tons of Hg have been released annually, of which 45% are discharged into river systems and 55% into the atmosphere (Preiffer and Lacerda, 1988). Owing to this metal, therefore, there is a possibility of causing two types of health hazards in the Amazon river basin: First, occupational inorganic Hg poisoning by direct inhalation of Hg vapor during the processes of burning and re-burning Hg-Au amalgam. Secondly, a part of Hg discharged into river systems is methylated and ultimately bio-accumulated to a significant level in fish. Thus, people living along the river and depending on riverine products are easily exposed to MeHg and may develop toxic levels through repeated consumption of these contaminated fish. The people living near gold mining areas may be contaminated with at least two forms of Hg - inorganic Hg and MeHg - simultaneously from surrounding air and diets. Though, in fact, high levels of Hg in hair and fish from the main tributaries of Amazon river have

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already been reported by several research groups (Martinelli *et al.*,1988; Pfeiffer *et al.*,1989; Malm *et al.*,1990), it is still difficult to predict to what extent these populations and biota are exposed to MeHg converted from inorganic Hg in the ecosystems, since the reported data are limited to T-Hg. Thus, the chemical speciation of Hg in various human as well as environmental samples is essential for better understanding of the environmental Hg pollution originated from metallic Hg.

To investigate the extent of Hg pollution and its health effects due to gold mining in Amazon, a three years collaborative study between National Institute for Minamata Disease (NIMD) and Universidade Federal do Rio de Janeiro (UFRJ) started 1993 as a part of the Global Environmental Research Project in the Environment Agency of Japan.

Previously, we conducted a preliminary survey to evaluate the actual extent of MeHg levels in human hair as well as in fish samples collected from five fishing villages at different distances from main gold mining area in the Tapajos river basin (Figure.I). The levels of MeHg in hair from fishing villages located near the gold mining area were higher than those downstream of the river and several samples among 136 contained MeHg exceeding 50 ppm the minimum threshold value for MeHg poisoning (WHO, 1990). The MeHg levels in hair of goldminers and gold shop workers were quite low at around the same levels as the general population without any specific Hg contamination (Malm *et al.*, 1990), however, the T-Hg showed particularly high levels (up to 113 ppm). Relatively high levels of MeHg up to 3.3 ppm were also found in fish collected near gold mining area. These results indicate that the inhabitants of fishing villages near gold mining areas are exposed to more MeHg than those far from gold mines, but, at the same time, the measurement of only T-Hg in hair samples is not sufficient for evaluating MeHg contamination in the areas being contaminated with inorganic Hg like such as gold fields.

Therefore, the present study aimed at evaluating more precisely the actual human

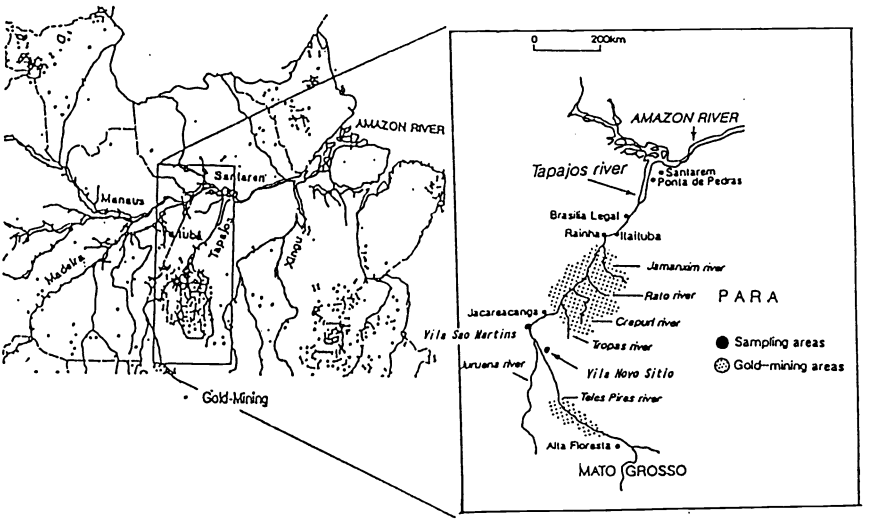

Fig. 1. Map of the study area

exposure to Hg due to gold mining activities by measuring not only T-Hg but also MeHg present in human hair, blood and urine samples collected from two different groups of people living in fishing villages and gold mining areas along the Tapajos river basin.

2.Study Area

Tapajos river basin, about 2,000 km long, is one of the main tributaries of the Amazon river system, and the first to be extensively exploited in the gold rush which has taken place since the late 1970's. It was originally a typical clear water river without turbidity, however, due to extensive gold mining activities, now it turned practically into a white water river. Gold mining has been carried out in several tributaries, mainly Teles Pires, Tropas, Crepuri, Rato, Jamanxim as well as the main channel of the Tapajos river (Figure.I). Alta Floresta (AF) is the most important city in northern Mato Grosso State as one of the main gold-trading centers in Tapajos river basin, with a population of around 136,000 in 1990 and a diversified food base. Most of the fish consumed there comes from the Teles Pires river. Jacareacanga (JA) is a typical fishing village located around 700 km downstream from AF. It has a population of 3,000 living for the most part on a combination of fishing small farms. Fish is the important protein source in this community.

As a part of our research project, we have conducted a field survey to investigate Hg contamination in two different types of communities, AF and JA, in September 1993, and collected human hair, blood and urine as well as fish samples in these regions. Human hair and blood samples were also collected from two other small and isolated fishing villages, Vila Sao Martins (VSM) and Vila Novo Sitio (VNS), located around 50 and 150km upstream from JA, respectively.

3.Materials and Methods

In AF, human blood and urine were collected from 25 gold shop workers including one female, aged 19 to 62 y, and three hair samples among these subjects were also collected. The sampling of urine was done the following day for most of the subjects. Human hair and blood samples were collected from 51subjects (22 males and 29 females, with ages ranging from 2 to 86y) in JA, VSM, VNS. Hair samples were taken from the scalp. Only 3cm long pieces from hair roots were used for Hg analysis. Forty five local fish samples were obtained from fish stores in AF and directly from fishermen in JA. At the time of sampling, we also collected information through questionnaire on eating habits, the amount and frequency of fish consumption, and so on. All these samples except for hair were frozen until the Hg analysis was conducted in both laboratories in Brazil and Japan.

In this study, the determinations of T-Hg and MeHg were conducted on the basis of the sensitive and reliable methods recently developed in our laboratory (Akagi and Nishimura, 1991), with some modifications. So far, the validity and reliability of these methods have been repeated checked by inter- and intra-laboratory comparisons (e.g. Matsuo *et al.*, 1989; Suzuki *et al.*, 1993) and confirmed to be widely applicable to various kinds of biological as well as environmental materials containing Hg down to background levels. In this study, the T-Hg determinations were also performed for urine and fish samples by a different method with an AA 1475 Varian and a cold vapor generator accessory VGA-76

Varian (Malm *et al.*, 1990), to check the accuracy of Hg analysis as well as possible of Hg contamination during the transportation and storage. The outline of the analytical procedures newly modified and used for this study is as follows. For T-Hg analyses in hair, blood and fish, a known amount of sample (1 to 10mg for hair, 0.1 to 0.5g for blood and fish flesh) was placed in a 50 ml volumetric flask, to which 2ml of HNO_3-$HCLO_4$(1+1), 5 ml of H_2SO_4 and 1ml of H_2O were added in order and digested at 230 to 250℃ on a hot plate for 20 minutes. In the case of urine sample, the mixture of these acids were placed first in the 50 ml volumetric flask, to which 5ml of urine sample was added dropwise with stirring the mixture using magnetic stirrer, and then digested in the same manner as described above. After cooling, the digested sample solution was made up to 50ml with Hg-free water. An aliquot of sample solution was introduced into the semi-automated Hg analyzer Model Hg 4000 (Sanso Seisakusho Co. Ltd., Tokyo, Japan) consisting of a Hg vapor generating system and atomic absorption spectrometer. The procedure is very simple and the determination of one sample completes within one minute and the detection limit is about 0.5 ng as Hg.

For analysis of MeHg in hair, around 10mg of finely cut hair sample was weighed and placed in a 10ml pyrex test tube with cap, to which two drops of ethanol, 5 ml of 2N HCl, and small amount of defatted cotton were added to prevent the floating of the hair sample. The tube was capped tightly and then heated at 100℃ for 5 minutes. After being mixed and cooled down to room temperature, 1ml of HCl extract was transferred to another 10ml test tube with cap and extracted with 4ml of benzene. MeHg in the benzene extract was subsequently measured with the ECD-gas chromatography (ECD-GLC, Yanaco G-6800). The determinations of MeHg in blood, fish and urine samples were done based on our dithizone extraction - ECD-GLC methods with modifications. The homogenized blood and fish samples (0.5 g or less) were digested with 10 ml of 1N KOH in ethanol in a 50ml screw-capped centrifuge tube at 100℃ for 1 hour. To the digested sample solution, 1ml of 20% EDTA (4Na-salt) and 10 ml of 1N HCl were added and the mixture was then washed with 5 ml of n-hexane to remove the fatty acids. After the hexane layer was discarded by suction, MeHg in the aqueous layer was extracted with 5 ml of 0.05% purified dithizone benzene (Dz-Bz) and centrifuged. The lower layer was discarded. For urine analysis, 20 ml of homogenized urine sample in the 50 ml centrifuge tube was simply shaken with 10 ml of 1N KOH in ethanol for 5 minutes using a mechanical shaker. The sample solution was then mixed with 1ml of 20% EDTA and 10ml of 1N HCl, extracted with 5ml of purified 0.05% Dz-Bz and centrifuged. After the lower layer was removed, the emulsified benzene layer was shaken with added anhydrous Na_2SO_4 (0.5g) for 5 minutes and centrifuged again (an emulsion was formed in most cases).

Each Dz-Bz extract was washed twice with 3 ml of 1N NaOH to remove the excess of Dz and an aliquot (usually 3 ml) of the extract was transferred to a 10ml test tube, followed by back-extraction with 2 ml of 5 ppm Na_2S in 0.1N NaOH - ethanol (1:1). After the benzene layer was removed, the lower layer was slightly acidified with a few drops of 1N HCl and then bubbled with N_2 gas through the solution for 3 minutes to eliminate the excess of S^{2-} ions as H_2S gas. To the sample solution, 2 ml of Walpole's Buffer (pH 3.0) was added and the mixture was re-extracted with 0.2 to 1ml of purified 0.05% Dz-Bz,

depending on the MeHg contents. The extract was washed twice with 2 ml of 1N NaOH and subsequently with 4 ml of distilled water, and finally acidified with a few drops of 1N HCl. The benzene layer was subjected to ECD-GLC for MeHg analysis. In these procedures, carrying the MeHg standard solutions throughout the procedure is needed the accurate determination, since the volume of the benzene layer varies due to partitioning.

The determination of creatinine in the urine samples was performed by an enzymatic assay method (Kainos Laboratories Incorp., Tokyo, Japan.), and the Hg concentrations were expressed as μ g/g creatinine.

4.Results and Discussion

4.1. T-Hg AND MeHg CONCENTRATIONS IN HAIR, BLOOD AND URINE SAMPLES

The interlaboratory comparisons of T-Hg measurements in urine and fish showed fairly good agreement, as is shown in Figure 2. These indicate not only that the two different analytical procedures gave comparable data, but also that no or very little Hg contamination occurred during the transportation (Brazil-Japan) and storage of these samples. The concentrations of T-Hg and MeHg in human hair, blood and urine samples collected from JA,VSM,VNS and AF are summarized in Table I., together with the results of the analyses of urine samples collected from people in Minamata City for comparison.

The hair samples from JA, VSM and VNS contained quite high T-Hg at 24.6, 37.4, 28.8 ppm on the average, respectively, and the variation was very large with individuals. Almost all of the T-Hg was in the methylated form and the ratio of T-Hg to MeHg was very close to 1 (Figure 3). Among all these hair samples, seven samples contained more than 50 ppm of MeHg, the minimum threshold value for MeHg poisoning established by WHO (WHO,1990). The contents in males were about 1.5 times higher than those in

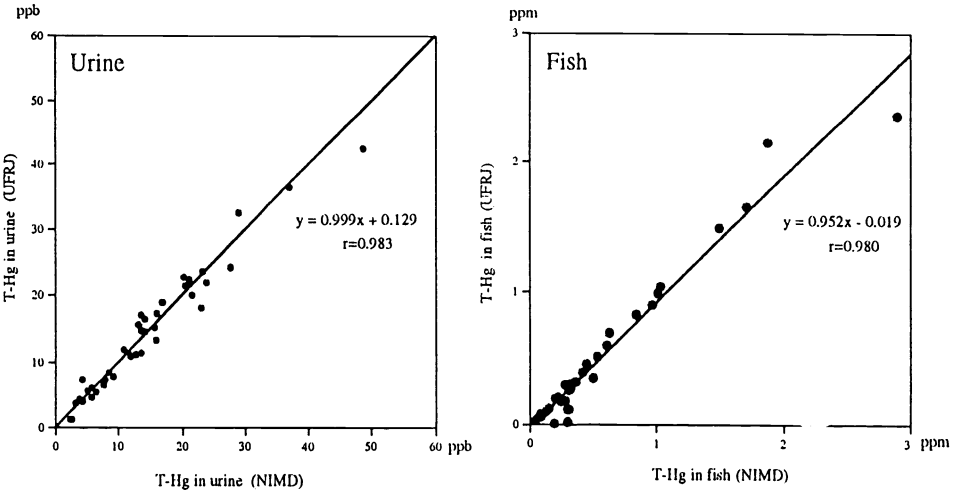

Fig. 2. Correlation of T-Hg determinations in two different laboratories, NIMD and UFRJ.

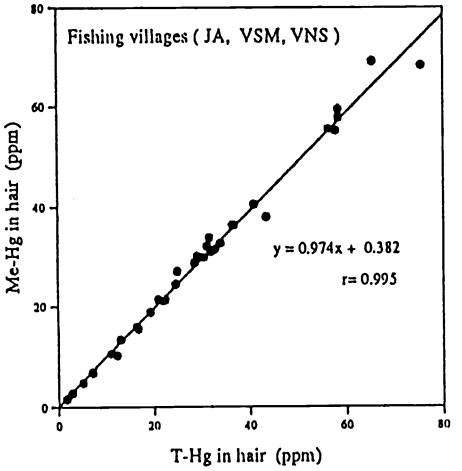

Fig. 3. Correlation between T-Hg and Me-Hg in hair.

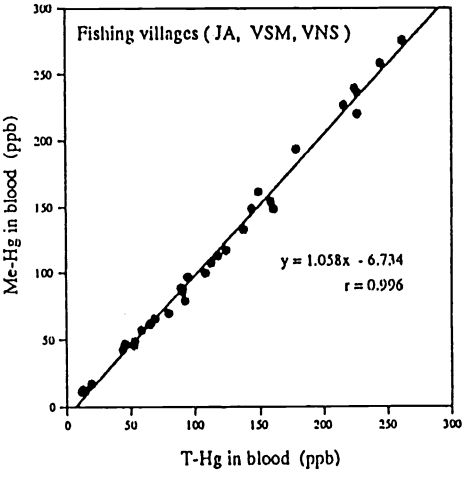

Fig. 4. Correlation between T-Hg and Me-Hg in blood.

females.

In contrast with the high MeHg contamination in people in the fishing villages, the hair Hg levels detected were very low (less than 5 ppm) in gold shop workers in AF, suggesting little external contamination with even Hg vapor. This was quite different from the previous results of hair analysis in gold shop workers and gold miners in Itaituba, which showed high contamination with inorganic Hg from air and/or sweat, in most cases (Akagi et al., 1994).

The blood Hg in JA, VSM and VNS showed a very similar pattern to hair Hg in the

TABLE I. Concentrations of T-Hg and MeHg in human hair, blood and urine samples.

sample origin	sample		n	T-Hg $\bar{X} \pm SD$	Me-Hg $\bar{X} \pm SD$	%MeHg $\bar{X}$
Jacareacanga	Hair	(ppm)	27	24.6 ± 17.8	24.1 ± 17.8	96.0
(JA)	Blood	(ppb)	19	90.4 ± 71.5	90.0 ± 76.6	97.2
Vila Sao Martins	Hair	(ppm)	14	37.4 ± 17.1	36.4 ± 17.1	96.4
(VSM)	Blood	(ppb)	8	149.8 ± 49.5	149.2 ± 52.5	99.0
Vila Novo Sitio	Hair	(ppm)	10	28.8 ± 13.0	27.3 ± 12.1	95.7
(VNS)	Blood	(ppb)	7	130.7 ± 78.4	131.9 ± 84.2	98.8
Alta Floresta	Hair	(ppm)	3	4.1 ± 1.3	3.1 ± 0.7	85.2
(AF)	Blood	(ppb)	25	12.2 ± 8.2	9.0 ± 6.7	72.2
	Urine	(μ g/g CR)	21	161.8 ± 95.3	0.4 ± 0.2	0.4
Minamata City	Urine	(μ g/g CR)	27	22.5 ± 14.9	0.7 ± 0.8	3.9

individuals. The T-Hg levels was 90.4, 149.8, 130.7 ppb on the average, respectively, of which average 98% was in the form of MeHg (Table. I). These average values of blood Hg were about 11-19 times as high as the reference value (8 ppb) in the general population (WHO, 1990). The blood Hg levels in males were approximately 1.5 times those in females. The correlation between T-Hg and MeHg was also very close to that observed in hair samples from the same group (r=0.998). In the blood samples from goldshop workers in AF, however, the Hg levels were very low at 12.2 ppb on the average, and the proportion of MeHg to T-Hg was found to be around 70%, with a large variation, showing the contribution of inorganic Hg due to exposure to Hg vapor. The correlation coefficient between the blood T-Hg and MeHg was 0.870, and the regression equation, (MeHg) = 0.708x (T-Hg) + 0.423, was obtained.

High levels of T-Hg were found in urine samples from AF with fairly large variation. Almost all of the urine samples except for one sample contained T-Hg above the level of 30 μ g/g creatinine, at which mild or minor adverse effects might occur among people exposed to Hg vapor (WHO, 1991). MeHg was also found to be present in urine samples, although the levels were extremely low, most of the urine Hg was in the inorganic form and % MeHg to T-Hg was in the range of 0.04 - 1.71 (average value of 0.36%). These were compared with the values of people living in Minamata, Kumamoto, Japan, as there were no data on urine MeHg in the literature. As shown in Table I, higher MeHg levels were found in the urine samples from people in Minamata than AF, and the percentage MeHg to T-Hg was 3.9% on the average, ranging from 0.26 to 20.1%. This fairly high proportion of MeHg in urine samples of the general population containing T-Hg at only normal levels is surprising, because it is well-documented that little MeHg is excreted in the urine (WHO, 1990).

The analyses of T-Hg and MeHg in 45 fish samples collected from JA and AF showed wide distribution of Hg levels. The 8 fish samples collected from AF contained quite high levels of T-Hg with the average of 1.26 ppm, ranging from 0.20 to 2.89 ppm, compared with the average of 0.28 ppm, ranging from 0.01 to 1.05 ppm in JA. Again, the major part (average 97%) of T-Hg in fish was in the form of MeHg in both groups. In AF the fish samples were collected from fish stores where mainly large fish (frequently weighing several ten Kg) were available. While, the fish samples (at most several Kg) obtained in JA were much smaller than those obtained in AF. Therefore, the difference in the levels of Hg in fish between JA and AF may be explained by the difference in body weight of fish in both local areas. The results of questionnaires indicated that almost all subjects in AF were meat-eaters, whereas in JA, they were living mainly on fish and ate fish almost everyday, although the amount of its daily consumption could not be estimated well in this study. From these results, it is apparent that the high MeHg contamination in the human population that occurs in the fishing villages is a result of frequent consumption of local fish.

4.2. CORRELATIONS OF MERCURY BETWEEN HAIR, BLOOD AND URINE

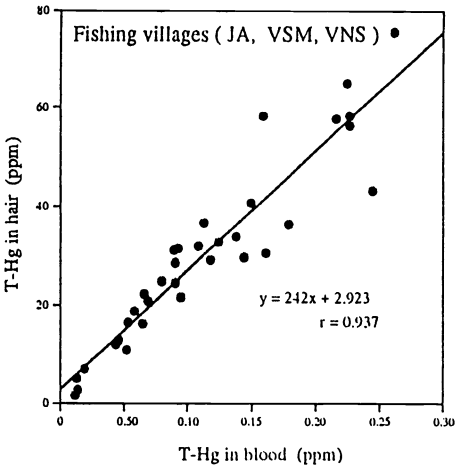

Fig. 5. Correlation between hair T-Hg and blood T-Hg.

The correlation between Hg in hair and blood for all subjects in the three fishing villages is presented in Figure 5. As expected from the above-mentioned results, the levels of T-Hg or MeHg in hair was significantly correlated with that in blood (correlation coefficient, r=0.937). From the regression equations presented in Figure 5, the overall average ratio of 242 was obtained for hair T-Hg versus blood T-Hg. This figure was in reasonable accordance with the value of 250, which has been estimated in various populations exposed to MeHg (WHO, 1990). These results indicate that, at least in the fish-eating people in JA,VSM and VNS, human exposure to Hg occurs mostly through the consumption of fish contaminated with MeHg, which is converted from inorganic Hg released as a consequence of gold mining activities, and moreover, the contribution of inorganic Hg to the human exposure through atmosphere or diet is small in these populations.

Based on the results of Hg analyses in blood and urine from AF, the relationships between T-Hg or inorganic Hg in blood and urine were investigated. No apparent correlation between T-Hg in blood and urine was found, but the T-Hg or inorganic Hg in urine was significantly correlated with the inorganic Hg in blood, with the correlation coefficient r= 0.688, as shown in Figure 6.

Although there are several studies reporting on the distribution of Hg between urine and blood among populations exposed to Hg vapor, the results vary considerably (Smith *et al.*, 1970; Lindsted, *et al.*, 1979; Roels et al., 1987). Also in the present study, a positive correlation was observed, when the relationship between T-Hg in urine and blood was investigated. It is reasonable that we have obtaind no apparent correlation between T-Hg in urine and blood, taking into account the fact that on average 73% of the T-Hg in blood samples tested was in the form of MeHg, not associated with exposure to Hg vapor. Therefore, the speciation of Hg at least in blood should be made to find the relationship between urine and blood Hg among populations exposed to Hg vapor particularly among populations with low exposure levels. In fact, we found a significantly positive correlation between inorganic Hg in blood and urine, in which the confounding effect by MeHg was

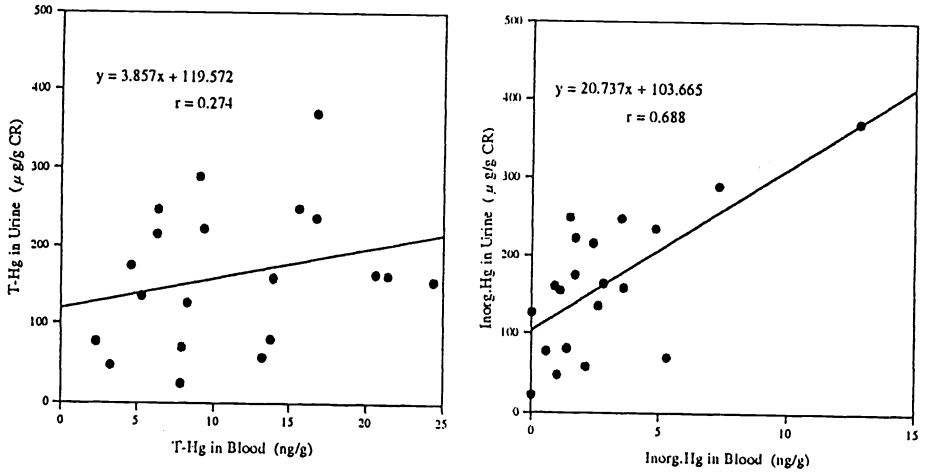

Fig. 6. Correlations between Blood Hg and Urine Hg in goldshop workers (AF).

eliminated (Figure 6). The scatter of the blood - urine ratios is not surprising, taking into account the facts that the exposure levels of Hg vapor vary considerably depending on the frequency of re-burning operations in the gold shop (each operation completes within 10 to 15minutes.), and that the urine samples were collected the day following the blood sample collection. Thus, the observed significant correlation between inorganic Hg in blood and urine from goldshop workers suggests the possibility of predicting the level of inorganic Hg retained in blood from Hg level in urine. Further extensive investigations are necessary to evaluate the actual extent of human as well as environmental Hg contamination in this and other river systems.

5.Conclusion

In the fishing villages, the hair and blood of inhabitants contained Hg at particularly high levels of Hg mostly in methylated form. Abnormally high levels of Hg mostly in inorganic form was found in the urine of goldshop workers. The hair and blood of goldshop workers contained Hg in both inorganic and methylated forms, though the MeHg levels were much lower than those in fishing villages.

A highly significant correlation was found between Hg in hair and blood, with a correlation coefficient, 0.97, and the obtained hair Hg - blood Hg ratio (242 : 1) was very close to the 250 : 1, already estimated in various populations exposed to MeHg. From these analytical results, it can be concluded that people living in these three fishing villages surveyed are mainly exposed to MeHg in fish, with little confounding exposure to inorganic Hg including Hg vapor, indicating that head hair is a very useful indicator for monitoring human contamination by MeHg in the fishing villages along the Tapajos river.

On the other hand, a significant correlation was also observed between T-Hg or inorganic Hg in urine and inorganic Hg in blood, suggesting the possibility of predicting the Hg in inorganic form in blood due to Hg vapor exposure from urine T-Hg. Thus, it would be apparent that chemical speciation of Hg is necessary for better evaluating the

contamination levels in the population in the area where contamination with both inorganic Hg and MeHg can occur, like in goldmining areas.

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INORGANIC MERCURY INTERACTIONS WITH LIPID COMPONENTS OF BIOLOGICAL MEMBRANES: ^{31}P-NMR STUDY OF Hg(II) BINDING TO HEADGROUPS OF MICELLAR PHOSPHOLIPIDS

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Abstract. Phosphatidylethanolamine (PE), phosphatidylserine (PS) and phosphatidylcholine (PC) in micellar phase in water have been studied by high resolution phosphorus-31 nuclear magnetic resonance (^{31}P-NMR), in order to follow inorganic mercury Hg(II) binding to the lipid headgroups. Decrease of the NMR peak area is observed upon $HgCl_2$ addition, with greater effect on PE and PS compared to PC. This is interpreted by Hg(II) binding to several phospholipid headgroups, linking different micelles together and forming by extension a large "insoluble" phospholipid-mercury network that is undetectable by high-resolution ^{31}P-NMR. The extent of phospholipid aggregation depends on the mercury-to-lipid molar ratio, and apparent Hg(II) affinities to phospholipid headgroups are in the order: PE>PS>>PC. When $HgCl_2$ is added to mixed micelles prepared with two lipids (PE/PC or PS/PC), co-precipitation is observed for both components in similar proportions.

1. Introduction

Mercury (Hg) interactions with epithelia barriers and biological membranes are necessarily the first step of Hg bioaccumulation and toxicity (Rothstein, 1976; Boudou *et al.*, 1991). Both organic and inorganic Hg compounds display strong thioloprive properties: they bind to the SH groups of various proteins, inducing severe structural and functional disturbances at the membrane level (Ralston and Crisp, 1981; Chávez and Holguín, 1988). However, thiol sites cannot account for total Hg binding on the erythrocyte membrane, as shown by Kinter and Pritchard (1977). It has been suggested that specific Hg interactions with membrane lipids could be responsible for lipid peroxidation (Ribarov and Benov 1981) and membrane rigidification phenomena (Delnomdedieu *et al.*, 1989; Boadi *et al.*, 1992), and could also facilitate the passive diffusion or transport of electro-neutral Hg complexes through the membrane barrier (Gutknecht, 1981; Foulkes and Bergman, 1993).

Recently, Shinada *et al.* (1991) and Delnomdedieu *et al.* (1989, 1992) have demonstrated by ^{1}H- and ^{199}Hg-Nuclear Magnetic Resonance (NMR), together with fluorescence polarization studies, that the uncharged $HgCl_2$ species specifically binds to phosphatidylethanolamine (PE) and phosphatidylserine (PS) in multilamellar dispersions. Hg(II) binding induced a strong rigidification of phospholipid (PL) bilayers, and the primary amine groups of PE and PS polar heads were proposed as the Hg binding sites. In ^{199}Hg-NMR studies, drastic chemical shift changes and peak area decrease of Hg NMR signals were observed and interpreted in terms of complexes formation between Hg(II) and the phospholipids. Formation of Hg/PL complexes depended on the metal chemical speciation, *i.e.* formation of chloro- or hydroxy-Hg(II) complexes in the dissolved phase, but not on the electrical charge of the lipid headgroups.

To obtain complementary informations on Hg(II) interactions with membrane phospholipids, ^{31}P-NMR of phosphatidylcholine (PC), PE and PS micelles in water was performed in controlled physico-chemical conditions, in the presence and absence of Hg(II). Effects of inorganic Hg on mixed micelles prepared with two lipids were also explored in order to study competitive Hg binding to the different phospholipids.

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2. Materials and Methods

2.1. SAMPLE PREPARATION

Phospholipids (PL) were kept in $CHCl_3$ at -18°C. To obtain multilamellar vesicles, $CHCl_3$ was evaporated under a nitrogen stream and phospholipids were dispersed by homogenization in acetate buffer (74 mM, pH 5.8). Micellar phases (15 mM) were prepared by Triton X-100 addition (10% weight/volume) to lipid dispersions.

Mixed micelles composed of two different phospholipids (PL1/PL2, 15 mM each) were prepared by mixing together both lipid aliquots in $CHCl_3$, followed by evaporation, dispersion, and solubilization with Triton X-100 as described above.

$HgCl_2$ was added to phospholipids at defined molar ratios (R_i = [Hg]/[PL]). For the two-lipid samples, R_i was calculated with respect to each individual lipid. Assuming that chloride, hydroxide and acetate ions are the only Hg(II) ligands to be considered in solution, chemical speciation models based on available thermodynamic data (MINEQL database - Schecher and Mc Avoy, 1991) predict that $HgCl_2$ soluble species accounts for 95% or more of total Hg(II) in our experimental conditions: pH = 5.8 and pCl = 2.8. The remaining 5 % corresponds to HgClOH and $HgCl_3^-$ species.

2.2. NMR

^{31}P-NMR phospholipid spectra were recorded on a Bruker WH 270 spectrometer, operating at 109.35 MHz, at controlled room temperature (23°C). Samples were spun at 40 Hz frequency, yielding a linewidth at half-intensity of about 30-50 Hz. Typical experimental parameters were: 7 µs $\pi/2$ pulses, 6 s recycle time, 5 kHz spectral window and gated broadband proton decoupling. All experiments were carried out in the presence of an external reference containing HPO_4^{2-} (41 mM, 80 µl, pH 10.5). Spectra were recorded in 100 scans, and a 40 min delay was kept after $HgCl_2$ addition, prior to signal acquisition.

Peak area integration was performed using Bruker standard programs. Reference peak area was used to calculate sample concentration with an average 10% accuracy.

3. Results and Discussion

^{31}P-NMR spectra of micelles made of a single phospholipid (PE, PS and PC) or of mixed lipids (PE/PC and PS/PC, Figure 1) in the absence and presence of $HgCl_2$ show well-resolved single NMR lines. The outermost left signal (+ 3.2 ppm) corresponds to the phosphate external reference. Chemical shift values (δ_{obs}) for PE, PS and PC are + 0.30, + 0.15 and - 0.40 ppm, respectively, in the absence of Hg.

Upon $HgCl_2$ addition at R_i = 2.4 to single-lipid micelles, an important peak area decrease is observed with every phospholipid, with a stronger effect for PE and PS compared to PC (data not shown). No changes are observed for PE and PC chemical shifts, whereas a + 0.30 ppm upfield shift is detected for PS in the presence of $HgCl_2$. A comparative study of Hg(II) effects for different R_i (0.8; 1.6; 2.4) reveals qualitatively similar results, and no significant changes in peak linewidth occur for all three R_i (data not shown). Each studied phospholipid shows a non-linear, progressive peak area decrease with increasing R_i. Decreases are in the order PE>PS>PC at a specific R_i.

Decrease of the phospholipid ^{31}P-NMR isotropic signal observed upon $HgCl_2$ addition can be explained by the appearence of a new, very broad (and thus beyond detection) NMR

line, in slow exchange with the isotropic sharp line. This powder-pattern spectra would correspond to the fraction of phospholipid micelles forming a large-sized "insoluble" complex with $HgCl_2$ (Tacnet *et al.*, 1991; Delnomdedieu *et al.*, 1992). This insoluble lipidic phase could result from the linkage by Hg of two or more distinct micelles, forming by extension an insoluble "network".

Inorganic Hg interaction with phospholipids is highly specific of the headgroup nature. Hg-PL reactivity order as observed by ^{31}P-NMR can be related to the affinity constants estimated by ^{199}Hg-NMR for the precipitation of $Hg(PE)_3$ and $Hg(PS)_3$ insoluble complexes, where it was found that the equilibrium constant was higher for $Hg(PE)_3$ than for $Hg(PS)_3$ (Delnomdedieu *et al.*, 1992). The "network" hypothesis also implies a stoichiometry of two or more phospholipid ligands per Hg, which is coherent with reported results for PE and PS. Binding and aggregation of several phospholipids by Hg(II) was also invoked to interpret the observed Hg-induced rigidification of model membranes (Delnomdedieu *et al.*, 1989).

Chemical shifts of the phospholipid isotropic signals are nearly unchanged upon $HgCl_2$ addition, indicating that no direct binding of Hg(II) on the lipid phosphate group occurs in the soluble fraction, as such a binding would greatly perturbate the phosphate electronic environment and cause δ_{obs} values to shift by several ppm (James, 1975). This is highly specific of the Hg(II)-lipid interactions, since other divalent cations, like Ca^{2+}, are known to bind phospholipids on the phosphate moiety in a charge-dependent interaction (Bevan *et al.*, 1983). The small δ_{obs} change observed with PS micelles in the presence of $HgCl_2$, is indicative of a soluble PS-Hg(II) species that involves a reactive group distant from the phosphate, most probably the amine. Formation of similar complexes with PE or PC cannot be infered nor excluded from ^{31}P-NMR measurements. The constant δ_{obs} values observed could be indicative of a greater distance between the phosphate group and the Hg binding site (amines) in PE and PC than in PS, due to different conformations of these headgroups in the presence of Hg(II).

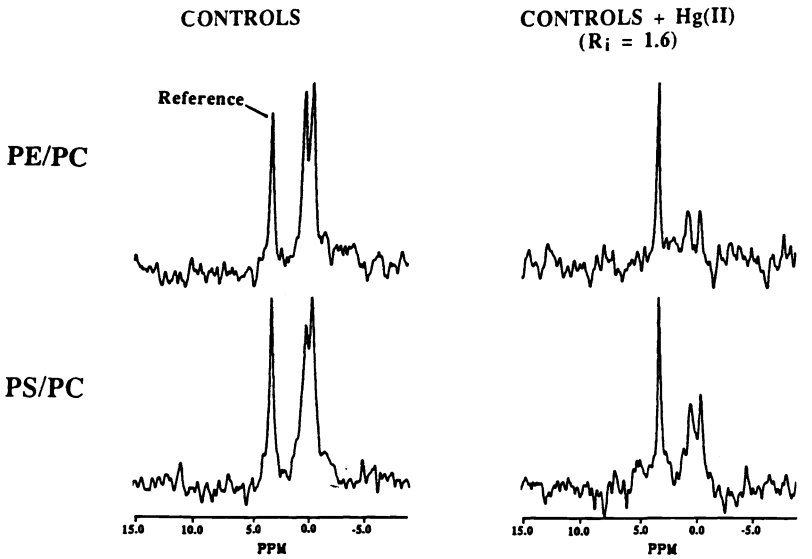

Fig. 1. ^{31}P NMR spectra of mixed micelles (PL1/PL2), in the absence and presence of $HgCl_2$. Outermost left NMR signal corresponds to the external reference (HPO_4^{2-}, 80 mM, pH 10.5). Right signal corresponds to PC and left signal to PE or PS, respectively. Chemical shifts are expressed relative to H_3PO_4, 85% (0 ppm).

When $HgCl_2$ is added to (PE/PC) or (PS/PC) mixed micelles at $R_i = 1.6$, both lipids show a simultaneous, comparable co-reduction of ^{31}P-NMR signals (Figure 1). This peak area reduction is R_i-dependent, leading to peak area values for both (PC and PE) or (PC and PS) signals similar to those obtained at the same R_i with PE or PS single micelles, respectively. This co-precipitation can easily be explained using the "network" model: a motional decrease of PC molecules incorporated in the mixed micelles is likely to be induced by Hg binding to either PE or PS and resulting aggregation.

These headgroup specificities and induced precipitation mechanisms observed with Hg(II)-phospholipids systems could be of great biological importance in the membrane rigidification, fusion and phase separation phenomena induced by numerous metal ions (Bevan *et al.*, 1983). The aminophospholipids are indeed an important component (up to 45%) of most eucaryotic cell membranes (Rothstein, 1981). Besides its thiol-binding properties, Hg high affinity for the phospholipid headgroups of PE and PS is certain to play an important role in its toxicological effects, depending on the pH and pCl conditions that control the metal chemical speciation in the dissolved phase and, consequently, its bioavailability and accessibility to membrane ligands.

4. Conclusion

This experimental approach shows that ^{31}P-NMR can be used to monitor aggregation phenomena induced by inorganic Hg binding to membrane phospholipids. Specificity of interaction can easily be derived from NMR parameters, providing a molecular basis for the understanding of Hg binding to biomembranes. Data are consistent with a network model for metal specific binding to phospholipid headgroups, in agreement with recent studies on the effect of Hg upon fluidity of model bilayers and erythrocyte membrane (Delnomdedieu and Allis, 1993).

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SWEDISH EXPERIENCES OF THE BAN ON PRODUCTS CONTAINING MERCURY

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ABSTRACT

The Swedish Parliament has decided that the use of mercury (Hg) must cease. Risk reduction measures are to be carried out with and without the support of legislation. According to decisions taken in May 1994 the aim is, with a few exemptions, to end the use of Hg in processes and products by the year 2000. Special attention has been paid to products containing Hg. Most uses of Hg-containing measuring instruments and electrical components have successively been phased out in Sweden. It can be concluded that most such uses have reliable Hg-free alternatives.

1. Introduction

Since January 1, 1992 clinical Hg thermometers have been prohibited for import, manufacture and sale. The same applies for other measuring instruments and electrical components containing Hg since January 1, 1993. It is not prohibited to use such products which were bought before the ban came into force.

The National Chemicals Inspectorate (KemI) is empowered to prescribe exemptions from the ban, and to grant exemptions in individual cases if there are exceptional reasons for doing so. Exemptions from the Prohibition (Ordinance 1991:1290) are found in KemI's Code of Statutes (KIFS 1992:9). General recommendations (1992:3) were issued at the same time.

The prohibition does not cover import of equipment containing banned products, but empowers KemI to prescribe such a ban. For the time being, KemI favours means of voluntary undertakings. A project is planned, aimed at informing different foreign industrial developing units of the technical and financial possibilities to replace the functioning of Hg in several types of equipment. Below, KemI's experiences on phasing out electrical components and measuring instruments containing Hg is briefly described.

2. Implementation of the Prohibition on Products Containing Mercury

Information-oriented efforts to reach those concerned of the ban were widespread. To use use traditional channels such as trade organizations and heads of company units was often unsuccessful because these bodies are often unaware of the presence of Hg-based technique. This knowledge is found in the development departments. Due to this, it has been

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hard to identify the kind of banned products and areas of use where there are special grounds for exemption from the prohibition.

Guidelines for exchange of information with the Board of Customs were drawn up. It was possible to include certain banned products under the customs tariff numbers.

3. Results

The Swedish prohibition does not cause any serious barriers to trade. On the other hand, consequences for companies vary. Companies specialised in technically advanced Hg relays may be loosing markets. Manufacturers of glass thermometers are among those most severely struck. Manufacturing of alternative precision instruments requires another type of machinery. Companies within the same country may be able to supply alternative Hg-free instruments. In other cases, companies in other countries are able to take on new markets.

Work on identifying environmental pollution has traditionally been focused on releases from point sources. We know little of the accumulated amount of Hg in products still in use and in landfills originating from disposed products. Hg has been used in measuring instruments for some hundred years and in electrical components since the beginning of this century. Considering that Hg and its compounds, are, and have been used in a vast range of other products, the amount can be far from negligible. Future emissions of considerable amounts of Hg, for the time being immobilized in landfills, are probably to be expected.

Hg contained in products on the Swedish market has been reduced with about 6 t. The implementation of the prohibition alone has reduced the flow with about 4 t. Additional amounts will be settled gradually in accordance with exemptions that are given. The policy is to exempt products when sufficient alternatives are not attainable and to encourage work on research and development. Special attention has been paid to security demands. Exemptions have also been made to make it possible for users to successively convert to other techniques and to prevent companies from loosing important parts of their markets. KemI has also taken into account the ongoing change of organization of the stations for weather observations.

When alternatives are not available, possible alternative techniques are often known but not developed to meet reasonable requirements for reliability, especially with respect to certain kinds of equipment. The construction of other parts of the equipment may be dependent on the design and capacity of the Hg-components. Therefore, a plan taking into account development efforts and the need for testing the safety of Hg-free constructions as a whole needs to be elaborated in order to guide a decision on exemption. KemI has made an extensive analysis of many instruments, devices and their alternatives. Measures taken have been guided by technical consultants. Exemptions are restricted in time.

The use of Hg in not sanctioned products is also decreasing by voluntary measures.

Several international standards seem to direct the use of Hg in instruments and electrical components. Most often, these are so-called product standards, designed for a certain Hg

instrument or Hg component. KemI has found that, in many cases, the same reliability can be reached with a Hg-free product. A product standard is therefore not sufficient reason to grant exemption from the prohibition.

In KemI's view, it is important to work on an international scale for a general elaboration of so-called method standards. These are not based on the measuring mode of a special instrument, but on the demands for reliability in a certain measuring situation, independent of the instrument used.

4. Discussion

There are several reliable alternatives, at a comparable price, to clinical Hg thermometers; both electrical and electronic ones, and those for single use. Other Hg in glass thermometers within the measuring area -38°C — +200°C could be replaced by thermometers with other liquids such as butyl alcohol, hexanol or xylen. The price is about the same. Electrical and electronic instruments would also work. For applications of up to 700°C, a Pt-100, also called a Resistant Termo Device (RTD), can be used. Different thermocouple are applicable within the measuring area 400°C — 1500°C. When measuring below -38°C and above +650°C, it never was possible to use Hg. Also other types of measuring instruments, like manometers, have reliable Hg-free alternatives.

The electrical and electronic instruments can be expensive if a very high accuracy has to be reached. But prices are continuously going down. A higher price per instrument is often compensated by the fact that a Hg-free instrument can be used in several measuring situations.

Hg is widely used in electrical contacts and relays. Conventional relays and other contacts with Hg, also when these are contained in switches and thermostats, can normally be replaced by a corresponding Hg-free component. This is not only applicable when fitting components into equipment being manufactured, but also when exchanging spare parts in the majority of older equipment.

Most Hg contacts can be replaced by electric ones, for example solid-state contacts. These contacts have no movable parts like mechanical ones. Therefore, they do not wear out as soon as other substitutes might do. Many tilt-switches and most level-switches can be substituted. The use of conventional Hg relays has ceased during the last ten years. On the other hand, the more technically developed Hg-wetted relays have become more common. The amount of Hg in those is continuously going down. For some applications it is possible to use semi-conductors or solid-state relays instead. What seems most complicated is to substitute tilt-switches when there is no fixed reference point.

5. Conclusions

The decline of Hg in products covered by the ban is shown in the table below. The need for development efforts is reflected in the gradual elimination of Hg in certain products. The main part of Hg contained in products marketed in 1991 (almost 70%) had, however, been eliminated by the end of the first six months of 1993.

TABLE I

Amount of Hg contained in certain products 1991-1999 (kg/year).

Product	Year						
	1991	1993	1994	1995	1996	1997	1999
Clinical thermometers	900	0					
Other glass therm.	110	16	16	16	0		
Industrial therm.	218	203	203	203	100	0	
Other measuring instruments	105	66	66	18	5	0	
Thermostats	40	30	0				
Float switches	2,640	1,190	0				
Relays	90	28	28	24	14	14	0
Circuit breakers	135	40	0				
Total	4,238	1,573	313	261	119	14	0
Reduction		2,665	1,260	52	142	105	14

The flow of Hg products mounted in imported equipment as pumps and cars has declined with about 500 kg a year as a result of the voluntary undertakings. It has not been possible to estimate the reduction of Hg contained in other types of equipment.

For exempted uses, Hg-containing spare parts may be appearing up to ten years after the equipment was marketed. For chemical/physical reasons it is not possible to replace the Hg in a few analytical instruments.

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MERCURY REACTIONS IN THE HUMAN MOUTH WITH DENTAL AMALGAMS

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Abstract. This is a preliminary study of the reactions of mercury (Hg) in the human mouth with dental amalgams. It was conducted by analysing saliva samples from subjects with amalgam fillings and control subjects with no amalgams. Samples were collected both prior to and after cleaning the mouth. These samples were analyzed for elemental mercury (Hg^0), inorganic mercury (Hg^{2+}) and methylmercury (MeHg). We concluded that the concentrations after cleaning represented the systemic concentrations. Hg^{2+} and MeHg were found in all systemic samples from both subjects and controls, while Hg^0 was found only in the samples from subjects with amalgams. In the control group, the concentrations found before and after cleaning the mouth were equivalent. In the amalgam group, concentrations of Hg^{2+} found before cleaning the mouth were 10 to 40 times higher than those found after cleaning, suggesting that the oxidation reaction of Hg^0 into Hg^{2+} takes place. For MeHg, a similar but less pronounced pattern as Hg^{2+} was found, supporting methylation in the mouth.

1. Introduction

Amalgam fillings in oral cavities are subject to a complex chemical/biological environment: air, oxidants, reductants, acidity, alkalinity, enzymes, and bacteria. Reactions occur in which Hg is released from amalgams. To better assess the toxicity of Hg released from dental amalgams, the reactions should be investigated first, because the reactions yield species other than Hg^0 (Marek, 1992). It is well known that different species cause dramatically different effects on human health. Studies show that Hg vapor may cross the lungs, rapidly enter the bloodstream, and be oxidized into Hg^{2+}. Hg^0 from amalgam has been considered to be the most toxic species (Clarkson, 1992; Reinhardt, 1992; Larsson, 1992). Another highly toxic species, MeHg, has been reported to be formed in vitro by methylation of Hg from amalgams due to the action of bacteria (Heintze *et al*, 1983). This compound has been found in the surface structure of a dental amalgam filling and a porcelain veneer crown (Sellars *et al*, 1994). If MeHg is formed in the mouth, it will be carried into the gastrointestinal tract, where it is easily absorbed and accumulated in the body. The effect of this compound on human health has been well documented (Choi, 1991; Sato and Nakamura, 1991). A non-volatile and dissoluble species of Hg is Hg^{2+}. In the human mouth, Hg^{2+} is carried into the gastrointestinal tract, and largely excreted in the feces. This pathway is much less toxic than Hg^0 and MeHg. It is probable that if Hg^0 released from amalgam was completely oxidized, the toxicity of Hg would be reduced dramatically.

The key questions regarding risk assessment of Hg from amalgams are what species are formed from Hg^0 in the oral cavity, and in what quantity? Little has been reported on in vivo conditions, due to the difficulty of developing experimental modeling and sampling in this very complex environment. Analytical techniques for Hg speciation have been quickly developed in the last few years (Liang and Bloom, 1993; Liang *et al*, 1994; Liang *et al*, 1994; Horvat *et al*, 1993; Horvat *et al*, 1993; Bloom and Fitzgerald, 1988), which can ensure success of the investigation for both in vivo and in vitro.

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2. Methods

For the investigation the following reactions were assumed to occur in the human mouth: Hg^0 reacting to enzymes, air, and oxidants becomes Hg^{2+}, and Hg^{2+} reacts to become methylmercury (CH_3Hg^+). Thus, the mercury concentration in saliva should include two parts: Hg^{2+} total = Hg^{2+} reaction products plus the systemic Hg^{2+} secreted. The same is true for CH_3Hg^+.

Hg found before cleaning the mouth is defined as Hg total. Hg found after cleaning is defined as systemic Hg which would include the effects of diet. The difference between concentrations before and after cleaning are defined as the reaction products.

Saliva was collected in three ways. (i) without cleaning, flushing or washing the mouth, 5 mL of saliva was collected into a cleaned Teflon vial, (ii) after cursory cleaning of the mouth by flushing with double di-ionized water 3 times just before sampling, (iii) after thoroughly cleaning the mouth by brushing carefully (not using paste) and rinsing with double di-ionized water.

The scrubbing water was also collected by swishing about 20 mL of water around in the mouth carefully and thoroughly twice, then spitting the water into a Teflon vial, to collect about 40 mL water in total. All sampling was done (with written instructions) by the donor.

The sampling schedule is illustrated in Figure 1.

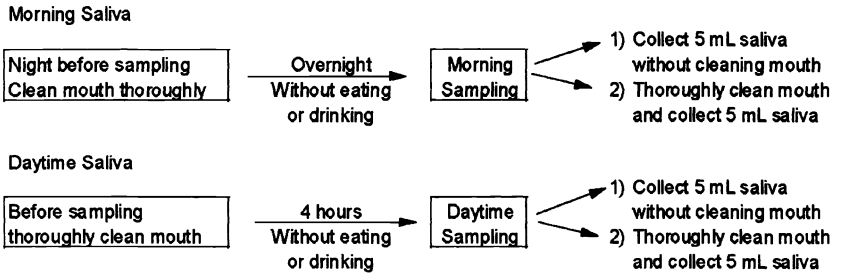

Fig. 1. Sampling schedule

The analysis was conducted as soon as possible after sampling. The samples were analyzed for Hg^0, Hg^{2+}, and HgMe using the method of Bloom & Fitzgerald, as improved by Liang *et al.*

3. Results and Discussion

About 150 saliva samples from subjects and controls in several countries were collected and analyzed. Systemic Hg^{2+} and MeHg were found in all analyzed samples from subjects and controls. Hg^0 was found only in samples from subjects with amalgams. Results were dependent upon the manner of cleaning, and a typical example is shown in Figure 2.

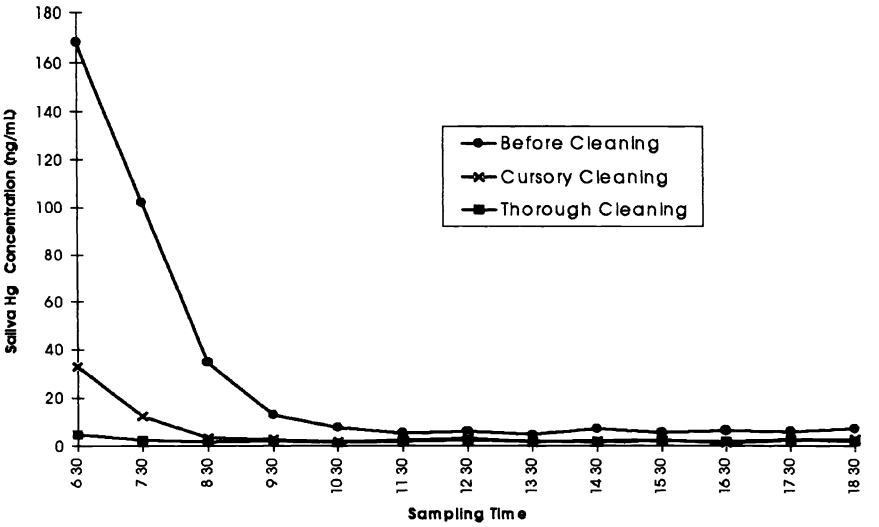

Fig. 2 Comparison of analytical results of Hg^{2+} in saliva from a subject with 12 amalgam surfaces obtained before and after cursory/thorough cleaning as a function of sampling time.

As shown, Hg^{2+} concentrations found in saliva collected before cleaning are significantly higher than those found after cursory and thorough cleaning. Those found after cursory cleaning are only slightly higher than those found after thorough cleaning. The Hg^{2+} concentration found in the morning sample is about 35 times higher than those found in samples collected several hours later. This suggests that the Hg^{2+} concentrations in systemic saliva are lower and relatively constant.

Figures 3 and 4 show the comparison of Hg^{2+}/MeHg found before and after thoroughly cleaning, for subjects and controls. Samples shown in Figure 3 were collected in the morning upon waking, while those shown in Figure 4 were taken before lunch, after 4 hours without drinking or eating. Again, the Hg^{2+} concentrations in saliva samples from amalgam subjects, collected before cleaning are dramatically higher than after cleaning and from the controls. Comparing the results in the two figures, the concentration found before cleaning in the morning (Figure 3) are about 5 times higher than those found before lunch.

Saliva samples from a person with 10 amalgam surfaces collected in the morning before and after cleaning had concentrations of 180 and 5 ng/mL Hg^{2+}. Samples collected before lunch, after four hours without eating or drinking were 30 and 3 ng/mL. Apparently, the dramatic difference in Hg^{2+} concentrations found before and after cleaning was caused mainly from reaction products. Samples from controls showed no significant difference before and after cleaning, indicating that the small amount of Hg^{2+} came naturally from systemic saliva. In the control group there were little changes with cleaning. The Hg^{2+} concentration was 0.27± .08ng/mL and the MeHg 0.009± 0.006. The results in Figures 3 and 4 show that MeHg has a similar pattern as Hg^{2+}, but the concentrations are lower. The MeHg data may not be sufficient at this point to prove

methylation in the mouth but the two to six fold increase over the systemic value tends to indicate that it takes place.

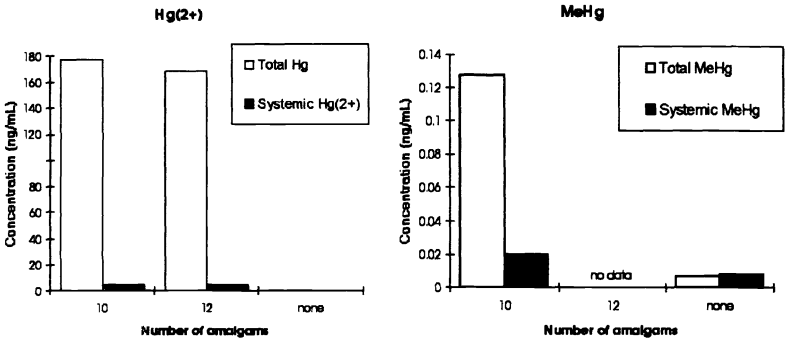

Fig. 3. Comparison of Hg^{2+} /MeHg concentrations in saliva samples collected in the morning, before and after cleaning the mouth.

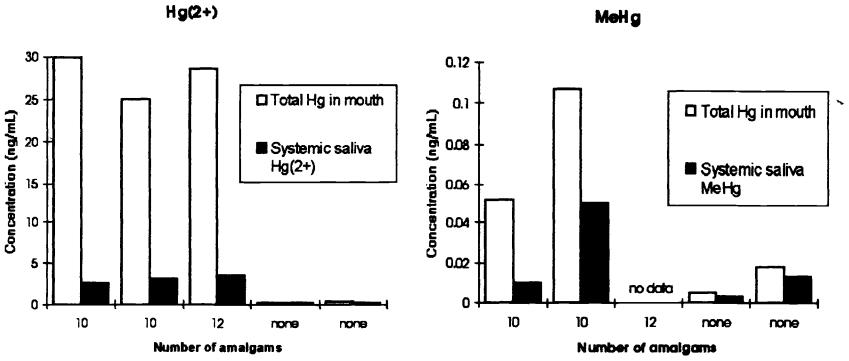

Fig. 4. Comparison of Hg^{2+}/MeHg concentrations in saliva samples collected after 4 hours without eating or drinking, before and after cleaning mouth.

Several scrubbing water samples from subjects and controls were collected and analyzed. (Table I). Hg^{2+}/Hg^{0}/MeHg were all found in the samples taken from amalgam subjects, and the amounts of Hg^{2+} in these samples were dramatically higher than those found in the control group.

TABLE I
Speciation of Mercury in 40 mL of Morning Scrubbing Water
(ng/sample, a Hg, n = 2)

Sample ID	No. of Amalgams	Hg^{2+}	Hg^{0}	MeHg
1	10	163 ± 4	19.6 ± 2.4	0.646 ± 0.102
2	10	40.6 ± 2	2.7 ± 0.4	0.082 ± 0.012
3	11	53.4 ± 3	11.4 ± 1.4	0.018 ± 0.003
4	0	0.32 ± 0.06	<0.01	0.006 ± 0.002

In summary, the preliminary evidence suggests that oxidation reactions occur in the human mouth with dental amalgams and methylation probably occurs. The oxidation reaction is an important pathway of Hg^{o}. This pathway may actually reduce the risk of human exposure to amalgams.

The oxidation results were significant and predicative. To accurately quantify the relationship of reactants and products in the complex conditions of the human oral cavity, the development of sophisticated techniques for sampling and modeling are required.

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MERCURY CONTAMINATION IN THE BRAZILIAN AMAZON. ENVIRONMENTAL AND OCCUPATIONAL ASPECTS

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Abstract. Mercury (Hg) contamination of miners, riparian and Indian populations and fish in the Amazon region, due to gold extracting activities, has been studied. Samples of hair, urine, and blood of Indians and prospectors, and hair from riparian fish-eating population and fishes from Madeira river, respectively, were collected and analyzed by Cold Vapor, Atomic Absorption Spectrometry (CV-AAS) techniques. The results obtained showed that the aquatic food chains in the Amazonian ecosystems are contaminated by methylmercury (MeHg), exposing Indians, prospectors and riverines to thr risk of severe health hazard. The highest levels of contamination, based upon hair analysis, were found in riparian of the Madeira river, followed by Cuniã Lake population, Indians (Fresco river) and prospectors, in that order. Blood analysis showed 59% of the samples from Indians and 33% from prospectors with Hg contents above 10 ng mL^{-1}. Analysis of urine, on the other hand, showed 44% of Indians with Hg levels below the detection limit (d.l.), and 30% above 20 ng mL^{-1}, whereas 38% of the prospectors presented Hg concentrations over 20 ng mL^{-1}, and 20% below the d.l. These results prove that prospectors, who hardly ever eat fish but are badly exposed to inorganic Hg vapor, are ocupationally contaminated, while the rest of the populations under survey are exposed to environmental contamination by Hg, through polluted fish ingestion.

1. Introduction

Mercury pollution in the Amazon region is one of the consequences of the gold rush that took place in the early 1980's. Since then, gold-mining has been the main source of mercury (Hg) contamination in Brazil. The estimated average gold prospectors in the Amazon region is 500,000 (Homero, 1989). Metallic Hg is utilized to agglutinate the fine gold particles through amalgamation. During this process, large amounts of Hg are lost to rivers and soil. In addition to this, the amalgamated gold (Au) is burned to release the precious metal, in most cases in open air and, consequently, emitting Hg vapor to the atmosphere. According to Malm et al. (1988), this is one of the main ways by which Hg enters the Amazonian ecosystem, the other one being *via* effluents from mining dredges. These authors estimate that the total Hg flux to the atmosphere is *ca.* 65 %. Nevertheless, the National Department of Mineral Production (Homero,1989) suggests a figure of 83%. In other words, out of the estimated 1,200 ton discharged into the Legal Amazon during the last ten years, between 800 ton and 1,000 ton of metallic Hg may have found its way into the atmosphere as vapor. Atmospheric Hg vapor undergoes oxidation to Hg(II) and may return on terrestrial and aquatic environments by precipitation. Divalent mercury is then subjected to organification under the Amazonian climatic conditions, yielding methylmercury (MeHg). Temperature, organic enrichment and dissolved oxygen have been shown to play an important role in Hg methylation (Jernelöv, 1970, 1973; Rada et al., 1986; Callister et al., 1986). Methylmercury is accumulated by fish through food intake and respired water (Fagerstrom et al., 1973; Jernelöv et al., 1971). For the human population, fish consumption is the most

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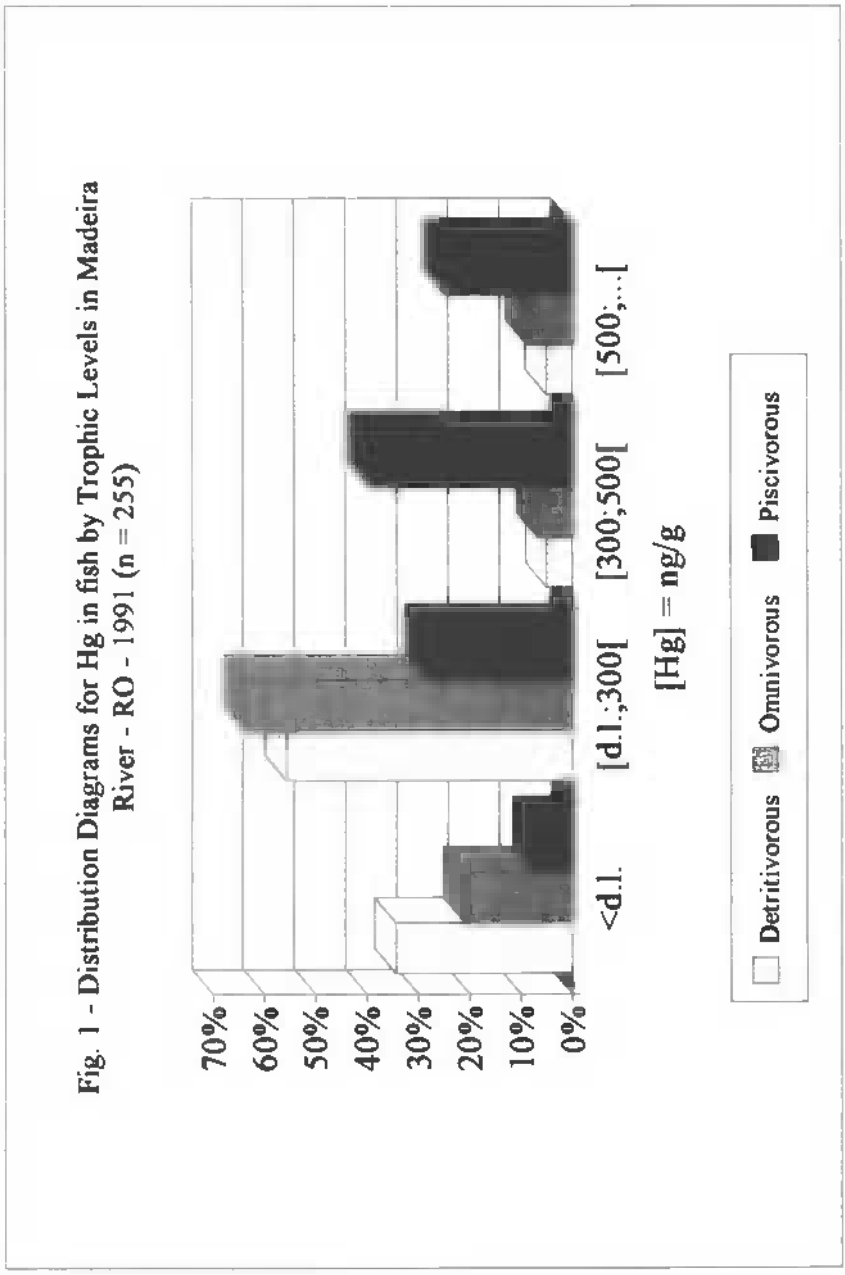


Fig. 1 - Distribution Diagrams for Hg in fish by Trophic Levels in Madeira River - RO - 1991 (n = 255)
70%
60%
50%
40%
30%
20%
10%
0%
<d.l.
[d.l.;300[
[300;500[
[500;...[
[Hg] = ng/g
Detritivorous
Omnivorous
Piscivorous

important route for MeHg ingestion (IPSC, 1990). The adverse effect of MeHg on the developing brain *in utero* differs both quantitative and qualitatively from that on the mature central nervous system (W.H.O.,1976). Clinical manifestation in infants includes a variety of cerebral palsy syndromes (Choi et al., 1978). Prenatally exposed infants show delays in the normal development and mild neurological disturbances (Clarkson, 1989). In the developing brain, the damage is diffuse and affects the cytoarchitecture of most areas in the brain (Choi, 1991).

A comparison of adult and prenatal exposure indicates that the practical threshold in adult dose response is between 50 and 100 $\mu g\ g^{-1}$ Hg in hair, whereas the prenatal threshold is in the range of 10 to 20 $\mu g\ g^{-1}$ Hg as peak concentration in the maternal hair during pregnancy period (Clarkson, 1992). At this range, mild symptoms such as psychomotor retardation in infants can occur (Marsh et al.,1987; McKeow-Eyssen et al., 1983; Kjesllstrom et al., 1989). The severity of the symptoms is dose-dependent and related to the gestional age the Hg ingestion occurs (Choi,1991).

Mercury contamination due to unregulated gold-mining activities upon the Amazonian environment and region's populations is, therefore, of the utmost concern. Consequently, two research projects have been undertaken to evaluate occupational and environmental contamination in gold-prospectors (*garimpeiros*), and Indian and riparian populations, respectively. One project studied the mercury pollution caused by the existence of an active and rather recent gold mining site (*garimpo*), Maria Bonita, in the Fresco river. This river is an important tributary of the Amazonian Xingu river, situated in southern Pará. Mercury utilized in this garimpo contaminates fish eaten at the Kayapó Indian Reserve. Fish is the main diet of Gorotire and Kikretum communities. About 90% of the Hg in fish occurs as MeHg (Fitzgerald, 1991, Huckabee et al., 1979). A second project involved determination of Hg in 75 hair samples from Cuniã Lake population and in 241 hair samples of riverines of Madeira River, 170 km downstream Porto Velho, Rondonia State's Capital, respectively. Gold mining activities in this region started in 1979 and the population seems to be more heavily affected. The riverside populations in this area use fish as their main protein food source. Two hundred and fifty-five fish samples, from 40 different species, were analyzed as well.

The aim of this study is to collect some basic data to evaluate the extent of occupational and environmental contamination of gold prospectors, directly involved with Hg handling, and Indian and riverine communities, indirectly exposed through dietary habits, respectively.

2. Materials and methods

Madeira river and Cuniã region inhabitants were questioned about their fish consumption habits. Specific data on fish species they eat more often and fish intake quantity were asked. Demographic and anthropometric measures (height and weight) data were gathered as well. A list of 40 fish species was presented and the interviewee was asked to grade their weekly consumption. Once the interviews were over, the population was classified by age and sex and hair samples were taken from one or several household members following well-known statistical criteria. Hair was cut close to the scalp with a pair of clean, stainless steel scissors and tied with a cotton string. The

Fig. 2A - Mercury contamination in hair - Riverines from Madeira River
(n = 241 ; average = 17.2µg/g)

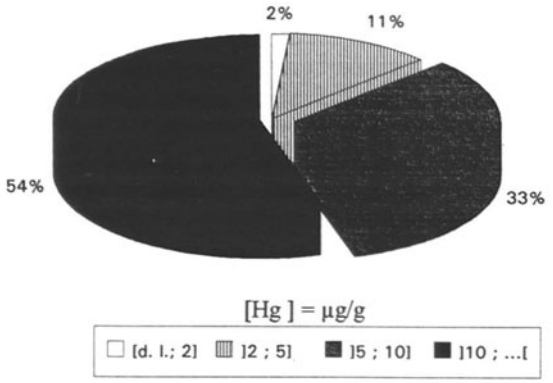


Fig. 2B - Riparian Population with Hg levels over 10 µg/g - Madeira River

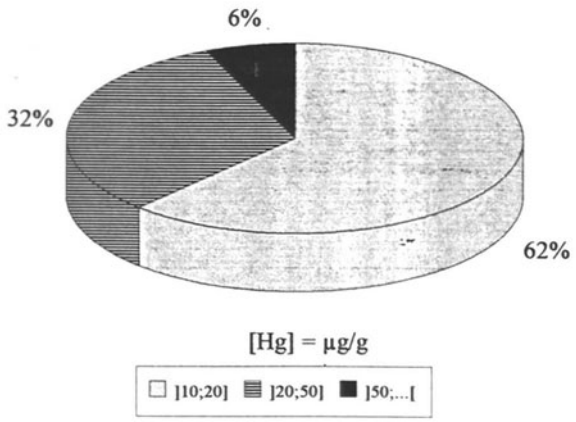


Fig. 3A - Mercury Contamination in Hair - Riverines from the Ecological Cuniã Reserve

(n = 75; average = 8.7 µg/g)

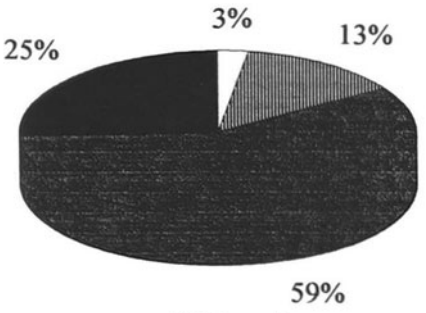
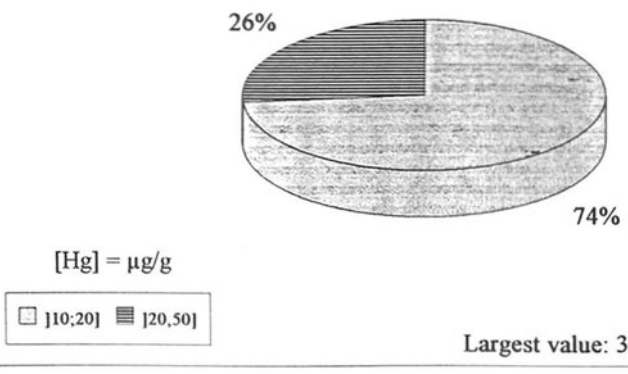


Fig. 3B - Riparian population with Hg levels over 10 µg/g - Ecological Cuniã Reserve

(n = 11)



Largest value: 31,9 µg/g

Fig. 4A - Mercury Contamination in Hair - Kayapó Indians
(n = 419 ; average = 8.0 µg/g)

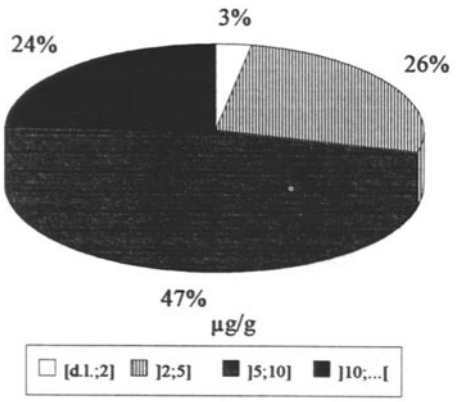


Fig. 4B - Mercury Contamination in Hair - Prospectors (Garimpeiros)
(145 samples; average = 3 µg/g)

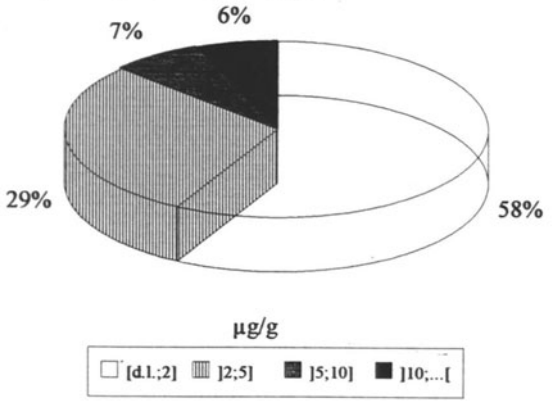


Fig. 5A - Mercury Contamination in Urine - Kayapó Indians

(n = 194; average = 14 ng/mL)

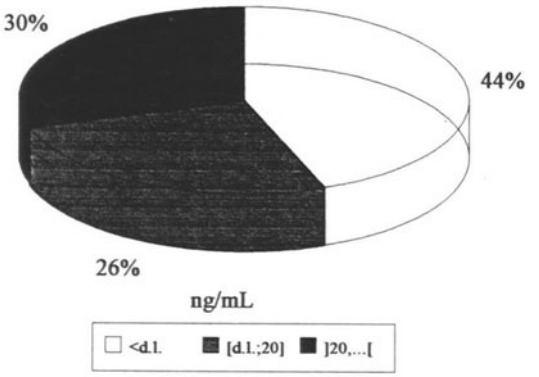
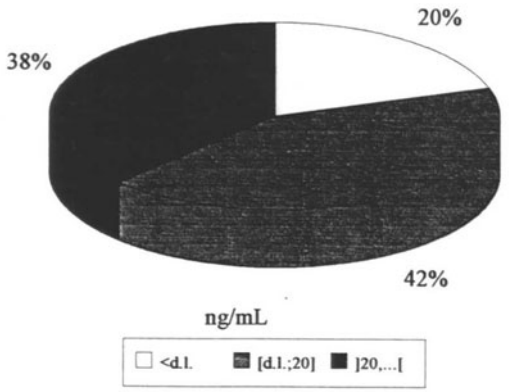


Fig. 5B - Mercury Contamination in Urine - Prospectors (Garimpeiros)

(n = 109; average = 25,3 ng/mL)



length was measured and the sample was saved in a labeled polyethylene bag. Only a few persons refused to have their hair cut by religious reasons. They were replaced by others of the same age group. Forty-one control samples were taken from residents of Porto Velho known to hardly eat fish, just 2 or 3 times *per* month. A similar procedure was adopted to collect the 419 hair samples from Indians and the 145 samples of hair from prospectors, but sampling of the already categorized population by age and sex, was made by simple draw without replacement. It was given (on purpose) priority to pregnant and child-bearing women, following World Health Organization (W.H.O., 1976) recommendations.

Fish samples were collected according to fish availability in households or directly obtained from local fishermen. After being identified, weighed and measured, about 50 g of the edible parts were taken and saved in plastic bags. Samples were kept cool with ice into a polyurethane box, until being frozen in Porto Velho. The samples, while still frozen, were next sent to Brasília to be analyzed. Two hundred and sixty-one fish samples, encompassing 40 species from three trophic levels, were collected. Collection was effected within the study area from different ecosystems: Madeira river, Machado river, local lakes and strings, Samuel Hydroelectric Reservoir, and Cuniã Lake area. The same method of sampling employed for hair, was used to collect blood and 24-hours urine samples from Indians (126 blood and 178 urine samples) and prospectors (130 sample of blood and urine). Samples of urine and heparinized blood were kept cool in ice within a polyurethane box. Analysis of Hg in urine was carried out *in situ* on a Mobile Laboratory.

It is worthnoting that every precaution was observed to prevent contamination during sample collection.

The procedure utilized in the analysis of total and/or inorganic Hg (organic is obtained from the difference between total and inorganic) in hair, blood and urine, was that of Magos and Clarkson (1972) using alkaline digestion. The amount of sample taken for Hg analysis was 10 - 20 mg of hair, weighed into vials previously weighed and labeled, 2.0 mL of urine and 1.0 mL of blood, respectively. Total Hg in fish was determined by pre-digesting, at room temperature, *ca.* 1.0000 g of the sample in a HNO_3 - H_2SO_4 mixture overnight or at least for 1 hour. Then, the digestion proceeds under reflux at *ca.* 85 °C for 3 hours. After this period of time, 2.0 mL of hydrogen peroxide are poured through the condenser to warrant complete destruction of the organic matter. The digest is then transferred into a 50.0 mL volumetric flask and completed to volume with water. The concentration of Hg in hair blood and urine, was determined by CV-AAS, using a LDC Analytical, Model 1255, Mercury Monitor. A Perkin Elmer, Model 403, Spectrometer, equipped with a modified spectrophotometric cell specially designed for this purpose (East et. al., 1990) was used to determine Hg in fish.

3. Results and discussion

3.1 Hg IN FISH

Figure 1 depicts a histogram giving the content of Hg in fish from Madeira river by trophic level. Biomagnification of Hg is occurring in this aquatic food chains as

Fig. 6A - Mercury Contamination in Blood - Kayapó Indians
(n = 132 ; average = 31,5 ng/mL)

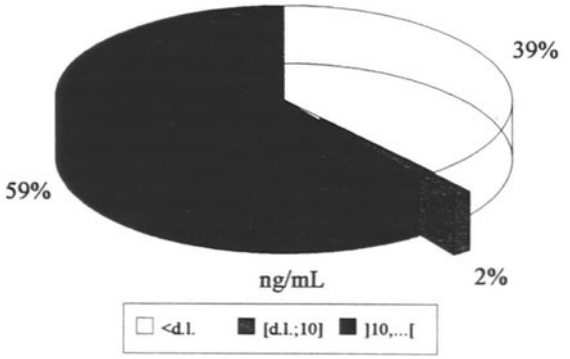
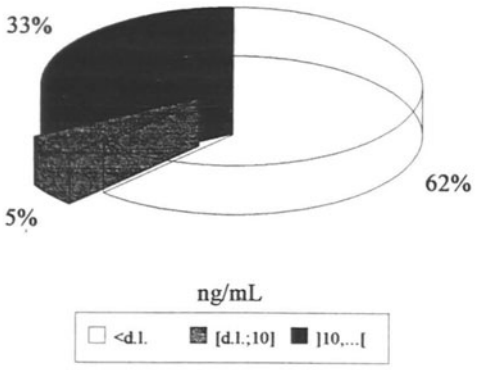


Fig. 6B - Mercury Contamination in Blood - Prospectors (Garimpeiros)
(n = 129; average = 17,3 ng/mL)



demonstrated by the rather large number of specimens of piscivorous with Hg concentrations above 300 ng g^{-1} (approximately 75%) with 45% of the results over 500 ng g^{-1}, i.e., exceeding the safety limit established by the W.H.O.,when the consumption is up to 400 g *per* week. On the other hand, about 90% of the samples of detritivorous and omnivorous, respectively, have Hg levels below 300 ng g^{-1}. Despite these lower values, some specimens of these species present elevated concentrations of Hg, e.g., one sample of *Osteoglossum bicirrhosum*, Aruanã, weighing 1,500 g, from the Madeira river area, had the highest value found in the present study, 11.15 μg g^{-1}. The fate of Hg through the food chain is related to environmental factors such as fish ecology, mostly in terms of feeding habits, trophic levels, habitat and migration patterns. The diversity and variation of ecological factors in the Amazonian ecosystems are responsible for the wide range of Hg concentrations found in fishes of this region.

3.2. Hg IN HAIR

Figure 2A shows chart pie representing hair contamination of riverside people along the Madeira river due to environmental exposure to Hg through fish consumption. A general analysis of the results indicates that about 53% of the samples present concentrations of Hg, as MeHg, above the threshold value of 10 μg g^{-1}. Furthermore, there exist eight people (Fig. 2B) with concentrations above 50 μg g^{-1} MeHg in this area, with a peak value of 303.1 μg g^{-1} MeHg (Boischio and Barbosa, 1993). MeHg level of 50 to 125 μg g^{-1} is considered the minimum level at which clinical symptoms may occur (W.H.O., 1976). Among the population of the Cuniã Lake area (Fig. 3A and 3B) only 25% of the samples analyzed presented concentrations of MeHg above 10 μg g^{-1}. Most of the individuals (59%, n=75) present MeHg concentrations in the range of 5 to 10 μg g^{-1}. Out of 419 hair samples collected at the Kayapó Indian community (Pará), 24% showed MeHg levels above 10 μg g^{-1} (Fig. 4A). Prospectors, on the other hand, present a different pattern with scarce 6% of the specimens analyzed having MeHg contents above 10 μg g^{-1} (Fig. 4B). In addition, 58% reached levels below 2 ng g^{-1}, against only 3% amidst the Kayapó population. In other words, it can be ascertained that riparian and Indian populations are much more exposed to MeHg than gold miners. This is consistent with the different dietary habits of the groups involved. While Indian and riparian populations rely mainly on fish in their diets, prospectors eat fish only occasionally. These results show that people most affected have nothing to do with gold extraction.

A segment of these populations to whom special attention should be given, includes women at child-bearing age with MeHg levels above 10 μg g^{-1}, considering the vulnerability of perinatal life to the compound. Thirty-eight women (n = 70) from Madeira river and Cuniã Lake populations at child-bearing age, presented MeHg concentrations above 10 μg g^{-1}. Seventeen of them (24%) had levels above 15 μg g^{-1}. The peak value was 145.0 μg g^{-1} (Boischio et al., in preparation). Mercury speciation was accomplished in 142 hair samples with Hg levels above 10 μg g^{-1}. In 97 samples, organic Hg accounted for 80% or more of the total Hg content, while 24 specimens presented organic Hg levels equivalent to 70% - 79% of total Hg. The control group presented an average of 1.6 μg g^{-1}.

3.3. Hg IN BLOOD AND URINE OF INDIANS AND PROSPECTORS

Figure 5A shows Hg concentrations in urine of prospectors and Indians. It is evident from there that the number of prospectors (20%) with Hg levels below the d.l. is lower than in Indians (44%). Furthermore, while 42% of the prospectors present concentrations between d.l. and 20 ng mL^{-1}, just 26% of the Indians are within this range. It is also worthnoting that among prospectors 38% present Hg levels above 20 ng mL^{-1}, which can be compared to 30% of Indians within the same level. The average of Hg concentration found in 109 samples of prospectors was 25.3 ng mL^{-1}, meanwhile the average for 194 urine samples from Indians was 14.0 ng mL^{-1}. These results show that the contamination is mainly due to occupational activities, since prospectors are directly exposed to Hg vapor.

Analysis of organic and inorganic Hg in blood of Indians ans prospectors showed higher levels of contamination among the former group (Figs. 6A and 6B). As a matter of fact, for Indians the average of 132 samples is 31.5 ng mL^{-1} and for prospectors, the average of 129 samples is 17.3 ng mL^{-1}.

3.4 ESTIMATE OF Hg INGESTION BY THE MADEIRA RIVER POPULATION

The daily consumption of fish *per capita* was estimated as 200 g of edible portion during the whole year. Thus, the current estimate of MeHg intake can be compared with Hg concentrations found in fish and hair samples[1]. A daily Hg intake within 40 and 200 μg is consistent with MeHg concentrations in the range between 10 to 50 μg g^{-1}, as it has been observed in 53% of the sampled population from Madeira river. This is also consistent with the daily consumption of about 200 g of fish with Hg concentration in the range of 200 to 1,000 ng g^{-1}, as it has been observed in 47% of the fish samples analyzed coming from the same area. The maximum range of Hg intake estimated for this population is 200 - 1,200 μg, which corresponds to a MeHg concentration in hair from 50 to 300 μg g^{-1}, as it has been observed in 3% of the persons.

Table 1 summarizes some ranges of Hg daily intake as related to the increased risk of paraesthesia (the earliest MeHg effect in adults), the F.A.O./W.H.O. suggested maximum dose (W.H.O., 1976), the EPA Reference Dose (discussed in Stern, 1992) and some estimates for the study population. By comparing the Hg levels one can see that the study populations are exposed to MeHg at potentially toxic levels, specially if we consider perinatal exposures.

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[1] The interconversions of Hg concentration in hair, blood and Hg intake are (Clarkson,1988):
Hg daily intake (μg) = fish (200 g) x Fish Hg concentration (μg g^{-1})
Blood Hg concentration (ng L^{-1}) = 0.95 x daily intake (μg)
Hair Hg concentration (ng g^{-1}) = 250 x Blood Hg concentration (ng mL^{-1})

TABLE 1

Hg daily intake according to some indicators of health effects and suggested doses as related to hair MeHg concentration

Indicator	Daily Intake* $\mu g\ kg^{-1}$	[MeHg] in Hair $\mu g\ g^{-1}$
Paraesthesia	160 - 380	50 - 100
F.A.O./W.H.O. max.allowable	27	7
EPA Reference Dose	16	4
53% of Madeira riverines	40 - 200	10 - 50
3% of Madeira riverines	200 - 1,200	50 - 300

* Assuming a body weight of 55 kg that is equal to the average for the Madeira river adult population (For details, see Boischio et al., in preparation)

4. Conclusion

The results of the present study clearly show, through hair analysis, a direct relationship between environmental contamination by Hg and dietary habits. As a matter of fact, Madeira river and Cuniã Lake populations present higher Hg levels than Kayapó Indians because they eat fish more often. Kayapó Indians include hunting games in their diet, relaying not so heavily in fish food. In addition, gold mining in the Madeira river has been more intense and older than in Maria Bonita area.

Another corroboration is the diversity of fishes, belonging to different trophic levels, usually consumed by riverside populations of Madeira river and Cuniã Lake, as evidenced in the interviews carried out in these communities. This fact is responsible for the wide range of Hg concentrations found in hair of these groups.

Prospectors, on the other hand, present low Hg values in hair as they hardly eat fish. Besides, the higher levels of Hg in urine is consistent with occupational exposure to inorganic Hg vapor, inhaled during amalgam burning.

In other words, there exist strong evidences that the aquatic food chain in the Amazon ecosystems is getting differentially contaminated by organic mercury, through mercury methylation. This fact represents a real threat to local fish-eating populations.

For the sake of verification, the average Hg content in hair of riparian populations from Madeira river of 17,2 $\mu g\ g^{-1}$ (n = 241), must be compared to that of a control group 1.6 $\mu g\ g^{-1}$ (n= 49), of people living at Madeira riverside in Porto Velho. They only eat fish twice or three times a month. The mean value, 1.6 $\mu g\ g^{-1}$, is in agreement with that quoted as "reference mean" for total Hg in hair in IPCS (1990), 2.0 $\mu g\ g^{-1}$. As long-term consumption of fish is the chief determinant of Hg intake in humans, the high

average value, 17,2 μg g^{-1}, found in riverines of Madeira river, who eat large amounts of fish, confirm our initial forecast

The most serious concern is regarding to perinatal MeHg exposure. The threshold level of Hg concentration in maternal hair within the range of 10 to 20 μg g^{-1} needs to be compared with the 54% of the individuals from Madeira river who presented hair Hg concentrations above 10 μg g^{-1} . This level is the same among women at child-bearing age from the Madeira river and Cuniã populations: 54% (38 out of 70) present Hg concentrations above 10 μg g^{-1}.

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HgEx - A HEURISTIC SYSTEM ON MERCURY POLLUTION IN THE AMAZON

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Abstract. HgEx is an Expert System that addresses the complex problems surrounding the pollution of the Amazon with Hg by informal mining operations. The system integrates information on biology, chemistry, geochemistry, medical, social and political issues in order to evaluate contamination for a single site or region. The program attempts to diagnose the possibility of hazardous Hg transformations such as oxidation and methylation. An extensive tutorial section containing over 1500 electronic pages provides guidelines for Hg monitoring fieldwork, sampling and analytical steps, amalgamation practices improvements and remelioration procedures for a polluted site. The system is structured for use by either highly-skilled personnel or those without technical-training.

1. Introduction

Use of Hg in informal mining operations ("garimpos") in the Amazon has been an efficient and cheap method for gold recovery, however improper use is causing pollution at rates of about 1 kg per kg of gold produced. About 70 tonnes of Hg is emitted annually from these operations (Veiga and Meech, 1992). Some miners who burn amalgam show signs of mercurialism and fish-eating people living distant from mining activities show high Hg blood levels (Malm, 1991; GEDEBAM, 1992).

Education can help to address this problem since pollution derives from miners' lack of concern for the environment together with ignorance about efficient gold extraction methods. As well, skilled professionals in contact with miners, such as doctors, priests, hygienists, social workers, nurses, mine inspectors and union leaders have limited knowledge about Hg transformations in the environment, its accumulation into the food chain and the symptoms manifested by a mercurialism victim. Such individuals can play a significant role in working with this problem but they need information and knowledge provided in an understandable and convenient way.

Computer programs can contribute to education. We have developed such a program - an Expert System called HgEx which combines technical factors with the power of heuristic observations to diagnosis bioaccumulation risk and recommend remedial procedures for a specific site. Developed in a natural-language programming-environment under MS-Windows, HgEx can be used by non-technical persons. A comprehensive Hypertext tutorial section gives details on Hg chemistry and distribution, amalgamation practices, bioaccumulation and the design of a site-specific monitoring program.

Conventional approaches that correlate natural variables with Hg biota levels rely on empirical regression models that often yield poor predictions of bioaccumulation (Håkanson *et al.*, 1988). Predictions are fraught with uncertainties and unknowns such as internal correlations between variables and site-specific aspects of biota contamination. The effect of some natural variables is controversial (Richman *et al.*, 1988; Verta *et al.*,

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1986) but the influence on bioaccumulation of pH, humosity, conductivity, biomass, suspended solids and Hg in sediments would seem appropriate.

In this work, a heuristic approach is used in which mining and amalgamation methods together with natural variables are dealt with using Inference Equations to conclude about belief in bioaccumulation risk. The system can handle uncertain or vague data using Fuzzy Logic and Neural Network techniques. The procedure reduces the need for extensive monitoring programs of a mining site and provides a preliminary diagnosis about bioaccumulation risk from an Expert's point of view (Veiga and Meech, 1992). Despite sparse data and uncertainty, a diagnosis can still be made about the likelihood of a critical situation.

2. System Overview

Field observations are the main source of information that allow evaluation of critical situations. HgEx conducts its diagnosis in three steps using the structure shown in Fig. 1:

- Determine the extent of Hg emissions from a site or region
- Determine the dangerous environmental factors and sediment adsorption ability
- Evaluate the potential bioaccumulation risk

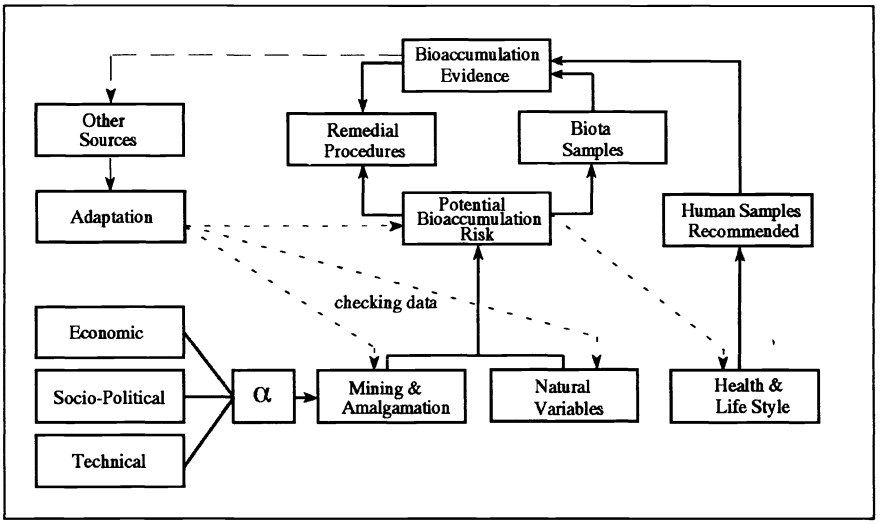

Fig. 1. System Structure

Potential bioaccumulation risk predicted by the system is compared with analyzed biota samples, when available, and conclusions about current and future bioaccumulation are provided (Fig. 1). When a high potential for bioaccumulation is indicated but the biota does not show high Hg levels, the system suggests frequent monitoring programmes and remedial procedures to look for future problems that may develop.

Occasionally, the system may predict a low bioaccumulation risk at a time when reliable biological samples provide evidence of a mercury accumulation process. The system will check the user inputs, searching for imprecise data (e.g. chemical analyses). If conflict persists after a hierarchical process of checking, the system uses the consultation data to adapt its diagnosis for the case study. Other sources of emission are considered the main reason for discrepancies between the predicted and evidenced bioaccumulation level. For example, forest fires have been estimated to contribute 26% more Hg to the Amazon than garimpos (Veiga *et al.*, 1994).

3. Mercury Emissions

The mining method and amalgamation procedure determine how Hg is released into the environment. At "garimpos", Hg entering the atmosphere can be as much as 45% of that introduced into the amalgamation process, when retorts are not used (Fig. 2). When metallic Hg is discharged with tailing, its relatively low mobility in watercourses creates points with very high concentrations ("hot spots"). These spots can be identified at the bottom of creeks or close to their margins.

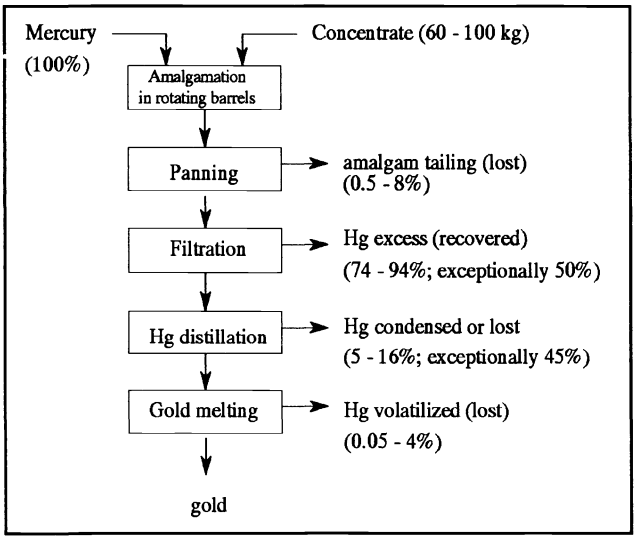

Fig. 2. Mercury balance in amalgamation in Poconé, Brazil. (adapted from Farid *et al.*, 1991)

To predict the extent of Hg emission, a number of events involved with mining and amalgamation have been examined from observations at different Amazon operations. The following factors are combined to predict the extent of emission:

- Region or site analysis
- Size of operation
- Mining method
- Portion of ore amalgamated

- Amalgamation method
- Amalgam/mineral separation method
- Fate of amalgamation tailing
- Gold/amalgam separation method
- Gold melting method

Rules can be developed to comprise all situations adopted by the miners with conclusions about emissions obtained from a suitable method which combines all pieces of evidence. Conventional expert systems apply the Minimum Degree of Belief of the premise statements. Unfortunately a large number of rules and possibilities must be established to represent the expertise precisely. If all options listed above are considered, there are over 70,000 rules required. Although all of these combinations are not actually practiced by the miners, representation of sensible situations is not a simple matter.

The method used in this work is adapted from a basic neural equation which propagates weighted evidence to a conclusion. The model is based on the now famous Perceptron neural network developed by Rosenblatt in 1957 (Minsky and Papert, 1969; Meech and Kumar, 1992). All inputs to a node are summed after multiplying by a "suitable" weighting value between 0 and 1.

A term called "High Emission Factor" (HEF) is used to collect evidence that a high emission of Hg exists. The higher the Degree of Belief in High Emission Factor (DoB_{HEF}) the higher our belief that high Hg emission is occurring. DoB_{HEF} is shown to the user in the form of linguistic expressions such as: "high", "low", "very low", etc. to characterize the level of emissions from an operation. We know, however, that these expressions are context-sensitive. What is "low" for some people may be "very high" for others. This depends on the concern and reaction of a society to the technical and economic factors which promote gold mining activity. So, the DoB_{HEF} is raised to an exponent value (alpha factor) which shifts the linguistic expression definition (Fig. 3). The following Weighted Inference Equation provides the DoB_{HEF} in high Hg levels by considering the importance of each variable on Hg emission:

$$DoB_{HEF} = [MIN\ (100, \sum_{i=1}^{n} W_i \cdot DoB_i)]^{\alpha_{HEF}}$$

where:

DoB_{HEF} = Degree of Belief in HEF

W_i = weight (importance) of the event *i*

DoB_i = degree of belief in *i*

α_{HEF} = α–factor - determined from external parameters

The alpha factor was devised to accommodate differences in the intensity of man-made Hg emissions. We observe that the behaviour of workers depends on society incentives and reactions. As a result, the development of a society will change our definition of high

and low levels of Hg emissions. To map these differences, an alpha factor is calculated based on Socio-Political, Technical and Economic aspects of a society which relate to the acceptance or rejection of Hg use in gold mining operations. A high alpha factor indicates acceptance of amalgamation practice and low control of Hg emissions enforced by a society, which may be a country, a region or a city. For the Amazon situation, $\alpha = 1$. For Canada, where Hg is practically banned and well monitored by authorities, the alpha factor is much lower (0.1 or 0.01). For Canada 150 years ago, when the hazardous effects of Hg were unknown and thousand of miners were colonizing the West, alpha would be much higher (about 10 or 100).

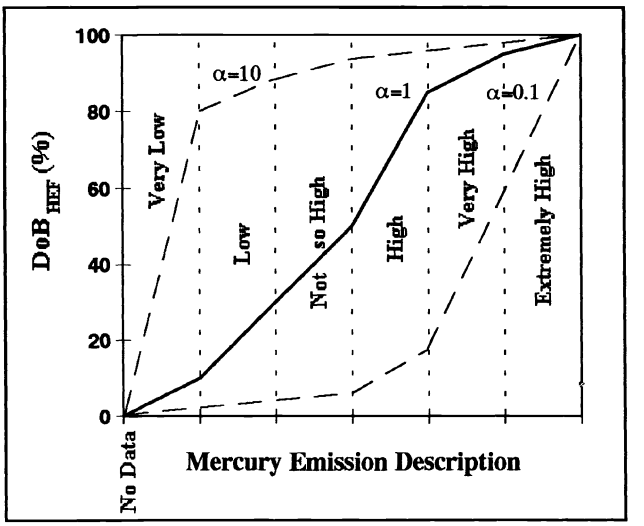

Fig. 3. Linguistic output of Degree of Belief in High Emission Factor

The main advantages of this method are:

- Dependent variability can be handled.
- A single network node can represent multiple output values.
- Outputs are easily adjusted for other situations using one simple equation..
- It is easy to explain the knowledge accumulation process.
- A User can input uncertainties and multiple choices or leave a step unknown.

Eight real cases of mining operations were used to formulate the weight (W_i) of each event in concluding about DoB_{HEF} (Table I). These cases represent most "garimpeiros" behaviour and mining activity in the Amazon. While exceptions may exist, we consider that the Inference Model used in this work will be able to cope with any unusual cases.

From the data in Table I, we can observe that amalgamation operations on board vessels are the main source of Hg emission to the environment. Most "garimpeiros" conduct amalgamation and separate amalgam-heavy minerals in a water box on board. When the box is full, they simply dump contaminated tailing into the river. Substantial reduction could be achieved by using retorts and by reprocessing tailing separately in a plant.

Table I. Correlation of Model Output with Observations at Mining Sites

Case	DoB_{HEF}	Hg emission	Reference
Madeira River - dredges	100	extremely high	Pfeiffer *et al.*, 1991
Madeira River - rafts	100	extremely high	Pfeiffer *et al.*, 1989
Rato River - monitor	100	extremely high	CETEM, 1993
Poconé - mill	65	high	author's visit
Poconé - mill	40	not so high	CETEM, 1989
Teles Pires - rafts	100	extremely high	CETEM, 1991
Serra Pelada - mill	40	not so high	author's visit
Roraima - manual	100	extremely high	Feijão and Pinto (1992)

The weights used to calculate DoB_{HEF} range from 0.3 to 0, i.e. from "very-high" to "low". Examples of the relationship between importance and weights are shown below:

Importance	Weight	Example of Event
very high	0.3	amalgam is burnt in pans
high	0.2	making amalgamation at the creek margin.
medium-high	0.15	amalgamation tailing recycled to primary gravity circuit
medium	0.1	amalgamation uses pots or copper plates
medium-low	0.05	dredges or rafts are used; blenders are used
low	0	miners use retorts

There is a clear logic associated with the process of establishing weights for events that are directly or indirectly related to the amalgamation operation itself. For example, the size of the mining operation is a relevant consideration. If a mine uses poor amalgamation procedures, this should derive a high DoB_{HEF}. However, it is obvious that the smaller the operation, the lower the emission. So large mining operations using amalgamation have a weight of 0.2 while a small one has 0.05. If all other factors are not present, the DoB_{HEF} for a large mine would be 20% or low for the Amazon region but high in a Canadian context. This seems acceptable and reflects the fact that no large gold mining operations in North America uses amalgamation.

The weight of some events are associated with a judgment of the operation itself. For example, since it is "known" that most dredges and rafts are the main emitters, we increase the HEF factor by using a weight of 0.05 for the fact that a dredge is in operation. This weight mirrors the fact that frequently Hg is spilled on board and amalgamation is carried out less carefully than on land. Similarly, we know dispersion is higher when high speed blenders are used to mix Hg with gravity concentrates. So a weight of 0.05 is also used to mirror the fact that this tailing carries more Hg than tailing generated by manual panning but less than tailing from continuous amalgamation processes, such as pots, plates or sluices. These latter methods have higher weights.

4. Dangerous Environmental Factors and Sediment Adsorption

The next step is to determine dangers in the environment to which Hg is being emitted. This analysis takes into account field observations and biogeochemistry of Hg.

Dark water rivers play an important role for Hg incorporation in biota (Mannio *et al.*, 1986). Unfortunately, little is known about the process by which organic substances in solution transform liquid Hg into methylmercury (Me-Hg). We have conducted some preliminary experiments in which tannic acid and fulvic acid solutions exposed to metallic Hg increase Hg levels in solution by 100 times. As most dark water rivers are not impacted directly by gold mining activities, natural Hg from organic soils or atmospheric Hg must be contributing to the high levels in the biota from these environments.

Methylation and bioaccumulation are controlled by a number of environmental factors. Variables that contribute to enhanced methylation and bioaccumulation are combined into a Dangerous Environmental Factor (DEF). These variables are:

- water colour
- water conductivity
- sediment Eh and pH
- biomass
- presence of "hot spots"
- Hg analyzed in sediments
- Hg background

Variables able to reduce Hg availability are defined as Mercury Adsorption Factor (MAF). The following items determine the importance of MAF:

- presence of hydrous ferric oxides - quantified by sediment colour
- presence of clayey sediments
- suspended solids

A methodology similar to that used for DoB_{HEF} is applied to determine DoB_{DEF} and DoB_{MAF}. This approach mirrors the concept that bioaccumulation risk is a function of the Hg emission level and the extent of Hg transformation. Mercury abatement by adsorption on fine ferruginous sediments is the only way in which risk can diminish.

5. Bioaccumulation Risk

Finally, belief in the Potential Bioaccumulation Risk (DoB_{PBR}) is calculated from:

$$DoB_{HEF} + DoB_{DEF} - DoB_{MAF}$$

Conclusions are then output using linguistic terms which depend on the value of DoB_{PBR} such as:
"*This condition is highly favourable for bioaccumulation. Check the fish. We suggest remedial procedures*" or "*It seems that bioaccumulation is controlled by natural factors*".

As an example of diagnosis, a case study of the Poconé region is presented below. The proximity of an important Ecological Park in South America ("Pantanal") makes this region a target of environmental groups and constant monitoring programs. Data input for bioaccumulation assessment were as follows :

This is a *small* "garimpo" region in which *milling* is the predominant extraction method. The amalgamation process is typically applied to *concentrates* in rotating *barrels* rather than to the whole ore. Some *manual panning* is also observed. Amalgam is separated from heavy-minerals in *water boxes*, in excavated *pools* or simply *panned at creek margins*. Amalgamation tailings are either *discharged to watercourses, recycled to plants* or *safely stored in pools*. Retorts are the preferred technique to recover the gold from amalgam, however there are some miners who *burn amalgam directly in a pan*. There are only a *few gold shops* but *no special fume hoods* are in use.

The above description input to the system derives a DoB_{HEF} for the region of 100%

The ferruginous sediment has a background level *inferred at 0.15 ppm Hg*. The water colour of the main drainage (Bento Gomes River) *is almost dark*, conductivity is *moderate (60 μS/cm)* and the biomass is *high*. Hot Spots are *visually identified* in many creeks of the region indicating *high Hg level*. The contaminated sediment is *rich in clay* and is *red-maroon* in colour. Analyses showed more than *20%* Fe_2O_3 and *0.1 ppm Hg*. The redox potential of interstitial water was *0.390 V at pH 6.3*. Near the mining activity, the watercourses are *a bit cloudy*. Samples of *20 carnivorous fish* gave an average of *0.1 ppm Hg* while the average of *100 snails* (*Pomacea canaliculata*) showed *0.23 ppm Hg*

When input to the system, the above data (italicized words) derive a DoB_{DEF} of 55% (relatively dangerous) and a DoB_{MAF} of 100% (definitely possible). These factors combine to yield a DoB_{PBR} of 55% while the biota results suggest a DoB_{BE} is only 30%. The system will conclude that evidence of bioaccumulation is currently moderate but the risk of increasing bioaccumulation in the future is moderately-high and so continued monitoring programs are advised as well as remedial procedures for "hot-spots".

Testwork with caged organisms demonstrated that adsorption of Hg was controlling the process of bioaccumulation at that time (CETEM, 1989).

6. Human Risk and Health Problems

Inhalation of Hg vapours is more significant for "garimpeiros" (informal miners) and gold shop workers (gold melters). A level of 60,000 $\mu g/m^3$ was measured by Malm (1991) in the air when amalgam is burnt in pans. Urine samples have shown Hg levels >20 ppb for "garimpeiros" burning amalgam daily, whereas levels between 10 and 20 ppb were observed for those burning amalgams 2 or 3 times per week. Normal levels are <10 ppb. Symptoms such as visual constriction, irritability, decreased memory and metallic taste were detected among the workers of gold shops in Alta Floresta (CETEM, 1991).

When intoxication takes place via food, Hg accumulates in methylated form (Huckabee *et al.*, 1979). High Hg levels (21 to 206 ppb) have been found in the blood of individuals living far from mining activities in the Amazon (GEDEBAM, 1992). Mercurialism is not clearly identified owing to differences in the amount of Hg burnt, fish consumed and origin as well as masking effects such as tropical diseases, alcohol consumption, etc.

Based on the environmental picture established by belief in a Potential Bioaccumulation Risk, a questionnaire is available to evaluate human risk. The conclusions do not yield a definitive clinical diagnosis but rather, give advice on whether hair, urine or blood samples should be collected. If such analyses are available, the system will compare them with normal ranges and based on symptoms observed, will suggest if an individual is subject to mercurialism or not. When human samples are taken indiscriminately without prior environmental evaluation, suspicion can spread among affected communities, since the analytical results and treatment methods are rarely given to the sample donors. In addition, the cost involved in collecting and transporting chilled samples to laboratories is high. Rationalization of this operation is required to obtain reliable data.

The questionnaire investigates undue occupational exposure of workers and possible indirect intoxication of ordinary people. A user inputs information from interviews with individuals using questions related to the following factors :

- Diet Habits: habit of eating fish, how many times per week and which kind of fish.
- Symptoms: general symptoms of mercurialism and masking factors.
- Occupational Exposure : how Hg is handled and how frequently.
- Life Style : storage of Hg and work clothes in the home; proximity to a source.

When inorganic Hg poisoning is likely, the system recommends urine samples. When methylmercury poisoning is suspected, hair analysis is suggested. If suspicion becomes stronger, blood analysis is recommended instead.

Methylmercury symptoms are the main factors in suggesting hair or blood sampling. However, many fish-eating individuals in the Amazon do not show symptoms of "Minamata disease" although Hg levels as high as 100 ppm in hair have been measured (Malm *et al.*, 1994). This leads us to place higher importance on diet habits and bioaccumulation evidence (biota analyses) rather than medical symptoms. When high Hg is analyzed in fish and/or other biota samples, bioaccumulation evidence (DoB_{BE}) is provided, otherwise the predicted bioaccumulation risk (DoB_{PBR}) is used to suggest hair or blood analyses. This stresses the concept that a prior evaluation of bioaccumulation potential in a region or site should be conducted before collecting human samples.

As before, linguistic terms are used to provide conclusions such as: "*Urine samples are recommended.*", "*Blood samples are strongly recommended.*", "*Hair samples can be helpful*", "*Evidence is insufficient to recommend blood or hair analysis.*", etc.

9. Conclusions

Expert Systems can play an important role in transferring heuristic knowledge to non-technical people who may be exposed to Hg. Since the subject is fraught with uncertainties about the effects of natural variables, the knowledge base accommodates imprecise data based on field observations. Heuristic Equations are suitable techniques to mimic the reasoning of an Expert, conferring elasticity to the Degree of Belief calculated for conclusions. In this particular case, linguistic terms have the same practical effect as complex mathematical models which usually demand high costs, much data and skill to quantify the relationship between each factor and bioaccumulation. Rapid diagnosis can bring rapid decisions.

HgEx was designed to integrate common-sense knowledge with observations and field samples of variables that usually correlate positively with Hg pollution. The system alleviates evaluation difficulties of monitoring programs by accepting vague data and by estimating the importance of variables to the final conclusion based on Expert opinion.

Acknowledgments

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PART II

MERCURY SOURCES AND TRANSPORT

MERCURY STACK EMISSIONS FROM U.S. ELECTRIC UTILITY POWER PLANTS

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Abstract. Literature estimates for worldwide anthropogenic mercury (Hg) emissions range from 900 to 6200 t/yr. EPA recently estimated that U.S. electric utilities emit about 93 t/yr. EPRI, DOE, and others have recently conducted field measurements to better quantify electric utility emissions of Hg and other trace substances. Hg emissions inventories based on these recent measurements indicate that total electric utility Hg emissions are about 40 t/yr - about half of these previous estimates. Furthermore, the results have indicated that Hg emissions are quite variable and are not consistently captured by conventional air pollution control technologies - electrostatic precipitators, fabric filters, and flue gas desulfurization systems.

1. Introduction

Title III of the 1990 Clean Air Act Amendments (CAAA) mandated that the U.S. Environmental Protection Agency (EPA) evaluate emissions and health risks associated with 189 hazardous air pollutants from electric utility steam generating stations. Hg was singled out for two separate studies that will examine emissions from utilities and other sources and define the thresholds at which Hg affects health and ecology. In anticipation of the CAAA, the Electric Power Research Institute (EPRI) initiated the Power Plant Integrated Systems: Chemical Emission Studies (PISCES) research program in 1988 (Chow 1991).

As part of the PISCES program, the Field Chemical Emission Monitoring (FCEM) program was undertaken to fill critical data gaps in the literature. To date, the EPRI FCEM program has sampled at 35 utility sites - encompassing a range of fuels, boiler configurations, particulate control technologies, flue gas desulfurization systems, and NOx control technologies. Parallel to EPRI's efforts, the Department of Energy (DOE) has conducted field measurements as part of two DOE studies - the Clean Coal Technology program and the Comprehensive Assessment of Air Toxic Emissions from Coal-Fired Power Plants (Schmidt and Brown 1994). The combined studies provide the most extensive quality-controlled data set extant for estimating Hg (as well as other trace substances) emissions from electric utilities.

Parallel to the FCEM program, EPRI's work in Hg cycling highlighted the need to characterize the various species of Hg in stack emissions. EPRI sponsored development of a technique to speciate Hg, and at select sites, Hg speciation measurements were conducted. This paper summarizes recent Hg field results and quantifies total Hg emissions from electric utility power plants.

2. Literature

Various authors have estimated global anthropogenic Hg emissions. Using the geometric mean of the range of Hg emissions compiled by Nriagu and Pacyna (1988), present day worldwide fossil-fuel combustion was estimated to produce about 1500 t(1000kg)/yr (290 from electricity generation and 1210 from other industrial use). The U.S. EPA has compiled information about present day estimates of Hg emissions from many sources to the atmosphere in the U.S. that amount to about 300 t/yr in 1990 (MRI 1993). This study estimated that coal-fired power plants emit 89 t/yr, with total power plant Hg emissions of 93 t/yr. This estimate was based largely on Hg in coal data from the U.S. Geological Survey (USGS). The USGS analyzed thousands of channel and core samples of coal for various coal quality

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parameters, including Hg content. These data represent "in-the-ground" coals which are often different in Hg content from "as-fired" coals. After the coal is mined, the coal may be washed before it is pulverized and burned.

3. Recent Field Studies

The PISCES program was initiated in 1988, and the initial phase involved a compilation of an interim chemical emissions database based on literature information. EPRI and the Utility Air Regulatory Group (UARG) concluded that the literature data (1) contained significant gaps -- especially with regard to internal plant streams, (2) were highly variable for a given plant characteristic, and (3) were conducted using inconsistent sampling and analytical procedures (Radian 1992). The limitations in the database became the impetus for EPRI and DOE's intensive field data acquisition efforts. To date, 48 fossil fuel-fired power plants have been sampled by EPRI and DOE. Because some sites were tested under different configurations (i.e. pilot facilities, pre- and post-low NOx burners, upstream and downstream of an flue gas desulfurization (FGD) system), more than one data set was obtained at some sites. The combined field studies include every significant coal type, boiler configuration, and particulate, SO_2, and NO_x control technology. The two sampling programs followed generally consistent sampling and analytical protocols. Triplicate samples were collected at each field site over a period of about 3 to 5 days. The results of these field studies provide a reasonable estimate of expected Hg emissions from utility power plants. However, because of the low concentrations of Hg and the nature of Hg, sampling and analysis have generally been difficult and significant uncertainty exists in the data.

3.1 HG IN FOSSIL-FUELS

The U.S. electric utility industry burns three major classifications of fossil fuels - coal, fuel oil, and natural gas. Figure 1 compares the measured Hg concentrations from the recent field sites with those in the literature for the three fossil fuels - coal, oil, and gas. The recent measurements have indicated Hg levels in U.S. coal range from 0.02 to 0.25 μg/g (emissions in the range: 0.5 to 10 μg/MJ; multiply μg/MJ by 2.3 to obtain lb/10^{12} Btu). Hg levels in coal tend to be 1 to 4 orders of magnitude greater than in fuel oil and natural gas; thus it makes sense to discuss Hg emissions by these different fuel types.

3.1.1 Coal

The more recent measurements tend to be within the data range of the literature values, but do not include some of the high literature results. Because of the limited sample size from EPRI's field studies and in order to better quantify Hg concentrations in coal, EPRI and UARG sponsored a study to analyze 123 different "as fired" coals (Baker, Bloom). At select power plants, multiple samples were taken at different time intervals in order to evaluate variability. A total of 154 samples (106 bituminous, 37 sub-bituminous, and 11 lignite) were analyzed. These coal samples represent a significant portion of the current and anticipated future coal supplies for the U.S. utility industry. These include samples of coal from a total of 76 counties in all 18 major coal-producing states in the U.S. In aggregate, this study provides a broad-based representation of the Hg content in U.S. coals. The results are summarized in Table I. The overall mean Hg concentration in the 154 samples was 0.085 μg/g (standard deviation of 0.074 μg/g). The multiple samples from the select plants varied within 10 percent but did not significantly affect the mean. The mean of the 123 different coals was 0.088 μg/g.

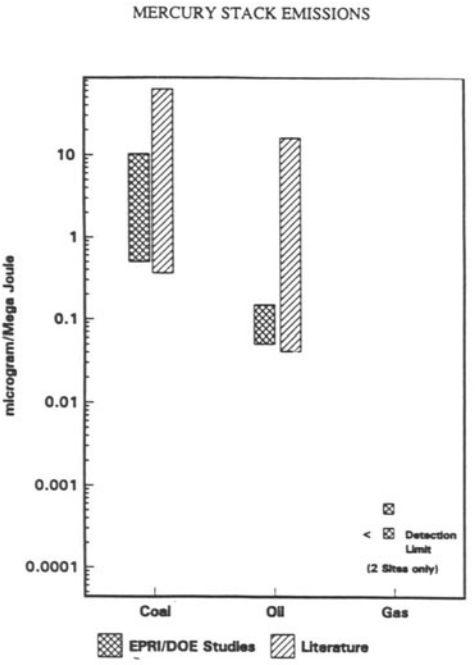

Fig. 1. Hg Levels in Fossil Fuels

TABLE I
Summary of Hg Concentrations by Coal Rank (Baker 1994)

Coal Type	Number of Samples	Arithmetic Mean (µg/g)	Standard Deviation (µg/g)
Bituminous	87	0.087	0.070
Sub-bituminous	37	0.053	0.027
Lignite	11	0.177	0.118
All Ranks	154	0.085	0.074

The results showed lower levels of Hg in the coal than the revised USGS coal database. The mean Hg concentration for bituminous coals from the EPRI/UARG study was 0.087 µg/g. This compares with an average of 0.21 for bituminous coals based on the USGS database. As noted earlier, the USGS database represents as-mined core samples, while the EPRI study represents as-fired coal samples. Thus process steps such as coal washing remove some Hg and are not accounted for in the USGS analyses.

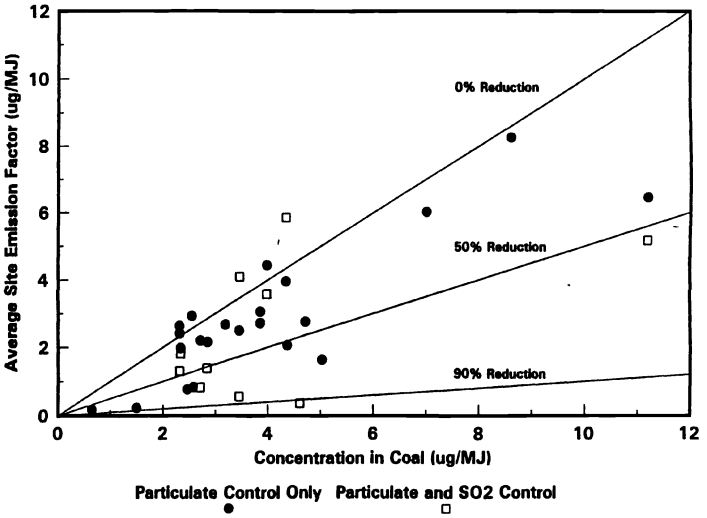

Fig. 2. Hg Emissions from Coal-fired Power Plants

3.1.2 Fuel Oil and Natural Gas

In the EPRI fuel oil sites, Hg was initially not detected in most of the fuel oil samples. To obtain lower detection limits, INAA (instrument neutron activation analysis) was used instead of CVAAS (cold vapor atomic absorption spectrophotometry). Using INAA with standards and blanks to ensure no loss of Hg, Hg was measured in the 0.002 to 0.008 μg/g range (0.04 to 0.13 μg/MJ). This is 1 to 2 orders of magnitude less than in coal. Natural gas samples were analyzed for Hg at only two sites. Hg was detected at 0.02 $\mu g/m^3$ (0.00056 μg/MJ) at one site and below the detection limit of 0.01 $\mu g/m^3$ (0.00028 μg/MJ) at the other site.

3.2 FLUE GAS STACK EMISSIONS

All coal-fired plants employ some type of particulate control technology and some plants also include an FGD system. This is significant because particulate and SO_2 control systems may remove Hg. Only a fraction of the oil-fired plants have a particulate control device, and no commercial oil-fired plants use an FGD system. Gas-fired power plants are generally uncontrolled.

3.2.1 Coal-fired Power Plants

Figure 2 compares the Hg specific emission factors with the inlet coal feed for coal-fired units. Both the individual Hg emission rates and the inlet coal concentration are normalized to mass of Hg per unit of heat input (μg/MJ) to calculate Hg removals for each site. Hg removal is defined as the reduction in total Hg stack emissions relative to potential Hg emissions based on the Hg in coal concentrations. The results are presented for the two general air pollution control technologies - dry particulate control (ESP and fabric filters) and FGD systems (spray dryer absorbers and wet FGD systems).

TABLE II
Hg Emission Factors for Coal-fired Power Plants[a] (μg/MJ) [b]

	Dry Particulate Control [c]			Combined Particulate and FGD Systems [d]		
Coal Type	Range	Number	Mean	Range	Number	Mean
Bituminous	1.7 - 6	15	2.8	0.3 - 1.5	4	0.6
Sub-bituminous	< 0.2 - 4.4	7	1.4	0.8 - 3.6	3	2.1
Lignite	4.5 - 6.4	2	5.5	4.3 - 5.2	2	4.7

[a] Based on recent field measurements as part of EPRI's PISCES program and DOE's field test efforts. Results obtained using the EPA multi-metals train (EPA Method 29).
[b] Multiply by 2.3 to convert to $lb/10^{12}$ Btu.
[c] This includes both ESPs and fabric filters.
[d] This includes both wet and dry FGD systems.

ESPs and Fabric Filters. Because Hg is generally present in the vapor phase at particulate control temperatures (120 to 150°C, Hg is not consistently well controlled by an ESP or fabric filter. Hg removal varied among the test sites—including some sites where the outlet Hg was greater than the inlet coal Hg, likely due to sampling and analytical variability. By contrast, Hg removals greater than 60% were measured at several sites, with the Hg accounted for in the collected fly ash. However, an explanation could not be found why certain plants or coals yield more particulate phase Hg The mean removal efficiency for all coal-fired plants with dry particulate controls was about 30%.

Wet FGD Systems. Hg removal efficiencies for a combined ESP (or fabric filter) and wet FGD systems were highly variable and gave poor correlation with the FGD design, coal composition, or measured Hg valence (oxidation) state. The Hg removal efficiencies for ESP/FGD systems ranged from as low as 0% to as high as 90%. Research has shown that oxidized Hg appears to be removed to a greater degree than elemental Hg (Peterson et al. 1994). However, only poor correlation was obtained with oxidized Hg or with Hg removal efficiency by FGD systems. The mean Hg removal efficiency for the combined ESP/FGD system was about 45%. EPRI, DOE, and other organizations are continuing work in this area to better understand Hg chemistry.

Emission Factors - The Hg emission results for coal-fired plants are presented for the three major coal classifications as well as the two general air pollution control technologies - dry particulate control (ESP and fabric filters) and FGD systems (spray dryer absorbers and wet FGD systems). The database is quite small for most of the categories, and this should be considered when applying the results in Table II. For example, the average Hg emission factor for units burning sub-bituminous coals with only particulate controls was actually less than the average Hg emission factor for the combination of the particulate and FGD system. This artifact was due to the small number of units studied. Two of the FGD systems had less than 25% Hg removal, while four of the dry particulate control sites achieved greater than 65% removal. Only two sites were tested that burn lignite coal; thus the confidence interval around the average emissions for these units is broad. The sites tested include both North Dakota and Texas lignite coals.

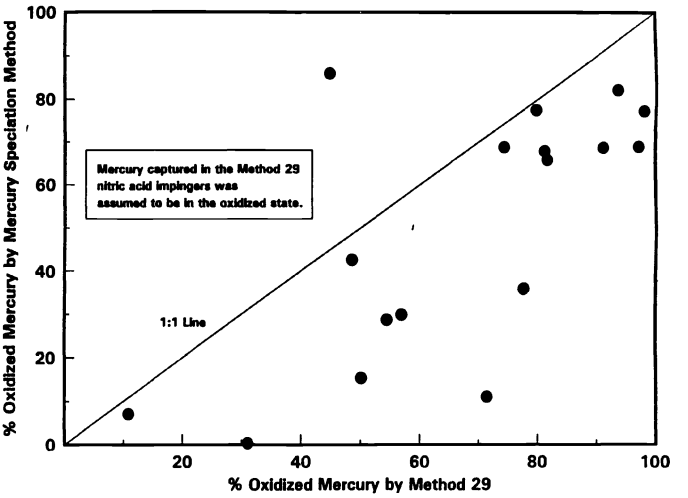

Fig. 3. Comparison of Hg Speciation Methods

Hg Speciation. Hg emissions may be present in several valence states - elemental (Hg^0) and oxidized (Hg^{+2}). This has significance for several reasons. The chemical form of the Hg may affect the degree of removal, as well as atmospheric fate, health effects, and risk assessment. EPRI has applied two sampling methods to quantify Hg emissions - the EPA multi-metals train (EPA draft Method 29) and the mercury speciation adsorption (MESA) method (Prestbo and Bloom 1995). EPRI has used both methods to provide some estimate of oxidized and elemental Hg. Neither method has been validated for Hg speciation. At some sites, the flue gas was sampled downstream of the ESP and some oxidation/reduction of Hg may occur before exiting the stack. In addition, oxidation/reduction of Hg may occur in the sampling system as well. Both methods are still experimental for Hg speciation, and further validation studies are planned. The multi-metals train uses two sets of impingers to capture the vaporous Hg. The first set of impingers consists of HNO_3/H_2O_2 and the second set consists of $KMnO_4$. Method 29 was not designed to speciate Hg, but it has been suggested that only oxidized Hg is captured in the HNO_3/H_2O_2 impingers, thus all remaining Hg (which should be elemental Hg) is captured in the $KMnO_4$ impingers. The MESA method, designed to speciate flue gas Hg, follows a similar approach except it uses a different medium to capture the Hg. This method employs solid sorbent traps - consisting of soda lime and iodated carbon - to capture the oxidized and elemental Hg, respectively.

The oxidized Hg concentrations from Method 29 (this assumes that the Hg captured in the HNO_3/H_2O_2 impingers is oxidized Hg) generally appear to be higher than the oxidized Hg concentrations from the MESA method. Figure 3 compares the measured levels of oxidized Hg based upon these two methods. Because the two methods generally agree for total Hg (some sites having large discrepancies), it would appear that one or both methods does not accurately quantify oxidized Hg. The purpose of the HNO_3/H_2O_2 impingers in Method 29 was to capture the volatile trace metals (such as arsenic, chromium, and nickel) and was not intended to selectively capture oxidized Hg. Thus, some elemental Hg may be captured in the HNO_3/H_2O_2 impingers. The other possibility is that the MESA method does not efficiently capture all the oxidized Hg. Recent research has shown that the oxidized Hg capture efficiency in the soda lime traps is a function of the sampling temperature. Some of the early runs were

not conducted at optimum temperatures and it is possible some of the oxidized Hg was not captured in the soda lime traps—thus underestimating oxidized Hg. In addition, the MESA was not designed to sample flue gas isokinetically, thus the train may not obtain a representative sample of particulates. However, when detected, the particulate phase Hg has generally been a small fraction (<1%) of the total Hg. In addition to being present at very low levels in the particulate phase, the ESP or fabric filter would be expected to capture most of the particulate phase Hg.

For dry particulate controls (ESPs and fabric filters), the mean percentage of oxidized Hg levels based on the sorbent speciation and Method 29 trains were 55 and 70%, respectively. The mean percentage of oxidized Hg for FGD systems were 25 and 45%, respectively.

The ratio of oxidized and elemental Hg is potentially a function of the coal type and composition as well as flue gas conditions. Data were insufficient to determine any definitive correlations to predict levels of oxidized and elemental Hg—other than by direct measurement. Figures 4 and 5 compare the concentration of oxidized Hg (in $\mu g/Nm^3$ - normal [25°C, 1 atm]) as a function of Cl in the coal for the multi-metals and sorbent speciation methods. The results from the MESA method show a trend toward higher oxidized Hg concentrations with increasing Cl content in the coal. This trend was not apparent with the Hg speciation results from Method 29. It is important to note that some results appear to be "outliers" and there is significant scatter among the data. This may be due to other factors that affect Hg speciation and that have not been completely considered. In addition, some of this scatter may be due to process variability as well as sampling and analytical methods.

3.2.2 Fuel Oil-fired Power Plants

As part of the State of California AB2588 study, utilities attempted to measure Hg (as well as other trace substances) emissions from oil-fired power plants. The method detection limits were not sufficient to quantify the concentrations of Hg in either the fuel oil or the stack. In EPRI field sites, more sensitive analytical methods were used to achieve lower detection limits in both the fuel oil and stack measurements. INAA was used to analyze the fuel oil - instead of CVAAS. Using INAA, Hg in fuel oil was measured in the 0.002 to 0.008 µg/g (0.04 to 0.13 µg/MJ) range. Assuming that all the Hg in the fuel oil is emitted in the stack, the Hg concentration in the flue gas would be approximately 0.1 to 0.4 $\mu g/Nm^3$. Because the Hg method detection limit (flue gas measurements) have ranged from 0.1 to 0.5 $\mu g/Nm^3$, these low levels of Hg have led to difficulties in quantifying the Hg concentration in flue gas for oil-fired power plants. Measured Hg stack emissions have ranged from 0.2 to 1.7 $\mu g/Nm^3$ (0.07 to 0.6 µg/MJ). The measured emission levels have been highly variable and have sometimes been much greater than the inlet fuel levels. Trace metals emissions data from fuel oil plant appear to be log normal, thus a geometric mean for Hg appears to be more appropriate than an arithmetic mean. A geometric mean reduces the emphasis on the very high measurements which are likely due to sampling and analytical difficulties. The geometric mean is 0.2 µg/MJ (Table III); this emission factor is conservative since this is higher than the Hg levels in the fuel oil.

3.2.3 Gas-fired Power Plants

Field tests were conducted at two electric utility gas boiler sites. Hg was not detected at the stack at either site. The detection limit was about 0.5 $\mu g/Nm^3$ (0.17 µg/MJ) which was three orders of magnitude higher than the expected levels based on the natural gas analyses. The Hg concentration in the natural gas was measured at 0.00056 µg/MJ (near the detection limit) at one boiler and less than the detection limit of 0.00027 µg/MJ at the other. This yields an average of 0.00034 µg/MJ (assumes half of the detection limit for the not detected value). The best estimate for Hg emissions would be to use the natural gas analyses and assume all the Hg is emitted in the stack (Table III).

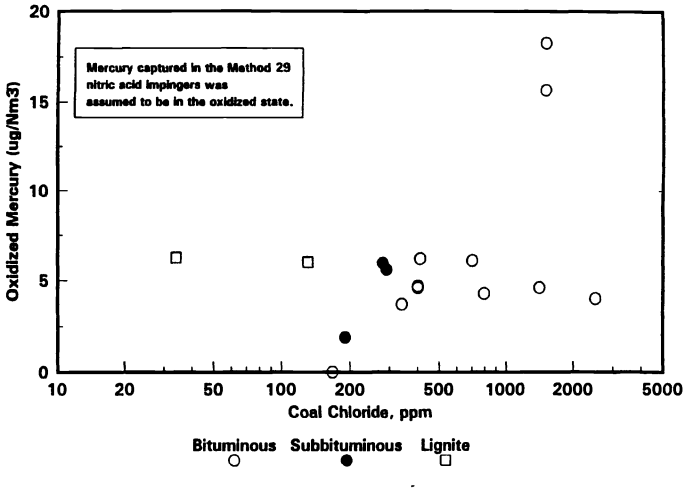

Fig. 4. ESP Outlet Oxidized Hg Concentration (Method 29) as a Function of Chloride Level

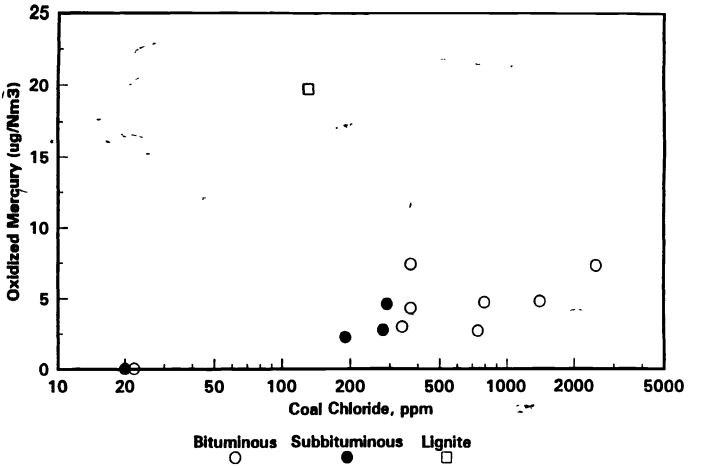

Fig. 5. ESP Outlet Oxidized Hg Concentration (MESA) as a Function of Chloride Level

TABLE III
Hg Emission Factors for Oil and Gas-fired Power Plants (μg/MJ) [a]

Fuel Type	Range	Number	Mean
Fuel Oil	0.07 - 0.6	5	0.20 [b]
Natural Gas	<0.00026 - 0.00056	2	0.00034 [c]

[a] Multiply by 2.3 to convert to $lb/10^{12}$ Btu.

[b] Hg stack emission results for oil plants were assumed log normally distributed. This emission factor is a conservative estimate for oil-fired plants with ESPs.

[c] Natural gas emission factors are based upon Hg in the inlet natural gas analyses, assuming that all Hg was emitted in the flue gas.

4. Total Electric Utility Emissions

Based on these recent and relatively extensive fuel and stack measurements, two approaches additional to MRI (1993) were employed to estimate total electric utility emissions from fossil-fuel fired power plants.

1. The more detailed approach incorporated the coal purchases for each individual power plant (EIA/DOE 1993) and average Hg concentrations based on the Hg coal analyses study (Baker, Bloom 1994) to estimate input Hg. Average removal efficiencies as calculated from the recent EPRI/DOE studies were then applied to estimate Hg emissions at each power plant. The individual Hg emissions were then summed to yield about 39 t/yr for the U.S. electric utility coal fired plants. Hg emissions from oil- and gas-fired utility plants estimated based on heat input data (MRI 1993) and average emission factors (Table III) were less than 0.3 t/yr.

2. An alternative approach applied the average emission factors for each category of fuel type and control technology from Tables II and III and the total heat input data for the U.S. utility industry. The UDI Power Statistics Database (1989) was used to calculate a weighted emission factor based on each of the categories of fuel type and control technology. This simplistic approach is similar to the methods used by other surveys such as MRI (1993), and yields a similar Hg emissions estimate as the detailed approach (described above) of 41 t/yr for the coal-fired power plants.

The estimated Hg emissions from these two approaches are compared with MRI's estimates in Table IV. Both approaches provide estimates of utility Hg inventory on the order of 40 t/yr for the 1990 period - less than half of MRI's estimate. Thus the revised U.S. total for Hg from all sources would likely be on the order of 250 t/yr (MRI 1993) - assuming the Hg emissions data for all other sources were correct. Power plants would amount to about 15 to 20% of the U.S. total, a number likely to decrease as newer generation technologies coming on-line.

TABLE IV
Total Hg Emission from Fossil Fuel-fired Power Plants (t/yr - in 1990)

Fuel Type	MRI [a]	EPRI Estimates	
		Fuel/Removal Efficiencies Methodology [b]	Emission Factors Methodology [c]
Coal	89	39	41
Oil	3.8	0.3 [d]	0.3
Natural gas	not estimated	0.001 [d]	0.001
Total	93	39.3	41.3

[a] Midwest Research Institute (1993).

[b] This methodology employs recent data on Hg in fuels and average removal efficiencies for ESP/fabric filters and ESP/FGD systems for coal fired power plants.

[c] This methodology employs average emission factors and heat inputs. The emission factors were based on actual measured Hg concentrations in flue gases. This calculation is the same approach as MRI (1993), but uses the recent emission factors in Table II.

[d] Based on recent emission factors in Table III.

5. Conclusions

Recent field measurements by EPRI and DOE better quantify Hg levels in fossil fuels and in flue gas emissions from electric utility power plants. These measurements show total Hg emissions from electric utility fossil-fuel fired power plants are about half of previous estimates. Hg is relatively volatile at nominal power plant stack temperatures, and is not consistently captured in conventional particulate and SO_2 control devices. The factors that affect Hg removal efficiencies could not be determined from the limited results available. Further, experiments on Hg speciation show the need for additional development work to develop reliable methods.

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MERCURY SPECIATION ADSORPTION (MESA) METHOD FOR COMBUSTION FLUE GAS: METHODOLOGY, ARTIFACTS, INTERCOMPARISON, AND ATMOSPHERIC IMPLICATIONS

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Abstract. Chemical speciation of mercury (Hg) in a wide variety of combustion flue gas matrices has been determined using the mercury speciation adsorption (MESA) method. The MESA sampling system for gas phase Hg species employs a series of heated, solid phase adsorbent traps. Flue gas oxidized Hg species (Hg(II) and MMHg) are adsorbed by a potassium chloride (KCl) impregnated soda lime sorbent. Elemental Hg (Hg^0) is collected by an iodated carbon sorbent after passing through the KCl/soda lime sorbent. Total Hg (Hg_t) is determined by summation of species. In the laboratory, cold vapor atomic fluorescence spectroscopy (CVAFS) is used for detection of Hg collected on the solid sorbents, after appropriate sample digestion and preparation. The MESA method has been evaluated for species stability, matrix effects, breakthrough, artifacts and precision. Based on eight duplicate samples a mean precision of 6.8% 11% and 4.5% (relative percent difference) has been calculated for Hg^0, Hg(II) and Hg_t respectively. Intercomparison of the MESA method with other methods shows very good agreement for Hg_t. Mass balance calculations at 5 sites range from 75 to 140%, with a mean of 97±25%. Overall mean speciation results from 19 separate determinations suggest that Hg(II) has a 1 sigma range of 40 to 94% in coal combustion flue gas at, the inlet to pollution control devices.

1. Introduction

Mercury elicits both interest and concern because of its known toxicity, mobility, bioaccumulation, atmospheric transport, and potential for new regulations by state and federal agencies in North America (Fitzgerald and Clarkson, 1991; Lindqvist, 1991). Atmospheric deposition has been shown to be the principal route for Hg to enter the relatively pristine lakes of the Northern U.S. and Sweden (Watras et al., 1994; Lindqvist, 1991). Although there are many sources of atmospheric Hg, combustion processes (i.e., fossil fuel and municipal waste) are estimated to be the largest single source of anthropogenic atmospheric Hg in the northern hemisphere. One global mass balance calculation estimates that 34% of the Hg emitted to the atmosphere each year is from coal combustion (Nriagu, 1989). In addition, with the prospect of rapid industrialization in several large countries such as China, India and Brazil, the contribution of Hg emissions to the atmosphere from fuel combustion could increase rapidly in the future.

Until recently, very few reliable Hg combustion emission values have been documented for North America, and essentially no comprehensive data was available on Hg species in coal combustion flue gas. Thermodynamic calculations predict that Hg will

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be in the form of $HgCl_2$ and Hg^0 at temperatures typical in flue ducts (80-250° C) (Mojtajedi et al., 1987). Unlike other trace metals in combustion flue gas, Hg, due to its low boiling point, is not generally associated with particulate material, but rather exists almost exclusively in the vapor phase (Lindberg, 1980; Germani and Zoller, 1988) Empirical measurements support this position as very little Hg is retained on flyash collected in particulate control devices. However, more recent measurements not reported in the literature suggest that under certain conditions (for example, low temperature or high soot levels) it is possible for a significant fraction of the flue gas Hg to be observed on particulate material. It is likely that the particulate Hg fraction will increase as the flue gas cools to temperatures below 100°C, especially if vapor phase Hg is in an oxidized form (Meij, 1991a). At the exit of the stack, or in the cooling plume, particulate Hg could be a significant fraction of the total Hg (Danilchik et al., 1994) contradicting an earlier study (Lindberg, 1980).

The accurate measurement of Hg emission from combustion sources is important to our understanding of the global Hg budget. More importantly, quantification of individual Hg species from combustion sources will be critical to address questions concerning Hg control, toxicity, and fate and transport, as each species has dramatically different chemical and biological properties.

The advantages and disadvantages of the commonly used impinger method for flue gas Hg determination (EPA draft method 29 and 101A) have been discussed elsewhere (Meij, 1991b). Briefly, the major disadvantages of the impinger method are the cost, hazardous chemical transport, large sample volume needed to overcome high Hg blanks, SO_2 interference, and wall losses. These disadvantages and the need for Hg speciation have prompted the development of the method described here and other methods (Schlager et al., 1993; Cooper, 1994; Larjava et al., 1993).

This paper discusses the research and results of a mercury speciation adsorption (MESA) method which uses solid sorbent collection and cold vapor atomic fluorescence spectroscopy detection (CVAFS). The method determines the species as Hg(II), Hg^0, monomethyl (MMHg), and total Hg (Hg_t) by summation of species. In particular we will discuss the methodology, analytical evaluation of speciation, results, and atmospheric implications of our findings.

2. Materials and Methods

2.1 SAMPLE COLLECTION

The MESA sampling system for gas phase Hg species employs a series of heated, solid phase adsorbent traps (Figure 1) (Bloom, 1993). The flue gas is drawn through a heated, quartz tube followed by a series of two KCl/soda lime traps and two iodated carbon traps. Oxidized Hg species ($HgCl_2$ and MMHg) are adsorbed by the KCl/soda lime sorbent while Hg^0 passes through and is collected by the iodated carbon sorbent.

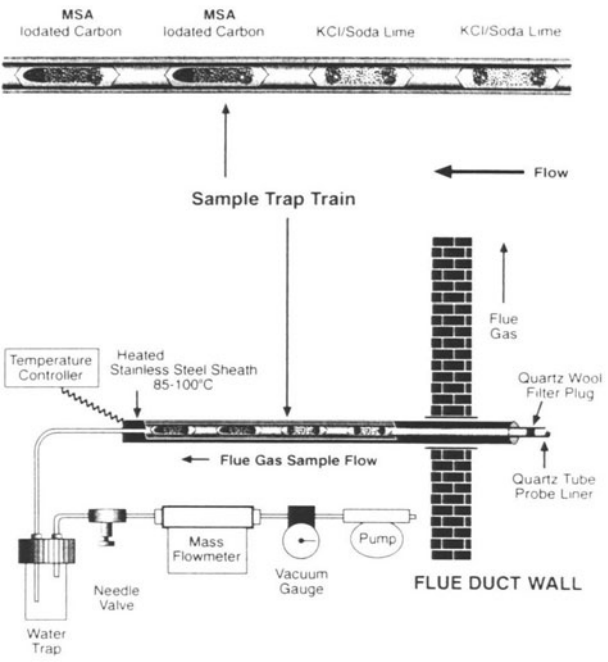

Fig. 1. Schematic of the MESA method sorbent trap configuration and associated equipment for gas phase Hg speciation sample collection. Two traps of each solid sorbent are used to determine Hg species collection efficiency. The quartz wool filter collects particulate material and is analyzed separately.

The MESA sampling system was designed to collect gas phase Hg species and no attempt was made to sample isokinetically in order to obtain a representative particulate Hg sample. The MESA method uses a perpendicular sampling orientation, low flow rate, and small (0.32 cm) inlet orifice for gas phase Hg sampling (Figure 1). Incident particulates entering the system are collected on either an inserted quartz wool plug or on the glass wool plug of the first KCl/soda lime trap (Figure 1). When particulate material collected in this way is separately analyzed for Hg, it typically accounts for less than 2% of the total Hg measured. In the results below, Hg measured on the quartz probe and quartz wool particulate filter are added to the Hg(II) value measured on the KCl/soda lime trap.

The KCl/soda lime traps are manufactured in an ultra clean laboratory by dissolving 250 g of powdered CaO (Strem, phosphor grade), 50 g of KCl (J.T. Baker, Baker Analyzed) and 25 g NaOH (J.T. Baker, Baker Analyzed) in approximately 1 liter of

double deionized water (DDW) to make a viscous liquid. The mixture is oven-dried at 110° C, ground and sieved between 10 and 20 mesh, and then ashed at 600° C for 1 hour. Approximately 2 g of the KCl/soda lime granules is packed into Teflon®/Halon® tubing (10 cm x 8 mm o.d.) between plugs of silanized glass wool (Supelco). The two traps are friction fitted to each other by means of an acid cleaned 6.4 mm, 2 cm long piece of FEP tubing (Cole Parmer). The KCl/soda lime traps are then packaged with acid cleaned Teflon® end plugs and stored in a clean poly ziploc bag.

The iodated carbon traps are commercially available (MSA, Pittsburgh). They are designed for the collection of Hg vapors (Braun and Metzger, 1987; Moffit and Kupel, 1971). The two traps are connected in series using 0.251 cm i.d. expanded PTFE heat shrink tubing (Cole Parmer). The iodated carbon traps are packaged with acid cleaned Teflon™ end plugs and stored inside a clean poly-ziploc bag. Once made and sealed, the KCl/soda lime and iodated carbon traps can be stored indefinitely without degradation or contamination if kept in a low Hg environment.

Samples are collected non-isokinetically from a single point away from the walls of the flue duct. This is accomplished with a 6.0 mm o.d. quartz tube which also has a quartz fiber filter plug inserted in the end to collect incident particulate material (Figure 1). The sample train temperature is maintained, using a proportional thermocouple feedback controller (Cole-Parmer Digi-sense®), at 90±10° C to avoid condensation of water. Dry gas volume is measured using a mass flow meter (Sierra, Side Trak III) after passage through a desiccant (silica gel). The mass flowmeters are periodically calibrated with bubble flowmeters and intercompared with an in-house flow meter (Sierra, Side Trak III). Because flue gas contains approximately 10% CO_2, a correction must be made to the flue gas volume (approximately -0.2% in volume per 1% CO_2). Concentrations reported are relative to dry flue gas at 21.1° C (70° F). Sample flow rate ranges from 0.35 to 0.5 standard liters per minute (slpm) over a 2 to 4 hour period for a total sample volume range of 36 to 120 liters. Trace element clean techniques are applied throughout sampling and analysis to minimize sources of contamination (Bloom, 1994).

2.2 ANALYSIS

Quantification of Hg was made using cold vapor atomic fluorescence spectrometry (CVAFS), following appropriate sorbent digestion and preparation (Bloom and Fitzgerald, 1987; Bloom, 1993; Bloom and Crecilius, 1983; Bloom et al., 1994; Liang et al., 1994). All standards were ultimately traceable to the lab stock standard for total Hg supplied by the National Institute of Science and Technology (NBS-3133, lot #290702). Methyl Hg standards, prepared in the lab, were cross-compared to this NIST primary standard. Also, where possible, certified standard materials were analyzed along with the samples.

The entire contents of the iodated carbon traps were gently refluxed for 1.5 to 2.0 hours in closed 25.6 mL Teflon vials with 10 mL of a mixture of 7:3 (v/v) concentrated HNO_3/H_2SO_4. The iodated carbon digests were then diluted to volume with 5% (v/v) BrCl reagent. Mercury on iodated carbon traps was determined by aqueous $SnCl_2$ reduction of small aliquots (100-500 µL) of the HNO_3/H_2SO_4 acid digest, then dual gold

amalgamation (Bloom and Crecelius, 1983; Moffitt and Kupel, 1971; Bloom et al., 1994), followed by CVAFS detection.

Analysis for MMHg and Hg(II) is currently performed by first dissolving each trap in 100 mL of a mixture of 5% HNO_3 and 0.39 M citrate in a 125 mL Teflon™ bottle. Methyl Hg is determined by aqueous phase ethylation, purging onto a Carbotrap®, gas chromatographic separation, and CVAFS detection (Bloom, 1989; Liang et al., 1994). Once the digestate has been properly analyzed for MMHg, an additional 10 mL of BrCl reagent is added to the HNO_3:citrate digest to ensure that Hg(II) is fully dissolved and all MMHg is converted to Hg(II) in solution. Aliquots are then analyzed by $SnCl_2$ reduction, dual gold amalgamation, and CVAFS detection.

If MMHg analysis is not needed, total oxidized Hg can be determined by digesting the individual KCl/soda lime traps in 100 mL of a mixture of 8% HCl and 2% BrCl (v/v). Aliquots (0.1-1.0 mL) of the KCl/soda lime digest can then be analyzed by aqueous $SnCl_2$ reduction, dual gold amalgamation, and CVAFS detection.

Most of the values reported in this paper for Hg(II) were produced by digestion of KCl/soda lime in 10% (v/v) acetic acid, with an additional 5% (v/v) concentrated HCl. This digestion and analysis procedure was shown to be precise and accurate for the measurement of Hg(II). However, this digestion procedure caused spurrious formation of MMHg. This artifact will be discussed in greater detail below.

Coal Hg values used for mass balance calculations were determined using a newly developed microwave digestion procedure followed by CVAFS detection (Bloom and Prestbo, 1994). The analysis of Hg in certified reference material and intercomparison with a neutron activation method for coal [Hg] provided a check on the overall analytical methods and standards.

3. Analytical Evaluation of the MESA Method

3.1 SPECIES STABILITY, MATRIX EFFECTS, BREAKTHROUGH AND ARTIFACTS

Anytime that Hg speciation methods are developed, a rigorous evaluation of the method with respect to sample collection and analysis must be performed. At the present time, interconversion and accuracy of speciation cannot be directly evaluated under field conditions, due to the lack of an Hg species spiking method for combustion flue gas. Only laboratory and indirect field tests exist to evaluate the MESA method for Hg speciation accuracy. The following described tests were initiated to challenge and evaluate the MESA method for species stability, matrix effects, trap breakthrough and artifacts in both sample collection and analysis.

Stability of Hg species on the solid sorbent traps has been investigated by collecting a parallel triplicate (or duplicate) sample and analyzing one sorbent trap immediately after collection and the remainder weeks to months later. This test was done on three separate occasions. The traps were stored in the laboratory (low in Hg) under ambient temperature

and light conditions. It has been determined that once collected, both Hg(II) and Hg^0 are stable on KCl/soda lime and iodated carbon respectively for 3 months.

The stability of Hg collected on iodated carbon traps after digestion in 7:3 (v/v) HNO_3:H_2SO_4 was investigated for a range of acid concentrations. Full recovery (100±10%) of Hg from the iodated carbon digest which contained 39% (v/v) HNO_3:H_2SO_4 was observed over a period of 30 days. For all digests with lower acid concentration, the recovery of Hg dropped off significantly in the first 24 to 48 hours. Qualitative data suggests that the Hg is re-adsorbed onto the carbon particles and not lost to the walls or the atmosphere. The concentration of acid must be at least 39% (v/v) for iodated carbon digestion or else Hg^0 will be underestimated in flue gas. For the flue gas data presented below, either the proper concentration of acid was used or the analysis was completed within 24 hours.

Hg(II) collected on KCl/soda lime then digested in 8% HCl:2% BrCl is stable in solution for a minimum of 30 days. The time period of stability for Hg in 8% HCl:2% BrCl solution should be indefinite, based on experience.

Experiments are currently underway to evaluate the stability of MMHg in HNO_3:citrate digest solution. In lab studies, MMHg spiked onto KCl/soda lime is stable in 5% HNO_3: 0.3 M citrate solution for 9 days. However, for a limited number of field samples that were spiked with MMHg during digestion, the spiked MMHg decreases between 30 to 40% in 24 hours. Therefore, using this digestion procedure requires immediate (< 6 hours) MMHg analysis for accurate results. However, when KCl/soda lime is digested in HNO_3:citrate solution, then further acidified and oxidized with 10 mL of BrCl reagent, Hg(II) is stable in solution for a minimum of 30 days.

A test was conducted to evaluate matrix effects during digestion and laboratory analysis. For eight consecutive days, a set of 3 MESA method sample trains were collected in parallel. In the laboratory, the traps from one of these sample trains were spiked with Hg(II) at the onset of digestion. The spiking levels ranged from 2 to 10 times the collected level of Hg on each trap. The recovery of digestion spikes was 103±3.6% for Hg^0 and 102±9.7% for Hg(II). This experiment provides at least two important quality assurance measures. First, as stated above, Hg was not lost during digestion or storage to either the walls or by reduction to Hg^0 followed by evasion. Secondly, the excellent recovery provides a measure of confidence in the accuracy of the digestion and analysis procedure.

We have found that the iodated carbon traps are nearly ideal for the collection of Hg. No observable breakthrough from the analytical iodated carbon trap to the backup iodated carbon trap has occurred at any combination of temperature (25-200°C), flowrate (20-1000 mL/min), sample vacuum (0.5-0.9 atm), or flue gas composition. Even when using iodated carbon to collect total Hg in flue gas (high Hg loading), no breakthrough has been observed. Iodated carbon traps have been shown to be highly efficient for the collection of gaseous Hg^0 (Bloom et al., 1994).

Breakthrough of Hg(II) can occur on the KCl/soda lime sorbent. Temperature has been investigated as the variable which controls breakthrough of Hg(II) on KCl/soda lime.

Results of temperature experiments indicate that a collection temperature above 120° C may result in breakthrough of approximately 30% and a collection temperature above 150° C may result in up to 50% breakthrough. At a KCl/soda lime temperature of 90±10° C, breakthrough is typically between 5-15% for an overall Hg(II) collection efficiency of greater than 97%. Accurate and uniform maintenance of KCl/soda lime traps at 90±10°C is essential for accurate Hg speciation results with the MESA method. The results of these temperature experiments suggest that Hg(II) is probably physio-sorbed rather than chemi-sorbed on KCl/soda lime.

Hg^0 in flue gas would be overestimated if there was breakthrough or breakdown (into Hg^0) of Hg(II) collected on KCl/soda lime. In order to evaluate breakthrough further and determine if Hg(II) breakdown occurs during sample collection, KCl/soda lime traps were spiked with 400 ηg of $HgCl_2$. These traps were then used to collect real flue gas samples. The mean spike recovery was 91.4 ± 5.9%. Unfortunately, these spiked KCl/soda lime traps were at a temperature of ~130° C during sample collection, exacerbating breakthrough. However, for one such sample, each trap was split into two samples, front and back half. Results of this analysis showed that each section of the two traps had Hg adsorbed to the KCl/soda lime in an overall decreasing trend. This behavior for the $HgCl_2$ spike suggests that breakthrough was occurring and not breakdown to Hg^0.

Conversion of Hg^0 to Hg(II) during sample collection would result in an overestimation of Hg(II) in flue gas. In order to ensure that this was not occurring, varying amounts of Hg^0, SO_2, HCl and H_2O were passed over KCl/soda lime in the laboratory to roughly simulate flue gas. Under certain conditions, Hg was found on the KCl/soda lime when SO_2 was also present. The conditions which were most favorable for Hg^0 retention were a collection temperature of 20° C, high levels of Fe and Mn (>1500 and 100 ppm respectively) in the KCl/soda lime, 750 ppm of SO_2 and dry nitrogen carrier gas. In one case, 30% of Hg^0 at an 1800 ηg Hg loading was collected on the KCl/soda lime trap under these conditions. It should be noted that these are not conditions typical of flue gas sampling for the MESA method. Soda lime from several different vendors were investigated to see if this phenomenon of Hg^0 collection in the presence of dry SO_2 could be repeated. Hg^0 was not collected in significant amounts (<4% at 2100 ηg loading) when the KCl/soda lime used was low in both Fe and Mn (1.1 and 0.97 ppm respectively). Further study showed that the addition of H_2O (~90% relative humidity) to the SO_2, Hg^0 mixture reduce the collection of Hg^0 on KCl/soda lime to less than 1%. for all the types of KCl/soda lime tested. Based on these experiments, it appeared that using KCl/soda lime which is low in trace element impurities may be very important to the accurate measurement of Hg speciation using the MESA method. Using KCl/soda lime which is high in trace element impurities could result in an over estimate of Hg(II) under field conditions. In order to address this concern a test was conducted where 4 parallel samples were collected, each one containing a different source of KCl/soda lime and therefore different levels of trace element impurities. All three of the KCl/soda lime types high in trace element impurities returned Hg(II) fractions of 0.82, 0.83 and 0.84, while the KCl/soda lime which was low in trace element impurities measured an Hg(II)

fraction of 0.99. This data suggests that in actual field collected samples, the composition of the KCl/soda lime may not be as important as suggested by the laboratory experiments. Further experiments are planned to address this important issue.

Finally, as mentioned above, MMHg can form during the digestion of KCl/soda lime in 10% (v/v) acetic acid. The formation reaction of MMHg involves the reaction of Hg(II), S(IV) and acetic acid in the presence of Fe on the surface of the digesting KCl/soda lime (Lee and Rochelle, 1987). S(IV) is present due to the co-collection of flue gas SO_2 by the KCl/soda lime traps. The chemistry of this reaction likely involves the production of methyl radicals in solution. The overall chemical equation is as follows:

$$Hg^{2+} + CH_3C(O)O^- + 2SO_3^{2-} + O_2 \longrightarrow CH_3Hg^+ + 2SO_4^{2-} + CO_2. \qquad (1).$$

Past reports have erroneously attributed from 2-15% of the total Hg in flue gas as MMHg (Prestbo and Bloom, 1993, Bloom et al., 1993). Currently, we use a non-methyl containing acid to digest KCl/soda lime in order to remove the potential for MMHg formation (see section 2.2). Subsequently, at two combustion facilities we have not quantitatively observed MMHg in flue gas above the 0.008 $\mu g/m^3$ detection limit using the new digestion procedure for KCl/soda lime. Another experiment supports this conclusion. Using impingers to collect flue gas, charged with either 0.1 M KCl or double deionized water (DDW), MMHg was not quantitatively detected above the 0.0003 $\mu g/m^3$ level. The MMHg spike recovery of the KCl and DDW impinger solutions was found to be 87 ± 23%. This reasonable MMHg spike recovery supports the conclusion that if MMHg was present in the flue gas, the KCl and DDW impingers would have collected and stabilized it. Future work is planned to more rigorously ensure that accurate and reliable measurements of MMHg can be made in flue gas.

3.2 INTERCOMPARISON WITH OTHER METHODS

As part of the evaluation of the MESA method a rigorous intercomparison exercise was completed at a commercial coal fired facility. A total of 5 different sample collection and analysis methods were employed during the intercomparison, including the most widely used, EPA Draft Method 29. Three of the methods use solid sorbent collection, while the other two, EPA method 29 and 101A, used liquid impingement. Each method collected 4 sample trains, in parallel, each day for 8 days. A rigorous protocol of digestion spiking, as well as duplicate analysis for each digested trap, was used to assess the precision, accuracy, artifacts, species interconversion, and matrix effects of the MESA method. Details of the intercomparison can be found elsewhere (Nott et al., 1994). Presented here are the results of the intercomparison with particular emphasis on the MESA method (Figure 2).

Excellent agreement with the mean value of all the methods was observed over Hg total concentrations which spanned a factor of 4 (Figure 2). Duplicate sample trains exhibited very good precision (Figure 2), with a mean relative percent difference (RPD)

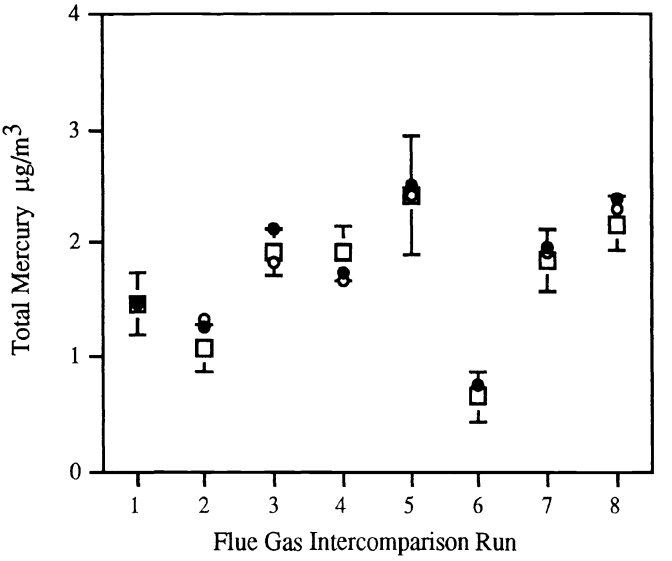

Fig. 2. MESA method intercomparison results. The square represents the mean of 10 measurements using 5 separate methods. The error bars are 1 sigma of the mean. Each filled and open circle represents a separate determination of total Hg using the MESA method. A single point indicates overlap of two separate points

of 4.5±4.1%. The recovery of digestion spikes was 103±3.6% for Hg^0 and 102±9.7% for Hg(II). Based on field blank results (3 σ) and a 90 liter sample volume, method detection limits were calculated to be 0.020 and 0.025 µg/Nm^3 for Hg^0 and Hg(II), respectively.

At yet another coal combustion site, a less rigorous, but more comprehensive three-way intercomparison was made between the MESA, HEST (Cooper et al., 1992), and EPA Method 29 (Figure 3 a and b). In this case, considerable variability in the flue gas concentration was observed over a three day period, probably due to changes in burn conditions and control technology. Fortuitously, from an analytical standpoint, the effect was an unprecedented intercomparison over more than an order of magnitude [Hg_t], while all analytical and sampling parameters remained constant. The correlation between the MESA method, EPA Method 29, and the dry sorbent HEST method was excellent over the entire range. The regression equation for Figure 3a is $x = 1.01y - 0.09$ ($r^2 = 0.95$) and for Figure 3b it is $x = 1.06y + 0.33$ ($r^2 = 0.91$).

Finally, for 5 sites where Hg mass balances could be calculated a mean value of 97.3 ± 25.2% was determined. This is within the target range of 100 ± 30%. Both the mean and standard deviation are skewed higher by the high recovery (140%) observed at an oil-fired power plant where measurements were close to the method detection limit. A summary of method detection limits, precision, spike recovery, stability and mass balance calculation results are listed in Table I.

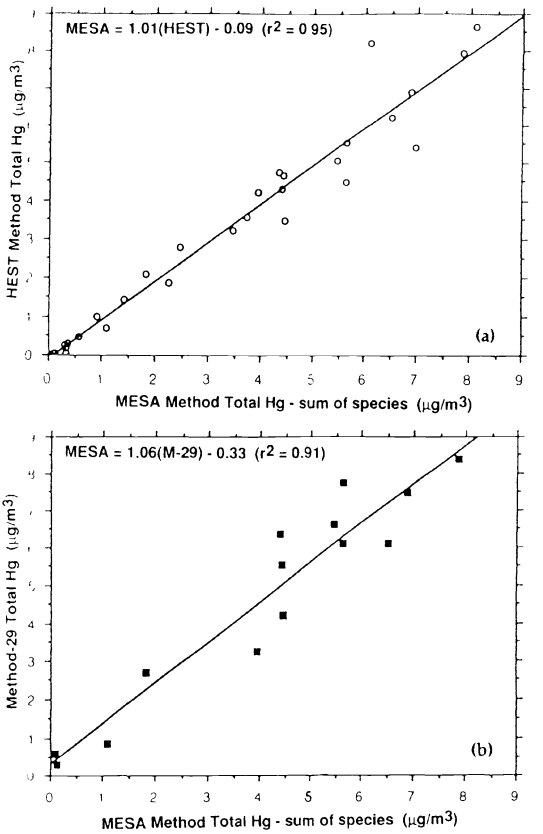

Fig. 3. Intercomparison of the MESA method (X axis) with (a) HEST method activated carbon/XRF and (b) EPA Method 29 for Hg_t, at a single site, over a four day period.

TABLE I

Summary of the analytical evaluation of the MESA method. Relative percent difference (RPD) was calculated for a set of 8 duplicate samples. RPD = ((|Duplicate1 - Duplicate2|)/Mean Duplicate) X 100%

	Hg^0	Hg(II)	MMHg	Hg_t
Method detect limit ($\mu g/m^3$)	0.020	0.025	0.007	-
Precision (mean RPD*)	6.8%	11%	23%	4.5%
Mean spike recovery	103%	102%	101%	-
On trap stability	3 months	3 months	na	-
Digest stability	>30 days	>30 days	24 hours	-
Mass balance (n=5)	-	-	-	97 ± 25 %

4. MESA Method Hg Speciation Results

The mean speciation results from all sites using the MESA method are presented in Table II. The Hg concentration value presented for each site in Table II is a mean of at least 3 sample trains. The sites include 3 oil fired steam plants, one municipal waste incinerator and several experimental pilot scale coal combustion facilities with the balance being full scale coal fired power plants. The coals burned represent a wide range of sulfur, ash, and chloride contents. In most instances the MESA method was used to evaluate the removal or change in speciation across pollution control devices. The values reported here are for the inlet side of pollution control devices. Therefore, the values presented here do not necessarily represent the actual concentration of Hg species emitted from the combustion facility. The actual concentration emitted is influenced by the pollution control technology and speciation of Hg (Chu and Schmidt, 1994).

The overall mean value of all sites measured, separated by fuel type, is presented in Table III. Site M was not included in the calculation of the mean for coal. Site D was not included in the calculation of the mean for oil. A standard deviation (1 sigma) is calculated for the coal results. Before pollution control devices (PCD) at coal-fired sites, oxidized Hg is the predominant form and relatively consistent. The overall mean value of 67±27% (1 sigma range of 40-94%) Hg(II) is consistent with other recent observations and estimates (Braun and Metzger, 1987; Cooper et al., 1992; Brosset, 1993). Interestingly, due to its relatively high water solubility and surface reactivity, Hg(II) should be easier to control than Hg^0.

Although there were only 2 oil sites measured, a comparison with coal indicates a much lower total Hg and relative percent oxidized Hg (Table III). The differences in speciation between coal and oil are likely due to differences in flue gas composition (i.e. sulfur and chloride).

5. Discussion and Conclusions

Two potentially very important ideas about atmospheric Hg have been identified as a result of this research effort. First, this is the most conclusive data base showing that a significant portion of Hg coal combustion flue gas exists in an oxidized form. This has important implications in terms of in-plant control and fate in the environment. Oxidized Hg is expected to have a relatively short half-life once emitted from combustion facilities as it is likely to be incorporated in rain and on particulate material and then be deposited locally or regionally. On a global scale, if we assume that roughly 35% of the total emitted Hg per year is from coal combustion (Nriagu, 1989; Nriagu and Pacyna, 1988), then roughly 23% of the global emissions are as Hg(II) based on the mean value for coal calculated here (67% Hg(II), Table III). This estimate assumes that there is no change in speciation across the pollution control device. If this estimated emission of Hg(II) is removed locally or regionally, then our understanding of the global cycle for Hg must be

TABLE II

Mean Hg speciation at a variety of combustion sites using the MESA method. Hg_t is obtained by summing the species Hg^0 and Hg(II). The fraction Hg(II) is calculated for each site. All values for coal listed in this table are from measurements made at the inlet to pollution control devices.

Fuel type	Hg_t $\mu g/m^3$	Hg(II) $\mu g/m^3$	Hg(0) $\mu g/m^3$	Fraction Hg(II)
(a) coal	6.27	5.01	1.26	0.80
(b1) coal	7.08	6.27	0.81	0.89
(b2) coal	5.52	4.09	1.43	0.74
(b3) coal	6.98	5.05	1.93	0.72
(b4) coal	6.47	3.02	3.45	0.47
(c) oil	0.19	0.04	0.15	0.21
(d) oil	<0.04	<0.02	<0.02	na
(e) oil	0.12	0.03	0.09	0.25
(f1) coal	3.16	3.00	0.16	0.95
(f2) coal	4.13	3.11	1.02	0.75
(g1) coal	10.1	7.08	2.99	0.70
(g2) coal	8.14	8.03	0.11	0.99
(h1) coal	7.05	4.73	2.32	0.67
(h2) coal	4.56	1.44	3.12	0.32
(i) waste	146	104	42	0.71
(j) coal	5.96	2.25	3.71	0.38
(k) coal	7.64	3.90	3.74	0.51
(m) lignite	23.5	20.0	3.46	0.85
(n) coal	8.04	0.02	8.02	0.00
(o) coal	7.63	2.20	5.43	0.29
(p) coal	6.93	6.61	0.32	0.95
(q) coal	2.08	1.81	0.27	0.87
(r) coal	5.62	4.56	1.06	0.81
(s) coal	6.24	5.37	0.873	0.86

TABLE III

Overall mean values for each fuel type calculated from Table II.

Fuel type	total Hg $\mu g/m^3$	Hg(II) $\mu g/m^3$	Hg(0) $\mu g/m^3$	Fraction Hg(II)
Coal				
Mean	6.3	4.1	2.2	0.67
1 sigma	1.9	2.1	2.1	0.27
n	19	19	19	19
Oil				
Mean	0.16	0.035	0.12	0.23
n	2	2	2	2
Waste				
Mean	146	104	42	0.71
n	1	1	1	1

reassessed in light of this finding. This also points out the need to initiate Hg speciation studies of combustion plume, atmospheric deposition and the historical Hg deposition record near coal combustion facilities. To do this more sensitive atmospheric speciation methods are needed.

Secondly, as part of this research we have identified a potential mechanism for the formation of MMHg in rainwater (Reaction 1). The mechanism involves the oxidation of S(IV) to S(VI) in the presence of Fe, whereby degradation of acetate occurs to form the methyl radical which can then bind to Hg(II) to form MMHg. In very preliminary laboratory experiments, using concentrations typical of polluted cloud water, we have found that Reaction 1 occurs at the pH commonly found in rain and cloud water (pH 4 to 5). To date, no other known reaction has been identified that would explain the methylation of Hg in the atmosphere. Again, this points out the need for more studies of aqueous reactions of Hg and comprehensive field cloud and rain water speciation studies.

The MESA method has been shown to be precise in the determination of Hg^0, Hg(II) and total Hg in combustion flue gas. Based on a rigorous intercomparison exercise, the MESA method appears to be accurate for total Hg. Furthermore, the method has several distinct advantages over the most commonly used EPA Method 29. The MESA method has a lower detection limit, sample collection is simple, fewer person-hours are needed to collect a sample and there is the added value provided by speciation information. The major disadvantage of the MESA method is the non-quantitative collection of particulate material. Further research and development is planned to attempt to overcome this disadvantage.

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Particulate Mercury in the Atmosphere: Its Significance, Transport, Transformation and Sources

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Abstract. The importance of particulate mercury (Hg(p)) in the transport, chemistry and deposition of this toxic metal has long been underestimated and largely ignored. While it was once believed to constitute a small percentage of total atmospheric mercury, Hg(p) may contribute a significant portion of the deposition of this metal to adjacent natural waters. Recent measurements of Hg(p) in several urban/industrial areas have documented that Hg can be associated with large particles (>2.5 μm) and in concentrations similar to those of the vapor phase Hg (ng/m^3). As part of ongoing effort to diagnose the sources, transport and deposition of Hg to the Great Lakes and other Great Waters, the University of Michigan Air Quality Laboratory (UMAQL) has investigated the physical and chemical properties of particulate-phase Hg in both urban and rural locations. It appears that particulate Hg may be the one of the most difficult of the Hg measurements to perform, and perhaps the one of the most important for deposition and source apportionment studies. Particulate Hg concentrations measured in rural areas of the Great Lakes Region and Vermont ranged from 1 to 86 pg/m^3 whereas Hg(p) levels in urban/industrialized areas were in the range 15 pg/m^3 to 1.2 ng/m^3.

Keywords: Mercury, dry deposition, particle phase mercury, size distribution, Great Lakes, Lake Champlain

1. Introduction

In recent years, the behavior of hazardous air pollutants (HAPs) has been receiving a great deal of attention from the scientific community. This is largely the result of recent changes in regulations including the Clean Air Act Amendments of 1990 and due to the scientific interest associated with compounds with inherent chemical and physical complexities. Mercury (Hg) continues to be of special concern because of its multitude of controllable sources, its volatility, mobility and strong tendency to bioaccumulate. In the Great Lakes Region, research on the sources, transport and deposition of atmospheric mercury has gained increasing attention as it is now believed by many to be the most important pathway for inputs to the natural waters.

The processes and deposition rates by which mercury enters the water column are still not adequately understood. In particular, the role of the various physical/chemical forms of mercury deposited from the atmosphere has yet to be determined. While vapor phase mercury is thought to constitute the vast majority of the atmospheric mercury burden, particle-phase mercury may actually play a disproportionately large role in the amount of Hg in the various environmental compartments. While the relative importance of wet deposition versus dry deposition in delivering Hg to the earth's surface is largely unknown, and location specific, most researchers agree that the particulate form of Hg is critical in understanding the cycling of this metal in the environment.

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An important aspect of this research was the ability to accurately collect and effectively analyze Hg(p) without artifacts. Measurements of Hg(p) has been limited over the past two decades but with recent advances in instrumental sensitivity and the application of clean techniques our knowledge of Hg(p) concentrations and behavior has improved. The precise determination of ultra-trace environmental concentrations (pg/m^3) of Hg(p) are now feasible. Until now, the number of studies with high quality Hg(p) data has been limited to a few intensive efforts.

The Air Quality Laboratory at the University of Michigan (UMAQL) has developed (Keeler, 1994; Lamborg *et al.*, 1994) and continues to improve the methods to reliably collect and analyze size fractionated Hg(p). These techniques are presently being utilized to gain a wider understanding of the atmospheric mercury cycle. Various analytical techniques have been utilized including dual-amalgamation preconcentration and cold vapor atomic fluorescence spectrometric (CVAFS) detection performed on Hg(p) extracted from glass fiber and other types of filters, and instrumental neutron activation analysis (INAA) performed on Teflon filters. The different techniques have distinct advantages and have been used to quantify Hg(p) in recent studies (Keeler *et al.*, 1994; Lamborg *et al.*, 1994; Olmez *et al.*, 1994).

Atmospheric Hg measurements reported here were performed as part of several UMAQL studies including: 1) ongoing urban atmospheric chemistry and deposition studies in Detroit, MI (Keeler *et al.*, 1994); 2) a two-year multi-site atmospheric Hg transport and deposition study in the State of Michigan (Hoyer *et al.*, this volume); 3) a long-term Hg and pollutant cycling study in the Lake Champlain Basin of Vermont (Burke *et al.*, this volume); and 4) a study of the atmospheric Hg levels in Broward County, Florida (Dvonch *et al.*, this volume). These investigations have provided an in-depth look at the relationship between particulate mercury and other aerosol constituents. In addition, mercury bound to particulate matter in precipitation is currently under investigation in event precipitation samples collected at the rural locations in Michigan and in the Lake Champlain Basin. This paper aims to evaluate the Hg(p) data collected by the UMAQL to date and to provide evidence of it's importance in the cycling of this critical pollutant.

2. Sampling and Analysis

Ultra-clean sampling and analysis techniques were required to obtain reliable Hg(p) data. Sampling equipment including filter packs, forceps, vials, petri dishes as well as other field sampling equipment were rigorously acid-cleaned in a 5-step, 11-day process. All sampling equipment, including filter packs and cyclones, were constructed of Teflon or were Teflon coated. Glass-fiber filters were pre-fired at 500 °C for > 1-hour prior to use in sampling. During sample collection, particle-free gloves were worn when field equipment was handled. Since outdoor concentrations of Hg in all forms are typically lower than indoor concentrations, most of the handling of filters and filter packs was done outdoors.

Total particulate mercury (Hg(p)) was collected using an open-faced Teflon filter pack onto 47 mm glass fiber filters (Gelman Type A/E) for 24 hours at a nominal flow rate of 30 L min^{-1}. Mercury in the fine particle size range(<2.5 μm) was collected onto 47 mm diameter glass-fiber filters using Teflon coated aluminum cyclones (URG, Carboro NC)

to remove larger particles upstream of the filter. Filters were placed into acid-cleaned petri dishes immediately after sampling, Teflon-taped and then stored at -40°C until analysis.

In addition, a microorifice cascade impactor (MOI) was used to collect size-fractionated aerosols (Marple and Rubow, 1984). This impactor was chosen because of its moderately high flow rate, 30 L min^{-1}, and relatively low pressure drop. With an ambient pressure of 0.973 atm the measured pressures at the nozzle exit of the five stages are 0.973, 0.971, 0.942, 0.929, and 0.893 atm, respectively. Regulation of the pressure drop is important as vaporization of particle associated water inside the impactor can result in a distortion of the size distribution (Biswas *et. al.*, 1987). This water loss could cause the particles to become smaller, resulting in an underestimate of the particles aerodynamic size. Experiments carried out with sulfuric acid droplets showed maximum changes in particle size of 3%. Since it is unclear whether the particulate Hg is associated with the sulfur containing particles in the atmosphere the actual size distortion of the Hg laden particles may be different but should not exceed that of highly hygroscopic sulfate. Teflon membrane filters (2 μm pore size) and glass-fiber filters were both utilized as impaction surfaces as they have low blanks for Hg. The particle cut-off diameters for the first 5 impactor stages are 5.0, 2.5, 1.0, 0.6, and 0.18 μm, respectively. The last stage collects all particles below 0.18 μm is aerodynamic size.

The filter extraction and analysis was performed in a Class 100 cleanroom using reagents that required further purification to maintain the consistently low blank values and detection limits. The present UMAQL protocol, utilized in the analysis of the MOI and Detroit filters, involved the extraction of each glass fiber filter in 30 mL of 10% HNO_3 followed by a digestion of the filter for 20 minutes at 160°C using a CEM MDS-2000 computer controlled microwave unit. The samples were then allowed to react for 12-hours at room temperature. After digestion, 10 mL of extract were removed with a pipet and placed into 30 mL acid cleaned polyethylene bottle for trace metals analysis using a Perkin Elmer ELAN 5000 ICP-MS. The remaining extract was utilized for Hg analysis by prior addition of 0.25 mL of BrCl to oxidize all the Hg to Hg^{2+}. The glass fiber filters used in the MOI were extracted with only 10 mL of 10% HNO_3 and were then treated as described above.

The UMAQL standard particulate protocol, applied to all filters collected in the Michigan Network, Vermont Studies, and Florida Study utilized acid digestion/CVAFS analysis of the samples extracted in a 10% solution of a 70% nitric acid/30% sulfuric acid mixture (approximately 2N) in Teflon vials. Extraction was performed by placing the vials in a sonic bath for 30 minutes. After extraction, the solution was oxidized with BrCl for one hour, converting all forms of Hg present into the inorganic, +2 oxidation state. The sample was reduced with NH_2OH and $SnCl_2$ was added to convert the Hg^{2+} to Hg^0 which is volatile and liberated from solution by bubbling with Hg-free N_2. The Hg released in this way was collected on Au-coated sand traps. The Hg was subsequently analyzed using the dual-amalgamation CVAFS method described by Fitzgerald *et al.* (1979). A calibration curve was generated by spiking vials containing blank filters with varying amounts of a 2 ng/mL standard (in 1% BrCl).

Flow rates through the sampling systems were measured using both calibrated rotameters with filter packs used only for flow-tests to prevent contamination, and

frequently calibrated dry test meters. Sampling pumps with mass flow-controllers were typically used to pull ambient air through the sampling equipment. All flow checking devices are calibrated before and after all intensive field projects with primary flow calibration equipment (e.g. spirometer).

2.1 QUALITY CONTROL AND QUALITY ASSURANCE

The UMAQL utilizes ultra-clean technique in all facets of the collection and analysis of our environmental samples (Keeler *et al.*, 1994). All equipment and supplies used in sampling are rigorously acid-cleaned in a 5-step, 11-day procedure (Rossman and Barres, 1991). Sample bottles, Au-sand traps and glass-fiber filter containers are Teflon-taped and triple-bagged before and after each use in the field. Particle-free gloves are always worn when handling the samples in the field as well as in the Class 100 clean laboratory at the University of Michigan.

Field and storage blanks were collected regularly with the particulate Hg samples. The field blanks were collected by loading the acid-cleaned filter packs and assemblies, connecting the sampling equipment, and then placing the filter pack assemblies or impactors in the sampling box for two minutes without drawing air through the system. Field and storage blanks for particulate Hg averaged < 7 pg Hg per filter (equivalent of <0.17 pg/m^3 for a 24-hour sample). Storage blanks for particulate mercury were obtained by placing an unused pre-fired glass fiber filter in a petri dish and shipping it to UMAQL for analysis.

A reagent blank was analyzed on each day of particulate Hg analysis. The appropriate amounts of reagents were analyzed to determine the contribution of the reagents to the concentration of Hg obtained for the sample. All samples were blank corrected using the corresponding reagent blank analyzed that day. The detection limit calculated as three times the standard deviation of reagent blanks, was less than 1 pg/m^3 for total particulate Hg. Initially, all particulate Hg samples were routinely analyzed in duplicate, and more recently, 50% of all samples were analyzed in duplicate. The analytical precision calculated from these replicate analyses was better than 10% for the routine analysis of Hg(p) in all of the studies. An initial analytical comparison was performed to compare the UMAQL extraction techniques to INAA performed on a "whole" undigested sample. Standard Reference Material No. 1648 from the National Institute of Standards and Technology (NIST) was obtained for this purpose. Urban Particulate Material (UPM) was extracted using the routine protocol as well as by INAA at the MIT Nuclear Reactor Laboratory. The two techniques gave equivalent results ($1.02\pm.05$ vs. $1.07\pm.1$) for the UPM (Olmez, personal communication). However, this does not guarantee that atmospheric aerosol samples would behave identically, therefore, additional experiments with collocated ambient filter samples are being completed to investigate this question.

3. Results and Discussion

3.1 MERCURY SIZE DISTRIBUTION IN URBAN DETROIT

The levels of vapor and particulate Hg have been previously measured in the City of Detroit during a short duration study in 1992 (Keeler *et al.*, 1994). Levels of particulate

Hg varied greatly from one site to the other with maximum concentrations at both sites of greater than 1 ng/m^3. In the present study the atmospheric Hg levels were measured at only one site during the spring of 1994. The fine and total Hg(p) concentrations measured in Detroit for 18 consecutive days during March of 1994 are displayed in Figure 1.

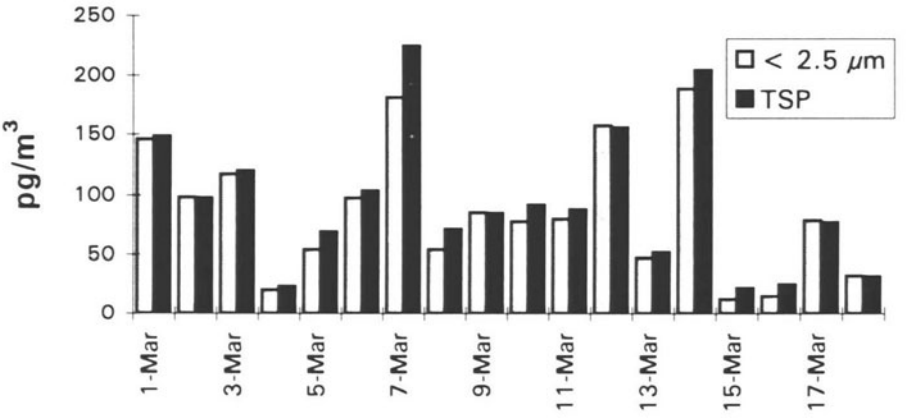

Figure 1. Fine and coarse particulate Hg concentrations measured in Detroit in March, 1994.

Ambient samples were collected every day during the study period for both fine particles (< 2.5 μm) and for total suspended particulates (TSP). The average total particulate Hg concentration during the study period was 94 pg/m^3 with a range of 22 to 225 pg/m^3. The percent of particulate Hg found in the fine size range (<2.5 μm) varied from about 60% to 100% during the 18 days of sampling. The mean %fine for the period was 88% as compared to Cd, another anthropogenically derived element which was measured concurrently, had an average of only 72% of its mass in the fine fraction.

The complete size distribution of the particulate Hg was measured with the MOI for each of the 18 days of sampling in downtown Detroit. The results indicate that particulate Hg was mostly collected on the fourth and fifth impactor stages. The mass median diameters (MMD) for these stages are 0.60 and 0.18 μm, respectively. Particles less than 0.18 μm were collected on the back-up filter. The results from the measurements in Detroit were compared to those compiled by Milford and Davidson (1985) from three references to particulate Hg measurements made in the late 1970s and early '80s. A total of five measurements in the three studies were utilized to calculate a MMD of 0.61 μm. The range in the five concentrations measured was 0.08-81 ng/m^3 with a geometric mean concentration of 1.9 ng/m^3. The MMD calculated from the 18 days of measurements in Detroit was 0.80 μm. The larger MMD observed in Detroit was associated with a much lower mean concentration than the older studies reported in the review paper by Milford and Davidson (1985).

The distribution of particulate Hg in Detroit was bimodal with an obvious fine and coarse mode. The average particle size for Hg(p) in the fine and coarse fractions was

determined using stages one and two of the MOI to calculate the average particle size of coarse fraction (> 2.5 μm), and stages three through six to calculate the particle size of fine fraction (< 2.5 μm). The average particle size of the Hg(p) in each mode was 0.68 μm and 3.78 μm for fine and coarse particles, respectively. The observation of the coarse particle mode was somewhat unexpected as previous studies have suggested that Hg (p), being primarily a combustion aerosol, should be submicron in size. In Detroit adsorption of vapor phase Hg onto existing aerosols was apparent with a positive relationship between Hg(p) and the total particulate mass in the atmosphere. The importance of the coarse particle Hg can be seen in the relative contribution of these large particles to the dry deposition flux. Modeling the dry deposition flux using the size distributions from this study demonstrated that the flux of coarse particle Hg was 4-5 times greater than the fine particle flux (Pirrone *et al.*, this volume).

An analysis of Hg(p) concentrations observed in Wayne County, MI at nine sites revealed that Hg levels increased by 11% annually over the period from 1986-1992 (Pirrone *et al.*, 1994). The significant increase in the annual particulate Hg levels was directly related to a 3% annual increase in coal consumption in Michigan together with an increase of 13% in the quantity of wastes being incinerated in the City of Detroit.

The concentrations observed in Detroit are similar to those recently reported for a long-term study of atmospheric particles in urban areas of the United Kingdom (Lee *et al.*, 1994). Quarterly average Hg(p) concentrations were in the range of 90 to 540 pg/m^3 for the ten UK sites discussed. The highest Hg(p) concentrations were observed at a site located near a smelter which also resulted in the highest concentrations observed for a variety of other heavy metals. The levels of particulate Hg in the UK study as well as those reported here are at the lower end of those reported for urban locations by Schroeder *et al.* (1987). The elevated concentrations of particulate Hg in urban areas suggests that more attention should be given to both nonferrous metal smelters and incinerators as sources of Hg(p) to the atmosphere.

3.2 PARTICULATE MERCURY IN RURAL MICHIGAN

In the previous section the levels of Hg(p) measured in the urban/industrial area of Detroit, MI were discussed. The typical levels in the urban/industrial areas and the variability of these levels was much greater than those typically observed at the more rural sites in Michigan, Pellston (PEL), South Haven (SHA), and Ann Arbor (ANN). Ambient measurements were performed every sixth-day for one-year at three rural sites in Michigan (Hoyer *et al.*, this volume). Particulate mercury levels averaged 10.5 pg/m^3 at PEL (n=47), 22.4 pg/m^3 at SHA (n=52) and 21.9 pg/m^3 at ANN (n=54). The range in particulate mercury concentrations observed at the South Haven and Ann Arbor sites was much greater than that recorded at Pellston (Figure 2).

Particulate Hg displayed a seasonal behavior at the rural Michigan sites. The maximum particulate mercury concentrations were recorded during the winter and early spring with a maximum 24-hour concentration of 32.2 pg/m^3 observed at Pellston (8 Apr. 94), 85.7 pg/m^3 at South Haven (20 Jan 94) and 76.9 pg/m^3 at Ann Arbor (8 Jan 94).

The range in the Hg(p) was also not as dynamic at the site in the northern-most part of the lower peninsula of Michigan. The maximum concentrations of Hg(p) at Pellston in northern Michigan were less than 50% of those observed at the two southern Michigan sites. Particulate Hg concentrations exceeded 30 pg/m^3 only 2 times during the year of measurement at Pellston. Air mass trajectories calculated for these days revealed that elevated concentrations were associated with transport was from the urban areas to the southwest and southeast to the site. Elevated Hg(p) measured at South Haven and Ann Arbor were typically associated with transport from the east and the southwest.

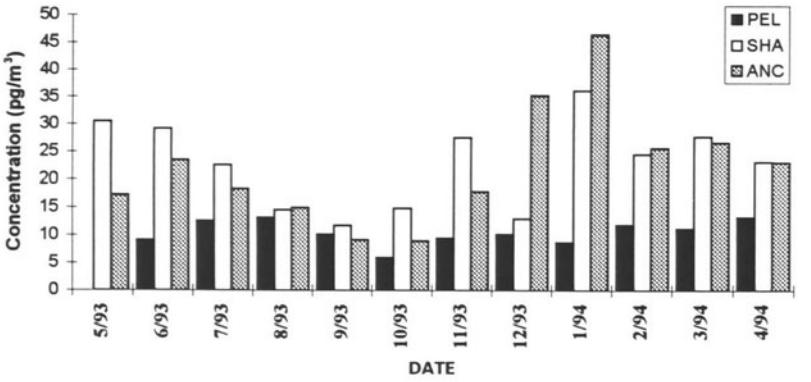

Figure 2. Monthly averaged particulate Hg concentrations at three Michigan sites.

3.3 PARTICULATE MERCURY IN RURAL VERMONT

Atmospheric Hg samples were collected twice per week with a total of 103 particulate phase Hg samples collected during 1993. The annual arithmetic average Hg(p) and vapor phase Hg concentration was 11.2 pg/m^3 and 2.0 ng/m^3, respectively. While the vapor phase concentrations at Underhill displayed no strong seasonal behavior a seasonal trend was observed in the Hg(p) with elevated concentrations during the winter months. This was especially evident in February where all samples were above the annual average. Increasing concentrations in November and December of 1993 provide further support for a seasonal influence on particulate Hg concentrations at this site. A similar increase in the concentration of other metals such as As and Se measured at Underhill (NESCAUM data) during the winter months was also observed. A similar increase in particulate Hg concentration during the winter months was observed at the rural sites in Michigan, as discussed in the previous section.

The seasonally averaged particulate Hg concentrations further illustrate this trend (Table I). The average for the winter months is significantly greater than the annual

mean, and the spring and autumn averages are somewhat higher than the average for summer.

Concurrent measurements of Hg in precipitation and ambient air (daily vapor and particulate) were obtained at the Underhill site (Burke *et al.*, this volume). Simple correlations were calculated between ambient and precipitation concentrations for the sampling days when precipitation occurred during ambient measurements. Ambient particulate Hg was correlated with reactive Hg in precipitation ($r=0.654$, $p<0.02$, $n=13$).

TABLE I

Seasonal averages for particulate Hg at Underhill, VT during 1993

Season	N	Hg(p) (pg/m^3)
Winter	24	15.8
Spring	26	9.7
Summer	26	9.4
Autumn	25	10.0

3.4 PARTICULATE MERCURY IN BROWARD COUNTY SOUTH FLORIDA

Particulate Hg samples were taken concurrently at three sites during the period 25 August to 7 September (Dvonche *et al.*, this volume). The average concentrations at the inland locations, sites 2 and 3, were 51 pg/m^3 and 49 pg/m^3, respectively. The average Hg(p) measured at site 1 near the beach, located about 9 km east of sites 2 and 3, was 34 pg/m^3. Particulate phase Hg comprised less than 5% of the total atmospheric Hg (vapor and particulate) which was consistent with values reported in northern locations (Burke *et al.*, this volume). The levels of Hg(p) in Broward County were generally higher than those typically measured (about 10-30 pg/m^3) at the rural sites in the Great Lakes Basin, discussed earlier. The levels measured in Broward County were not as high as other measurements made in large urban/industrial source areas such as Detroit, where short-term average particulate Hg concentrations were found to be near 100 pg/m^3. However, the elevated levels of particulate Hg observed in Broward County during were higher than those measured at rural sites with concentrations never exceeding 100 pg/m^3. The elevated levels in Broward county are suggestive of a local source influence. The elevated levels of Hg(p) in South Florida were somewhat surprising. While the average vapor phase Hg levels were 2-3 times higher in Broward County than those measured elsewhere, the PM10 and TSP levels were not significantly elevated with typical concentrations of PM10 in the range 15-20 $\mu g/m^3$.

4. Conclusions

Measurements of Hg(p) documented the importance of this form of the compound in the atmosphere. The levels and behavior of Hg(p) was investigated at several locations in the Great Lakes, Lake Champlain basin, and in South Florida. The magnitude and particle size of the observed Hg(p) varied dramatically from site-to-site as well as from day-to-day. Seasonal variability was observed in the levels of Hg(p) with higher concentrations typically found in the winter months than those measured in the summer. The observed correlation between the operationally-defined reactive Hg species and Cl^- in precipitation provides support for the speculation that this species may be $HgCl_2$. Also, the correlation observed between ambient particulate Hg and reactive Hg species in precipitation on days when ambient measurements were conducted and precipitation occurred, implies that this species may be associated with particles.

The average particle size of the Hg(p) measured in each mode was 0.68 μm and 3.78 μm for fine and coarse particles, respectively. The observation of the coarse particle mode was somewhat unexpected as previous studies have suggested that Hg(p) should be submicron in size. Near source adsorption of vapor phase Hg onto existing aerosols was apparent in Detroit with a positive relationship between Hg(p) and total particulate mass in the atmosphere. The importance of large particle Hg(p) should not be underestimated in determining the dry deposition flux. Modeling the dry deposition demonstrated that the flux of coarse particle Hg was 4-5 times greater than the fine particle flux in this study. The relative importance of Hg(p) in the fine and coarse fractions to the total dry deposition flux was site specific and varied with time and meteorological conditions.

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AN INTENSIVE MULTI-SITE PILOT STUDY INVESTIGATING ATMOSPHERIC MERCURY IN BROWARD COUNTY, FLORIDA

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Abstract. An intensive multi-site pilot study of atmospheric Hg was conducted in Broward County, Florida in August and September of 1993. Broward County, which contains the city of Fort Lauderdale, is located in southeastern Florida. The county borders the Florida Everglades on the west and the Atlantic Ocean on the east. A network of four sampling sites was set up for 20 days throughout Broward County to measure Hg in both the vapor phase and the particle phase as well as Hg in precipitation. The mean concentrations of total vapor phase Hg measured at two inland sites were found to be significantly higher (3.3 and 2.8 ng/m^3) than that measured at a site located on the Atlantic shore (1.8 ng/m^3). The mean concentrations of particle phase Hg collected at the two inland sites (51 and 49 pg/m^3) were found to be 50% greater than that measured at the coastal site (34 pg/m^3). In addition, event precipitation samples were collected at four sampling sites over the 20 day study period and were analyzed for both reactive and total Hg. The mean concentration of total Hg in the precipitation samples was found to be 44 ng/L, with a range of 14 to 130 ng/L. It was determined that further meteorological analysis and a more complete characterization of the aerosol and precipitation composition are needed to identify the probable source(s) contributing to the increased deposition of Hg.

1. Introduction

The importance of mercury (Hg) as an environmental contaminant stems from its ubiquitous nature due largely to the multitude of sources, its volatility, mobility and persistence in nature. While Hg was once thought to be a threat only in the locality of large industrial facilities, recent research has found that even remote and pristine waters have elevated levels of Hg compounds in fish. A statewide survey of Hg in sportfish was implemented in Florida after preliminary indications of Hg contamination in Florida freshwater fish (Hand and Friedemann, 1990). The study found concentrations of Hg in fish in the Savannas State Reserve and the Everglades that exceeded acceptable levels for human consumption. Hg concentrations sufficient to warrant limited consumption advisories were found in fish in numerous lakes, rivers, and wetlands. Other studies in Florida suggested that Hg is transported through the Everglades food web and that Hg bioaccumulation has diminished the viability of the endangered Florida panther (Roelke *et al.*, 1991). The risk of Hg biomagnification to other animal populations has not yet been quantified. However, the potential for perturbations of ecosystem structure and function seems apparent.

The studies described above provided an initial assessment of the magnitude of the Hg contamination in south Florida. However, they did not address issues regarding the origin, atmospheric transport and deposition, or availability of Hg in these habitats. The study reported here investigated the local impact of anthropogenic sources on the atmospheric Hg levels in Broward County, Florida, an area located immediately east of the Florida Everglades. This research was a collaborative effort between the Florida Department of Environmental Protection, the United States Environmental Protection Agency (AREAL and Region IV), the Broward County Department of Natural Resource Protection, and the University of Michigan Air Quality Laboratory (UMAQL). The

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project served as a pilot investigation for more comprehensive sampling to be performed in urban areas in south Florida. The study included a limited investigation of the sampling and analytical methods for atmospheric mercury determinations which could be utilized in selected ecosystems in the Everglades or surrounding areas.

2. Experimental Methods

Ambient measurements of vapor phase and particle phase Hg, as well as Hg in precipitation were made at four sampling sites located in the Fort Lauderdale area (see Figure 1). Samples were collected at each of these sites from 19 August to 7 September, 1993. Since the prevailing winds are out of the east/southeast during the late summer and early fall, a site along the coast was chosen to provide a "local background". Three additional sites were chosen along a path leading inland or "downwind" from the coast. A brief description of each site and the reasons for choosing the site follows.

2.1. SAMPLING SITES

The John Lloyd State Park was chosen as the "local background" site (1). The site is also used by the Broward County Department of Natural Resource Protection as a background site for their air monitoring network. The site was located at the end of a service road in the park about 100 m west of the shore of the Atlantic Ocean and approximately 100 m east of the Intercoastal Waterway. Samples were collected daily at this site to measure vapor and particle phase Hg as well as Hg in precipitation. Since the site was close to the Atlantic Ocean and with winds predominately from the east/southeast, the levels of atmospheric mercury at this site were expected to represent "local background" levels. Because of land-sea breeze circulation, it was understood that this site may not provide a true marine background. However, this site did provide a "local background" for comparison with the three inland sites when winds were out of the east/southeast.

The central site (2) was located on the Broward Community College campus, approximately 13 km west of site 1. During periods with winds out of the east/southeast, this site location was expected to provide adequate distance for homogeneous mixing in the boundary layer to assess the impact of local sources. The central site was located on the roof of the campus gymnasium, which was approximately 10 m high. At site 2, vapor and particulate Hg samples as well as precipitation samples were collected daily. Another inland site (3) was located approximately 20 km west of site 1 in the backyard of a residential home. The residential area was moderately populated with several houses in the area adjacent to the sampling site. At this site vapor, particulate and precipitation samples were collected daily. This site was chosen because it was approximately 8 km east of a conservation area of the Everglades. An additional site (4) was located 10 km west of site 1 and also approximately 300 m southwest of a municipal waste incineration facility. Precipitation samples were collected daily at this site which was located on the property of one of the South Florida Water Management District pumping stations on the South New River Canal.

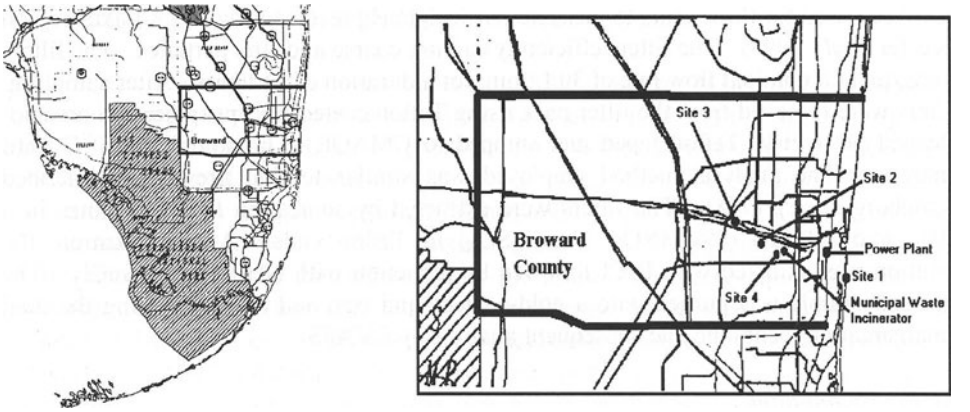

Fig. 1. Location of Sampling Sites in Broward County, FL

2.2. METHODS OF SAMPLE COLLECTION AND ANALYSIS

All equipment and supplies used in sampling were rigorously acid-cleaned in an 11-day cycle (Hoyer and Keeler, 1994). Sample bottles, gold sand traps and glass-fiber filter containers were Teflon-taped and triple-bagged. All of the samples collected were analyzed using ultra-clean techniques for trace metal analysis. The particulate and precipitation samples were processed and analyzed in a Class 100 ultra-clean laboratory at the UMAQL in order to minimize contamination. However, the vapor phase samples were analyzed on-site in Florida in a normal laboratory setting because the risk of contamination was minimal. Particle-free gloves were worn during all procedures of sample handling and analysis.

Vapor Phase Hg

Gold-coated sand traps were used at all of the sites because of their ability to quantitatively remove vapor species of Hg from an air stream. The quartz sand was gold-coated under vacuum in a gold plasma that uniformly deposited gold onto the sand. The collection efficiency of the sand traps for removal of gaseous Hg has been found to be >97% by the UMAQL and by Dumarey *et al.*, (1985). Two traps in series were used to characterize any amount of breakthrough during all measurements of vapor phase Hg. A pre-fired glass-fiber filter (Gelman type A/E) was used to remove particles from the air stream prior to reaching the gold-coated sand traps. Samples were collected at a flow rate of 300 cc/min. for durations varying from 3 to 24 hours. The gold-coated sand traps were analyzed by thermal desorption using a dual amalgamation technique and subsequent analysis by cold vapor atomic fluorescence spectroscopy (CVAFS) similar to the method described by Fitzgerald and Gill (1979). The instrument was calibrated daily by injecting Hg vapor standards.

Particle Phase Hg

Particle phase Hg samples were collected using pre-fired glass-fiber filters (Gelman type A/E). These filters have been proven to efficiently collect particulate Hg and have

now been used for three years to measure particulate Hg levels in the Great Lakes region (Keeler *et al.*, 1995). The filters efficiently capture coarse and fine particles. The filters were run at a nominal flow rate of 30 L/min. for a duration of 24 hours. After sampling, filters were removed from the filter pack using Teflon coated forceps, placed in an acid-cleaned petri dish, Teflon taped and shipped to UMAQL to be stored at -40°C until analysis. The analysis method employed was similar to that previously described (Lamborg *et al.*, 1994). The filters were extracted by sonication for 30 minutes in a 10% acid solution (7% HNO_3: 3% H_2SO_4) in Teflon vials. After sonication, the solution was oxidized with BrCl followed by reduction with NH_2OH and $SnCl_2$. The reduced sample was purged onto a gold-coated sand trap and analyzed using the dual amalgamation technique and subsequent analysis by CVAFS.

Hg in Precipitation

Daily event precipitation samples were collected manually at each site. The collectors consisted of an acid-cleaned 1 L borosilicate glass sample bottle and a 28 cm (diameter) polyethylene funnel supported in a polyethylene housing system. The collectors were elevated 2 m above the ground in order to avoid possible contamination from ground splashing during precipitation. The bottle and funnel were deployed at 8 AM for 24 hours and replaced each morning regardless of a precipitation event. In the event of precipitation occurring at 8 AM, the sample was not collected until the completion of the precipitation event. The precipitation samples were shipped to UMAQL by overnight mail for processing and analysis. The analysis method was similar to the one described by Hoyer and Keeler (1994). An aliquot of the sample was poured off for analysis of major ions and samples of sufficient volume were analyzed for the operationally-defined reactive Hg species by acidifying an aliquot of sample to a 1% HCl solution before reduction with $SnCl_2$. In addition, a subset of samples with sufficient volume were poured off into 125 ml polyethylene bottles and acidified to a 0.2% HNO_3 solution for analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The analysis method employed was a modification of the procedure described by Long and Martin (1992), using an ultrasonic nebulizer instead of chelation for pre-concentration. The remaining sample volume was oxidized to a 1% BrCl solution and refrigerated overnight prior to analysis for total Hg. The oxidized Hg was reduced and purged onto a gold-coated sand trap and analyzed using the dual amalgamation technique and subsequent analysis by CVAFS.

Additional Trace Constituents

Measurements of gaseous SO_2 were made continuously at site 2 from 28 August to 7 September. These measurements were made using a Differential Optical Absorption Spectrometer (DOAS) as described by Stevens *et al.*, (1993). In addition, aerosol trace metals were also collected at site 2 from 28 August to 7 September using 2-μm pore Teflon (PTFE) membrane filters (Gelman) in an all Teflon filter pack. Analysis of these filters was performed at USEPA-AREAL using X-Ray Fluorescence (XRF) similar to the method described by Dzubay *et al.*, (1982).

2.3. QUALITY CONTROL AND QUALITY ASSURANCE

For event precipitation, measurements of the sampling blank were obtained by rinsing the collection funnel with ultra-pure water and analyzing the rinse for Hg. The average concentration of Hg in 12 precipitation collector blanks was 0.26 ± 0.2 ng/L. The method of collection used for the present study was slightly different than the automated wet-only sample collection method used in the UMAQL Great Lakes data (Hoyer and Keeler, 1994). With the manual method, the collection bottle was exposed to dry deposition for the entire period that the funnel-bottle was deployed. Since the maximum amount of time that the funnel-bottles were deployed was 24 hours, the amount of Hg added by dry deposition was negligible relative to the magnitude of Hg present in the precipitation. The contribution of dry deposition was determined by performing collector rinses on funnels that had been deployed for 24 hours without collecting any precipitation. From the funnel rinses, dry deposition of Hg to the funnels was found to be insignificant. Furthermore, the manual method used in this study had been previously determined at UMAQL to compare very well to the automated method based on co-located sampling (Hoyer and Keeler, 1994).

Field blanks were collected regularly for vapor phase and particulate Hg samples. For both types of samples, field blanks were performed by assembling the sampling equipment and placing it in the sampling box without drawing air through the system. Field blanks for vapor phase Hg averaged 0.015 ng Hg on the trap, which corresponds to 0.03 ng/m^3 for a 24-hour sample or 1.3% of the average vapor phase Hg concentration. Particulate Hg field blanks averaged 17 pg Hg on the filter, which corresponds to 0.4 pg/m^3 for a 24-hour sample or less than 1% of the particulate Hg typically collected.

For precipitation and particulate samples, a reagent blank was analyzed on each day of analysis. The appropriate amounts of reagents were analyzed to determine the contribution of the reagents to the concentration of Hg obtained for the sample. All samples were blank corrected using the corresponding reagent blank analyzed that day. The current detection limit for Hg in precipitation (calculated as three times the standard deviation of the reagent blanks) is 0.15 ng/L.

All particulate samples and 50% of precipitation samples were analyzed in duplicate. Analytical precision calculated from these results was better than 10% for analysis of Hg in both precipitation and particulate samples.

3. Results and Discussion

3.1. VAPOR PHASE Hg

Vapor phase Hg levels in Broward County were slightly elevated, on average, above typical background levels reported elsewhere. As seen in Figure 2, concurrent 24-hour averaged vapor phase Hg concentrations at sites 2 (central) and 3 (house) were found to be significantly different and higher than those at site 1 (beach) as determined from t-tests (paired two-sample comparison of means, $p < 0.01$). The elevated Hg levels at sites 2 and 3 relative to the beach site were most evident for the period 30 August to 7 September. Vapor phase Hg values observed during the two-week period were elevated

when compared to typical vapor phase measurements (~2.0 ng/m^3) made using the same techniques in the Great Lakes Basin (Keeler *et al.*, 1994).

At site 2 (central) where day and night samples were collected, a strong diurnal relationship was observed in the vapor phase Hg levels. The average night time vapor phase concentration (4.5 ng/m^3) was nearly twice the concentration found during the day time (2.4 ng/m^3) at this site. The strong diurnal variation seen in the vapor phase Hg measurements can be explained by the diurnal changes observed during the study in the structure of the boundary layer in south Florida. During the day time, intense heating resulted in considerable vertical mixing of the ambient pollutants. However, calm winds (< 1.0 m/s), little vertical mixing, and lower mixing heights during the night resulted in higher concentrations.

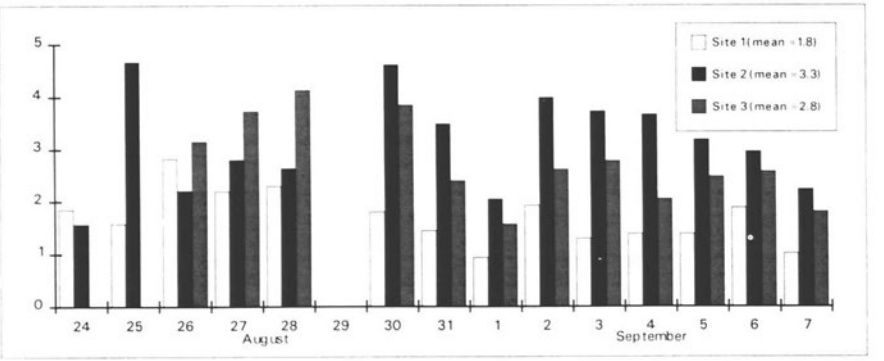

Fig. 2. 24-Hour Averaged Vapor Phase Hg Concentrations in ng/m^3 Measured in Broward County, FL

3.2. PARTICLE PHASE Hg

Particulate Hg samples were taken concurrently at sites 1, 2, and 3 during the period 25 August to 7 September. Figure 3 reveals that the concentrations of particulate Hg measured at site 2 (central) were significantly ($p < 0.01$) elevated with respect to those measured at site 1 (beach), a result also observed with the vapor phase Hg. The average concentrations at site 2 (51 pg/m^3) and site 3 (49 pg/m^3) were 50% greater than the average at site 1 (34 pg/m^3). As with the vapor phase Hg, this observation was most evident during the period 30 August to 7 September. For measurements made on the days before 30 August, the site to site differences were not as evident due to highly variable meteorological flow patterns that changed notably every several hours during the day. Since 24-hour ambient Hg measurements were performed at all sites except site 2, most of the time-averaged Hg measurements made during this study were not of short enough duration to observe site to site differences over short periods of time (less than 12 hours). However, for the period 30 August to 7 September when flow was much more consistent from the east/southeast, the trend of higher vapor phase and particle phase Hg at sites 2 and 3 compared to site 1 was strongly evident. Consistent air mass transport from the southeast was observed for the period 30 August to 7 September as a result of the semi-permanent Bermuda high.

Particle phase Hg comprised less than 5% of the total atmospheric Hg (vapor and particulate) for the days with both measurements. This was consistent with other values reported (Burke *et al.*, 1995). The levels of particulate Hg found during this study were generally higher than those typically measured (about 10-30 pg/m^3) at rural sites in the Great Lakes Basin (Keeler *et al.*, 1995). In addition, the two-week average of particulate Hg measured at all sites during this study was 5 to 10 times higher than other measurements made in south Florida (Guentzel *et al.*, 1994). The levels measured in Broward County were not as high as other measurements made in large urban/industrial source areas such as Detroit, where short-term average particulate Hg concentrations were found to be near 100 pg/m^3 (Keeler *et. al.*, 1994; 1995). The elevated levels of particulate Hg observed in Broward County during this study, however, do suggest a local source influence.

A significant relationship was observed between measurements of aerosol vanadium (V) and gaseous SO_2 made at site 2 as seen in Figure 4. Both V and SO_2 are emitted during oil combustion. A relationship was also observed between particle and vapor phase Hg, and V and SO_2, also seen in Figure 4. These relationships were strongest

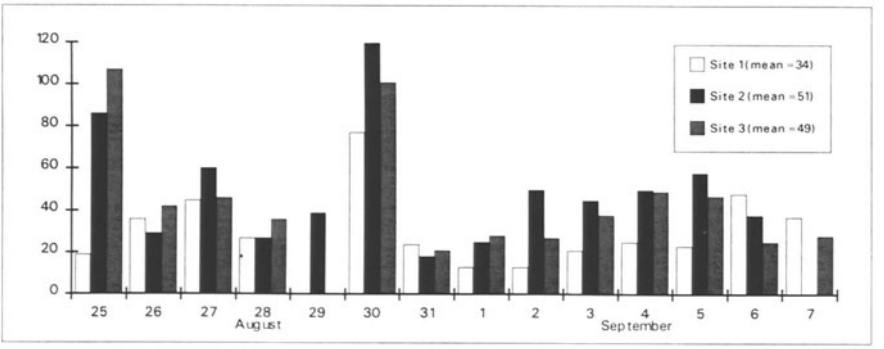

Fig. 3. Particle Phase Hg Concentrations in pg/m^3 Measured in Broward County, FL

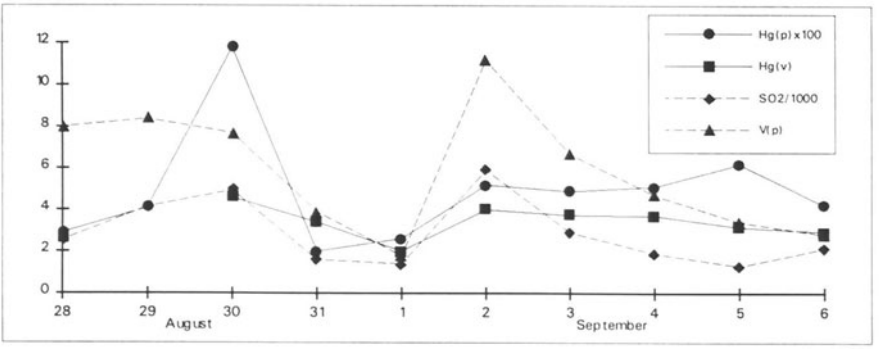

Fig. 4. Particle and Vapor Phase Hg, Particulate V, and Gaseous SO_2 in ng/m^3 Measured at Site 2

during the period 30 August to 2 September. As previously stated, a sea breeze circulation was observed with winds out of the east/southeast during the day, and calm conditions during the night. On 30 August, a sea breeze was present with winds out of the east/southeast corridor during the day. However, Hurricane Emily disrupted the pattern on 31 August and 1 September as it approached the Carolinas and rode up the eastern seaboard. The strong gradient flow caused by the hurricane prevented the typical sea breeze pattern during this 48-hour period. Sustained winds out of the south/southeast during the entire 2-day period resulted in the cleanest 2 days of the study, as seen in Figure 4. However, on 2 September the hurricane had moved far enough north allowing the Bermuda high to re-establish itself as the dominant feature. The sea breeze circulation was then again present, and as seen in Figure 4, the concentrations of all 4 components were again elevated.

3.3. Hg in EVENT PRECIPITATION

The levels of Hg measured in precipitation collected at the four sites are summarized in Table I. Average total Hg concentrations measured at sites 2 (central), 3 (house), and 4 (near incinerator) were elevated relative to concentrations measured at site 1 (beach). All samples collected were analyzed for total Hg and samples of sufficient volume were analyzed for reactive Hg. Table I suggests that the same pattern seen for total Hg was also present for reactive Hg since the average concentrations of reactive Hg were also elevated at sites 2, 3, and 4 relative to site 1. However, this trend was not as distinct for Hg in precipitation as it was for vapor phase and particle phase Hg.

It should be noted that most precipitation events during this study were the result of isolated convective systems rather than associated with frontal activity. With the convective storms, a strong spatial gradient would not be expected in 20-day averaged Hg concentrations measured at sites separated by relatively short distances (<10 km). However, spatial gradients may be seen in precipitation collected daily (individual events) at these sites, depending upon the source and transport of the feed air for each individual convective storm.

During this study, site-to-site differences in precipitation Hg concentrations were observed on several days. On 25 August air mass transport was from the east/southeast. Precipitation samples were collected at all four sites on this day, one of only two days during the entire study on which this occurred. Concentrations of Hg measured at the inland sites were all elevated when compared with site 1 located at the beach as seen in Figure 5. It is also clear from Figure 5 that a relationship existed between the measured concentrations of Hg, V, and Ni in the precipitation collected at sites 1, 2, and 4 (insufficient volume for ICP-MS analysis of the sample collected at site 3). Vanadium and nickel are both trace elements emitted during oil combustion (Gordon, 1988).

The levels of total Hg measured in event precipitation in this study were elevated 3 to 5 times over those made by the UMAQL in Vermont (Burke *et al.*, 1995) or the Great Lakes Basin (Hoyer *et al.*, 1995). However, it is difficult to make any definitive conclusions as to the source(s) responsible for the elevated levels of Hg in precipitation with the limited number of events collected during this study.

TABLE I
Summary of Hg in Precipitation in ng/L at Sites in Broward County, FL

	Site 1	Site 4	Site 2	Site 3
Total Hg Mean	35	57	40	46
Std. Dev.	16	15	19	28
Range	15 - 56	43 - 81	15 - 73	14 - 130
N	6	5	8	13
Reactive Hg Mean	1.0	2.5	1.9	2.0
Std. Dev.	0.4	1.0	1.1	1.1
Range	0.5 - 1.4	1.7 - 3.7	0.8 - 3.3	1.0 - 3.2
N	4	4	5	4

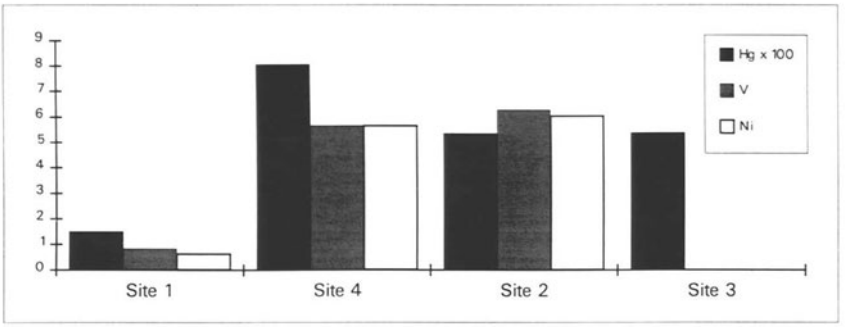

Fig. 5. Hg, V, and Ni in μg/L Measured in Precipitation Collected in Broward County on 25 August, 1993

4. Summary and Conclusions

The data obtained from this pilot study indicate that levels of vapor and particle phase Hg measured at sites 2 (central) and 3 (house) were elevated above levels measured concurrently at site 1 (beach). One explanation for this is that a source, or sources, located near or between site 1 (beach) and site 2 (central) was impacting the portion of Broward County which lies west of site 2. While the association of ambient Hg with V and SO_2, combined with elevated Hg in precipitation being found with elevated V and Ni suggest an oil combustion source, the present study was not designed for source apportionment of the Hg. Therefore, making any definitive conclusions as to the specific source(s) responsible for these elevated levels of Hg will require further meteorological analysis and a more complete characterization of the aerosol and precipitation composition.

Levels of total Hg in precipitation observed in daily event collections at several sites in Broward County during this study were significantly higher than those previously reported for more remote sites in southern Florida (Guentzel *et al.*, 1994). The

relatively large variation in Hg concentration measured simultaneously at multiple sites separated by relatively short distances (<10 km) suggests that more research is needed to adequately characterize atmospheric deposition to south Florida caused by sources in the two urbanized counties (Broward and Dade). The enhanced deposition in these areas may be quite important to the overall Hg loading to the sensitive ecosystems in south Florida due to the combination of the high amount of annual rainfall and high precipitation Hg concentrations.

Since wet deposition is the major removal process of atmospheric mercury, future studies in south Florida should include more comprehensive precipitation collection at a grid of sites in the two counties Also, vapor and particulate measurements at selected sites would provide a better understanding of the processes leading to Hg in precipitation. In addition, a more detailed elemental analysis of both precipitation and particulate samples is needed to characterize the probable source(s) contributing to the increased deposition of mercury The additional information obtained from the increased sampling and analysis would allow for a proper evaluation of the impact of local and regional source(s) to the Hg deposition to the region

Acknowledgments

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AMBIENT LEVELS AND DRY DEPOSITION FLUXES OF MERCURY TO LAKES HURON, ERIE AND St. CLAIR

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Abstract. Ambient concentrations and dry deposition fluxes of Hg in the gas and particle phase to Lakes St. Clair, Erie and Huron were estimated with a hybrid receptor-deposition model (HRD). The ambient gas and particulate phase Hg concentrations were predicted to vary by a factor of 12 to 18 during the transport of air masses traversing the lakes. The ensemble average deposition fluxes of fine particle Hg ranged from 7 pg/m^2-h to 15.3 pg/m^2-h over Lake St. Clair, 0.5 to 4.2 pg/m^2-h over Lake Huron and 5.1 to 20.6 pg/m^2-h over Lake Erie. The deposition flux of coarse particle Hg was in the range of 50 to 84 pg/m^2-h over Lake St. Clair, 4.7 to 24.2 pg/m^2-h over Lake Huron and 5.1 to 20.6 pg/m^2-h over Lake Erie. Gaseous Hg volatilized at a rate of 0.21 to 0.52 ng/m^2-h from Lake Huron and 0.13 to 0.36 from Lake Erie. Gas phase Hg was deposited at a rate of 5.9 ng/m^2-h and/or volatilized at a rate of 0.5 ng/m^2-h from Lake St. Clair depending upon the location of the sampling site used in the HRD model. The effect of meteorological conditions, particle size distributions and type and location of the sampling sites played an important role in the transfer of atmospheric Hg to and/or from the lakes.

1. Introduction

Mercury is emitted into the atmosphere from a multitude of natural sources and from previously contaminated natural waters. Emissions from anthropogenic sources including coal and oil combustion, municipal solid waste and sewage sludge incineration, and smelting operations are more significant (EPA, 1993). As a consequence of the increase of anthropogenic emissions in industrialized countries some investigations indicate that ambient Hg concentrations have increased by 1.5% per year in the Northern Hemisphere and by 1.2% per year in the Southern Hemisphere during the 1977-1990 period (Slemer and Langer, 1992). In addition, increases in Hg deposition rates have been reported for the north temperate lake systems in Wisconsin, Minnesota and Sweden (Slemer and Langer, 1992; Swain *et al.*, 1992; Meger, 1986; Lindqvist *et al.*, 1991; Nater and Grigal, 1992). Swain *et al.* (1992) reported a 2% increase in Hg deposition rates in remote lakes in Wisconsin and Minnesota. Moreover, analysis of lake sediments and dated soils (Rada *et al.*, 1989; Norton *et al.*, 1990) as well as peat bogs (Norton *et al.*, 1990) suggest that Hg deposition may have doubled during the last century. It is now widely accepted that atmospheric deposition is an important pathway in the transfer of Hg to natural waters.

This paper presents estimates of deposition fluxes and exchange rates of gas phase Hg to Lakes St. Clair, Huron and Erie. Ambient concentrations and particle size distributions of atmospheric Hg measured in the Detroit urban/industrial area in April 1992 (Keeler *et al.*, 1994a) and March 1994 are used as input to a hybrid receptor-deposition model (HRD) to estimate the ambient concentrations, deposition fluxes, and exchange rates of the gas phase Hg at the air-water interface. The HRD model accounts for temporal and spatial variations in the ambient concentration, deposition flux and gas exchange rate associated with changing meteorological conditions, particle size distributions, and hydrodynamics (i.e., wave frequency and spray formation).

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2. Methods

2.1 SAMPLING SITES

During a 10-day intensive study in April 1992 (Keeler *et al.* 1994a), ambient Hg concentrations for both gas and particle phases were measured at two urban sites: Site-5 was located in downtown Detroit close to Zug Island, which is one of the most industrialized areas in Southeastern Michigan. Anthropogenic Hg is emitted (in this area) from a large number of emission sources including coke ovens, iron and steel plants, incinerators, power generation facilities, and lime and cement operations (Pirrone *et al.*, 1994). The second site (Site-1) was located in a mixed residential/industrial land use area which is northwest of the Detroit Incinerator (GDRRA), one of the largest municipal solid waste incinerator facilities in the US which has been operating in Detroit since 1989.

In March 1994, an 18-day intensive study was performed in Detroit at the urban site (Site-5) to determine ambient Hg concentrations in the gas phase as well as the Hg associated with fine fraction (<2.5 μm) and total suspended particulate matter. In addition, a six stage-microorifice cascade impactor (MOI) was used to determine the particle size distribution of particulate Hg in the atmosphere. The dry deposition velocity of particulate Hg in each particle size over Lakes Erie, St. Clair and Huron was then calculated.

2.2 ANALYTICAL PROCEDURES

Total particulate Hg was collected using an open-faced Teflon filter pack (Savillex) with a 47 mm diameter glass fiber filter (Gelman Science Type A/E) for 24 hours at a nominal flow rate of 30 L/min. Particulate Hg in the fine fraction (<2.5 μm) was collected onto a 47 mm diameter glass fiber filter (Gelman Science Type A/E) after removal of particles in the coarse fraction using a Teflon-coated aluminum cyclone (University Research Glassware, N. C.). A six stage-MOI was used to measure the size distribution of the particulate Hg (Keeler *et al*, 1994b). Samples were collected onto 37 mm glass fiber filters at a nominal flow rate of 30 L/min for 24 hours. After sampling, the filters were individualy placed in acid-cleaned petri dishes and stored at -40 °C until analysis. Gas phase Hg was collected using gold-coated glass beads at a nominal flow rate of 300 mL/min for 12 and 24 hours.

Each glass fiber filter was extracted in 30 mL of 10% HNO_3, placed in a CEM MDS-2000 microwave oven for 20 minutes at 160 °C, and then allowed to react for 12 hours at room temperature. After digestion, 10 mL of extract were removed with an Eppendorf pipet and placed into 30 mL acid cleaned polyethylene bottle for trace metals analysis using an ICP-MS. The remaining extract was used for Hg analysis after addition of 0.25 mL of BrCl to oxidize all the mercury to Hg^{++}. The glass fiber filters from the MOI were extracted with 10 mL of 10% HNO_3 at 160 °C for 20 minutes, allowed to react for 12 hours at room temperature, and oxidized to Hg^{++} with 0.25 mL of BrCl.

The Hg analysis was performed using dual amalgamation with Cold Vapor Atomic Fluorescence Spectrometry (Fitzgerald and Gill, 1979). Excess BrCl was removed by adding 100 μL of hydroxylamine hydrochloride to 5 mL aliquots of filter extract and allowed to react for 5 min. Subsequently, 0.5 mL of stannous chloride were added to reduce the Hg^{++} to Hg^0, which was subsequently purged from the solution with an Hg-free nitrogen stream and concentrated onto a gold-coated sand trap. Calibration curves covering the expected concentration levels were analyzed on a daily basis and the check of standards was performed every six samples.

2.3 MODELING

The atmospheric transport of contaminants and their transfer to natural waters is affected by their chemical transformations and vapor-particle partitioning during transport, meteorological parameters, and wave dynamics and spray formation at the air-water interface. In order to estimate the deposition fluxes of particulate and gas phase Hg to Lakes St. Clair, Huron and Erie, the Hybrid Receptor-Deposition Model (Pirrone *et al.* 1994a; 1994b) developed to estimate the deposition flux of trace metals and semivolatile organic compounds (SOCs) to Lake Michigan was modified for Hg.

3. Results and Discussion

This study was aimed at assessing the levels of atmospheric Hg in the urban area of Detroit and estimating the ambient concentration, dry deposition flux and the air-water gas exchange rate of Hg over Lakes St. Clair, Huron and Erie. To accomplish these objectives, 24-hour integrated samples were used in the HRD model to evaluate the distribution of ambient concentrations and deposition fluxes of Hg in the particle and gas phase over the lakes. Dry deposition fluxes were determined for Hg in the gas phase and in the fine and coarse fraction measured at the industrial/urban sites in April 1992 and March 1994, and for particulate Hg with a mass median diameter (MMD) corresponding to the 50% collection efficiency of each MOI stage (see Table I). Major details on the particle size distribution of Hg measured with MOI can be found in Keeler *et al.* (1994b).

Table I shows ambient concentrations of Hg in the particle and gas phase measured in Detroit during April 1992 and March 1994. In March 1994 the particulate Hg concentration in the fine fraction ranged from 12 pg/m^3 to 190 pg/m^3, which represents 86% of the total suspended particulate Hg. This finding agrees very well with the MOI data (obtained as sum of the last four MOI stages) which show that 86% of the atmospheric Hg collected on glass fiber filters of the last four MOI stages was in the fine fraction. Particulate Hg concentrations measured in March 1994 were found to be lower than those measured at the same location in Detroit in April 1992. The particulate Hg concentration measured in April 1992 ranged from 57 pg/m^3 to 1230 pg/m^3 at Site-5 and from 69 pg/m^3 to 1086 pg/m^3 at Site-1 with arithmetic means of 297 pg/m^3 at Site-5 and 342 pg/m^3 at Site-1. Ambient concentrations of Hg in the gas phase during April 1992 ranged from 0.41 ng/m^3 to 3.5 ng/m^3 at Site-5 and from 9.5 ng/m^3 to over 70 ng/m^3 at Site-1. The high concentrations found at Site-1 suggest the impact of a significant local source. However, the lower particulate Hg concentrations measured in Detroit during March 1994 were likely due to the prevailing west-northwesterly winds during this period.

In April 1992 the prevailing winds were from the south-southeast suggesting transport of atmospheric Hg emitted from the industrial area of Detroit which includes coal combustion plants (e.g., coke ovens, iron and steel plants), municipal solid waste plants and sewage sludge incineration plants (Pirrone *et al.*, 1994). These source types account for a large fraction (>45%) of anthropogenic emissions of Hg in the United States (EPA, 1993).

Changes in the ambient concentrations of particulate and gas phase Hg with distance from the sampling sites are shown in Figure 2 for the forward trajectories which started in Detroit and traversed Lake St. Clair and Lake Erie on 9 April 1992 and on 7 March 1994 (Figure 1). The calculated Hg concentrations along the over-water trajectories were obtained using the Hg concentrations and particle size distributions measured at the sampling sites (Site-1 and Site-5) as input values in the HRD model.

TABLE I

Ambient concentrations of Hg measured at Site-1 and Site-5 in the fine and coarse fraction (pg/m^3), in the gas phase (ng/m^3), and on particles collected on each Micro-Orifice Impactor (MOI) stage (pg/m^3). The mass median diameters (μm) corresponding to a 50% collection efficiency of each MOI stage is given.

Particle Size	Sampling Period	Mass Median Diameter	Site - 1	Site - 5
Fine (<2.5 mm)	April 5-17, 1992	0.6	290	252
Coarse (>2.5 mm)	ibid.	5.0	51.3	44.5
Gas phase	ibid.		48.8	3.4
Fine (<2.5 mm)	March 1-18, 1994	0.6		86
Coarse (>2.5 mm)	ibid.	5.0		12
Micro-orifice Impactor :	ibid.			
Stage-1		5.0		6
Stage-2		2.5		6
Stage-3		1.0		14
Stage-4		0.6		33
Stage-5		0.18		30

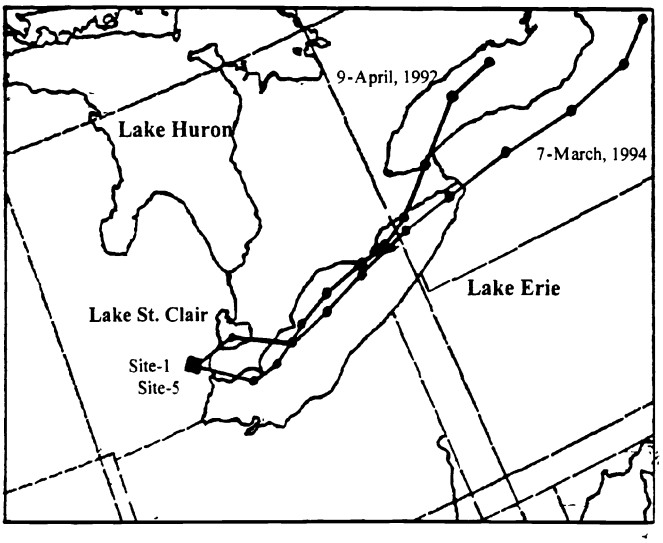

Fig. 1. Forward trajectories which started in Detroit and traversed Lake St. Clair and Lake Erie on 9 April 1992 and 7 March 1994.

The concentrations of particulate Hg in the fine and coarse fraction (Figure 2b) decreased by a factor of 12 and 18, respectively, when the air mass moved from the sampling site to the lakes. The decrease in ambient concentration was mainly due to atmospheric dispersion during transport with deposition accounting for only 10 and 22% of the overall decrease in the Hg concentrations in the fine and coarse fractions, respectively. The gas phase Hg concentrations decreased along the over-water trajectory by a factor of 15 compared to that measured at the sampling sites on 9 April 1992. Figure 1-c shows the decrease in the ambient concentration along the over-water trajectories that traversed Lakes St. Clair and Erie on 7 March 1994. The overall decrease in the ambient Hg concentrations are similar to those obtained for the fine and coarse fraction along the trajectory that traversed the lakes on 9 April 1992 (Figure 2b). However, the increase in the ambient concentration observed when the air mass was at a distance of 10-20 km from the sampling site (Figure 2c) was due to a decrease in the mixing layer depth (from 1080 m to 660 m) occurring over the lake during transport. The Hg levels over the lakes reached the minimum value of 10-20 pg/m^3 in the particle phase and 1.5-2 ng/m^3 in the gas phase at a distance > 40 km from the sampling sites. These Hg levels are similar to the regional background levels observed in the Great Lakes Region (Keeler *et al.*, 1994b; Burke *et al.*, 1994).

Figure 3 shows the change in dry deposition flux of Hg in the particle and gas phase with distance from the sampling sites when the air masses moved from Detroit over Lake Erie on 9 April 1992 and 7 March 1994. The exchange rates of gas phase Hg at the air-water interface, F-1 and F-5 (Figure 3a), were calculated using the measured concentrations at sampling sites Site-1 and Site-5, respectively, and a total Hg concentration in the dissolved aqueous phase of 0.5 ng/L (Gill and Bruland, 1990). Since measurements were not available to estimate the spatial and temporal variations of the total Hg in the dissolved aqueous phase, a Hg^0 concentration of 0.05 ng/L was assumed constant throughout the lakes area. This value was used to evaluate the exchange rate of gas phase Hg at the air-water interface. The exchange rate of gas phase Hg increased up to a factor of 2 during transport. Similar changes were found in other critical parameters effecting the gas exchange at the air-water interface such as the overall air-water transfer coefficient, KOL, which ranged from 1.1 to 4 cm/h, Henry's law constant, H, which ranged from 120 to 175 Pa/m^3-mole, the temperature at the air-water interface, Ta-w, which varied by 50% on average, the wind speed, Ws, which ranged from 2.3 to 0.8 m/h and the mixing layer depth, Zmix, which ranged from 1080 to 620 m. The increase found in the KOL was associated with a decrease in the Zmix which led to an increase in the ambient concentrations along the over-water trajectory with higher exchange rates of the gas phase Hg. However, it is likely that the air-water exchange rate is actually more variable than that found in this study since changes in the Hg^0 concentration in the lakes were not measured. The dry deposition flux of fine and coarse fraction Hg decreased 10-fold along the over-water trajectory (Figure 3b). Similar variations were found in the deposition flux of particulate Hg obtained using the MOI data (Figure 3c). These changes ranged from 20-fold for Hg associated with 0.18 μm diameter particles (Stage-5 of the MOI) to 10-fold for Hg associated with 5 μm diameter particles (Stage-1 of the MOI). Variations in the dry deposition flux of particulate Hg are mainly due to changes in deposition velocity and ambient concentration along the trajectories traversing the lakes (Pirrone *et al.*, 1994a). Figure 4 shows the volatilization rates from the lakes and/or deposition to the lakes for each forward trajectory that traversed each lake during April 1992. The exchange rates of the gas phase Hg ranged from 0.8 ng/m^2-h (deposition to the water surface) to -0.5 ng/m^2-h (volatilization from the water surface) when Hg concentrations measured at Site-5 were used. When Hg concentrations measured at Site-1 are utilized, the HRD model estimates that only volatilization occures from the

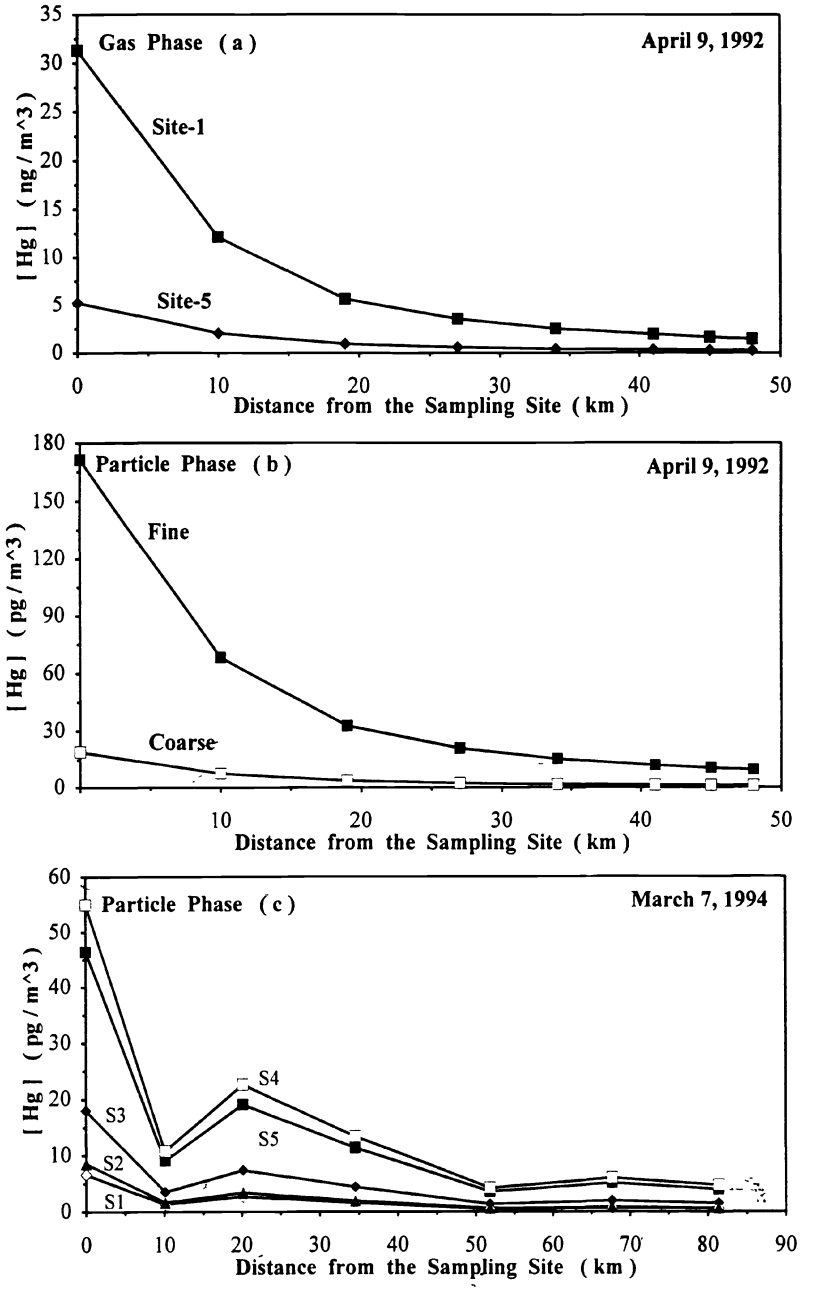

Fig. 2. Calculated Hg concentrations in the gas and particle phase along 24-hour forward trajectories traversing Lake St. Clair and Lake Erie on 9 April 1992 and on 7 March 1994 using the Hg concentrations measured at Site-1 and Site-5.

lakes. These findings suggest that based on the assumption of a constant Hg^0 concentration equal to 0.05 ng/L in the dissolved aqueous phase, the lakes are degassing Hg into the atmosphere.

The respective changes in dry deposition flux of particulate Hg in the fine and coarse fraction were 8-fold and 15-fold, respectively, when the concentrations measured at Site-1 were used, and 25-fold and 30-fold when the concentrations measured at Site-5 were used. The higher variations in the dry deposition flux of Hg over the lakes obtained using Site-5 data were likely due to larger variations in the activity of local emission sources located upwind of Site-5, since the effect of variations in the parameters controlling the transport of the air mass and particle deposition velocity over the water were similar for both sites.

The deposition flux of particulate Hg, obtained as averages of those obtained along each forward trajectory using the MOI data, shows 6-fold variations for the MOI-Stage1, 7-fold for the MOI-Stage2, 16-fold for the MOI-Stage3, 15-fold for the MOI-Stage4 and 7-fold for the MOI-Stage5 (Figure 5). The higher variations in the dry deposition flux of Hg associated with particles with a MMD=1 μm are in good agreement with results obtained by Pirrone *et al.* (1994a) for trace metals associated with 1.3 μm diameter particles.

Table II shows the estimated deposition fluxes of atmospheric Hg in the gas and particle phase using the measurements made at sites Site-1 and Site-5 in April 1992 and March 1994 as input values to the HRD model. Dry deposition fluxes of total particulate Hg (fine+coarse) obtained using the Hg concentrations measured in April 1992 at Site-1 were higher than those estimated using the Hg concentrations measured at Site-5. However, Lake Erie was more impacted by the urban plume generated in Detroit with dry deposition fluxes in the range of 112 to 125 pg/m^2-h, followed by Lake St. Clair 67 to 109 pg/m^2-h and Lake Huron 19 to 31 pg/m^2-h. In March 1994 the dry deposition flux of particulate Hg (fine+coarse) was lower than that obtained during April 1992. However, Lake St. Clair is more impacted by the transport of air masses of urban origin with an average deposition flux of 57 pg/m^2-h, followed by Lake Erie 24 pg/m^2-h and Lake Huron 5.2 pg/m^2-h. Hg volatilization rates from the lakes were predicted to range from -0.13 to -0.36 ng/m^2-h for Lake Erie and -0.21 to -0.52 ng/m^2-h for Lake Huron. Predicted Hg volatilization from Lake St. Clair was at a rate of -0.5 ng/m^2-h when Hg concentrations measured at Site-5 were used, while deposition to the lake at a rate of 5.9 ng/m^2-h was predicted when Hg concentrations measured at Site-1 were used. The volatilization rates obtained in this study were similar to those estimated by Vandal *et al.* (1991).

TABLE II

Dry deposition flux of Hg in the gas phase (ng/m^2-h), in the particle phase (pg/m^2-h) for each Micro-Orifice Impactor (MOI) stage, and in the fine and coarse fraction (ng/m^2-h) calculated for Lakes St. Clair, Huron and Erie during April 1992 and March 1994. Negative values imply volatilization of the gas phase Hg from the lake.

	Lake St. Clair			**Lake Huron**			**Lake Erie**		
	Apr-1992 Site-1	Apr-1992 Site-5	Mar-1994 Site-5	Apr-1992 Site-1	Apr-1992 Site-5	Mar-1994 Site-5	Apr-1992 Site-1	Apr-1992 Site-5	Mar-1994 Site-5
Gas phase	5.9	-0.5		-0.21	-0.5		-0.36	-0.13	
MOI:									
Stage-1			23.5			3 6			15.2
Stage-2			5.8			1			5.1
Stage-3			4.15			0 41			3.7
Stage-4			2.3			0.17			1.5
Stage-5			0.63			0.02			0.4
Fine	25	15.3	7.1	6.8	4.2	0.52	20.6	18.5	5.1
Coarse	84	51.4	50	24.2	15	4.7	104	93	19

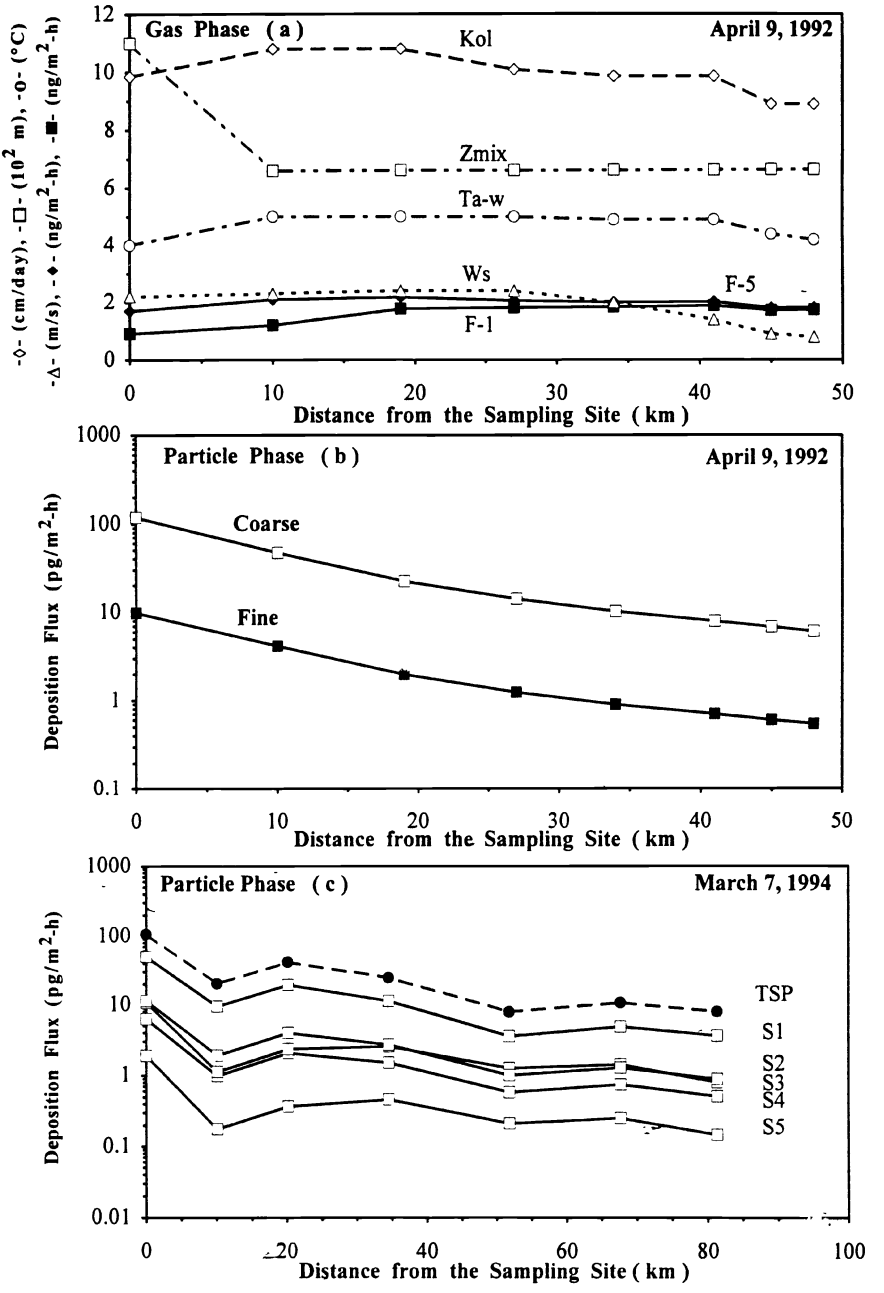

Fig. 3. Volatilization rates of the gas phase Hg and dry deposition fluxes of the particulate Hg along the forward trajectories that traversed Lake St. Clair and Lake Erie on 9 April 1992 and on 7 March 1994.

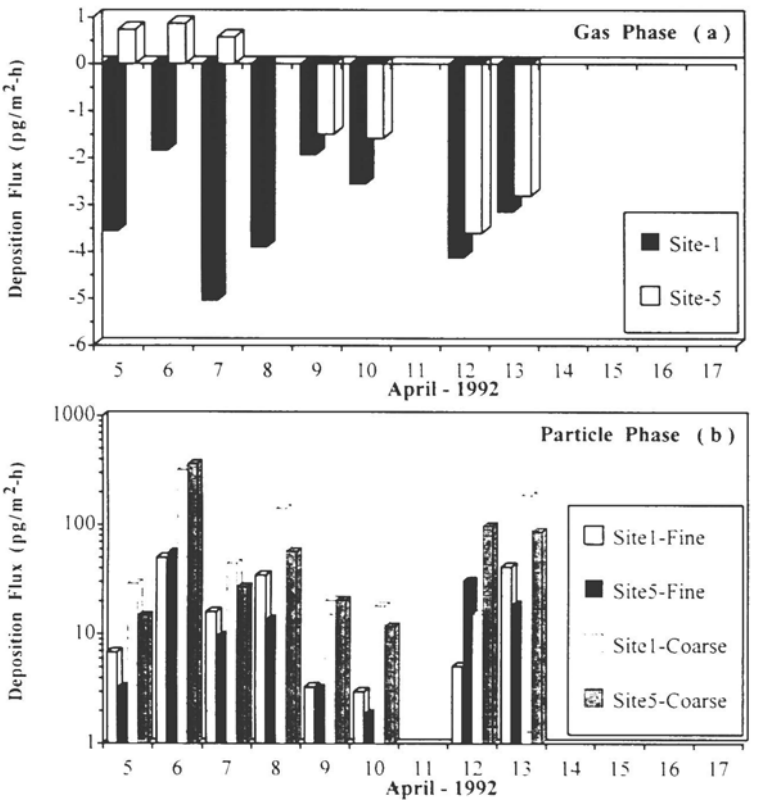

Fig. 4. Dry deposition fluxes of Hg in the gas and particle phase obtained as average of those calculated along each over-water trajectory traversing Lake St.Clair, Lake Huron and Lake Erie. Negative values imply volatilization of gas phase Hg from the lake.

4. Summary and Conclusions

Temporal and spatial variations of atmospheric concentrations and deposition fluxes of Hg associated with both the particle and gas phase over Lakes St. Clair, Erie and Huron were estimated using a hybrid receptor-deposition model (HRD). An evaluation of the variations in the particle deposition velocities and gas exchange rates of Hg during transport was performed. The overall variations in the deposition fluxes over the lakes ranged from 20-fold for 0.18 μm diameter particles to 10-fold for 5 μm diameter particles. The estimated exchange rates of the gas phase Hg were affected by the sampling site location and the fraction of Hg^0 in the total Hg dissolved in the aqueous phase. Therefore, gas phase Hg was predicted to volatilize from Lake Huron and Lake Erie at a rate of -0.21 to -0.5 ng/m^2-h and -0.13 to -0.36 ng/m^2-h, respectively. The model predicted that Lake St. Clair was degassing Hg at a rate of 0.5 ng/m^2-h when Site-5 data were used, and when the higher ambient concentrations measured at Site-1 were utilized gas phase Hg was deposited to Lake St. Clair at a rate of 5.9 ng/m^2-h. These results suggest that gas phase Hg can be deposited to the water surface (e.g., Lake St. Clair) when the air mass is near the emission sources, while it is re-emitted to the atmosphere at locations more distant.

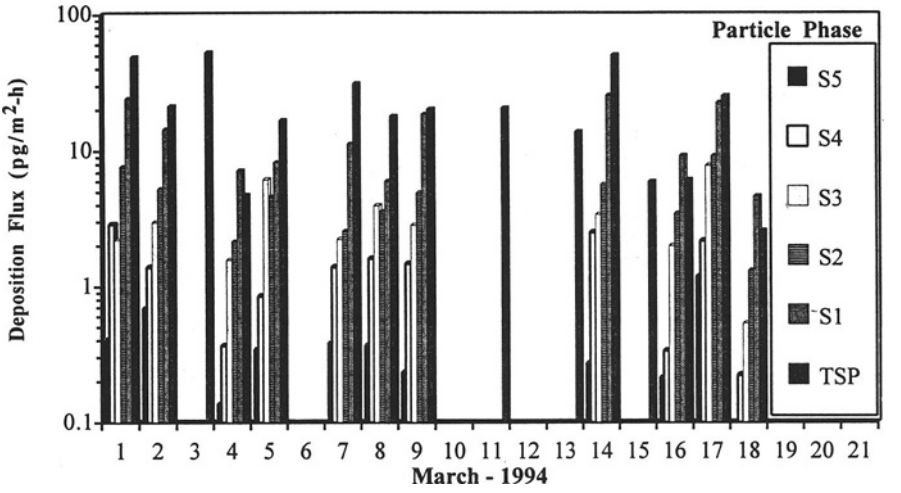

Fig. 5. Dry deposition fluxes of particulate Hg for each particle size range of the MOI stages, obtained as average of those calculated along each over-water trajectory that traversed Lakes St.Clair, Huron and Erie during March 1994.

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ATMOSPHERIC MERCURY IN NORTHERN WISCONSIN: SOURCES AND SPECIES

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Abstract. The atmospheric chemistry, deposition and transport of mercury (Hg) in the Upper Great Lakes region is being investigated at a near-remote sampling location in northern Wisconsin. Intensive sampling over two years and various seasons has been completed A multi-phase collection strategy (gas-, particle- and precipitation-phases) was employed to gain insight into the processes controlling concentrations and chemical/physical speciation of atmospheric Hg Additional chemical and physical atmospheric determinations (e g ozone, particulate constituents, meteorology) were also made during these periods to aid in the interpretation of the Hg determinations For example, correlations of Hg with ozone, sulfur dioxide and synoptic-scale meteorological features suggest a regionally discernible signal in Hg Comparison to isosigma backward air parcel trajectories confirms this regionality and implicates the areas south, southeast and northwest of the site to be sources for Hg Particle-phase Hg (Hg_p) was found to be approximately 40% in an oxidized form, or operationally defined as "reactive" However, this was quite variable from year-to-year Hg_p and other particle constituents (esp sulfate) show significant correlation and similarity in behavior (concentration ratios in precipitation and in particles) These observations are part of the growing evidence to support the hypothesis that precipitation-phase Hg arises in large part from the scavenging of atmospheric particulates bearing Hg Observed concentrations of rain and particle-Hg fit broadly the theoretical expectations for nucleation and below-cloud scavenging Significant increases in the Hg/aerosol mass ratio appear to take place during transport. Enrichment of aerosols is taken as evidence of gas/particle conversion which could represent the step linking gas-phase Hg with rain The refined budget indicates ca 24% of total deposition is from summer particle dry deposition, and that this deposition also contributes ca. 24% of all reactive Hg deposition Additionally, almost all (86%) deposition (wet and dry) occurs during the summer months

1 INTRODUCTION

Recent budgets of the biogeochemical cycling of mercury (Hg) in temperate latitudes have increased understanding of Hg accumulation in sensitive lakes (Fitzgerald *et al*, 1991, 1994, Lindqvist *et al*, 1991, Mason *et al*, 1994, Watras *et al*, 1994) In north central Wisconsin, the budget (Fitzgerald *et al*, 1991) outlined a total deposition of 10 3 $\mu g/m^2/yr$, with 66% arriving from precipitation and 34% from dry deposition While such budgets unequivocally implicate the atmosphere in the transport of Hg to the aquatic environment, little is known about Hg's atmospheric chemistry Determinations of Hg species in source plumes and in laboratory experiments (Mei, 1991, Prestbo, 1995, Munthe, 1992) have offered critical information about the chemical nature of Hg when released to the atmosphere and presented chemical-based mechanisms for its incorporation into rainwater Extensive receptor-based chemical investigation is required, however, to assess the importance of various Hg transformation pathways to Hg deposition

The University of Connecticut, with aid from the Wisconsin Department of Natural Resources and as a part of EPRI's Mercury Accumulation Processes and Pathways Project (MAPP) has established the Crab Lake Atmospheric Mercury Station (CLAMS) in north central Wisconsin to specifically address the need for receptor-based chemical information on atmospheric Hg Here, we are presenting some of the results from the on-going investigations

2. METHODS

The bulk of the results reported below were obtained at the Crab Lake Atmospheric Mercury Station (CLAMS) CLAMS is located in north central Wisconsin (Vilas County) near the town of Presque Isle (49 6° N, 89 0° W) The station consists of a 60' aluminum tower, field laboratory and pump enclosure The field laboratory is outfitted with a class 100 clean bench and

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Cold Vapor Atomic Fluorescence Spectrometer. During Aug. 1992, additional sampling was done at Max Lake, a small naturally acidic lake, approximately 30 Km south of CLAMS. This sampling was carried out at the end of a short 7m pinewood dock. The sampler inlets were approximately 1.5m from the lake surface.

At both sites, the following Hg collection procedures were used: 1) Gas-phase Hg (TGM) was collected on Au-coated quartz sand traps systems as described elsewhere (Fitzgerald and Gill, 1979; Fitzgerald, *et al.*, 1991) and the samples analyzed in the field. Samples for particle-phase Hg (Hg_p) were collected on polycarbonate (Nuclepore®) or quartz-fiber filters (Pallflex®), both capable of high efficiency collection of > 0.2 μm diameter particles, and moderately efficient for .2-.05 μm particles. All filter handling took place in the CLAMS cleanbench.

Precipitation was collected using ultraclean protocols and an acid-cleaned, manually-operated Teflon®-film funnel (Mason *et al.*, 1992; Fitzgerald, *et al.*, 1991). Snow was collected at CLAMS (and nearby Carlin Lake) by scooping up newly fallen material into acid-cleaned wide-mouth jugs, while the operator wore elbow-length gloves and stood downwind of the collection area. Some precipitation was filtered before analysis to study the physical distribution of the species present. This was done either with a peristaltic pump to remove liquid from the sample bottle and force it through a Teflon® in-line filter holder (Savillex®, for snow), or by suction through an aspirated polycarbonate filter funnel cassette (Nalgene®, for rain). In both instances, the precipitation was filtered using acid-cleaned 0.2 μm pore size polycarbonate filters (Nuclepore®)

Analysis of gas-, particle- and precipitation-phases of Hg was performed using techniques described elsewhere (Fitzgerald and Gill, 1979, Mason *et al.*, 1992; Lamborg *et al.*, 1994). Methylmercury (MeHg) analysis of particulates and precipitation was accomplished using the ethylation and chromatographic technique of Bloom and Fitzgerald (1988; Bloom, 1989). Inert distillation was used to separate the MeHg from precipitation and filter material (Horvat, 1993).

Sulfate determinations of precipitation or extracted filter material were made by ion chromatography (Miller and Nikolaidis, 1992). Isosigma air parcel back trajectories were prepared using the PC version of HySPLIT (Draxler, 1992) and interpolated meteorological data obtained from the National Climatic Data Center (NOAA). Aerosol mass was determined by gravimetric analysis of 47mm, 0.2 μm, Nuclepore® filters. Fine mass was selectively collected using a Teflon®-coated cyclone (University Research Glassware). Sulfur dioxide was collected behind the cyclone using a sodium carbonate-coated denuder (Koutrakis *et al.*, 1988). Ozone data were obtained from the Bureau of Air Management, Wisconsin Department of Natural Resources from Trout Lake Forestry Station, some 35 Km southwest of CLAMS. The sample inlet for the ozone determinations was located at approximately the same height as the Hg collection equipment at CLAMS.

3. RESULTS

Some results for gas-, particle- and precipitation-phase determinations of Hg at CLAMS are shown below in Figures 1-3 (where they are discussed). Summary statistics for Hg and other species for each sampling period can be found in Table I. Some values are missing from the figures, indicating voided samples. Error bars on the figures were generated in the following ways: for TGM, one standard deviation for duplicate or triplicate samples; for particle Hg, one standard deviation calculated as 15% of value from one system. Detection limits were nominally: TGM, 10 pg/m^3; particle Hg, 0.5 pg/m^3; precipitation Hg, 0.07 ng/L.

Table I. Summary of Hg measurements made during MAPP.

Sampling Period	TGM	Particle-Phase	Precipitation-Phase
Aug '92 (no gas & part figure)	1.21±0.49 ng/m^3	total: 63±32 pg/m^3 react: 38±18 pg/m^3	total: 2.58±2.23 ng/L react: 0.43±0.51 ng/L
Jan. '93	1.79±0.43 ng/m^3	total: 6±4 pg/m^3 react: 5±3 pg/m^3 methyl: 2 pg/m^3	total: 1.63±0.91 ng/L react: 0.22±0.11 ng/L methyl: n/a
Summer '93	1.8±0.4 ng/m^3	total: 14±23 pg/m^3 react: 1±2 pg/m^3 methyl: 0.95 pg/m^3	total:6.70±5.55 ng/L react: 4.04±4.74 ng/L methyl: 0.112±0.423 ng/L
May '94 (no gas & part figure)	1.68±0.26 ng/m^3	n/a	total: 8.74±2.59 ng/L react: 2.94±0.36 ng/L methyl: n/a

3.1 Gas-Phase

The high precision measurements (frequently with relative standard deviation of <5%) allow the temporal fine structure to be reliably documented. First it should be noted that the overall variability of gas-phase Hg is relatively low (rsd: 30%). This is consistent with the notion that Hg is a trace gas with a long residence time in the atmosphere (Slemr *et al.*, 1981; Fitzgerald *et al.*, 1981). However, the variability bears a connection with synoptic-scale meteorology (passage of fronts, etc.) as is noted on the January and Summer 1993 TGM time series (Figures 1 and 2). Frequently, the passage of fronts (noted by the arrows) was accompanied by rapid and significant changes in gas-phase Hg concentration. It should also be noted that these fronts were not always associated with precipitation (triangles) at the site or upwind of the site, and that changes in concentration cannot easily be attributed to a general cleansing of the air by rain.

Interestingly, there appeared to be little seasonal difference in the concentration and variability of TGM. The average value of 1.68 ng/m^3 is comparable to estimates made over the Pacific and Atlantic Oceans (Fitzgerald *et al.*, 1984, Slemr and Langer, 1992; Fitzgerald, 1995).

3.2 Particle-Phase

Unlike TGM, particle-phase Hg (Hg_p) shows a high level of temporal (60%) and seasonal (3-5x) variability. Wintertime collections made in January of 1993 (as well as previous measurements in Northern Wisconsin) suggest particulate mass which was dominated by fine fraction (< 2.5 μm) material. Indeed, collection of particles using a high-volume cascade impactor showed that the wintertime Hg resided entirely in the ultra-fine fraction (<0.5 μm). The dry deposition velocity for such material has been estimated to be 0.1 cm/s (Arimoto *et al.*, 1990). Analysis of the size distribution of summer Hg_p indicated that some coarse fraction Hg (> 2.5 μm) is present during the summer, effectively increasing the mass mean diameter to 2 μm and deposition velocity of Hg_p (0.5 cm/s). The amount of Hg observed in the coarse fraction during the summer was consistent with measurements of soil Hg made in the area (250 ng/g, Nater and Grigal, 1992) and amounts of total aerosol mass observed at the site (e.g. 250 ng Hg/g soil * 5 μg/m^3 = 1.25 pg Hg/m^3). While no direct observations are yet available, it can be assumed that the coarse/soil contribution to atmospheric Hg would be relatively constant throughout a season without snow cover (roughly 5 months of the year) with slight deviations due to soil moisture and local wind speed. Using this information, it can be estimated that dry

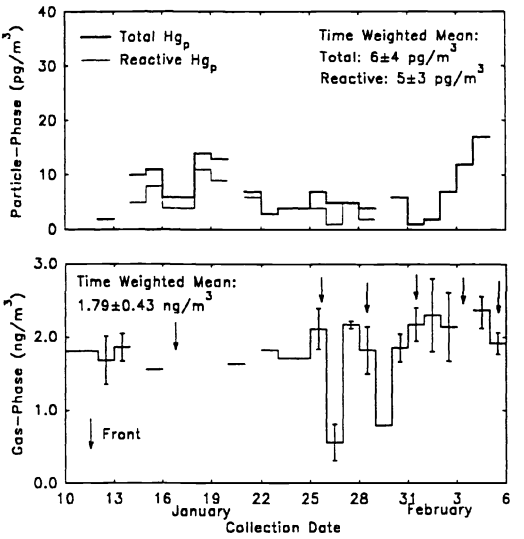

Figure 1. Atmospheric Hg measurements at CLAMS, Winter 1993

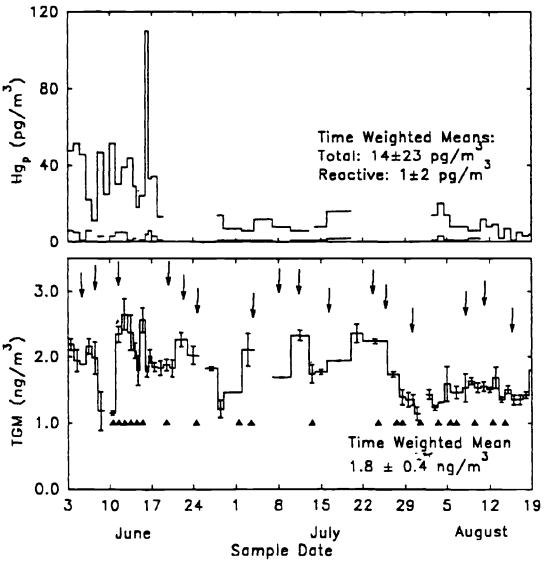

Figure 2. Atmospheric Hg measurements at CLAMS, Summer 1993

deposition of Hg from recycled soil material would equal only 0.2 $\mu g/m^2/yr$, which represents roughly 2% of total deposition. This also implies that excursions, or "events" in Hg_p most probably arise as a result of increased fine fraction contribution. Fine fraction material, in general, has a relatively long atmospheric lifetime (3-5 days) and is usually the result of anthropogenic emissions (Finlayson-Pitts and Pitts, 1986). This, too, must be confirmed through observations.

Speciation of the particle-phase is an important component in the current study. Operationally defined reactive particle-phase Hg was demonstrated to make up a significant fraction of total Hg during the Summer 1992 and Winter 1993. In both these sampling sessions, reactive Hg_p was approximately 50% of total, and sometimes more. In contrast, this species made up generally less than 30% of the total at CLAMS during Summer 1993. These values are of the same scale as the percentage of reactive Hg which is observed in precipitation (see below). One explanation for the generally lower Summer 1993 levels might be the heavy rainfall associated with the "Flood of 1993" which fell primarily to the south of the site. The results from 1994 collections will aid in understanding this observation.

Particle samples were also analyzed for MeHg. Only a few samples have been completed (N=4) and gave the following results: one sample from Jan. '93 showed 2 pg/m^3 MeHg, while one from Summer '93 contained 0.95 pg/m^3. It should be noted that the technique used for the analysis is still under development. If further determinations confirm these findings, it is plausible that MeHg in rainwater could be explained by invoking washout of MeHg on particles. However, as has been demonstrated, the amount of MeHg arriving to Wisconsin lakes through deposition (dry and wet) is not sufficient to account for MeHg accumulation in fish (Fitzgerald *et al.*, 1991).

The results of sulfate and mass determinations in Summer 1993 are as follows: SO_4=2.12±2.06 $\mu g/m^3$ [0.24 - 10.62]; Total mass=5.0±3.8 $\mu g/m^3$ [2.0 - 25.1]; Fine Mass=3.6±1.5 $\mu g/m^3$ [2.2 - 9.8]. Hg_p and particulate sulfate were statistically significantly correlated, but with a low correlation coefficient (r^2=0.23 $p>0.01$ mean $Hg/SO_4 = 2x10^{-5}$). However, as mentioned above, it appears that much of Summer 1993 may have been anomalous and obscured more striking connections between these two species. Hg_p likewise showed a weak but significant correlation with total aerosol mass (r^2=0.26, $p>0.002$) during Summer 1993 but no correlation during Winter 1993. It is interesting that particulate concentrations of Hg (mass/mass) were generally quite high (<1 - 30 ppm, avg.=7 ppm) during the summer. This is in stark contrast to primary particulate matter which was found to be < 1 ppm Hg after an electrostatic precipitator scrubbing coal-fired emissions (Meij, 1991) and to soil matter which may become entrained at the site (0.25 ppm; Nater and Grigal, 1992). Clearly, some enrichment of the aerosol takes place during transport and is assumed to be due to gas-to-particle conversion.

3.3 Regionality of Gas- and Particle-Phase Hg

During the Summer of 1993, both gas- and particle-phases of Hg at CLAMS showed weak but significant correlations with ozone (O_3) and sulfur dioxide (SO_2):

Hg-p and O_3: r^2= 0.14 $p>0.02$	Hg-p and SO_2: r^2=0.13 $p>0.05$
TGM and O_3:r^2=0.37 $p>0.001$	TGM and SO_2: r^2=0.16 $p>0.02$

Both of these species, particularly O_3, can be used as indicators for regional "air quality", or the general impact of anthropogenic activity on the atmospheric environment. Natural background levels of ozone (20 ppbv) and SO_2 (0.05 ppbv) were observed at CLAMS, as well as concentrations slightly elevated above these baselines (24h averages):

Species	Mean (ppbv)	Range (ppbv)
Ozone	30	10-50
Sulfur Dioxide	.1	<.05 - 10

While neither of these species were ever in "non-attainment" for their respective National Ambient Air Quality Standard (O_3: 120 ppb; SO_2: 30 ppbv), it is significant that maximum concentrations for ozone, SO_2 and Hg were coincident. This covariation is most probably the result of similar emission regions and transport. This example of atmospheric Hg's regional character is not a new observation (Lindqvist *et al.*, 1991; Schroeder and Markes, 1994; Lamborg *et al.*, 1994), but is perhaps more subtle (due to the site's remoteness) than those reported before.

The regionality of Hg's behavior can be verified using meteorological tools as well. Using the HySPLIT model (Hybrid Single Particle Lagrangian Integrated Trajectory, Draxler, 1992), isosigma (constant pressure, terrain following) backward air trajectories can be generated which indicate the most probable travel path for air arriving at a site. Grouping trajectories by sector (8 in all) and generating average Hg concentrations for each group allows examination of chemical data for meteorologically-based trends. It should be noted that trajectories (and concentration information) which were found to cross fronts, as indicated by surface weather maps, were not included in the analyses. However, trajectories which likely had precipitation upwind of the site were included in the treatment, and may have therefore contributed to de-emphasizing the impact of certain sectors (Keeler and Samson, 1989). When this treatment was applied to samples from June 1993, the following results were obtained:

Species	N	NE	E	SE	S	SW	W	NW
Hg_p (pg/m^3)	34		39	48	40	19	23	46
	n=5	n=0	n=1	n=2	n=2	n=3	n=1	n=2
TGM (ng/m^3)	1.83	1.85	1.82	2.22	1.39	2.01	1.94	1.86
	n=5	n=2	n=1	n=4	n=1	n=3	n=1	n=3

Although there are limited data, it appears that air arriving to northern Wisconsin from the industrial Midwest regions of southern Lakes Huron, Michigan and Erie may bear more Hg than from other regions. Interestingly too, Hg_p concentrations in air from the NW may be higher on average, indicating a source there as well. Here, the meteorological treatment has generally verified the correlation of Hg species with ozone and sulfur dioxide.

3.4 Precipitation-Phase

The precipitation collected since January 1993 at CLAMS (as well as collections made previously in Wisconsin) is shown in Figure 3. Speciation for 1993 was fairly typical of past years, with approximately 47% of the Hg present in the form of reactive Hg. For May 1994, this speciation was more skewed toward total Hg, but the samples collected were from small sized events, and possessed a large amount of filterable material. MeHg can be found in rain and snow, but only in small amounts. Samples from 1993 also show this behavior.

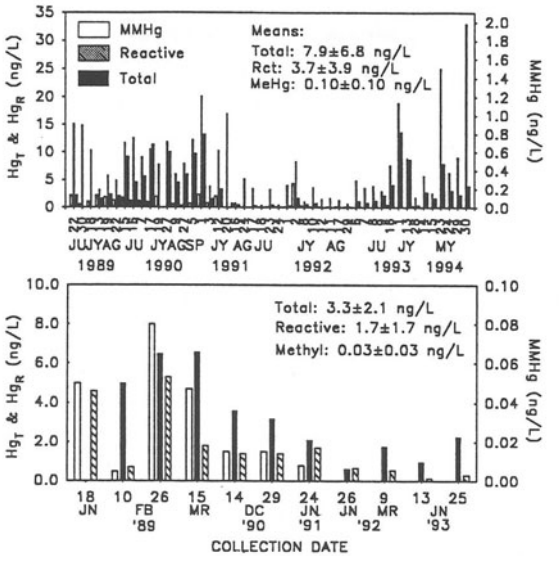

Figure 3. Rain (above) and Snow Hg measurements from N. Wisconsin

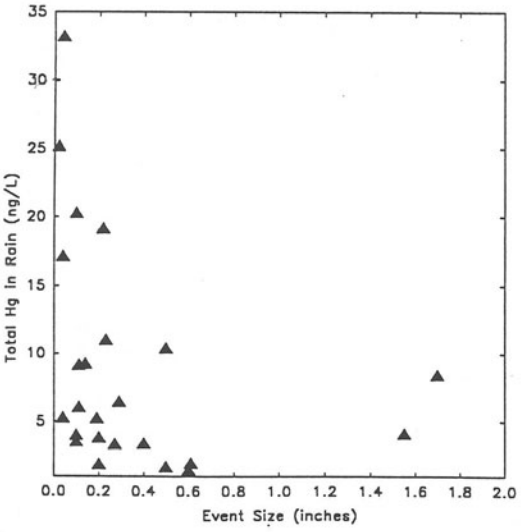

Figure 4. Washout of Hg in rain from 1991-1994

Some samples from January 1993 and May 1994 were filtered through 0.2 μm pore, acid-cleaned polycarbonate filters and the filtrate analyzed for total and reactive Hg. (Table II). The results suggest that large fractions of Hg in precipitation can be removed along with particulate matter. The effect is greater for total than for reactive Hg, but some reactive Hg can be removed by filtration. This was very dramatically demonstrated with the May 1994 samples (not shown), which came from small sized events and perhaps more heavily impacted by scavenging of aerosols. If the concentration of rain collected is plotted versus event size (Figure 4), a dramatic nonlinear relationship can be observed. This relationship has been frequently observed between events and even within individual events (Bloom and Watras, 1989; Iverfeldt, 1991; Hoyer *et al.*, 1993; Ferrara *et al.*, 1986) and has usually been attributed to the impact of particle scavenging by rain. The washout ratio ($w=Hg_{ppt}$ (ng/L) * 1.2 m^3/L /Hg_p (ng/m^3)) of samples collected during 1989 was 477±547. A similar value was found for 1993 (181±129). These values are similar to the range (200-2000) that might be expected for a precipitation-phase species which arises from particle scavenging (GESAMP Working Group 14, 1989).

Table II. Results from filtered precipitation Hg determinations.

Sample	Total Hg Unfiltered	Total Hg Filtered	Reactive Hg Unfiltered	Reactive Hg Filtered
Rain (N=3)	21.63±13.86 ng/L	5.08±1.55 ng/L	4.96±2.57 ng/L	2.76±1.29 ng/L
Snow (N=4)	1.42±0.74 ng/L	0.72±0.13 ng/L	0.40±0.23 ng/L	0.19±0.10 ng/L

There is a strong correlation between Hg and sulfate in rain from the 1993 collections (r^2=0.83 p>0.01, neglecting one outlier). Additionally, the Hg/SO_4 ratio in rain was $5\pm4x10^{-5}$, and of the same order as that in the particulate matter. Charlson *et al.*, (1983) using a parameterization scheme based on physical and chemical considerations, estimated that approximately 64% of the sulfate in rainwater in rural regions was the result of nucleation scavenging of particles bearing sulfate. Charlson *et al.* estimated that 3% of the sulfate arose from below-cloud scavenging by droplets, and the remaining 33% from in-cloud production from dissolving SO_2. Altogether then, particulate sulfate accounted for 67% of that which was found in rain. To the extent that Hg correlates with sulfate, it may be inferred that Hg in rain arises from perhaps analogous mechanisms. Not surprisingly, the end members of washout curves (appox. 40 ng/L at the start of, or for a small event and 2-6 ng/L at the end of, or for a large event), such as those from Wisconsin or Italy, reproduce fairly accurately the extreme predictions of Hg in rain from washout mechanisms (45 ng/L: Seinfeld, 1986) and in-cloud production (2-4 ng/L: Munthe, 1992).

3.5 Biogeochemical Budgetary Concerns

With winter, spring and summer determinations of all forms of atmospheric Hg now complete, a refined version of the budget for Hg (Fitzgerald *et al.*, 1991) deposition in northern Wisconsin can be constructed. The relevant information used is listed below as a summary:

Season	Total Hg_p	React Hg_p	Methyl Hg_p	Total Hg_{ppt}	React Hg_{ppt}	Methyl Hg_{ppt}
Winter	7 pg/m^3 Vd=0.1 cm/s	7	2	3.27 ng/L 26 cm/yr	1.68	.03
Summer	26 pg/m^3 Vd=0.5 cm/s	10	0.95	7.86 ng/L 55 cm/yr	3.66	.1

These values yield the following

Species Deposited	Dry ($\mu g/m^2/yr$)	Wet ($\mu g/m^2/yr$)	Total ($\mu g/m^2/yr$)
Total Hg	1 8 (93% Summer)	5 2 (84% Summer)	7 0 (86% Summer)
Reactive Hg	0 8 (84% Summer)	2 5 (82% Summer)	3 3 (82% Summer)
MethylHg	01 (60% Summer)	06 (88% Summer)	0 07 (84% Summer)

The refined budget is essentially identical to that from 1991 The total deposition was estimated to be 7 0 $\mu g/m^2/yr$ This value is somewhat lower that the 1991 estimate Lower rain concentrations measured during 1992 lowered the wet depositional flux estimate Wet deposition was found to furnish 74% of the deposition This is a somewhat higher estimated contribution than calculated in 1991 This is due to the discovery that wintertime particulate Hg is located on ultrafine material, and therefore contributes less to dry deposition The refined version demonstrates that the summer is the period when the majority (86%) of Hg is deposited Furthermore, the refinements highlight the contribution of summertime dry deposition to annual reactive Hg fluxes (24%) This implies the existence of a supply of the substrate for methylation which is independent of precipitation amounts

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ATMOSPHERIC SOURCES, TRANSPORT AND DEPOSITION OF MERCURY IN MICHIGAN: TWO YEARS OF EVENT PRECIPITATION

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Abstract. To assess the sources, transport and deposition of atmospheric mercury (Hg) in Michigan, a multi-site network was implemented in which Hg concentrations in event precipitation and ambient samples (vapor and particulate phases) were determined. Results from the analysis of 2 years of event precipitation samples for Hg are reported here. The volume-weighted average Hg concentration in precipitation was 7.9, 10.8 and 10.2 ng/L for the Pellston, South Haven and Dexter sites, respectively. Yearly wet deposition of Hg for 1992-93 and 1993-94 was 5.8 and 5.5 $\mu g/m^2$ at Pellston, 9.5 and 12.7 $\mu g/m^2$ at South Haven and 8.7 and 9.1 $\mu g/m^2$ at Dexter. A spatial gradient in both the Hg concentration and wet deposition was observed. Northern Michigan received almost half the deposition of Hg recorded at the southern Michigan sites. The concentration of Hg in precipitation exhibited a strong seasonal behavior with low values of 1.0 to 2.0 ng/L in winter and maximum values greater than 40 ng/L in summer. The spring, summer and autumn precipitation accounted for 89 to 91% of the total yearly Hg deposition. Mixed-layer back trajectories were calculated for each precipitation event to investigate the meteorological history and transport from potential Hg source regions. Elevated Hg concentrations were observed with air mass transport from the west, southwest, south, and southeast. At each of the sites precipitation events for which the Hg concentration was in the 90th and 10th percentile were analyzed for trace elements by ICP-MS to investigate source impacts.

Keywords: Mercury, wet deposition, precipitation, trace elements, regional transport, trajectories

1. Introduction

Atmospheric transport and deposition of Hg has been recognized as an important link in the cycling of Hg in the environment (Lindqvist, 1985; Lindberg *et al.*, 1991). Anthropogenic Hg sources in the U.S. and initial estimates of their annual emissions into the atmosphere have recently been reported (U.S. EPA, 1994). Since anthropogenic sources for Hg in the U.S. are numerous and generally not well characterized, an accurate emissions database which includes both anthropogenic and natural sources is not yet available. This fact coupled with an incomplete understanding of atmospheric processes for Hg limit the applicability of deterministic models in predicting the atmospheric behavior and deposition of Hg over short temporal and large spatial scales. To investigate the local and regional transport and deposition of Hg, accurate, long-term measurements at multiple receptor locations should be obtained. To attempt to diagnose the source(s) and source regions culpable for the observed Hg, concentrations of Hg in ambient air (both vapor and particle phases), and in event precipitation should be measured together with complementary chemical and meteorological parameters at multiple sites over time periods longer than one year.

Research conducted in Scandinavia (Brosset, 1987; Iverfeldt, 1991) identified a spatial gradient in the concentration of Hg in precipitation from northern to southern Sweden. Meteorological analysis indicated that the elevated levels of Hg observed in precipitation were associated with transport from the heavily industrialized region to the south and southeast of Sweden. In addition, Hg concentrations were correlated with concentrations of sulfate, Cd and Pb in precipitation, which suggested a connection

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between the Hg found in precipitation and anthropogenic emissions upwind (Iverfeldt, 1991).

In the Great Lakes, indirect evidence suggesting a gradient in the deposition of Hg has been reported by Nater and Grigal (1992). A two fold increase of Hg content in surficial soils was observed from western Minnesota to northeastern Michigan. To investigate these findings and to determine the sources of the Hg deposition in the Great Lakes region, sampling for Hg and other chemical and meteorological parameters was conducted in Michigan from 1992 to 1994. Measurements included event precipitation for the two years of the study, and vapor and particulate phase Hg, as well as other atmospheric constituents on an every 6th day basis for the second year of the study. Data reported in this paper are limited to Hg, major anions and trace elements. Sites were chosen to provide an adequate spatial resolution to characterize regional transport and to document spatial differences in the deposition of Hg in Michigan. In addition, source regions and source types culpable for the Hg measured were investigated using meteorological, elemental, and chemical data for precipitation events with elevated Hg.

2. Materials and Methods

Event precipitation was collected for two years (March 1992 - March 1994) at three sites in Michigan: Pellston, South Haven and Dexter (Figure 1). The site near Pellston located at the University of Michigan Biological Station is also a National Atmospheric Deposition Program (NADP) site. The region around Pellston is mixed forest with areas of low intensity farming. The site in South Haven was located in a rural agricultural area 3 km east of Lake Michigan. The Hg monitoring at that site was collocated with atmospheric measurements as part of several studies investigating the loading of Hg and other toxic compounds to the Great Lakes. The Dexter site, located 25 miles northwest of Ann Arbor, MI is a U.S. EPA National Dry Deposition Network (NDDN) Site.

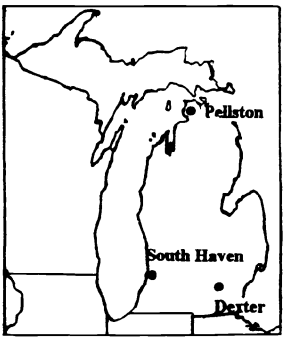

Fig. 1. Hg Measurement sites in Michigan

Precipitation samples were collected into a 10 L borosilicate glass (BSG) vessel using an MIC-B automatic collector (MIC Co., Richmond Hill, Ontario) with a Teflon-coated funnel. After each precipitation event, the sample was transferred from the 10 L collection vessel to a 1 L BSG bottle. With a funnel inlet area of 0.2 m^2, precipitation events of 0.13 cm or greater provided sufficient volume for analysis. The 10 l vessel was rinsed with ultra-pure water (containing <0.2 ng Hg/L) after collection of each sample and was replaced biweekly. A field blank was performed biweekly to ensure that the system was contaminant-free. A Teflon-covered pad was installed on the undersid-

of each funnel cover to shield the funnel from windblown dust and other particulate matter.

All sample bottles and glassware used in sample analysis were rigorously cleaned in an 11-day procedure involving an acetone rinse, detergent wash, multiple rinses with ultra-pure water, heating in 3M HCl at 80°C, and two separate soaking periods in 0.6M HNO_3 followed by extensive rinsing in ultra-pure water in a Class 100 clean room (Rossmann and Barres, 1991). Ultra-clean techniques were used in all phases of sample collection and analysis. Samples were shipped by overnight mail to the University of Michigan Air Quality Lab (UMAQL) in Ann Arbor, MI. A Belfort rain gauge located at each site was used to determine the volume and time of each precipitation event.

When samples were received at UMAQL a subsample was poured off and acidified for analysis of trace metals by inductively coupled plasma mass spectrometry (ICP-MS). A separate subsample was poured off for analysis of pH and major ions by ion chromatography. The remaining sample was oxidized with bromine monochloride to a 1% solution for analysis of total Hg by cold vapor atomic fluorescence spectrometry (Fitzgerald and Gill, 1979). At the start of the study, the detection limit for total Hg, defined as 3σ of the reagent blank, was 0.095 ng/100 mL sample. The detection limit was reduced to the current level of 0.015 ng/100 mL sample with the use of more purified HCl and bromine salts. All samples were initially analyzed in duplicate. After the first 6 months through the end of the study 50% of the samples were analyzed in duplicate. The average analytical precision over the duration of this study was 6%.

Procedures required to implement and operate a multi-site network for collection and analysis of event precipitation for Hg are described in Hoyer and Keeler (1994a). The manuscript details experiments including collocated manual and automatic collectors, interlaboratory comparisons and investigation of the stability of Hg in precipitation. Results from the first year of network operation are reported elsewhere (Hoyer *et al.*, 1993).

Three-day backward mixed-layer trajectories were calculated for each day on which precipitation was collected. Air mass trajectories define the most probable path of an air mass before arriving at a specified receptor site. Trajectories were calculated from upper air data collected at National Weather Service monitoring stations (Heffter, 1980).

3. Results and Discussion

3.1 Hg CONCENTRATION IN PRECIPITATION

During the two years of event precipitation collection, a total of 153 samples were collected at Pellston, 188 at South Haven and 181 at Dexter. The two year mean Hg concentration in precipitation was 7.9 ng/L at Pellston, 10.8 ng/L at South Haven and 10.2 ng/L at Dexter (Table I).

Variability in the precipitation Hg concentration between the sites was clearly evident. The maximum concentration observed at the northern Michigan site in Pellston was approximately 20% lower than the maximum at the southwestern Michigan site in South Haven and the southeastern Michigan site in Dexter. Precipitation events with elevated Hg were also less frequent at the Pellston site than at the two southern Michigan sites. The standard deviation of the Hg concentration in precipitation at South Haven was

higher than at the other two sites largely due to the elevated Hg concentrations in several summer samples collected at the site.

TABLE I
Total Hg in precipitation in Michigan (ng/L), Mar 1992-Mar 1994

SITE	n	Volume-Weighted Average	Std Dev	Range	90th Percentile
Pellston, MI	153	7.9	7.4	1.4 - 47.6	16.6
South Haven, MI	188	10.8	11.2	1.2 - 59.5	25.7
Dexter, MI	181	10.2	9.8	1.8 - 55.2	19.6

The concentration of Hg in precipitation varied seasonally at each of the sites (Figure 2). Average Hg concentrations for the spring and summer were a factor of two greater than those in winter, except at the Dexter site where two high concentration events occurred in winter 1994 which elevated the mean. Year-to-year differences in the seasonal average Hg concentration in precipitation are evident (Figure 2). The average Hg concentration was 14% and 25% lower in the summer of 1992 at South Haven and Dexter, respectively, than in summer of 1993. This may have resulted from lower than average ambient temperatures during the summer 1992, but more years of sampling would be required to adequately characterize seasonal differences on a year-to-year basis. The average Hg concentration in precipitation in winter 1994 at Dexter was higher than that in winter 1993. This was uncharacteristic when compared to measurements at the other sites. This elevated average was due to one event in Feb 1994 and two events in Mar 1994 for which the concentration of Hg was greater than 20 ng/L. These storms deposited precipitation with slow transport from the east (Detroit metropolitan area).

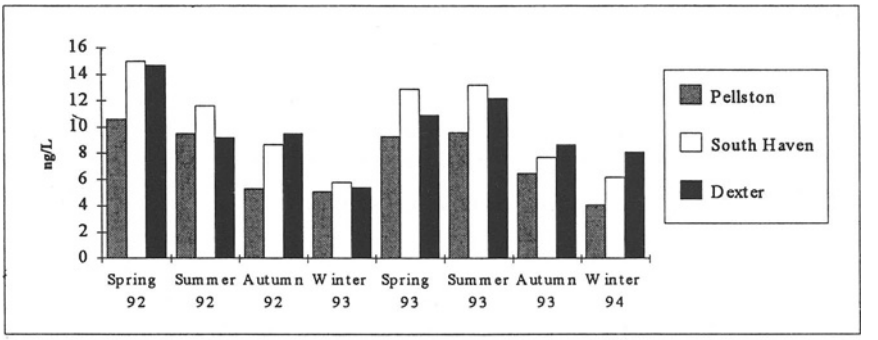

Fig. 2. Volume-weighted average Hg concentration in precipitation 1992 - 1994.

Many factors, both chemical and physical, may influence the seasonal variation in the concentration of Hg in precipitation. Those factors include precipitation type, source influences, atmospheric oxidant concentration (Munthe *et al.*, 1991), in-cloud processes (Borys *et al.*, 1988), meteorology and chemical/physical aspects of the aerosol population. Borys *et al.* (1988) reported that the concentration of constituents in frozen precipitation may be strongly influenced by in-cloud growth processes (accretion and vapor deposition). Several in-cloud processes are potentially important factors which

may control the concentration of Hg in cloud droplets and subsequently in precipitation. These include in-cloud temperature, turbulence, aerosol size distribution, and chemical properties of the atmospheric aerosol incorporated into the cloud system. Chemical parameters of importance include oxidant concentrations and the particulate and vapor species in the air which feeds the precipitating cloud system (Munthe *et al.*, 1991).

3.2 Hg WET DEPOSITION

During the first year of measurement, the total Hg wet deposition observed at South Haven was 9.45 $\mu g/m^2$ while at Pellston and Dexter the wet deposition was 5.79 and 8.66 $\mu g/m^2$, respectively (Table II). The wet deposition of Hg was substantially higher in the second year of sampling at South Haven, but nearly identical for both years at Pellston and Dexter. The increase in deposition measured at South Haven resulted from an increased precipitation rate. Event Hg wet deposition measurements in Underhill, VT made from Dec 1992-'93 also demonstrate the importance of precipitation amount on yearly loading (Burke *et al.*, this volume). During this one year period, the average volume-weighted Hg concentration at the site in Vermont (8.3 ng/L) was similar to that observed at Pellston (7.9 ng/L). However, Hg deposition observed at the Vermont site was 9.26 $\mu g/m^2$, substantially higher than that measured at Pellston. The measured values at the Pellston site are also lower than values estimated from measurements in northern Wisconsin at similar latitudes (Fitzgerald *et al.*, 1991), and from measurements of weekly precipitation collected in Ontario (Mierle, 1990). These differences may be due to sampling frequency, precipitation amount and/or differences in source impacts.

A spatial gradient in the deposition of Hg was observed in Michigan in this study. South Haven received 1.6 and 2.3 times more Hg deposition than Pellston in the two respective years of sampling. While the spatial differences in Hg wet deposition are clearly a function of the different amounts of precipitation received, the difference in Hg concentration at the sites also contributes substantially to the regional gradient in wet deposition of Hg. In 1992-'93 South Haven received 1.2 times more precipitation than Pellston and 1.6 times more Hg was deposited in South Haven. In 1993-'94 South Haven received 1.6 times more precipitation than Pellston, but 2.3 times the Hg wet deposition. The yearly precipitation totals in 1992-'94 were within 10% of the 30-year climatological average for these regions in Michigan (NOAA, 1992). However, the precipitation received at South Haven in 1993-'94 was 24% higher than the 30-year average.

Seasonal variation in the wet deposition of Hg was also observed in both years of measurement with summer storms delivering 3 to 5 times more Hg than winter storms (Figure 3). Note that while the volume-weighted average concentration of Hg in precipitation collected at Dexter was elevated in winter 1994 compared to winter 1993, the deposition for this season was similar in the two years of study. Hg wet deposition occurring during winter of 1992-'93 accounted for only 6% of the total Hg deposition at Pellston, 7% at South Haven and 15% at Dexter. Wintertime Hg wet deposition in 1993-'94 contributed 7% of the yearly total at both Pellston and Dexter and 8% at South Haven. The largest portion of the annual Hg wet deposition occurred in the spring and summer months at each of the sites with 34% of the total being deposited during those seasons. Hg wet deposition during the autumn periods averaged 22% of the total annual wet deposition at the three sites.

Table II
Deposition of Hg in precipitation ($\mu g/m^2$), Mar 1992-Mar 1994

SITE	Event Avg	Event Max	1992-'93 Deposition	1993-'94 Deposition	1992-'93 Precip Amnt, cm	1993-'94 Precip Amnt, cm
Pellston, MI	0.07	0.51	5.79	5.54	73	71
South Haven, MI	0.12	0.85	9.45	12.67	89	116
Dexter, MI	0.10	0.98	8.66	9.11	87	88

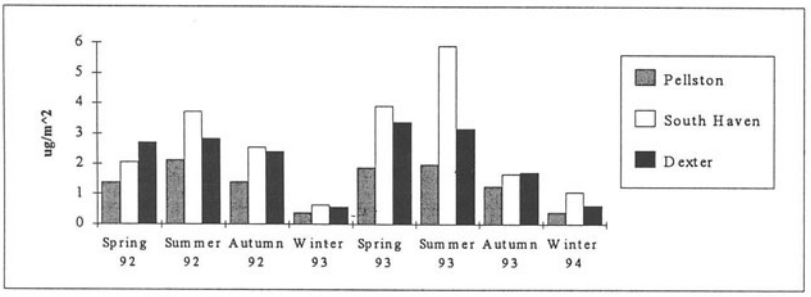

Fig. 3. Mercury wet deposition by season in Michigan 1992 - 1994.

Individual precipitation events resulted in Hg wet deposition from 0.002 $\mu g/m^2$ to a high of 0.984 $\mu g/m^2$ measured at Dexter in 1992-'93 which represented 10.8% of the total annual deposition. Elevated Hg deposition events (90th percentile by site) were generally the result of large volume precipitation events with average or above average Hg concentration. At all sites precipitation events in the 90th percentile for Hg concentration accounted for 18 to 22% of the cumulative Hg wet deposition for the two-year period while the 10th percentile events accounted for only 3 to 6% of the Hg wet deposition.

For this study, precipitation events which accumulated less than 0.13 cm did not produce sufficient volume for a complete chemical and elemental analysis. The contribution of these events was estimated using the average concentration in events which accumulated 0.13 to 0.25 cm for the month during which the low-volume event occurred. This estimation procedure was used because of the seasonal variation in Hg concentration and the relationship between precipitation and concentration amount (lower volume events have a higher Hg concentration, Hoyer and Keeler, 1994b). The estimated deposition from these events was not included in Table II. These small events were estimated to have contributed 4% of the two year total at Pellston, 2% at South Haven and 3% at Dexter. These data indicate that collection of events less than 0.13 cm is not important in accurately assessing wet deposition when event samples are collected throughout the year.

3.3 TRANSPORT AND SOURCE CHARACTERISTICS

Air mass trajectories are a useful tool in the analysis of air and precipitation chemistry measurements (Pierson *et al.*, 1986; Keeler *et al.*, 1990; Moody and Galloway, 1988). However, interpretation of trajectory measurements should not be undertaken without full knowledge of the associated uncertainties and the limitations inherent in the meteorological measurements on which they are based (Kahl, 1993). An initial investigation of the meteorological associations and potential sources influencing the Hg concentrations measured in event precipitation samples was performed. Mixed-layer back trajectories were plotted for each event and a suite of trace elements in samples with elevated Hg were analyzed. The relative abundance and combination of the elements quantified were used to characterize potential sources. Previous work has demonstrated that trace element components of a transported aerosol mass and metal ratios reveal specific source influences (Rahn and Lowenthal, 1984; Keeler and Samson, 1989).

The highest Hg concentrations (90th percentile) were typically associated with air mass transport from the west, southwest, south and southeast of the sites in Michigan (Figures 4a-b). Although less frequently, events elevated in Hg were also observed with transport from the north and east to each of the sites. Upwind stagnation was evident for a few of the 90th percentile events which has been previously shown to result in elevated anion levels in precipitation (Pierson *et al.*, 1989; Moody and Samson, 1989). Trajectories plotted for 10th percentile events indicated that transport from the north, northwest, and east (frequently accompanied by rapid advection) often resulted in low Hg concentration in precipitation.

Trace element concentrations in precipitation events with high Hg at the South Haven site were investigated for potential source markers. On 11 May 94 and 24 May 94 transport to South Haven was from the northwest and these events had elevated concentrations of Hg, V, Pb, Fe, Zn, Mn, Cu, NO_3^- and SO_4^{2-} (elevated in comparison to concentrations in other samples in the 90th and 10th percentile for Hg). The sample collected on 24 May 94 also contained elevated levels of As and Se and especially elevated NO_3^- and SO_4^{2-} concentrations. These elemental concentrations indicate potential contributions from metals processing, iron and steel manufacturing, and oil and coal combustion.

During the summer months, with prevailing winds from the southwest, the South Haven site received storms with feed air from one of the largest Hg emission source areas in the region. According to the draft EPA Emissions Inventory (U.S. EPA, 1994), Cook County and the three counties surrounding it at the southern tip of Lake Michigan emit more than 5.0 tons of Hg/year. The number and variety of Hg and other trace element source types are diverse in this region so that characterization of Hg sources using measurements at receptor sites requires analysis of the intersection of a large number of precipitation events representing different meteorological conditions. Events elevated in Hg concentration arriving at the South Haven site from the southwest all had elevated concentrations of Pb, Fe, Zn, Mn, As, Cd, Se, V, NO_3 and SO_4^{2-} reflecting a variety of possible source influences including coal combustion, oil combustion, metals processing (ferrous and non-ferrous) and incineration.

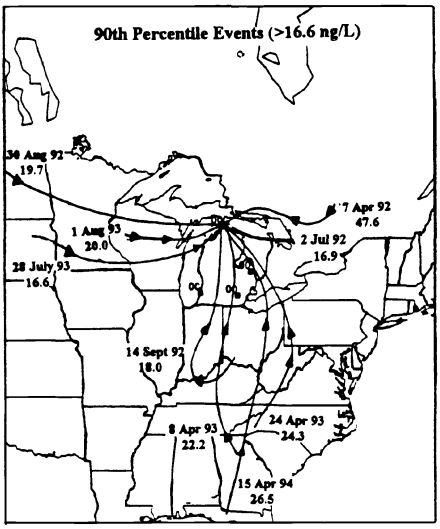

Fig. 4a. Pellston Mixed-Layer Trajectories

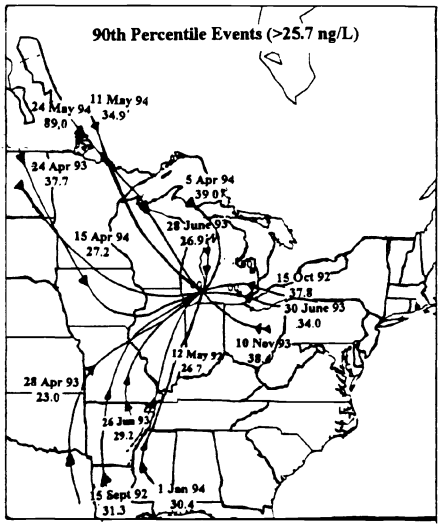

Fig. 4b. South Haven Mixed-Layer Trajectories

Each trajectory is labeled with the date of precipitation and concentration of Hg in ng/L.

In general, when Hg was elevated other trace metals in the sample were also elevated indicating common source(s) and/or source regions. Also, when a sample was low in Hg concentration it was generally accompanied by low elemental and anion levels. However, for samples in the 10th percentile for Hg concentration, there were two events at Pellston, one at South Haven and one at Dexter which had an elevated level of one or more other elements. A snow storm at Pellston on 19 Dec 1993 with Hg concentration of 2.0 ng/L was highly elevated in Ni, Pb, Fe, Zn, As, Cd, Se, Cu and Cr and slightly elevated in Mn and V. The trajectory for this event indicates air mass transport from west-southwest of the site. On a second occasion at Pellston (10 Sept 1993) a precipitation sample had 2.6 ng/L of Hg but contained highly elevated Pb and Cd. Air mass transport for this event was very rapid and directly out of the northwest traveling over potential metals sources in the Upper Peninsula of Michigan. On 19 Feb 1994 a snow sample at Pellston contained 2.8 ng/L Hg and elevated Mn, V and Cr indicating potential input from oil combustion sources and non-ferrous metal manufacture.

At South Haven only one of the 10th percentile events contained elevated levels of trace metals other than Hg. Frozen precipitation that fell on 25 Feb 1994 contained 3.1 ng/L Hg but had elevated Cu and a moderate level of Pb, Zn and Mn. Trajectories plotted for events in the 10th percentile for Hg concentration indicated that a source region contributing to elevated Hg may, on occasion, contribute to very low levels of Hg in precipitation. Clearly, factors other than air mass origin were affecting the constituent load in precipitation. Precipitation type, storm type (convective vs. frontal), wind speed, other boundary layer parameters, and the Hg chemistry itself could have affected the Hg concentration in precipitation from storms which arrive from known source regions.

4. Conclusions

Analysis of two years of event precipitation samples at three sites in Michigan has resulted in several findings to date. A gradient in both the Hg concentration and wet Hg deposition in Michigan was observed with the northern Michigan site receiving less Hg than the southern Michigan sites. The Hg concentration in event precipitation samples varied by season with Hg concentrations two times greater during spring and summer months than during winter. The data suggest that the sources of Hg measured at the sites are of regional origin (within and outside of Michigan) and that proximity to known anthropogenic sources significantly influence the concentration and wet deposition of Hg in the Great Lakes basin. Assessment of event deposition over a two-year period has enabled an accurate measurement of total Hg loading to the lower peninsula of Michigan in the Great Lakes basin. This study provides the first spatially resolved event Hg wet deposition data in the region. These results can be used to improve model estimates of the wet Hg flux in this region.

Several studies have now documented a seasonal trend in the Hg concentration in precipitation and in the wet deposition of Hg (Burke *et al.*, this volume; Glass *et al.*, 1986). This observation is possibly due to combined effects of chemistry and physical processes (e.g. ozone and other in-cloud oxidant concentration, physical factors in-cloud involved in the growth of rain droplets and ice crystals). To elucidate the dominant factors controlling the seasonal variation of Hg in precipitation, further investigations of the concentrations and reaction rates for Hg and other ions and constituents in

precipitation are needed as well as better understanding of Hg-containing aerosols, their size distributions, concentrations, and their role in precipitation formation

Mixed-layer trajectories indicate that the dominant sources of Hg to the Michigan sampling sites are located to the west, southwest, south and southeast Investigating the cross-section of several events that contained elevated Hg concentration provides the ability to separate meteorological influences from source effects on precipitation chemistry Specific source types can also be identified with the use of tracer compounds measured in the precipitation

In order to investigate sources utilizing the receptor-based approach employed in this study, short duration (event) precipitation samples need to be collected for at least one year in order to assess sample to sample variability, inter-site differences, seasonal variation and meteorological factors which can drastically alter precipitation chemistry

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U S EPA Emission Inventory Mercury Study Report to Congress 1994

Impact of the State-of-the-Art of Flue Gas Cleaning on Mercury Species Emissions from Coal-Fired Steam Generators

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Abstract. When balancing the element mercury (Hg) two coal-fired power plant units - one with slag tap boilers (ST, 2 x 220 MW) and one with a dry bottom boiler (DB, 475 MW) were compared. Both systems are provided with electrostatic precipitators (ESP), nitrogen oxides removal ($DeNO_x$) and flue gas desulfurization (FGD) systems. The Hg in the flue gas is predominantly in gas phase. Only 15 % of the Hg introduced by the coal leaves the unit with the bottom or fly ash. Depending on the operating mode, 30 to 40 % of the Hg is separated in the FGD systems. The overall separation rate for the total system ranges between 45 to 55 %, the residue is emitted in the form of gaseous Hg species. At full load, the Hg concentration in the cleaned gas is less than 6 $\mu g/m^3$ [2)].

In the flue gas path of another dry bottom boiler (DB1, 480 MW) the concentrations of the gaseous species of bivalent mercury (Hg^{2+}), elemental mercury (Hg^0), and total mercury content (Σ Hg) were determined. The sum of the concentrations of Hg^{2+} and Hg^0 is in agreement with the measurement of Σ Hg. Directly downstream of the boiler Hg^{2+} dominates with 77 %, while Hg^0 amounts to 23 %. In the high-dust $DeNO_x$ system Hg^0 is oxidized almost completely to Hg^{2+} (96 %). Air heater and electrostatic precipitator do not influence the Hg species concentrations. The FGD system eliminates approximately 80 % of the Hg^{2+}. At the same time the quantity of Hg^0 increases by the factor 10. In the cleaned gas Hg^0 dominates with 76 % as compared to Hg^{2+} with 24 %. At full load the concentration of Σ Hg in the cleaned gas is also below 6 $\mu g/m^3$.

1. Introduction

Approximately 80 % of the Hg in the atmosphere consist of Hg^0 in gaseous phase. Because of the long residence time of several months it is evenly distributed throughout the troposphere (mean concentration 1-2 ng/m^3). After oxidation to divalent water-soluble Hg compounds, such as $(CH_3)_2Hg$, the residence time decreases to a few days as a result of wet deposition. The compounds of Hg^{2+} may be deposited also in dry form on the ground. (Lindqvist, 1985). Anthropogenic Hg emissions arise predominantly from chlorine alkali electrolyses, metal melting, cremation sites, waste incinerating plants, and coal-fired power plants (Hall 1991).

With the large-scale combustion of hard coal in pulverized-coal boilers, depending on the boiler type, between 15 and 60 % of the introduced Hg quantity are separated with the residual substance flows bottom ash (slag) and electrostatic precipitator ash (Meij 1989; Maier 1992). Balancing experiments around a modern limestone desulfurization system established separation rates of 30 to 70 % for Hg (Maier 1992). In a power plant consisting of a dry bottom boiler, a high-dust $DeNO_x$ configuration and a limestone-based desulfurization plant Hg separation rates ranging from 30 to 60 % were found (Gutberlet 1984; Maier 1992; Fahlke 1994).

[2)] All flue gas concentrations are related to a standard cubic meter, dry. For the dry bottom boiler unit the reference oxygen level is 6 % and for the slag tap boiler unit 5 %.

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The low degree of Hg separation is explained by the amount of insoluble Hg^0 in the flue gas. This Hg species is practically not scrubbed out in the FGD, as opposed to Hg^{2+}. From laboratory analyses Hg^{2+} dissolved in the scrubber suspension is known to be reducible by sulfur dioxide (SO_2) to monovalent mercury (Hg_2^{2+}). Hg_2^{2+} may disproportionate to Hg^{2+} and Hg^0 as a function of the chloride concentration and pH. Hg^0 is expelled by air already from the scrubber suspension. As a result of this mechanism, downstream of the scrubber a higher Hg^0 concentration forms than initially produced by combustion (Braun 1988).
In German hard coal-fired power plants the chemical reactions of the Hg species were studied in only two plants (Gutberlet 1992). In order to increase the Hg separation rates of limestone desulfurization plants and to minimize thus the emission rate, indepth understanding of these processes in the various plant types is necessary.

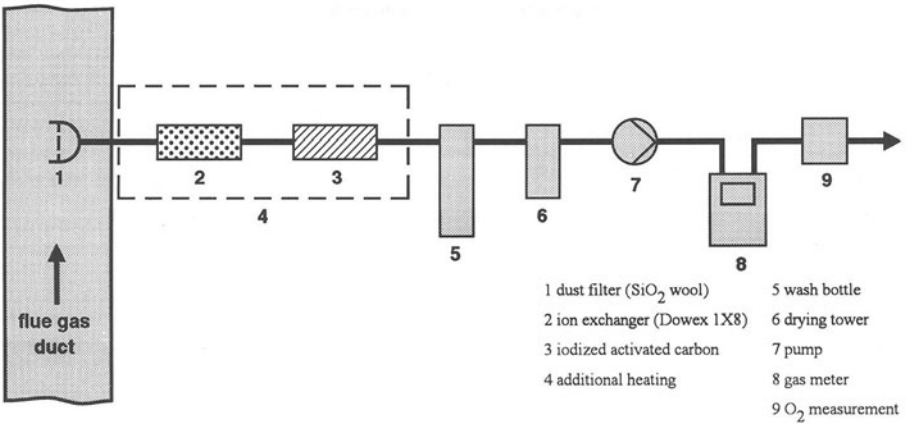
2. Materials and Methods

2.1. MERCURY BALANCING OF THE TOTAL PLANT

Mercury emissions from coal-fired power plants are difficult to measure because of the very low concentrations. For verification of the results of the cleaned gas measurements balancing of the total plant is an adequate method. Because of the natural Hg concentration variations in the coal during balancing only coal from one mine (Hg 0.13 mg/kg mean value) was burnt. 6,000 tons of coal were burnt for each test series, 4,500 tons of which were used in the pretest period to bring the plant to steady state with respect to Hg loads. After this, over 12 hours, samples were taken at regular intervals from all incoming and outgoing solid, liquid, and gaseous constituents flows. In the cleaned gas gaseous and particle-bound emissions were classified. The applied sampling systematics yields recovery rates close to 100 % (Fahlke 1993, 1994).

2.2. DETERMINATION OF GASEOUS MERCURY SPECIES

For differentiating between the Hg species Hg^{2+} and Hg^0 a sampling system with solid absorbers (Figure 1) was used which was developed in the Karlsruhe Nuclear Research Center (Braun 1986 I+II, 1988). The fly ash in the flue gas was separated already in the flue gas duct by way of quartz wool filters. In the first adsorption stage, a strong base anion exchanger (Dowex® 1X8, chloride form) $HgCl_2$ is selectively complexed to $[HgCl_3]^-$ or $[HgCl_4]^-$ and attached as complex anion. In the second stage, iodized activated carbon is used adsorbing all remaining Hg species. The mean flue gas flow amounts to 1.5 l/min at a temperature of 140 °C. The comparative measurements with gas wash bottles (washing medium: HNO_3, concentrated), conducted parallel to the measurements with the solid substance adsorber, were in good agreement.
Mercury oxide (HgO) which may form with a small quantity by conversion with nitrogen dioxide (NO_2) (Hall 1991), is not adsorbed on the ion exchanger and, therefore, determined by this method as Hg^0.



3. Results and Discussion

3.1. RESULTS OF MERCURY BALANCING

The Hg loads and their distribution (in percent) to the residual constituents flows are compiled in Figures 2 and 3.

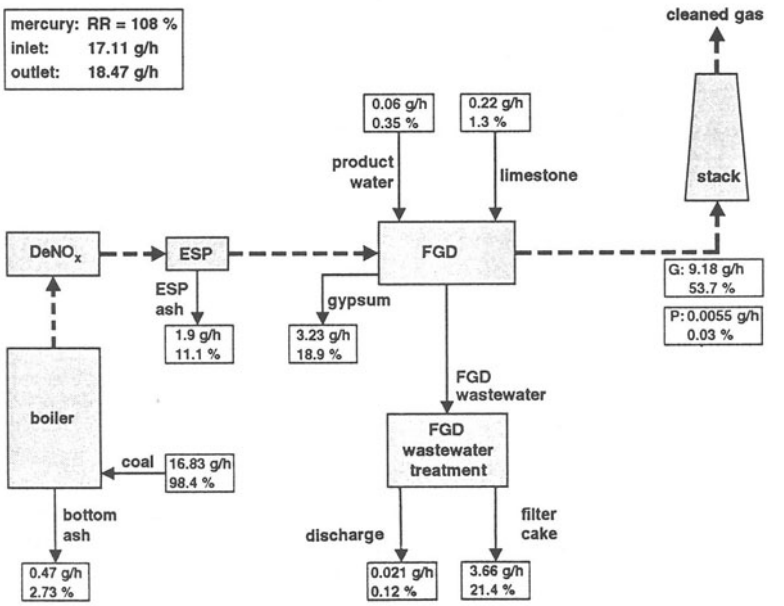


Figure 2. Results of Hg balancing in the dry bottom boiler unit (full load operation).

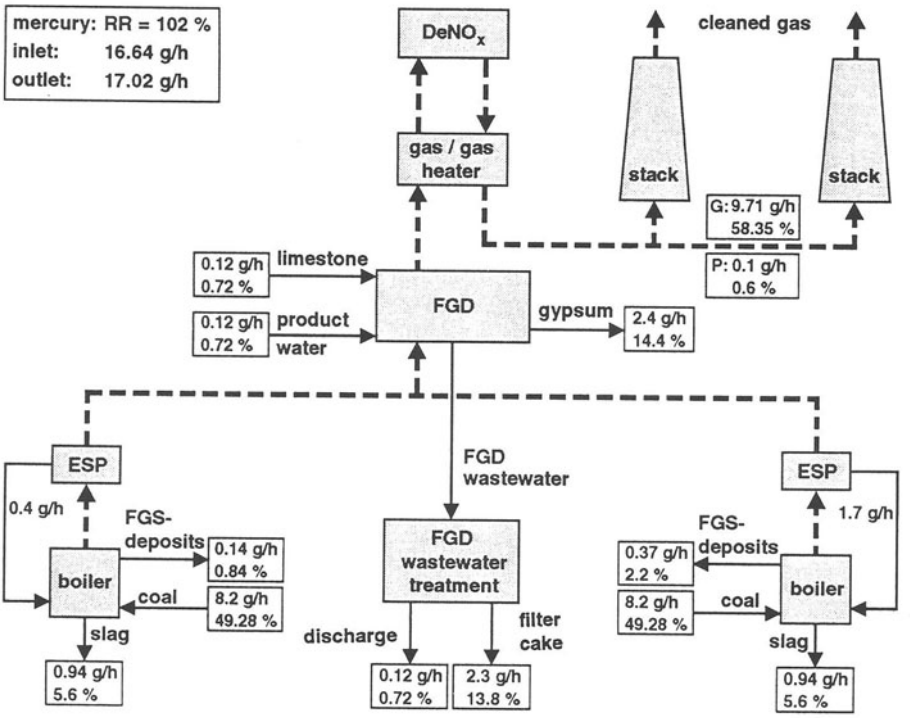


Figure 3. Results of Hg balancing in the slag tap boiler unit (full load operation).

In both units only about 15 % of the Σ Hg were separated because of the high temperatures in the ESP (see also Bergström 1986; Braun 1986). In the DB unit the separation rate for Σ Hg amounts to 46 %, that for the ST unit, to 42 %. At full load, emissions are less than 6 μg/m^3 Σ Hg (mass flow 9 g/h).

3.2. GASEOUS MERCURY SPECIES IN THE FLUE GAS

With the system as described under Sect.2.2., flue gas samples were taken from two sampling points in the DB1 unit. The sampling points were located upstream/downstream of the DeNO$_x$ system, upstream/downstream of the ESP, and upstream/downstream of the FGD system. In Table I the individual concentration values of Hg^{2+}, Hg^0 (percentage distribution) and Σ Hg are listed. The measurements conducted simultaneously are displayed in the same font (normal, underlined or italics). The chloride concentrations of the coal used in the measurement period amounted to a mean value of 1.35 g/kg, ± 0.4 g/kg.

Table I

Concentrations (a) and distribution (b) of Hg^{2+} and Hg^0, DB1 unit, (mv) = mean value

Concentrations

Hg Species	Sampling Points				
	upstream of $DeNO_x$	downstream of $DeNO_x$	upstream of ESP	downstream of ESP = upstream of FGD	downstream of FGD
Σ Hg [µg/m³]	81/76/68/50	72/77/69/58	93/88/55	91/71/45 *56/59/60*	*51/37/46*
Hg^0 [µg/m³]	25/20/12/08	04/05/03/03	05/03/03	03/03/02 *03/03/02*	*42/28/32*
Hg^{2+} [µg/m³]	56/56/53/42	68/72/66/55	88/85/52	88/68/43 *53/56/58*	*09/09/14*

Percentage Distribution

Σ Hg [%]	100	100	100	100	100
Hg^0 [%] (mv)	31/26/18/16 (22 75)	6/7/4/5 (5 5)	5/3/5 (4 3)	3/4/2 *5/5/3* (3 7)	*82/76/70* (76)
Hg^{2+} [%] (mv)	69/74/82/84 (77 25)	94/93/96/95 (94 5)	95/97/95 (95 7)	97/96/98 *95/95/97* (96 3)	*18/24/30* (24)

igure 4 shows also the mean values of the distribution (in %) in the course of the flue as path

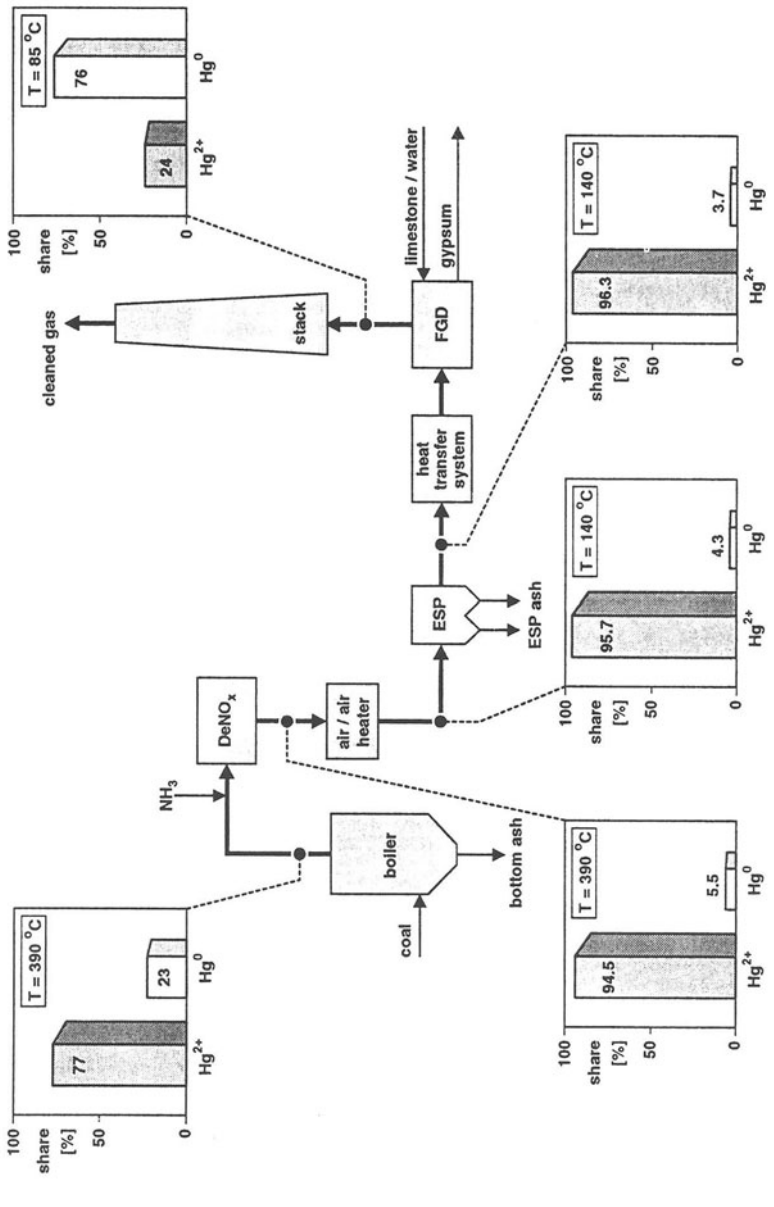


Figure 4. Percentage ratio of Hg^{2+} and Hg^0 in the flue gas path (dry bottom boiler, full load).

4. Conclusions

- When establishing the Hg balance in the two units (slag tap boiler with limestone FGD and tail-end $DeNO_x$ and dry bottom boiler with high-dust $DeNO_x$, limestone FGD) only 15 % of the Hg quantity introduced are separated via bottom and fly ash. The remainder is in gaseous form. In the FGD system in the two units another 30 to 40 % are separated. The separation rate for Σ Hg of the entire two units amounts to 45 and 55 %.
  The Hg speciation was analyzed in another unit with dry bottom boiler, high-dust $DeNO_x$, system and limestone FGD. The results may be summarized as below:

- Under the existing flue gas conditions 77 % are present as $HgCl_2$ already downstream of the boiler. By oxidation in the $DeNO_x$ catalyst this portion increases to 95 %. The residue is Hg^0.
- In the scrubber approximately 80 % of the Hg^{2+} are separated. A portion of the removed Hg^{2+} is reduced at a pH of approximately 4.0 to Hg^0 which is discharged with the flue gas and emitted.
- The Σ Hg separation rate of the total system amounts, therefore, only to 40 % maximum.
- In the cleaned gas of all units described the concentration of Σ Hg is less than 6µg/m^3.

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ATMOSPHERIC MERCURY CONCENTRATIONS ABOVE MERCURY CONTAMINATED MILL TAILINGS IN THE CARSON RIVER DRAINAGE BASIN, NV

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Abstract. During processing of the historic Comstock Ore, Virginia City, NV, an estimated 5.5 x 10^9 g of metallic mercury (Hg) were released into the Carson River Drainage Basin. The Bessels Mill site is one of at least 75 locations where Hg was used to amalgamate the gold and silver from the ore. Although the mill is no longer standing, Hg contaminated tailings attest to its past location. Mercury concentrations in samples of tailings from the Bessels Mill site are as high as 1570 μg/g. Mercury concentrations vary spatially over the site. Total Hg concentrations in air measured directly over the site are well above regional background levels (1 to 7.1 ng/m^3). The highest average atmospheric Hg concentration measured at the site was 240 ng/m^3 for October 1993. The estimated range of Hg flux to the atmosphere from the site was 37 to 500 ng/m^2 hr. Atmospheric Hg concentrations varied seasonally, diurnally and spatially. Atmospheric Hg concentrations varied as a function of Hg concentration, soil and air temperature, wind speed and surface morphology.

1. Introduction

In processing of the gold and silver rich Comstock Ores, metallic Hg was used to remove gold and silver from finely crushed rock. It is estimated that during processing approximately 5.5 x 10^9 g of Hg were discharged into the Carson River Drainage Basin of central western Nevada (Figure 1) (Smith, 1943). Mercury, originally concentrated in mill tailings, has been redistributed throughout the Basin by eolian and fluvial processes (Miller *et al.*, 1993).

This paper discusses both substrate and atmospheric Hg concentrations associated with the Bessels Mill tailings deposit. Data are presented on Hg concentrations measured in the atmosphere directly over the tailings on both seasonal and diurnal time steps. Factors affecting Hg concentration in the atmosphere over the site are addressed.

2. Methods

Mercury concentrations in substrate were measured using a Buck Scientific hydride cold vapor generation system attached to a Perkin Elmer 2380 atomic absorption spectrophotometer at the Nevada Bureau of Mines and Geology, Reno, NV. Accuracy was 19%, analytical precision was 21% and the limit of detection was 10 ppb (Desilets, 1994). Surface concentrations shown in Figure 2 were obtained from a 15 cm deep homogenized sample.

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Figure 1. General location of the Carson River Drainage Basin.

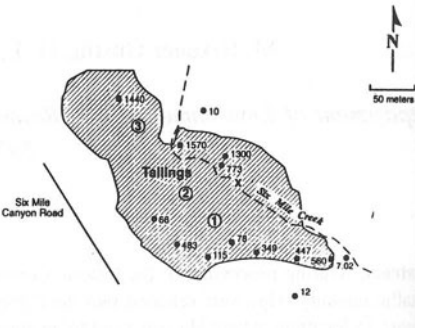

Figure 2. Map showing surface distribution of Hg at the Bessels Mill site in μg/g.

Atmospheric sampling for total Hg was done 1 m above the ground using three in-parallel sampling trains, each of which included an in-line Teflon 0.2 μm filter and two gold-coated quartz sand traps in series. Sampling flow rates were controlled by high precision mass flow controllers. Atmospheric samples were taken in October, January, March and June (1993-94).

Atmospheric sample traps were processed using a nondispersive atomic fluorescence spectrophotometer at the University of Nevada, Reno (UNR) and the analytical precision was less than or equal to 1.5%. Precision for atmospheric samples averaged 12.6% at concentrations between 2 and 300 ng/m^3. Data QA/QC were checked by sending sample splits to Brooks Rand and Frontier Geosciences (Seattle, WA).

3. Results and Discussion

Mercury concentrations in surface samples of tailings and soil from the Bessels mill site ranged from 7 to 1570 μg/g. Mercury concentrations in tailings varied over the site (Figure 2). In soils surrounding the tailings Hg concentrations were 7 to 12 μg/g, two orders of magnitude greater than characteristic background levels reported for substrate of 0.01 to 0.05 μg/g (Andersson, 1979).

Atmospheric concentrations over the Bessels Mills site for each month were one to two orders of magnitude greater than global background concentrations of 1 to 3 ng/m^3 (Lindqvist *et al.*, 1991) and measured regional background values for western Nevada of 1.1 to 7.1 ng/m^3 (Gustin *et al.*, 1994) (Figure 3). The highest average concentration of 240 ng/m^3 was in October. Atmospheric concentrations of Hg are expected to be higher for late summer given that Hg evasion rates increase with temperature (Lindberg *et al.*, 1979)

At the Bessels Mill site Hg concentrations in atmosphere were found to vary with sampling location. In June, atmospheric Hg concentrations were measured at the three circled locations shown on Figure 2. Atmospheric Hg concentrations at sites 2

and 3 were similar, with average values of 46 and 45 ng/m^3, respectively. The Hg concentration at site 1 averaged 181 ng/m^3. Unfortunately mercury concentrations for substrate immediately beneath the sampling sites were not available. It is hypothesized that the variation in atmospheric concentrations is a function of surface Hg concentrations and atmospheric turbulence. Site 1 was located in a topographic low surrounded by mounds of tailings, whereas sites 2 and 3 were located on flat open areas.

A diurnal sampling was completed in June at Bessels Mill (Figure 4). Atmospheric Hg concentrations were highest at mid-day, a function of increasing air and soil temperatures and stagnant air over the site. The Bessels Mill site is located in a canyon which would allow for entrapment of contaminated air during stagnant periods. Atmospheric Hg concentrations decreased as late afternoon winds increased in velocity (Figure 4). Concentrations of atmospheric Hg increased between 0100 and 0400 hours and this increase occurred concurrently with decreasing soil and air temperatures. This observation suggests that air movement is a critical factor influencing Hg concentrations over the site.

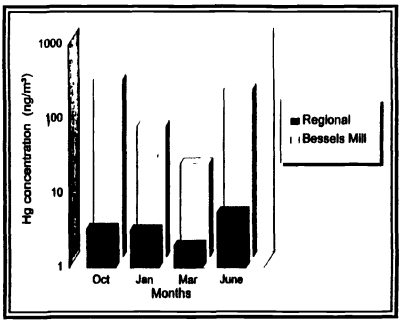

Figure 3. Bar graph showing monthly variation of atmospheric Hg concentrations at Bessels Mill and average concentrations for western regional Nevada.

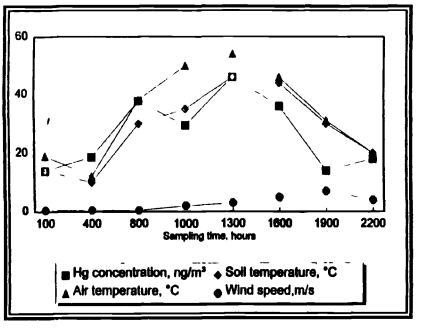

Figure 4. Graph showing the diurnal variation of Hg in the atmosphere for June at Bessels Mill. Average standard deviation for Hg concentrations $\pm$ 0.8.

Using the maximum and minimum concentrations of Hg measured in the atmosphere over the Bessels Mill site (240 and 18 ng/m^3), Hg flux rates necessary to sustain the atmospheric Hg concentrations would be 500 and 37 ng/m^2 hr, respectively. The maximum value is higher than the rates of 14-160 ng/m^2 hr measured by Kim *et al.* (1993) for the Hg contaminated East Popular Fork site (EPF). The higher values for the Bessels Mill site may be a function of the substrate Hg species being predominantly in an elemental form, whereas at EPF it is Hg sulfide (Kim *et al.*, 1993).

4. Conclusion

Mercury concentrations in the atmosphere over Hg contaminated tailings vary spatially, seasonally and diurnally. Factors influencing these variations are surface Hg concentration, soil and air temperature, wind velocity and surface morphology.

Acknowledgments

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Methylmercury in Runoff from the Svartberget Catchment in Northern Sweden during a Stormflow Episode

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Abstract. The dynamics of MeHg during rain-driven runoff episodes are important in calculating the output of MeHg from forested catchments. These dynamics may also provide insight into the processes controlling MeHg output from soils to surface waters. The concentrations of MeHg, Hg-tot, TOC and associated chemistry were observed during a rain-driven, July runoff episode on two forested tributaries of the Svartberget Catchment, as well as at the outlet of a mire in the headwaters of that catchment. TOC concentrations in runoff increased during the episode. Hg-tot concentrations also tended to increase (from 3 to between 4 and 7 ng L^{-1}), though the timing of that increase varied. MeHg concentrations, on the other hand, tended to decrease. The decrease was slight in the two forested tributaries (ca. 0.1 ng L^{-1}), but greater in the mire runoff (from 0.8 to ca 0.3 ng L^{-1}). These data are set in relation to a hypothesis about the processes which control MeHg output.

1. Introduction

Mercury (Hg) contamination in the food chain of freshwater ecosystems is widespread in Sweden (Håkansson *et al.*, 1990). The accumulation in soils of anthropogenic Hg deposited from the atmosphere has shielded aquatic ecosystems from the full impact of anthropogenic Hg-tot deposition (Aastrup *et al.*, 1991). Nonetheless, the fraction of a percent of the soil store of Hg and especially the methylmercury (MeHg) store which moves from soils to surface waters each year may be an important source of the Hg in the aquatic food chain (Hultberg *et al.*, 1994).

In the organic rich surface waters of northern Sweden where many lakes have fish with unacceptable Hg levels, stream chemistry varies markedly during stormflow episodes (Bishop *et al.*, 1990). Both total organic carbon (TOC) and acidity have been found to increase with flow while many mineral substances become diluted. A relationship between dissolved organic carbon (DOC) and MeHg in lakes has been found (Lee and Hultberg, 1990). Thus, to better understand the transfer of MeHg from soils to surface waters, it is important to understand the dynamics of MeHg concentrations in runoff during stormflow episodes when DOC/TOC concentrations can increase. This paper documents the concentration of MeHg and other elements in runoff from different portions of the Svartberget Catchment during a rain-driven episode in July 1993.

2. Study Site and Methods

The 50 ha Svartberget Catchment is located in northern Sweden (64° 14' N, 10° 46' E). It is afforested with a mixture of mature Norway Spruce (*Picea abies*) in low-lying areas and Scots Pine (*Pinus sylvestris*) on higher ground. There is an 8 ha mire at the upper end of the catchment that drains into the Kallkällbäcken tributary. A second

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tributary, Västrabäcken, joins Kallkällbäcken just above the outlet of the catchment (See Bishop *et al.*, (1995b) for maps and a more complete description of the catchment.)

Hourly average flow was measured or calculated at the outlet of the mire (Site M), Kallkällbäcken (Site K), and Västrabäcken (Site V) just above their confluence, as well as for the entire catchment at Site S, just below the confluence of Kallkällbäcken and Västrabäcken. Unfiltered water samples were collected at sites M, K and V using ultra-clean sampling methods. Sampling protocol and analytic methods are described in Lee *et al.* (1995). Replicate analyses of both MeHg and Hg-tot using these procedures have a standard deviation of 0.05 ng/l.

4. Results

The stream was sampled immediately prior to the rain episode during a period of low flow on July 23, 1993. During the next three days, 36 mm of rain fell and generated 12 mm of runoff between July 23 and July 31, which was the period over which element outputs were calculated for this episode. In the week preceding the episode, 17 mm of rain fell but were too dispersed in time to generate a storm hydrograph. The intensity of the runoff on July 27 has been exceeded, on average, twice a year during the snow free half of the year (June 1 - November 31) over the last 10 years.

During the episode, stream pH fell to 4.8 at Site V, 4.5 at Site K and 4.2 at Site M (data not shown.) The TOC concentration increased at all locations during the episode, to over 30 mg L^{-1} at site V and over 40 mg L^{-1} at sites M and K (Figure 1a). Hg-tot concentration in runoff was ca. 3 ng L^{-1} at all sites on 23 July (Figure 1b). The subsequent concentrations in the runoff from each subcatchment were usually higher, but sometimes lower than this initial value. The MeHg concentration decreased to a greater or lesser extent from the pre-event concentration. The decrease was greatest in the mire runoff, while the decrease of ca 0.1 ng L^{-1} in the runoff from the forested subcatchments was at the limit of what could be detected (Figure 1c).

5. Discussion

The positive relationship between TOC and flow is consistent with that seen at most other times in the catchment. Total mercury at each sampling point also increased at some time during the event, but not as uniformly as TOC. In contrast to TOC and Hg-tot, MeHg tended to decrease during the event, if only slightly on the forested subcatchments. This resulted in a sharp decline in the TOC/MeHg ratio (Figure 1a) to values at the lower end of those seen during the course of 1993 (Pettersson *et al.*, 1995). It is intriguing to note the inter-subcatchment consistency of the TOC/MeHg ratio. Due to the changing TOC/MeHg ratio during the event, though, MeHg output is not a linear function of TOC output.

The variation in the Hg-tot/MeHg ratio was less consistent than the TOC/MeHg ratio (Figure 1b). This variability suggests that any connection between the export of Hg-tot and MeHg is a weak one over short time scales.

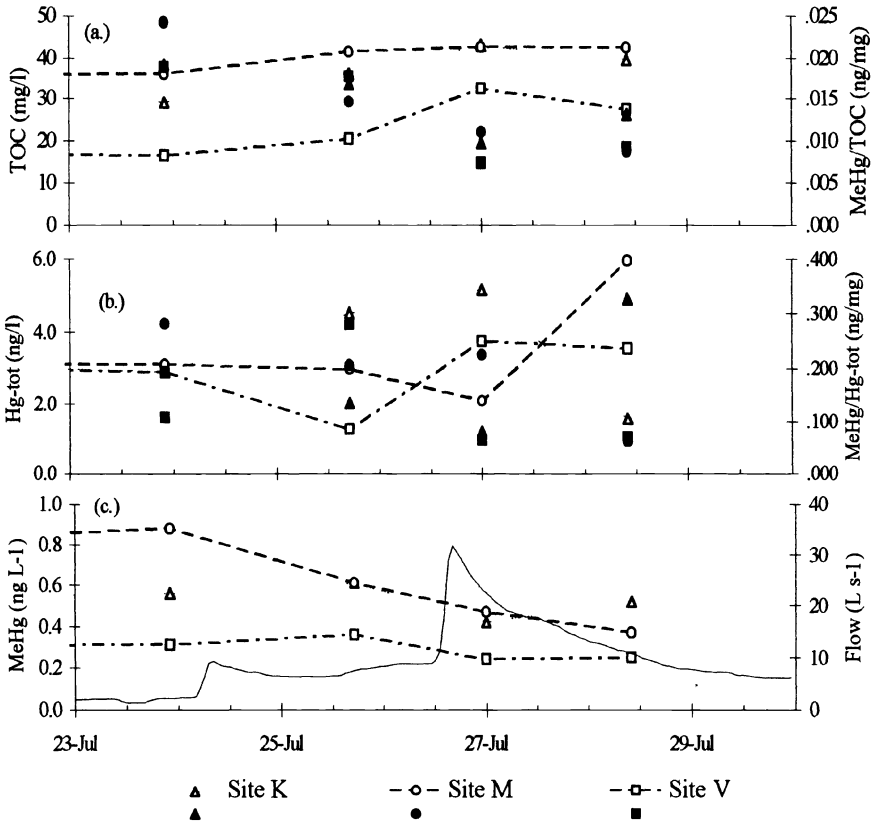

Figure 1. Chemistry at the different sampling points during the July rain event. (a.) TOC and the TOC/MeHg ratio (b.) Hg-tot and the Hg-tot/MeHg ratio, and (c.) MeHg together with hourly runoff from the catchment at Site S. In (a.) and (b.) the open, connected symbols are concentrations, while the closed symbols are the ratios.

During the year, MeHg concentration, the MeHg/TOC ratio and MeHg output vary with temperature and flow (Lee *et al.*, 1995; Pettersson *et al.*, 1995). During spring flood, MeHg concentration declined while TOC and Hg-tot either remained steady or increased (Bishop *et al.*, 1995a). From these data, and what was seen in the episode reported here, a mechanism for controlling MeHg output is hypothesized in which MeHg is produced from the larger, riparian pool of anthropogenic Hg-tot in the solid or dissolved form by a temperature dependent process in which organic carbon has a central role, both as a complexing agent to mobilize MeHg and as a facilitator of the MeHg production. Increasing runoff rates reduce water residence time in the catchment and thus dilute MeHg concentrations in runoff.

According to this mechanism, the rain-driven episode resulted in only small declines in the concentration of MeHg from the forested tributaries because the MeHg production rate was comparable to the rate of loss in runoff. The production may also have been enhanced by the increased TOC concentrations during the episode. This is in contrast to

the situation in the spring when lower temperatures give a lower MeHg production rate and runoff rates are several times higher, resulting in greater concentration drops. The mire has a higher production rate due to the greater amount of organic carbon available, but the residence time of water is shorter there, making MeHg concentration more vulnerable to dilution as runoff rates increase, as seen during both the spring flood and the rain-driven episode reported here (Bishop *et al.*, 1995a).

The riparian zone has been identified as the location in which the much of the MeHg in runoff arises from forested catchments (Bishop *et al.*, 1995b). The efficacy of production there is apparent from the areal rate of production during the July episode where the forested MK subcatchment has a greater output of MeHg per unit area than the mire subcatchment (Table I). The mire, however, is a larger source of both Hg-tot and TOC. The output of MeHg from the riparian zone of the forested subcatchments may well be sensitive to the geometry of the riparian zone given the large differences in the output from the forested V and MK subcatchments. The former subcatchment has shallower riparian peats that are further from water's main flow pathways (Bishop, 1994).

Table I

Output per unit area during the July Rain Event (July 24 - 30, 1993)

Subcatchment	Area	Water	TOC	Hg-tot	MeHg
	(ha)	mm	g/ha	mg/ha	mg/ha
M (Mire)	14.8	13.0	5.6	0.55	0.059
V (Västrabäcken)	8.6	8.1	2.2	0.26	0.022
MK (Kallkällbäcken below the mire)	26.2	12.4	4.6	0.36	0.065
S (whole catchment)	49.6	11.8	4.5	0.40	0.056

Acknowledgments

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PART III

ATMOSPHERIC MERCURY

LONG-TERM CHANGES IN CONCENTRATION AND DEPOSITION OF ATMOSPHERIC MERCURY OVER SCANDINAVIA

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Abstract. Samples for measurements of total gaseous mercury (Hg) in air have been collected since 1980 in south-western part of Scandinavia. A collection program for precipitation samples used to determine changes in depositional fluxes of total Hg has been in operation since 1987. A comparison of today's total gaseous Hg levels in air and the total Hg concentrations in precipitation with the ones found earlier, shows a clear decrease with time. At the Swedish west-coast, yearly average air concentrations and median levels of 3.3 and 3.1 (1980-1984), 3.2 and 2.8 (1985-1989), and 2.7 and 2.6 ng Hg/m^3 (1990-1992), respectively, were found. Increased average and median winter concentrations were always found, with levels at 3.7 and 3.4, 3.7 and 3.3, and 3.0 and 2.7 ng Hg/m^3 for the respective time period. Higher winter values were expected due to increased anthropogenic emissions and changes in the mixing height of the atmosphere. The corresponding total wet deposition rates decreased from 27 (1987-1989) to 10 μg Hg/m^2 yr. (1990-1992). A finding of special interest was the decreased number of episodic events of high total gaseous Hg levels in air, from 1990 and further on. In addition, the frequency distribution of the concentrations of Hg in air seems to be different for these years compared to the other two time periods. A frequency distribution of air concentrations of Hg more resembling a normal distribution was found for the years 1990 to 1992. The decrease of the atmospheric burden of total gaseous Hg and deposition of total Hg are most probably connected to lower emissions in source areas on the European continent. It seems logical to state that the problem of high Hg depositional fluxes to Scandinavia, is best solved by abatement strategies on the regional scale.

1. Introduction

The importance of the atmospheric pathway as the main route for introducing mercury (Hg) to terrestrial ecosystems in Scandinavia has previously been discussed (Iverfeldt, 1991a). A greater future impact on surface waters by run-off of Hg released from the catchments pools can be expected, since the Hg pools in soil are still increasing (Driscoll *et al.*, 1994; Hultberg *et al.*, 1994). Based on the situation with ongoing accumulation of Hg in terrestrial systems and a too large Hg export via run-off to surface waters, Johansson *et al.* (1991) suggested that an 80% decrease in the wet depositional Hg flux must be reach not to increase the terrestrial pools. This mass-balance approach was formulated as a critical load concept.

Already in 1982, the source of the atmospheric Hg deposited in Scandinavia was shown to be located on the European continent, i.e. Hg was found to be a typical example of a long range transported air pollutant (Brosset, 1982). At the same time, it was found that part of the airborne Hg was related to soot particles in the air. Later on, a decreasing south-north gradient in the wet deposition of airborne Hg was demonstrated (Brosset, 1987; Iverfeldt, 1991b). Even in the northern part of Scandinavia an impact from regional Hg sources on the level in both air and precipitation was evident, if compared to more clean sea areas in both the southern and northern hemisphere (Fitzgerald *et al.*, 1984; Slemr and Langer, 1992). However, the smaller impact from the continental sources on the

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northern part of Scandinavia could be seen in trajectory analysis of Hg in air and less skewness of the corresponding frequency distribution plot of the individual data (Iverfeldt, 1991b).

An emission inventory of Hg species for 1987 formed the basis for a model calculation of the long range transport of Hg from the European continent to Scandinavia (Petersen *et al.*, 1994). The model results were verified against measured values of Hg in air and precipitation in Sweden. The importance of continental sources of Hg was clearly demonstrated in this study. Today, we have started to experience a decrease in the Hg levels in air as well as in precipitation, with time. The individual Hg numbers in air that we measure today at one of the most exposed regional background stations in Scandinavia (Rörvik), are often lower than the previously estimated average concentration in northern Norway between 1987 and 1988. However, no new official information on drastic changes in European Hg emissions is yet available. In a parallel work we try to derive a relationship between emissions and measured Hg concentrations changes, using a much larger data set (Munthe *et al.*, 1994).

Here we present a compilation of all individual measurement data on total gaseous Hg in air and total Hg in precipitation, collected at the Swedish west coast from 1980 to 1992. Besides previously unpublished material, the data used by Brosset (1982, 1987) and Iverfeldt (1991b) are included. The present study is focused on finding indications of possible changes in levels and fluxes. The same research group has been involved in both the collection and analysis of all samples, which is very important considering the quality of the data compilation.

2. Materials and methods

Collection and analytical techniques used for Hg measurements in air and precipitation at the IVL monitoring sites and in the laboratory have been described in detail elsewhere. Total gaseous Hg in air was collected on three gold traps in series (Brosset, 1982, 1987; Brosset and Iverfeldt, 1989; Brosset and Lord, 1991; Iverfeldt, 1991b). Until 1989, individual precipitation samples were collected on an event basis. The sampling protocol was described by Iverfeldt (1991a, b). From 1990, monthly samples were collected using a bulk sampler, which was protected from interferences by dry deposited Hg through a capillary attached to the funnel (e.g. Iverfeldt, 1991b). In an intercomparison study, no difference was detected between the two sampling techniques (Iverfeldt and Munthe, 1993). For preservation, the collection bottles used for monthly sampling were preacidified with 2.5 mL Suprapur HCl. Handling, cleaning, blank determinations, calibration, reproducibility tests and intercomparisons, have been reported previously (Iverfeldt, 1991b). The analytical procedure applied initially used a plasma-atomic emission detector, which was changed to an atomic fluorescence detector at the end of 1990. No difference have been detected in the accuracy of two detectors. The change in detector has also been evaluated in a separate study (Jensen and Iverfeldt, 1994).

3. Results and Discussion

The measured total gaseous Hg concentrations in air at Rörvik were first divided into two periods, before and after an expected change in the relatively large emissions from East-Europe, following the introduction of a new economical/political system. Then, the first and second half of the initial ten-year period were compared to find differences. In Table I, the respective total gaseous Hg average and median concentrations are given. A decrease in the Hg levels in air is indicated, even if the change is not yet statistically significant. It is interesting to note that the absolute standard deviation also has decreased and that the relative standard deviation is similar for all periods. The wet deposition fluxes for the two last periods show a very dramatic decrease. Even if the collection of single events during the 1980's may have resulted in an over-representation of high Hg levels in precipitation, a comparison with other stations in the Nordic network (Iverfeldt, 1991b) show that a value around 20 μg $Hg/m^2/yr.$, is reasonable. The relative standard deviation, based on the respective yearly value and taking parallel samples into account, is less than 10% for the last time period. Therefore, the deposition rate during the last period seems to be only half of that at the end of the 1980's.

TABLE I

Average and median concentrations of total gaseous Hg in air and corresponding deposition rates of total Hg at the Swedish west-coast, 1980 to 1992*

Period	Hg in air Average (ng/m^3)	1 SD	Hg in air Median (ng/m^3)	n	Deposition rate of total Hg ($\mu g/m^2/yr.$)
1980-1989	3.2	1.4	2.9	618	-
1980-1984	3.3	1.3	3.1	209	-
1985-1989	3.2	1.4	2.8	409	27
1990-1992	2.7	1.0	2.6	124	10

*Data taken from Brosset (1982, 1987); Iverfeldt (1991); and Munthe *et al.* (1994)

The decrease in total gaseous Hg levels in air between the winter time periods is of the same order of magnitude as calculated for the whole year (Table II). As expected, all average and median winter levels are higher than the comparable yearly averages.

TABLE II

Average and median concentrations of total gaseous Hg in air during various winter periods (October to March) at the west-coast of Sweden*

Winter periods	Hg in air Average (ng/m^3)	1 SD	Hg in air Median (ng/m^3)	n
1980-1989	3.7	1.6	3.3	264
1980-1984	3.7	1.6	3.4	93
1985-1989	3.7	1.7	3.3	171
1990-1992	3.0	1.1	2.7	70

*Data taken from Brosset (1982, 1987); Iverfeldt (1991); and Munthe *et al.* (1994)

A finding of special interest is that occasions of episodic events with high total gaseous Hg levels in air, nearly stops 1990 (Figure 1).

In addition, the frequency distribution of the concentrations of Hg in air is different for these later years compared to the other two time periods (Figures 2, 3, and 4). A frequency distribution of the air concentrations of Hg more closely resembling a normal distribution is found for the years 1990 to 1992.

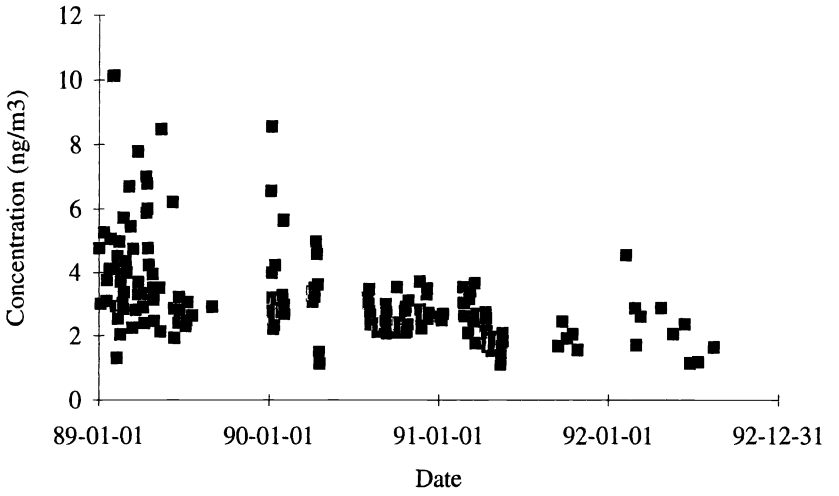

Fig. 1. Concentrations of total gaseous Hg in air from 1989 to 1992 at the west-coast of Sweden.

The same result is also found if the 1990 to 1992 period is compared to the frequency distribution previously found for Hg in air in northern Norway, 1987 to 1988 (Iverfeldt, 1991b).

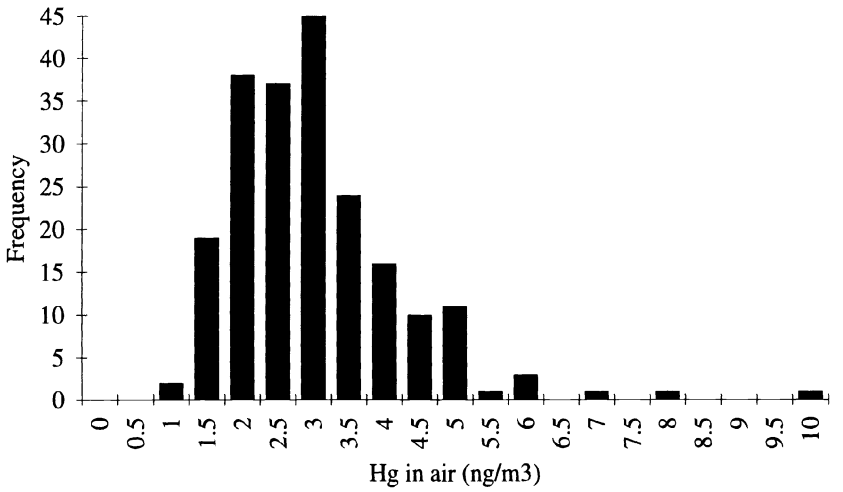

Fig. 2. Frequency histogram of total gaseous Hg in air at the Swedish west-coast, 1980 to 1984.

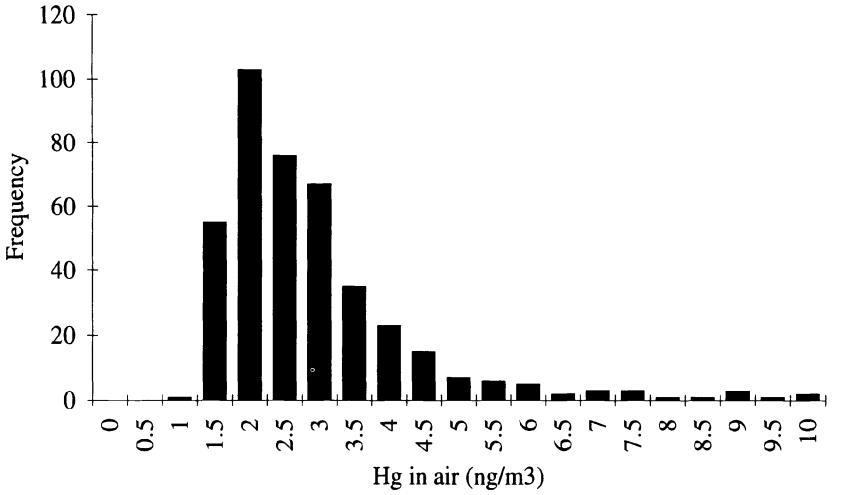

Fig. 3. Frequency histogram of total gaseous Hg in air at the Swedish west-coast, 1985 to 1989.

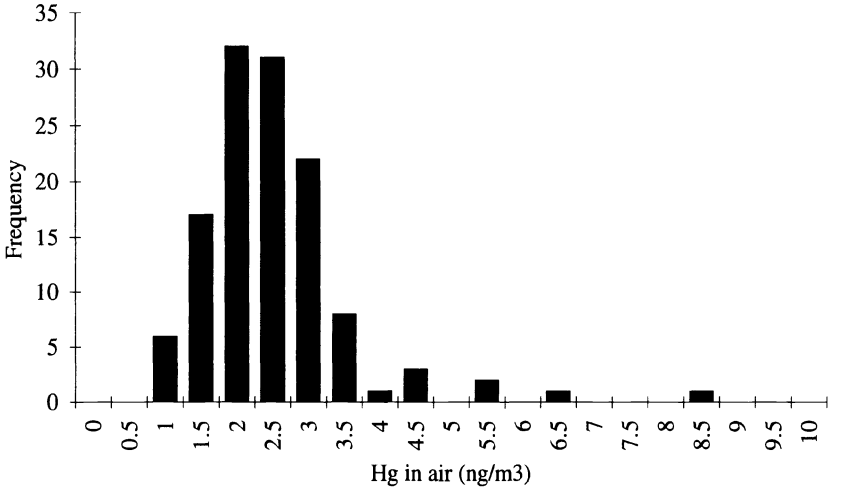

Fig. 4. Frequency histogram of total gaseous Hg in air at the Swedish west-coast, 1990 to 1992.

4. Conclusions

A comparison of today's total gaseous Hg levels in air in south-western Sweden, with the ones found during the 1980's, showed a decrease with time. In addition, the higher average winter levels (compared to summer concentrations of total gaseous Hg in air) were also

found to be lower during the first three years of the 1990´s. Further, the corresponding total Hg wet deposition rate decreased also from the 1980´s to 1992.

The indicated decrease of the atmospheric burden of Hg is most probably connected to much lower emissions in source areas on the European continent. However, the lack of episodic events may be connected to both decreased emissions of Hg and to a different weather situation.

It seems logical to state that the problem of high Hg depositional fluxes to Scandinavia, must be solved by abatement strategies on the regional scale. The findings in this paper clearly stress the need for a monitoring network for atmospheric Hg, focusing on the regional transport scale, to be able to follow up emissions reductions. Also, it is important to detect any changes in a favourable trend. This may occur, for example, due to a rapid economical development in large areas of the eastern part of the European continent followed by an increased usage of energy. If this is not accompanied by the installation of efficient cleaning equipment, a rise in airborne Hg may be seen again in Scandinavia.

Acknowledgements

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TOTAL GASEOUS MERCURY MEASUREMENTS IN FLORIDA: THE FAMS PROJECT (1992-1994)

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Abstract. Measurements of Total Gaseous Mercury (TGM) in the atmosphere are being conducted as part of the Florida Atmospheric Mercury Study (FAMS). FAMS is a multi-year study focusing on the atmospheric transport and deposition of Hg and other trace metals at several locations in central and south Florida. A major component of this study, which this paper addresses, involves determining regional TGM concentrations and seasonal variability patterns at the various collection sites. Occasional problems were encountered in the collection efficiency of TGM on Au. The reason for this interference was not identified, but it was dramatically reduced by heating the collection columns to 80 °C. Atmospheric Hg samples are currently being collected using Au-coated silica sand traps from atop 48 ft. aluminum sampling towers using an unattended and automated sampling and data recording system. We currently have approximately a two year record of TGM, beginning in the summer of 1992, for the Lake Barco Site, located in central Florida approximately 30 miles east of Gainesville, FL. The records at the south Florida sites are shorter, ranging from one month at Andytown to 16 months at both Fort Myers and Fakahatchee Strand. Average TGM concentrations (ng/m^3) for 3 to 6 day integrated samples at the various sites are: Lake Barco, 1.59 ± 0.58 (n=78); Fort Myers, 1.59 ± 0.40 (n=42), Fakahatchee Strand, 1.42 ± 0.41 (n=30); Tamiami Trail 1.46 ± 0.80 (n=27); Everglades National Park 3.11 ± 1.52 (n=13); and Andy Town, 1.78 ± 0.62 (n=3). The mean Hg concentration for all the sites is 1.64 ± 0.76 ng/m^3 (n = 191).

1. Introduction

The recent discovery of elevated levels of Hg in freshwater fish (Hand and Friedman, 1990), and the deaths of three panthers, believed to result from Hg toxicosis, in remote areas in S. Florida (Roelke, et al., 1991) has prompted State and Federal agencies to investigate the sources of Hg to Florida ecosystems. The Florida Atmospheric Mercury Study (FAMS) was initiated in the Fall of 1992 to address concerns related to the atmospheric introduction of Hg into Florida waterways. The main objective of this program is to provide temporal and spatial information on the atmospheric concentration and deposition of Hg and other trace elements in Central and South Florida. A general overview of the FAMS project is given by Pollman et al. (1995). This paper presents information on the Total Gaseous Mercury (TGM) measurements made as part of the FAMS program. Other measurements conducted as part of the FAMS program are discussed in companion papers in this issue (see Guentzel et al., 1995 and Landing et al., 1995, this volume).

2. Materials and Methods

2.1 SAMPLING LOCATIONS

TGM measurements are currently being collected at 7 sites in central and south Florida: Lake Barco, Fort Myers, Fakahatchee Strand, two sites in the Everglades National Park

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(Tamiami Trail Ranger Station and Baird Research Center), Andytown, and Little Crawl Key (Figure 1). A description of the FAMS sampling network and the environmental setting of these sampling sites is given in a companion paper (Pollman et al., 1995, this volume). Sampling was initiated at the Lake Barco site in the Fall of 1992, at the Fort Myers and Fakahatchee Strand sites in January of 1993, at the Everglades sites in June of 1993, and the Little Crawl Key and Andytown sites in May of 1994. The Caryville and Everglades Nutrient Project Removal Sites are scheduled to begin in late 1994.

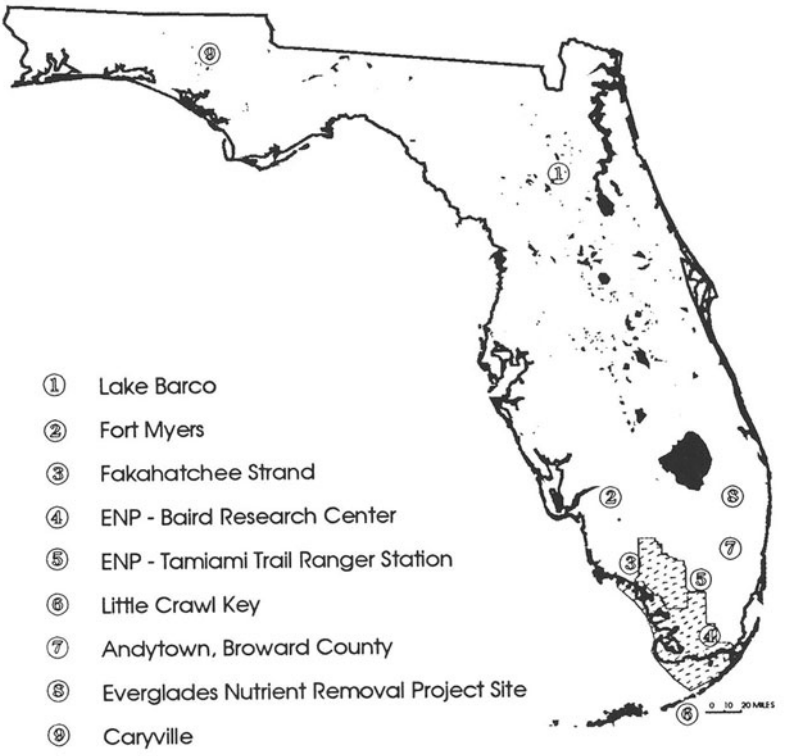

Figure 1. FAMS Sampling Locations in Florida

2.2 COLLECTION METHODS

TGM measurements were collected atop a 48 ft. aluminum tower (Upright, Inc.) using a series of three quartz tubes filled with Au-coated quartz sand grains. The collection columns are placed in series. The first column in the series (Column A) collects the TGM sample. The second column in the series (Column B) serves as a blank and also as a recovery check on the efficiency of the collection column. The final column in the

series prevents back diffusion of Hg from the vacuum lines and pumps from reaching Column B when the flow is off. Because particulate Hg levels in Florida (Landing et al., 1995, this volume) are typically less than 1% of TGM values, we felt it was unnecessary to filter the incoming air to remove particles. However, at selected sites, we have placed a column packed with quartz glass wool in front of the Au collection column to collect particulate Hg. On all occasions, the particulate Hg observed on this column was ≤ 20 pg/m^3.

Four TGM samples are collected each month using a meteorological data recording system (CR-10, Campbell scientific) to control sample collection periods. Currently, each TGM sample consists of an integrated 6 day collection period each week beginning midnight on a Wednesday and ending midnight the following Tuesday. Earlier sample collections used a 3 or 5 day sampling period each weekly period. Sample column sets are changed on approximately a monthly basis. To estimate a field blank, a fifth series of sample columns is employed which is identical to the sample collection sets except that no air is drawn through them. The 5 sets of Au collections columns are mounted in a rain tight Plexiglas box. Air is drawn into the columns through a small length of Teflon tubing which protrudes out the bottom of the sampling box. This arrangement helps protect the sample inlet from rain. The A column remains exposed to the atmosphere for the entire month long deployment period. Ambient air is pulled through each sampling train using a vacuum pump housed in a small shed at the base of the tower. A single vacuum line runs between the vacuum pump and a series of 4 in-line solenoid valves mounted in the TGM box. Each Au column sampling train is connected to one of the solenoid valves. Air is drawn through a different Au column sampling train each week by programming the datalogger to activate, in sequence, a different solenoid valve each week. A rain sensor was employed to halt sampling during rain events. Sampling usually resumed 5-10 minutes after the rain storm ceased.

The volume of air drawn through each sampling train was determined using a mass flow meter, MFM, (Sierra Instruments) placed in-line between the vacuum pump and the TGM sampling box. MFM readings are continually sent to the meteorological data logger which averages the readings for a 6 minute interval and records this value in memory. At the end of each monthly sampling period, the MFM readings were retrieved from the data logger and integrated over the appropriate sampling period to determine the volume of air drawn through each sample. At typical flow rates of 80-300 mL/minute, the volume of air drawn through an individual sampling train varied between 0.5 and 2.5 m^3. Air flow rates were controlled using a precision needle valve positioned between the vacuum pump and the MFM. MFM readings were periodically verified with a second in-line MFM and with a rotameter placed on the sampling inlet.

2.3 TGM DETERMINATIONS

Mercury collected on the Au-coated quartz sand columns was analyzed using the two-stage Au amalgamation technique described by Fitzgerald and Gill (1979)

employing non-dispersive resonance atomic fluorescence detection (Gill and Bruland, 1990). Prior to analysis, any moisture that may have collected on the Au collection column was removed by flushing the Au column for 10 minutes in a dry helium gas flow sampling train system, independent of the analysis system. This "drying train" is similar to the gas flow system used for sample analysis. Gold trap columns are used on the inlet gas to the the drying train to remove any elemental Hg from the He carrier gas.

The detection limit associated with a TGM measurement can be estimated based on three times the standard deviation associated with Au collection column field blanks (i.e. the A and B columns with no air passed through them), divided by the volume of air sampled. For 1993, the A and B Au collection column field blanks averaged 0.089 ± 0.053 ng Hg (n=31) and 0.082 ± 0.043 ng Hg (n=32), respectively. For 1994, the average column blanks were 0.060 ± 0.050 ng Hg (n=23) and 0.047 ± 0.045 ng Hg (n=25) for the A and B columns, respectively. This corresponds to detection limits ranging between 0.29 ng Hg/m^3 and 0.057 ng/m^3, for sample volumes ranging between 0.5 and 2.5 m^3. The reproducibility of the TGM measurements is 2-8% (RSD), based on five sets of three simultaneously collected samples.

Notice that there is a very slightly larger mean blank (6-13 pg Hg) on the A column field blank compared to the B column field blank. This indicates that very little atmospheric Hg diffuses onto the exposed Au collection column during the month long deployment period. Also, it suggests that the majority of the field blank signal on the Au columns comes from the combined contributions of: blanking, shipment to the field, deployment, retrieval, shipment back to the laboratory, column drying, and analysis. This procedural or handling blank contribution is only slightly higher than most investigators observe with shorter duration and on-site TGM analysis protocols. Our field blank signal is almost always less than 10% of the sample signal and more typically it represents only about 5% of the sample signal. We feel this is a reasonable blank level for a long term and unattended sampling network.

3. Results and Discussion

3.1 TGM COLLECTION RECOVERY PROBLEMS

We occasionally experienced interference problems in the collection of TGM on the Au collection columns at some of our sampling sites. The problem was manifested by two features: minimal or no signal on the "A" column (sample column); and a sample signal much greater than the blank on the "B" Column (second column in the train). The severity of this problem was greatest at the Fakahatchee Strand, Tamiami Trail, and Everglades National Park Sites. Problems only occasionally occurred at the Lake Barco and Fort Myers sites. Collection problems of TGM onto Au have also been observed by Brosset and Iverfeldt (1989). These investigators found that reducing the volume of air sampled improved the collection efficiency. We also found evidence that large volumes

were more likely to experience interference's in the collection of TGM, so we reduced the amount of sample volume collected from approximately 2 to 0.8 m^3. This significantly reduced the frequency of problems, but never eliminated it.

We conducted several laboratory and field tests to determine whether placing a precolumn containing different absorbents in front of the Au collection column would eliminate the interference. The precolumns we tested were: a heated quartz wool column, a moisture adsorbent (K_2CO_3), and a collection column packed with grains of high purity nickel. We tested a moisture absorbent to determine whether the columns were developing a layer of water from the normally high humidity present which prevented efficient contact between the Hg^o and the Au. The heated precolumn was tried to determine whether combusting the incoming air at temperatures >600 °C would remove any interfering (presumably organic) substances that was preventing the efficient recovery of TGM on a Au collection column. Pure nickel was also tried since it serves as a medium for the collection of volatile sulfur compounds. Prior to field testing, the precolumn substrates were tested in the laboratory and found not to collect Hg^o from ambient air. Four simultaneous collections of TGM were conducted in the field, two of the collection lines having a precolumn and two normal collections lines. Unfortunately, none of these approaches proved effective.

Laboratory investigations were also conducted to determine if it was possible to "poison" a Au collection column and prevent TGM collection. Tests were conducted using the gases dimethylsulfide, ozone, sulfur dioxide, hydrogen sulfide, and methyl iodide and aerosols of diammonium sulfate and ammonium chloride. These potential interferents were introduced into an ambient air collection stream in front of a Au collection column. A simultaneous TGM collection was also made without introduction of the interferent. None of these compounds showed any interference in the collection of TGM on Au.

Our most recent efforts to eliminate this interference consists of wrapping a heating tape around the Au collection columns and using a variable transformer to warm them to approximately 80 °C. Based on several months of testing, this modification appears to have reduced the frequency of occurrences and slightly reduced the severity (the amount of Hg breakthrough onto the B column above a blank signal) of TGM collection problems. Currently, about one out of every four or five collections shows evidence of inefficient collection on the A column.

To further verify the accuracy of our TGM collections, we are conducting simultaneous 6 day integrated collections of TGM using Au-coated sand and iodated carbon collectors (Mine Safety Appliances Co.) at the Lake Barco and Fakahatchee Strand sites. Initial results suggest that both collection methods produce comparable TGM concentrations (Table 1). Results from a two sample t-test indicate no significant difference between the two collection methods at the 95% confidence level ($P = 0.369$).

TABLE 1
A Comparison of TGM Determinations Using Iodated Carbon and Au-Coated Quartz Sand Collection Columns

Sample Number	Gold Column (ng Hg/m^3)	Iodated Carbon (ng Hg/m^3)
LB 1	1.12	1.49
LB 2	1.29	1.19
LB 3	0.91	1.14
LB 4	0.98	1.28
LB 5	1.00	1.14
LB 6	1.18	0.89
LB 7	0.80	1.10
LB 8	1.17	0.97
FS 1	1.11	1.39
FS 2	1.13	1.07
FS 3	1.66	1.37
FS 4	1.33	1.08
FS 5	1.11	1.08
FS 6	0.80	1.37

3.2 TGM MEASUREMENTS IN FLORIDA

Results obtained for TGM at the FAMS network sample sites are illustrated in Figure 2 and summarized in Table II. For this compilation, we have excluded any samples where the amount of Hg observed on the B column was greater than that on the A column. This arbitrary exclusion resulted in eliminating approximately 10% of the sample collections. We currently have greater than a one year TGM record at four sites: Lake Barco, Fort Myers, Fakahatchee Strand, and Tamiami Trail. There does not appear to be any distinctive temporal or spatial trends in TGM at these sites. At this point, we have too few data to make any statements about temporal or spatial variability for the Everglades National Park, Little Crawl Key or Andytown sites. The Everglades National Park site has a higher mean Hg concentration than the other sites, but this may be due to the paucity of data available. Note that the most recent data available for this site are in much more agreement with longer term trends at the other sites.

On two occasions elevated TGM measurements (i.e. greater than 2x the normal value) were observed which lasted for only one or two sample collection periods (see Figure 2). Perhaps the most striking of these is for Lake Barco. For a two week period in the summer of 1993, TGM concentrations exceeded 4 ng/m^3. While these values are not unusual, based on TGM observations from other terrestrial areas (see next section), they are well outside normal trends for this site. There were no unusual wind directions or

duration's during this sampling period (based on comparison with long term wind direction patterns for this site) which might offer an explanation for these few high points. We are currently investigating whether there is any correlation with high aerosol or rainfall Hg, trace element, or major component parameters during this time period.

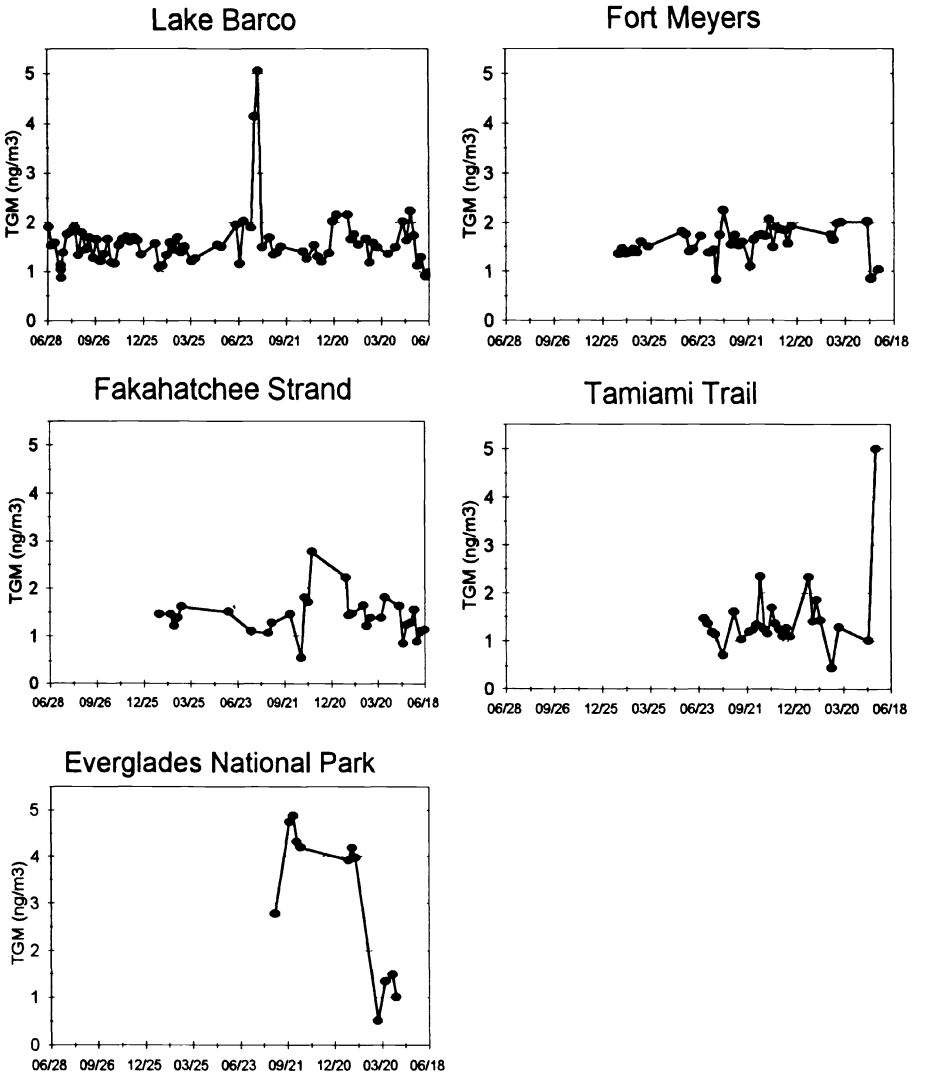

Figure 2 Total Gaseous Mercury Measurements at the FAMS Network Sites

TABLE II
FAMS: Summary of TGM Measurements (1992-1994)

Location	Number of Observations	Range (ng Hg/m^3)	Mean (ng Hg/m^3)
Lake Barco	78	0.87 - 5.06	1.59 ± 0.58
Fort Myers	42	0.83 - 2.25	1.59 ± 0.40
Fakahatchee Strand	30	0.56 - 2.77	1.42 ± 0.41
Tamiami Trail	27	0.45 - 5.00	1.46 ± 0.80
Ever. Nat. Park	13	0.51 - 4.88	3.11 ± 1.52
Andy Town	3	1.26 - 2.31	1.78 ± 0.62

3.3 Comparison with other Terrestrial TGM Measurements

Table III gives a comparison of the TGM measurements made by FAMS in Florida with other terrestrial TGM measurements. While there are only a few terrestrial TGM measurements with which to compare, it appears that TGM values in central and south Florida are similar to sites studied by Fitzgerald and coworkers in remote Wisconsin regions and ambient air measurements near the Oak Ridge National Laboratories in Tennessee. Moreover, the TGM values we observed in Florida are very similar to northern hemisphere marine background TGM values obtained by Fitzgerald (1989) and Slemr and Langer (1992).

TABLE III
A Comparison of Terrestrial TGM Measurements

Location	Number of Observations	Range (ng/m^3)	Mean ± STD (ng/m^3)	Reference
Walker Branch, TN	39	1.52 - 3.68	2.15 ± 0.51	Kim et al., (1995)
Egbert, Ontario	46	1.30 - 13.3	3.83	Schroeder (1992)
Little Rock Lake, WI	36	1.00 - 2.45	1.57 ± 0.40	Fitzgerald et al., (1991)
Crab Lake, WI	-	-	1.79 ± 0.43	Lamborg et al., (1993)
Nordic Countries	~ 900	1.0 -4.0	~ 2.6	Lindqvist et al., (1991)
Great Lakes Basin				Keeler et al., (1994)
Chicago, IL	59	-	9.7	
South Haven, MI	39	-	2.0	
Florida	191	0.45 - 5.06	1.64 ± 0.76	This Study

4. Summary and Conclusions

Atmospheric TGM concentrations in Central and S. Florida do not appear to be elevated by comparison with other terrestrial and marine background TGM observations. At present, no spatial or temporal gradients in TGM are apparent at the FAMS network sites where more than one year of data are available. Additional sampling from sites recently established need to be obtained before any clear trend can be established. More importantly, spatial and temporal trends in atmospheric Hg deposition patterns do not appear to be directly related to atmospheric TGM (see Guentzel et al., 1994). Future efforts need to address the relationship between atmospheric TGM and Hg deposition. Of particular importance is the potential contribution of water soluble Hg (II) species to atmospheric Hg deposition and the relationship between TGM and the factors responsible for water soluble Hg (II) species production.

Acknowledgments

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IS MERCURY INCREASING IN THE ATMOSPHERE? THE NEED FOR AN ATMOSPHERIC MERCURY NETWORK (AMNET).

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Abstract Mercury uses in human endeavors will lead to a general, though variable, volatilization of Hg Current estimates for anthropogenic interferences range from about 50 to 75% of the total annual Hg emissions to the atmosphere Recent modeling suggests that the present atmospheric Hg burden has increased by a factor of 3 during the last 100 years with a current rate of increase of about 0 6% yr^{-1} (ca 0 01ng $m^{-3}yr^{-1}$) This impact, which is significant, can be examined and assessed empirically To date, however, atmospheric Hg programs have not employed an experimental design sufficient to account for short time scale atmospheric Hg variations of natural and anthropogenic origin, and to resolve the long term temporal pattern I am proposing an international research program, AMNET, or Atmospheric Hg Network, to address the important question, "Is Hg increasing in the atmosphere?" AMNET would examine temporal and spatial variations in atmospheric Hg and assess the influence of natural and anthropogenic sources on the global atmospheric Hg cycle This program requires international support and cooperation The experimental design of AMNET would follow the successful Atmospheric Lifetime Experiment Program (ALE), which examined the contemporary temporal changes in the atmospheric concentrations of the freons, methyl chloroform, carbon tetrachloride, and nitrous oxide Following the ALE design, AMNET sampling stations would be maintained in both hemispheres and at sites free from strong local pollution sources of Hg (e g , remote islands) Measurements would be made for a period of three to five years The precision and accuracy of the Hg^{o} determinations must be $\geq$ 1% The accurate resolution of the variability and secular trends in the atmospheric Hg burden can provide (1) a direct quantitative assessment of the scale to which anthropogenic processes are affecting the natural biogeochemical cycling of Hg, (2) an essential refinement and constraint currently lacking in mass balance models, (3) an enhanced knowledge of the behavior of Hg in the atmosphere, and (4) an accurate data base required for global circulation atmospheric chemical Hg models

1. Introduction

There are a variety of significant human health concerns, and critical environmental issues associated with the geographically wide-spread incidence of elevated levels of Hg (i.e., monomethylHg, MMHg) in fresh water and marine fish. A linkage is evident between the bioaccumulation of MMHg in aquatic systems and the atmospheric mobilization and deposition of Hg, which has local, regional, and global components (e.g., Lindqvist *et al.*, 1991; Fitzgerald, *et al.*, 1991; Iverfeldt, 1991; Wiener *et al.*, 1990; Hudson *et al.*, 1994; Mason *et al.*, 1994). Furthermore, it is increasingly apparent that human-related inputs of Hg to the air exceed natural inputs, with the principal sources being coal combustion, smelting and waste incineration (Nriagu and Pacyna, 1988). Estimates for annual amounts of Hg released into the air by human activities range between 3600 and 4500t, which represents about 50 to 75% of the total yearly input (6000 to 7500t) to the atmosphere from all sources (Fitzgerald, 1986; Lindqvist *et al.*, 1991; Nriagu, 1989). Active Hg uses and indirect mobilization associated with human endeavors will lead to a general, though variable, volatilization of Hg to the atmosphere. Identification of the sources for temporal variations in Hg^{o}, and the accurate determination of secular trends in the atmospheric Hg burden will provide a direct quantitative assessment of the scale to which anthropogenic processes are affecting the natural geochemical cycle. This information will provide refinement and precision to Hg cycle mass balance simulations at the present time. In a

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manner analogous to contemporary research on the carbon cycle (i.e., CO_2), it will also allow more realistic and sophisticated Hg models to be developed and tested (Hudson *et al.*, 1994a).

To achieve these goals, an international research program, AMNET, or Atmospheric Hg Network is proposed. The principal focus of AMNET would be the accurate determination ($\geq$ 1%) of the temporal and spatial variations in atmospheric Hg^0 and the assessment of the influences from natural sources and the interferences from anthropogenic emissions on the global atmospheric Hg cycle. A suggested experimental approach for AMNET would be based on the very successful Atmospheric Lifetime Experiment Program (ALE) which examined and modeled the atmospheric cycling of the industrial freons, methyl chloroform, carbon tetrachloride, and nitrous oxide (Prinn *et al.*, 1983). The ALE Program employed stations in both hemispheres, and at sites free from strong local pollution sources (e.g., remote islands). Measurements would be made for a period of three to five years.

2. Global Hg Cycling: Current and Historical Mass Balances

The question of whether Hg is increasing in the environment with rising Hg concentrations in the atmosphere serving as a sensitive signal can be placed readily in perspective using state-of-the-art mass balances to simulate the current and premodern global Hg cycle. We used a well-constrained Hg budget approach to: (1) to scale and evaluate the major aquatic biogeochemical processes of methylation, Hg^0 production and evasion, (2) to assess the influence of anthropogenic emissions on the behavior and fate of Hg in the environment by simulating the situation that existed 100 years, and (3) to provide a framework for the development of more realistic models of the biogeochemical cycling of Hg (Mason *et al.*, 1994). The current global Hg cycle is presented in Figure 1, where the estimates for annual direct anthropogenic Hg releases to the atmosphere were averaged and taken as 4000t (20 megamoles, Mmol). Total emissions were taken to be 7000t (35Mmol) yr^{-1}. The premodern view of the global Hg cycle is presented in Figure 2 and corresponds to the 1890 period. We assumed that today's Hg mass balance was achieved through a linear increase in anthropogenic emissions over a 100 year period.

A comparison of the budgets presented in Figures 1 and 2 provides a revealing and insightful assessment of the extent to which anthropogenic Hg emissions may have perturbed the Hg cycle over for the past century. It is evident that terrestrial systems, ocean waters and the atmosphere are significantly contaminated with Hg released by human activities over the 100 year period considered in these simulations. Complex biological and chemical interactions, especially those involving methylation, Hg^0 production and volatilization prolong insidiously the activity of anthropogenic Hg releases to the environment. Of the estimated 200,000t (1000Mmol) of Hg emitted to the atmosphere since 1890, 189,000t (95%) reside in terrestrial soils, 7,200t in the ocean surface waters (3.6%) and 3,400t (1.7%) have been added to the atmosphere. Thus, contemporary Hg releases are adding to active reservoirs that are significantly contaminated by the integrated impact of atmospherically derived Hg as a pollutant.

It appears that Hg accumulating in soils will be released slowly to terrestrial and coastal waters. Swedish studies (Lindqvist *et al.*, 1991; Johansson *et al.*, 1991, Aastrup *et al.*, 1991) and lacustrine research by Swain *et al.* (1992) suggest that < 30% of the atmospheric Hg deposition to a watershed reaches a lake. Thus, the effects from the anthropogenic Hg

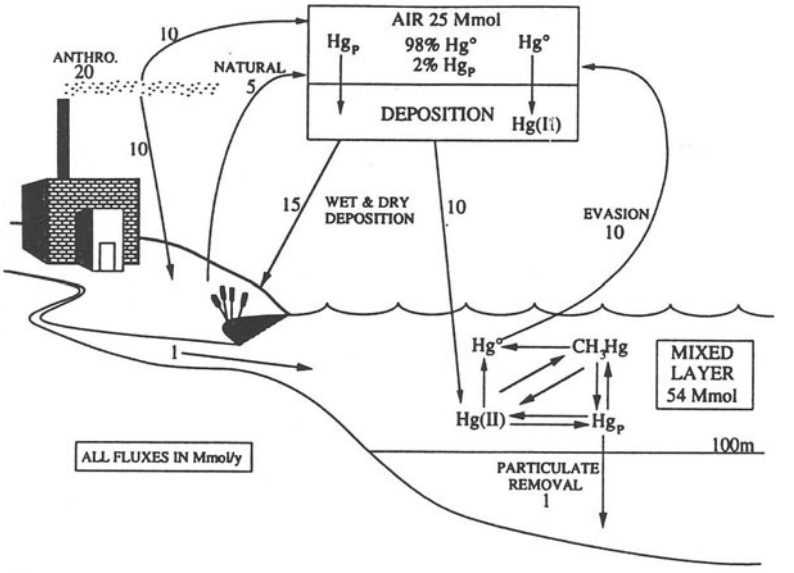

Fig. 1. The current global Hg cycle (as adapted from Mason *et al.*, 1994).

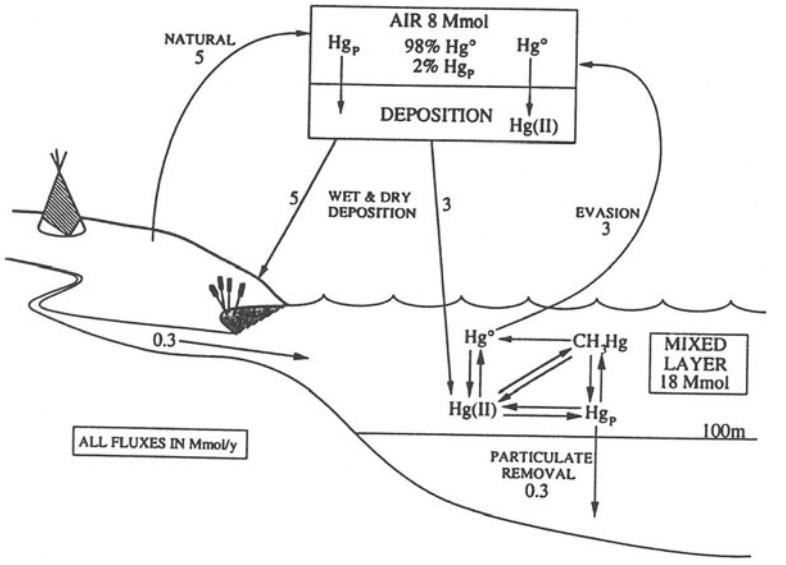

Fig. 2 A premodern view of global Hg cycle (as adapted from Mason *et al.*, 1994)

loadings will persist and affect fish in fresh waters and estuarine/coastal regions for a long period (decadal time scales) even after a cessation in Hg emissions. In contrast, the atmosphere, open ocean waters and biota would return to 1890 Hg concentration levels in a short time, ca. 15 to 20 years.

The simulations show that about 1/2 of anthropogenically related Hg emissions to the atmosphere contribute to the global cycle, and about 1/2 will be deposited on a local/regional scale. Since the mass balancing uses empirical data for Hg deposition, this analysis suggests that the localized/regional component has not been measured. This is a most significant result. This work suggests that atmospheric Hg fluxes have increased by about a factor of 4.4 over the last century as a consequence of human activities. However, the net increase in the atmospheric burden is a factor of three, due to the predicted significant near source removal of Hg in the form of particles and ionic species. As a consequence, 60% of the direct or recycled component is contributing to the Hg burden in the atmosphere even though 77% of the present day inputs are directly or indirectly of anthropogenic origin. The present annual rate of increase of Hg in the atmosphere is estimated to be 0.01 ng m^{-3} (i.e., 0.6% yr^{-1}). This prediction is testable, and points directly to the use of a valuable program such as AMNET.

The conclusions and predictions associated with these mass balance budget simulations of the global Hg cycle have far reaching implications. The importance of Hg^{o} in controlling the production of MMHg is quite evident. Evasion of Hg^{o} is balanced by total atmospheric deposition of Hg(II) or "reactant" to the oceans. The mechanisms by which Hg(II) is reduced to Hg^{o} are poorly known. However, the reduction appears to be biological and involves microorganisms. In view of the significance of Hg^{o} in affecting the speciation, behavior and fate of Hg in the environment, the Hg^{o} cycle in the atmosphere and waters deserves much scrutiny. The Hg^{o} and MMHg cycles are intimately linked. Environmental studies of Hg must view the biogeochemistry of Hg as a unified system. An unilateral focus on one aspect of the system must be avoided. For example, human exposure to MMHg in fish is related to anthropogenic emissions of Hg, atmospheric transport and deposition processes, and *in situ* biological interactions and chemical reactions that lead to MMHg and Hg^{o} production and recycling between water and air.

In summary, and although Hg(II) reduction and evasion removes Hg from the waters where it might be methylated, the recycling between surface waters and the atmosphere will prolong the impact of anthropogenically derived Hg on aquatic systems. The present day surface waters of the oceans contain enhanced Hg levels that promote increased methylation, and concomitant increases in the content of MMHg in biota. Oceanic emissions reflect the presence of this increased burden. About 70 to 80% of today's emission of Hg are related to human activities. A substantial portion of the emissions are predicted to be deposited locally. Regional deposition would reflect the presence of ionic and particulate Hg species in emissions. Elemental Hg emission would contribute to far field and more global effects. A 3 fold increase in the Hg burden in the atmosphere and in ocean is predicted. Accordingly, surface soils contain most of the pollution derived Hg released over the past 100 years. The simulations indicate that current emissions are exacerbating the problem by adding Hg to seriously contaminated active reservoirs of surface soils, watersheds, the atmosphere, and the oceans. As most Hg deposited on the oceans is recycled to the atmosphere, the terrestrial environment becomes a principal sink. Mercury deposited on land is mobilized slowly to enter the watershed and tributaries of fresh and coastal waters. The

insidious consequence of the complex and interesting biogeochemical cycling of Hg is to lengthen the influence and active lifetime of anthropogenic Hg in regions where methylation can occur.

3. Atmospheric Hg Distributions: Temporal Changes?

The mass balance comparison of the current and premodern global Hg cycle is reasonably well constrained and supported by recent research. It provides a strong foundation for remedial action and a foundation for future work. Further, a recent paper based on non-synoptic data from 7 oceanographic cruises of short duration, Slemr and Langer (1992) concluded that annual atmospheric Hg increases of ca. 1.5% for the Northern Hemisphere and ca. 1.2% for the Southern Hemisphere had occurred for the period between 1977 and 1990. While the inferred increases do agree with expectations, the precision of measurement appears inadequate, and the experimental design does not account for short time scale variations of both a natural and anthropogenic origin. For example, in a two-month study, we found spatial and temporal variations in atmospheric Hg over the northeast Pacific ocean that were comparable to the changes reported for the 13 year period in the Slemr and Langer work. The data from our work in the Pacific Ocean and the 1990 results from Slemr and Langer are shown in Figure 3.

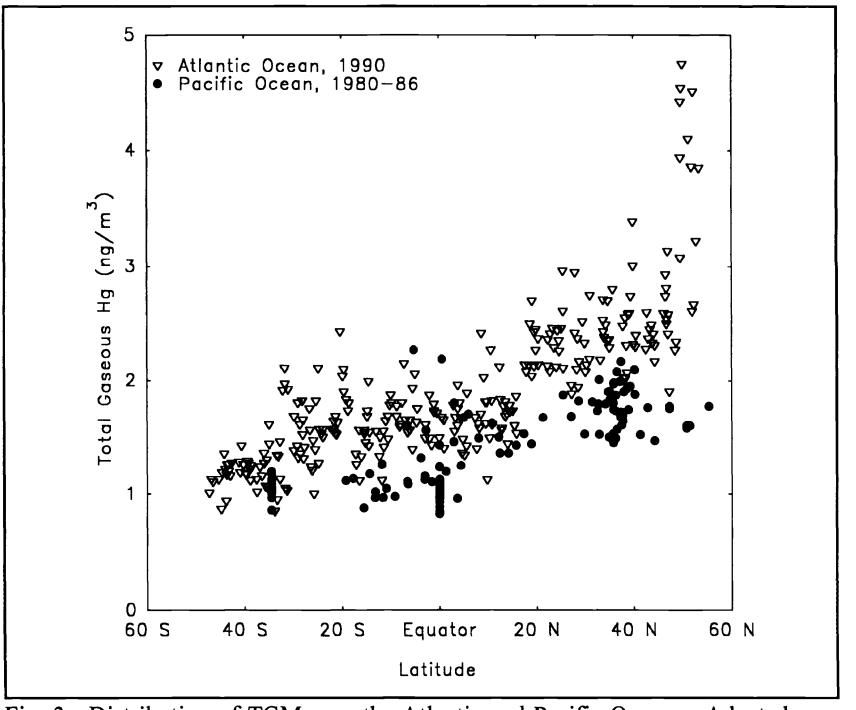

Fig. 3. Distribution of TGM over the Atlantic and Pacific Oceans. Adapted from Slemr and Langer, 1992 and Fitzgerald, 1989.

Total gaseous Hg concentrations (>99%Hg^o) in the marine boundary layer decrease between the northern and southern hemisphere over the Pacific and Atlantic Oceans. This interhemispheric distributional pattern characterizes a trace atmospheric gas whose primary sources, on a unit area basis, are continental and in the case of Hg include significant anthropogenic sources. Trace gas modelling for Hg yielded an average tropospheric residence time of total gaseous Hg, assumed to be Hg^o, of about a year (Fitzgerald, *et al.*, 1981). The mass balances presented in Figures 1 and 2 yields a similar value. Thus, Hg^o from both natural and anthropogenic sources can be readily mixed intrahemispherically. Interhemispheric mixing will allow northern hemispheric emissions of Hg^o to be transported to the atmosphere of the southern hemisphere. As suggested, the broad dispersion of Hg^o has contributed to the geographically large problem of elevated Hg concentrations in fresh and marine fish.

In general, the TGM values over the Pacific Ocean are smaller compared to similar latitudes for the Atlantic Ocean. There is significant variability in both studies with the Atlantic data showing slightly more scatter. These results are consistent with the size of the ocean basins and the proximity of terrestrial and anthropogenic Hg sources to the smaller Atlantic Ocean. The highest values (4 - 5 ng/m^3), for example, in the Slemr and Langer survey are from stations in the North Sea that were quite close to Germany and continental Europe. The issue of variability associated with Hg emissions from natural sources such as the oceans, volcanoes, and mineralized regions, as well as those from human activities which also vary in strength and in time and space must be addressed before secular changes in atmospheric Hg concentration can be quantified. The Hg distribution will be also be affected by meteorological conditions, and seasonal variations in the oceans and on land. In view of potential problems posed by atmospheric Hg variability, the very important question of whether Hg is increasing, decreasing or remaining constant in the atmosphere has not yet been properly considered.

4. Atmospheric Hg Network: AMNET

Fortunately, the temporal variations and secular trends in Hg^o can be resolved, and the experimental design has been provided, as indicated, by the highly successful Atmospheric Lifetime Experiment Program. An analogous atmospheric Hg program would focus on frequent atmospheric measurements and utilize a sampling and analytical strategy similar to that employed by ALE. The ALE studies of contemporary temporal changes in the atmospheric concentrations of the freons, methyl chloroform, carbon tetrachloride, and nitrous oxide showed that 3 to 5 years of on-site continuous measurements are necessary to deal satisfactorily with questions of natural variability and to resolve the influence of pollution on constituents such as Hg^o in the atmosphere (Prinn *et al.*, 1983). In addition, measurements must be carried out in a network context, with stations selected in both the northern and southern hemispheres. The ALE network used primarily island sites that were relatively free of localized sources. The stations were located on the west coast of Ireland at Adrigole (52°N, 10°W), Cape Meares, Oregon (45°N, 124°W), Ragged Point, Barbados (13°N, 59°W), Point Matatula, American Samoa (14°S, 171°W) and Cape Grim, Tasmania (41°S, 145°E). Monthly means and standard deviations for several years of data for freon 11 ($CFCl_3$) at the ALE sites is presented in Figure 4 (Cunnold *et al.*, 1986, 3 yrs of data shown as mixing ratio in ppb by volume). The increases in atmospheric $CFCl_3$ is readily

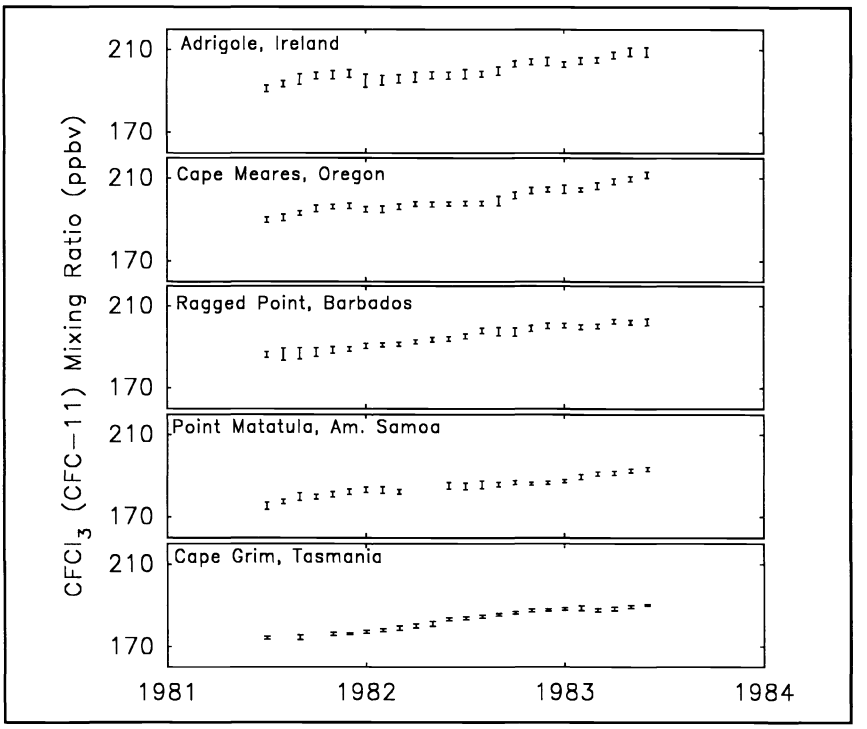

Fig. 4. Monthly avg. $CFCl_3$ conc. from the 5 ALE stations (Cunnold *et al.*, 1986).

resolvable and the averaged rate of increase of the mixing ratio was reported to be 15.3 ppptv yr^{-1} (or approximately 8.6% yr^{-1}) during the period of study (1978-84).

Critical information concerning the biogeochemical cycling of Hg and the role of anthropogenic inputs can be derived from the temporal and spatial variations in atmospheric Hg^{o}. As suggested, this research program might be called AMNET or Atmospheric Hg Network and would be international in scope. As noted and following the ALE format, sampling stations would be in both hemispheres and at sites free from strong local pollution sources of Hg. A precision and accuracy of $\geq$ 1% is required over a 3 to 5 year period. This is a challenging analytical undertaking, but one that is achievable. Nitrous oxide provides an example of the fine resolution that is possible by careful long term atmospheric measurements. Data for secular trends in N_2O as measured at Cape Meares, Oregon between 1980 and 1989 are reproduced in Figure 5 (Trends '91). The averaged rate of increase during this 10 year period is about 0.2% yr^{-1}, and as with $CFCl_3$, it is readily determined.

AMNET needs international support and cooperation to provide the high quality data necessary to constrain global models, to determine the influence of natural and anthropogenic sources on the global atmospheric Hg cycle, and to assess their effects on the biogeochemical activity of Hg in natural waters. Fortunately, there are a variety of suitable atmospheric Hg sampling sites that could be included in a network. Most importantly, the accurate resolution of the variability and secular trends in the atmospheric Hg burden can

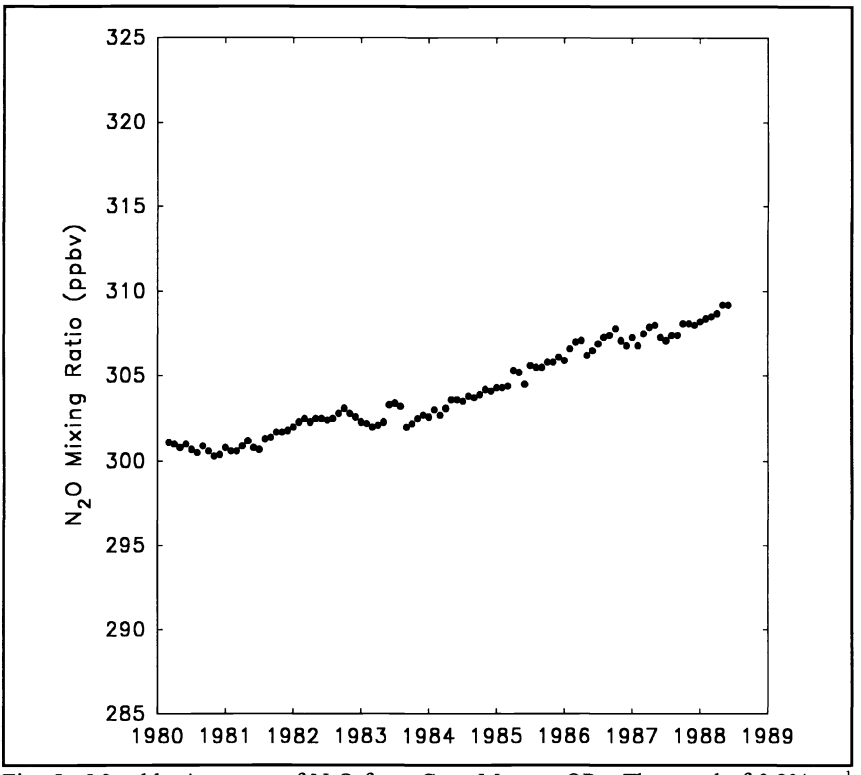

Fig. 5. Monthly Averages of N_2O from Cape Meares, OR. The trend of 0.2% yr^{-1} was readily determined. Adapted from Trends '91

provide (1) a direct quantitative assessment of the scale to which anthropogenic processes are affecting the natural biogeochemical cycling of Hg, (2) an essential refinement and constraint that is currently lacking in mass balance models, (3) an enhanced knowledge of the behavior of Hg in the atmosphere, and (4) an accurate data base necessary for the development and validation of global circulation atmospheric chemical Hg models.

5. Conclusion

Finally, AMNET is a long term program designed to resolve the important geochemical and anthropogenic questions associated with atmospheric Hg variations, with secular trends in the atmospheric Hg burden and with fate controlling atmospheric chemical reactions. AMNET stations will also provide the opportunity for intensive studies of the chemical reactions and processes affecting the behavior and fate of Hg in the atmosphere. A complete program would combine both long-term monitoring and shorter time scale reaction oriented studies of the gas and particulate phases of Hg, chemical speciation investigations, and depositional studies using the AMNET air sampling sites.

Acknowledgments

The idea for AMNET had its inception during my participation in the SEAREX Program (1977-1987). I am grateful to my students and colleagues who provided assistance and a stimulating atmosphere for our Hg studies over the Atlantic and Pacific Ocean. I thank the numerous investigators who are currently obtaining high-quality data for Hg in the atmosphere. These are the individuals who can make AMNET a reality, thereby enhancing our understanding of the atmospheric Hg cycle, the influence of anthropogenic interferences, and the efficacy of remedial measures. This work has been supported in the past by NSF grants in association with the SEAREX Program, and recently by the MAPP Program, which in term is supported by The Wisconsin Department of Natural Resources and the Electric Power Research Institute. This is contribution 265 from the Marine Sciences Institute of the University of Connecticut.

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AN UPDATE OF THE MERCURY INVENTORY AND ATMOSPHERIC MERCURY FLUXES TO AND FROM FINLAND

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Abstract. Finland, the northern-most agricultural/industrial country in the world, has been for some time steadily improving environmental mercury (Hg) research. This paper focuses upon Hg recovery during zinc production, uses of Hg, updating of information on Hg emissions and atmospheric transport of Hg to and from Finland. The recovery of Hg as a by-product of zinc production began in 1970. The highest amount of recovered Hg was noted to be 160 t in 1989. Total uses of Hg in different sectors were about 7.4 t in 1992, which had decreased by 50% since the year 1987. In 1992, the estimated Hg emission to air was 2 t yr^{-1}, whereas to water and land the emission was about 0.20 and 3.67 t yr^{-1}, respectively. Natural Hg emission in Finland was estimated to be about 0.4 t yr^{-1} (range: 0.3 to 0.5 t yr^{-1}). In addition, an initial attempt was made to estimate the atmospheric Hg flux to and from Finland; these values were noted to be 2.7 and 2.1 t yr^{-1}, respectively.

1. INTRODUCTION

Mercury has been identified as a toxic pollutant discharged into the ecosystem from anthropogenic and natural sources. Its toxicity, atmospheric cycling, deposition and accumulation as methyl-Hg (MeHg) in fish have been well established (Schroeder *et al.*, 1991; Fitzgerald, 1993). Great interest has been shown in Hg transport and inventory after the health effects of the discharges of Hg to Minamata Bay in the 1950s were observed (Irukayama, 1967; Nriagu, 1979, 1990; Nriagu and Pacyna, 1988). Recently, there have been increases in fossil fuels combustion, pesticide uses, waste incineration and industrial emissions, suggesting a need to update the national inventories of Hg. Estimating national or regional emission inventories and updating of emission factors provide emission scenarios from different facilities (Pacyna, 1993).

It is accepted that a large fraction (about 90%) of atmospheric Hg is in the form of elemental Hg (Hg^0) in air, and that the remainder is in the form of divalent Hg compounds which are either in gaseous form or bound as compounds of sulfur or carbon (Lindqvist and Rodhe, 1985; Fitzgerald, 1986; Lindqvist and Schroeder, 1989). A new pattern of Hg pollution has been observed in species of lakes in remote areas of Scandinavia and North America, which is believed to be due to long range transport of pollutants (Verta *et al.*, 1986; Håkanson *et al.*, 1988; Gibbons *et al.*, 1993).

Many papers have been published on anthropogenic Hg emissions in Europe and in Finland (Pacyna, 1989; Mukherjee, 1989, 1991; Aunela and Larjava, 1990). The present study has its main objectives to (a) estimate the flow of Hg into the Finnish ecosystem; (b) estimate natural emission of Hg in Finland; (c) update the Hg emission inventories to air, water and land from different facilities in Finland; (d) update the emission factors, and (e) estimate the atmospheric Hg fluxes to and from Finland.

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2. MATERIAL AND METHODS

In this work, production and uses of Hg have been considered for 1991, and emissions of Hg have been considered for the year 1991/92. The whole study is based on information provided by provincial authorities, facility operators, the National Board of Waters and the Environment, available statistics, literature-cited emission factors, and calculated emission factors based on simplified mass balance and the efficiency of pollution control equipment.

The calculated atmospheric Hg flux to Finland is based on the works of Iverfeldt (1991) and Petersen and Iverfeldt (1993). Calculated atmospheric Hg flux from Finland is based on the works of Keeler *et al.* (1993).

3. RESULTS AND DISCUSSIONS

3.1. FLOW OF Hg TO THE FINNISH TECHNOSYSTEM

In Finland, Hg recovery as a by-product during the production of zinc began in 1970. During the Hg recovery process, Hg-containing gases from the zinc roaster are passed into the Hg recovery plant where the gases are washed by strong and weak H_2SO_4 in different towers. Hg containing residue is then washed with water, mixed with lime and heated in a rotary kiln where the Hg is vaporized. During cooling, the Hg condenses, and is recovered at a purity of 99.999% (Outokumpu News, 1981). The highest amount of recovered Hg was noted to be 160 t in 1989; this value decreased to 80 t by 1991.

The import of Hg through raw materials to Finland is given in Table I. The Hg import through copper concentrate increased by three-fold since 1987 (Mukherjee, 1991); the recent increase of Hg in raw material is due to consumption of 90% imported concentrate by the copper smelter at Harjavalta. It should be noted, however, that the total import of Hg through raw materials in 1991 decreased by 50% since 1987. The reason for this decrease is that, at present, Hg content in zinc concentrate is about 45% less than in 1987, and there are no separate import statistics for Hg oxide in the Finnish custom office for the year 1991.

Radical changes have occurred in the principal uses of Hg in recent years in Finland (Table II). The end uses of Hg have decreased by 50% since the year 1987 due to (a) lower demand for chlorine in the pulp and paper industry, as well as the recent closure of a chlorine production facility; (b) less use of amalgamation; (c) limited use of Hg-cell batteries, and (d) replacement of Hg compounds by less toxic materials in the pharmacological sector.

3.2. UPDATING OF EMISSION INVENTORIES FROM NATURAL AND ANTHROPOGENIC SOURCES IN FINLAND

3.2.1. Natural sources

In the past, no attempt has been made to estimate natural emissions of Hg in Finland. However, knowledge of atmospheric emission from natural sources is necessary to assess the extent of local or global pollution by toxic metals (Nriagu and Pacyna, 1988). Literature studies indicate that natural sources of Hg include: (a) degassing from mineral deposits; (b) volcanoes; (c) photoreduction of divalent Hg in natural waters;

(d) forest fires, and (e) biological formation of elemental Hg (Nriagu, 1989; Lindqvist *et al.*, 1991).

Global natural emission of Hg has been estimated by many authors; recent estimations vary between 2.5 to 3.0 x 10^3 t yr^{-1} (Nriagu and Pacyna, 1988; Lindqvist *et al.*, 1991), which lead to an average global natural emission rate of 6 g km^{-2} yr^{-1}. In addition, it has been concluded that the maximum natural emission of trace elements stem from forested regions (Orsini *et al.*, 1982; Nriagu, 1989).

TABLE I

The import of Hg through raw materials and other sources in Finland in 1987 and 1991.

Source category	Period 1987* kg Hg yr^{-1}	Period 1991
Zinc concentrate	150 000	82 000
Copper concentrat	760	2 030
Heavy fuel oil	10	2
Hard coal	210	510
Batteries	6 640 (4 580-8 700)	1 650 (1 500-2 000)
Lamps	105 (100-110)	200
Instruments	1 500 (1 200-1 800)	1 500 (1 200-1 800)
Metallic Hg	1 500	1 000
Hg-oxide	13 100	-
Total	174 000	89 890

*Source: Mukherjee (1989); Totals are rounded; - The data are not available

There are no data for Finnish natural Hg emissions from either lake waters or coniferous forest soils. Considering the geographical position of Finland, the natural Hg emission rate for land areas can be estimated as less than 1 g km^{-2} yr^{-1}, and for waters as 5 g km^{-2} yr^{-1}. These values have been taken from the works of Xiao *et al.* (1991) and Lindqvist *et al.* (1991). Hence, calculated natural Hg emissions are as follows:

Land = 304 625 km^2 x (< 1) g km^{-2} yr^{-1} = < 0.3 t yr^{-1}
Waters = 33 522 km^2 x 5 g km^{-2} yr^{-1} = 0.2 t yr^{-1}
Total = 0.4 t yr^{-1} (Range: 0.3 - 0.5 t yr^{-1})

Estimation of natural emission of Hg in Europe is under consideration (Petersen *et al.*, 1990). There is a lack of natural emission data for Hg and other trace elements at present. Such emission data will be quite valuable while studying Hg or other trace elements modeling.

TABLE II

Use categories of Hg in Finland in 1987 and 1991/92.

Use	1987[#] Consumption t yr^{-1}	1991/92
Batteries	6.65 (4.6-8.7)	1.65 (1.5-2.0)
Thermometer		1.50 (1.2-1.8)
Tooth fillings	4.7	1.20 (1.0-1.4)
Agriculture[*]	4.7	4.0
Laboratory use (including instruments)		1.0
Chloralkali plants	3.5 (3.0-4.0)	2.0
Paint		0
Pharmaceuticals		0
Others	7.1 (6.3-7.9)	0
Total	22.0	7.4 (11.4)

Note: Data from (a) National Board of Waters and the Environment, 1993; (b) Orion Oy, 1993; (c) Mukherjee (1989).
[*]Hg compound used in seed dressing stopped on 1.1.1992;
[#]Source: Mukherjee (1989)

3.2.2. Anthropogenic sources

In Finland, anthropogenic sources of Hg released to the environment have both point and diffuse origins. Hg discharged into the air, water and soils from industrial sources is given in Table III. It is observed that, at present, non-ferrous metallurgical plants still represent the greatest fraction of atmospheric emission in the Finnish Hg inventory, followed by power plants. Recent studies in the European Union's coal-fired power plants indicate that about 89% of Hg is emitted from coal-fired power plants in vapor form to the atmosphere (Bignoli, 1989). In our study, Hg content in fly ash is noted to be 0.19 mg kg^{-1} (Imatran Voima Oy, 1993), and it is assumed that Hg retention in Finnish fly ash is about 11%. The total estimated fly ash produced was about 0.458×10^6 t, based on 9% ash content in coal. Hence, total Hg in fly ash is about 0.087 t, of which 65% is dumped in disposal sites/landfills. Due to the economic depression in 1991/92, recycling of fly ash in the construction industry dropped from 60% in 1987 to 35% in 1991/92. In addition, it should be noted here that in Finland, there are now ten wet scrubber units in coal-fired power plants, but that no information is available on retention of heavy metals in the residues of calcium sulphite and sulphate present in the units. Clarke and Sloss (1992) indicated that in the flue gas desulphurization system, retention of Hg in the residue is about 30%. In peat-fired boilers, Hg retention in fly ash is assumed to be the same as in coal-fired boilers. The production of ash was about

160 000 t yr^{-1}, containing 0.28 mg Hg kg^{-1} (Wahlström and Pohjola, 1987). One third of the ash was reused as a building material, and the remaining 100 000 t were dumped in landfills.

This study indicates that total Hg emission to air has decreased by 40% since the year 1987. This decrease is due to substantially lower emissions from the copper smelter at Harjavalta as well as decreased chlorine production by the Hg cell process. In addition, Hg discharge to land via jerosite decreased from 10 t in 1987 to 1.5 t in 1992 (Karlman, 1993).

3.3.3. Atmospheric Hg fluxes to and from Finland

High Hg concentration in fish and lake sediments has been reported in remote areas of Scandinavian countries. These concentrations are not only attributable to long range transport of Hg from central Europe, Czechoslovakia, Poland and the former U.S.S.R. (Steinnes, 1987; Iverfeldt, 1991; Münch *et al.*, 1991; Schroeder *et al.*, 1991; Petersen and Iverfeldt, 1993), but also due to local sources (Nilsson *et al.*, 1989). Hg^0 has a long atmospheric residence time (Lindberg, 1987), estimated to be between 0.7 to 2 years (Wollast *et al.*, 1976; Andren and Nriagu, 1979; Lindqvist and Rodhe, 1985).

In Europe, major sources of Hg emissions include: (a) coal combustion, as well as emissions from industrial, commercial and residential boilers (68%); (b) chlor-alkali plants (18%); (c) waste incineration (7%), and (d) roasting and smelting operations in non-ferrous metallurgical plants (6%) (Petersen *et al.*, 1990). The presence of MeHg in precipitation, in fish and in sediments raises the question of whether atmospheric MeHg is also transported globally.

Recently, long range transport of trace elements in European and Scandinavian countries has been cited in literature (Iverfeldt and Rodhe, 1988; Iverfeldt, 1991; Lindqvist *et al.*, 1991; Münch *et al.*, 1991; Petersen, 1992; Petersen and Iverfeldt, 1993; Pacyna, 1993). In our study, dry and wet precipitation data of Hg cited by Iverfeldt (1991) and Petersen and Iverfeldt (1993) for Scandinavian countries have been considered for calculation of atmospheric Hg flux to Finland. The wet and dry deposition rates of Hg in northern and southern Finland are calculated as follows (Stations refer to Fig. 1):

Wet deposition rate of Hg

Northern Finland = 160 500 km^2 x 6 g km^{-2} yr^{-1} (this value is selected as mean value from the north Norwegian town Överbygd, close to the Finnish border and a central Swedish town, Vindeln (Iverfeldt, 1991).

= 0.96 t Hg yr^{-1}

Southern Finland = 177 000 km^2 x 11 g km^{-2} yr^{-1} (this value has been selected from the Finnish station Tikkakoski) (Iverfeldt, 1991)

= 1.95 t Hg yr^{-1}

Dry deposition rate of Hg

Northern Finland = 160 500 km^2 x 0.2 g km^{-2} yr^{-1} (the value is selected as per mean value from Överbygd and Vindeln) (Petersen and Iverfeldt, 1993)

= 0.03 t Hg yr^{-1}

Southern Finland = 177 000 km^2 x 0.75 g km^{-2} yr^{-1} (the value is selected as per mean value from the Swedish towns Vindeln and Aspvreten) (Petersen and Iverfeldt, 1993)

= 0.13 t Hg yr^{-1}

TABLE III

The total release of Hg (t yr^{-1}) into the Finnish environment, 1992.

Category	Air	Water	Land
Zinc plant[1]	0.9	0.002	1.5
Copper smelter[2]	0.08	0.02	-
Fuel combustion in elec. power plant[3]			
- Coal	0.45	0	0.06
- Oil	0.008	0	0
- Peat	0.23	0	0.03
- Wood	0.001	0	-
Chlor-alkali plants[4]	0.162	0.025	0.008
Refuse incineration[5]	0.04	0	0.02
Iron & Steel industry[6]	0.03	0	-
Cement industry	0.02	0	0
Sludges			
-from pulp & paper industry[7]	0.022	0	0.022
-from waste water treatment plants	0	0.15	0.42
Hazardous waste treatment plant[8]	0.055	0	?
Domestic wastes & batteries	0	0	1.6
Crematories[9]	0.008	0	0.008
Tooth fillings[10]	-	-	0
Seed-dressing & fungicides[11]	0	0	0
Total	2.0	0.20	3.67
Hg discharaged in 1987**	**3.5**	**0.15**	**20.0**

**Source: Mukherjee (1989)

Note: A dash indicates that the quantity discharged is not known.

Note: 1. Emission Factor (EF) 5 g Hg t^{-1} Zn produced. 2. EF = 1 g Hg t^{-1} Cu produced by the Flash Smelting Process. 3. Air emission calculated on the basis: Hg content mg kg^{-1} (Coal: 0.1; Oil: 0.005; Peat: 0.1 and Wood: 0.01); Fuel burned: Coal: 5.09 x 10^6 t; Oil: 1.86 x 10^6 t; Peat 5.2 x 10^6 t (containing 50% H_2O) and Wood: 0.068 x 10^6 t; 4. EF = 4 g Hg t^{-1} Cl produced by Hg-cell method. 5. EF = 1 g Hg t^{-1} waste (Mukherjee, 1989). 6. EF = 0.01 g Hg t^{-1} sinter produced (Hg in coke: 0.03 and lime: 0.01 mg kg^{-1}); total sinter produced: 3.228 x 10^6 t. 7. About 113 800 t (d.w.) of sludge containing 0.2 mg Hg kg^{-1} was burned and the same amount dumped in the landfills. 8. Wahlström et al. (1993) 9. EF = 1 g Hg $cadaver^{-1}$; based on a certain number of amalgam fillings in each body. It was reported that over 60% were aged and had false teeth (Lauren, 1993). 10. About 400-600 kg of Hg are passed into the sewage system as a result of dental amalgam use; it is still uncertain how much Hg is passed into the aquatic system (Malm, 1994); 11. Hg use in seed dressing stopped on 1.1.92.

The above data are for the year 1988, and have been also considered for the year 1992, as no other recent information is available on the deposition rate of Hg in the Scandinavian countries.

Hence, total wet and dry deposition rate of atmospheric Hg to Finland is estimated to be about 3.1 t Hg yr^{1} and Hg flux to Finland is about 2.74 t yr^{1} (3 1 - 0.36 t yr^{1}). As per Keeler *et al.* (1993), it is considered that 15% of Hg emissions from point sources (stack height ≥ 150 m) are deposited locally as particulates (0 36 t yr^{1}), while the remaining 85%, in gaseous form, are transported by wind out of the emission region. We consider that 85% of atmospheric Hg emission from point and natural sources crosses the border of Finland; therefore, atmospheric Hg flux from Finland is approximately 2.1 t yr^{1} (Fig. 2)

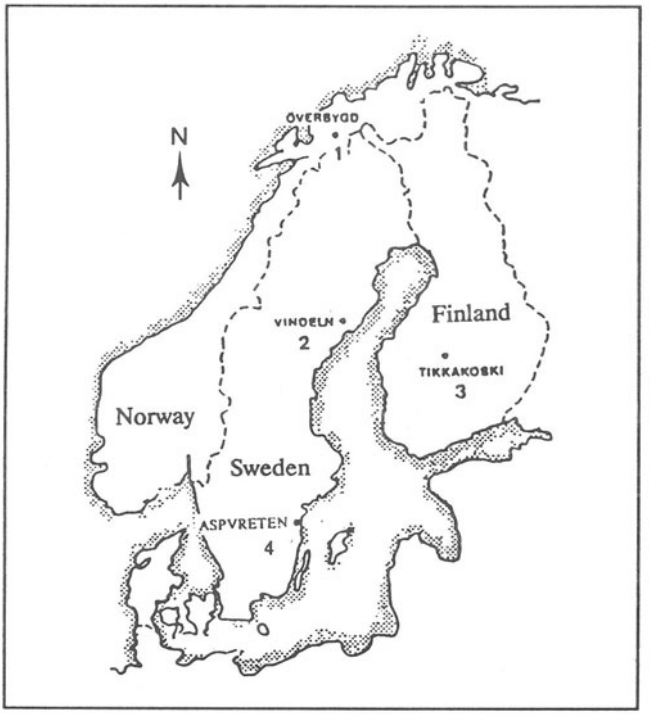

Fig. 1. To calculate Hg flux to Finland, Hg precipitation data at stations 1, 2, 3 and 4 were considered.

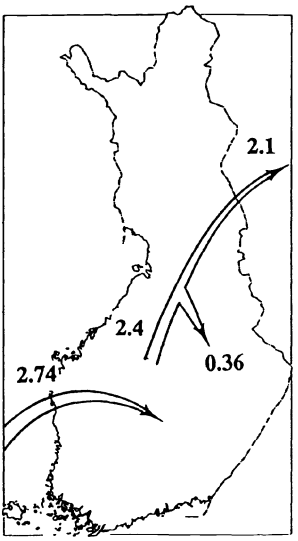

Fig. 2. Atmospheric Hg fluxes to and from Finland (t yr^{-1}).

4. SUMMARY

The present study indicates that atmospheric Hg emissions from industrial sources have decreased from 3.48 t in 1987 to 2.0 t in 1992, due to decreased atmospheric emission of Hg from copper smelter at Harjavalta, as well as decreased chlorine production in Finland. The Hg discharge through jerosite has also decreased from 10 t in 1987 to 1.5 t in 1992. Simultaneously, the use of Hg in Finnish society has also decreased by 50% since the year 1987 (mean value: 22 t yr^{-1}).

In the past, no attempt was made to estimate the natural emission of Hg in Finland and atmospheric fluxes of Hg to and from Finland. In this study, estimated natural emission of Hg was estimated at 0.4 t yr^{-1} (mean). The Hg flux to and from Finland was estimated as 2.7 t and 2.1 t yr^{-1}, respectively. In Finland, Hg discharged from industrial sources to air, water and soils is about 2.0, 0.20 and 4.0 t yr^{-1}, respectively.

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ANTHROPOGENIC INFLUENCES ON THE GLOBAL MERCURY CYCLE: A MODEL-BASED ANALYSIS

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Abstract: A model of the global Hg cycle is presented and applied to analyze modern Hg budgets and historical changes in deposition Our modeling suggests that mixing into the ocean interior is a significant sink of Hg and likely has limited any anthropogenically-caused increase in surface ocean Hg concentrations to about 50% above natural levels rather than 200% as has recently been argued Additionally, both the increase in air pollutants during the industrial era and their recent decrease in North America likely have affected atmospheric Hg scavenging and the resulting records of Hg deposition rates in lake and bog sediments

1. Introduction

The anthropogenic influence on the global Hg cycle is evident from the 2- to 5-fold higher current rates of Hg accumulation in lake sediments (Swain *et al.*, 1992), and peat bogs (Benoit *et al.*, 1994) relative to preindustrial fluxes. Although in some cases a decline in deposition is evident over the past 20 years, global atmospheric Hg^0 concentrations appear to have increased at an annual rate of 1.2 to 1.5 percent between 1977 and 1990 (Slemr and Langer, 1992). Recently, Mason, Fitzgerald and Morel (MFM, 1994) argued that Hg in the surface ocean is now 3-times the natural level and, consequently, two-thirds of oceanic Hg emissions are actually anthropogenic in origin. MFM concluded that two-thirds of all Hg now entering the atmosphere each year is ultimately derived from anthropogenic sources.

To understand the link between anthropogenic emissions, atmospheric concentrations, and deposition of Hg, models of regional and global Hg transport and deposition are needed. To date, modeling of the global Hg cycle has primarily consisted of budgets of natural and anthropogenic fluxes to and from the atmosphere. Although a mechanistic Hg cycle model was developed by Milward (1982), that work predated the recent significant revisions in geochemical data. In this paper, we present a Global Mercury Cycling Model (G-MCM) calibrated using the MFM synthesis of recent global Hg budgets and use it to identify key assumptions that influence the response of the Hg cycle to anthropogenic activities over the past few centuries.

2. A Global Mercury Cycling Model (G-MCM)

Since Hg is an atmophilic element, the principal global transport fluxes occur through the atmosphere. Inputs to the atmospheric Hg^0 pool A_{Hg} include a constant flux from volcanoes W_{atmo} and variable emissions from terrestrial systems E_{terra}, the oceans E_{ocean}, and anthropogenic activities E_{anthro}. Atmospheric Hg^0 removal is approximated

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as a first-order process with rate coefficients k^D_{terra} and k^D_{ocean} defining the rate of wet plus dry deposition of Hg^{II} to terrestrial systems D_{terra} ($= k^D_{terra} \times A_{Hg}$) and to the oceans D_{ocean} ($= k^D_{ocean} \times A_{Hg}$). The resulting mass balance for a single box atmosphere is:

$$\frac{dA_{Hg}}{dt} = W_{atmo} + E_{terra} + E_{ocean} + E_{anthro} - D_{terra} - D_{ocean} \quad (1)$$

Hg in terrestrial systems T_{Hg} exists primarily as Hg^{II} in soils (Hg in vegetation is not well quantified at present, but the limited data available suggest that it is insignificant in mass compared to Hg in soils). The sinks for T_{Hg}, reduction and subsequent evasion of Hg^0 from soils $E_{terra}(= k^E_{terra} \times T_{Hg})$, burial in inland drainages and deltaic sediments $B_{terra}(= k^B_{terra} \times T_{Hg})$, and fluvial export to the oceans X_{terra} ($= k^X_{terra} \times T_{Hg}$), are all first-order processes. The mass balance for the single box terrestrial system is:

$$\frac{dT_{Hg}}{dt} = D_{terra} + W_{terra} - E_{terra} - X_{terra} - B_{terra} \quad (2)$$

where W_{terra} is the constant rate of mercury input to soils from weathering.

In the oceans, G-MCM represents the cycling of both Hg^0 and Hg^{II}, but not mono- and dimethylmercury since they do not contribute significantly to the exchange of Hg between the oceans and atmosphere (Mason and Fitzgerald, 1993). Oceanic mixing and circulation is parameterized according to a multilayer, box-diffusion model calibrated for the oceanic uptake of ^{14}C and cycling of $\sum CO_2$, ALK, DOC, and P (Hudson *et al.*, 1994). Since Hg^{II} sorbs on settling particles in proportion to its concentration, scavenging generates a downward flux out of each layer and a net burial in pelagic sediments B_{ocean}, which depends on the particle flux and the Hg^{II} concentration at the sea bottom. The rate of Hg^{II} reduction to Hg^0 in surface waters R ($= k^R_{ocean} \times O^{surface}_{Hg^{II}}$) is proportional to the amount of Hg^{II} present $O^{surface}_{Hg^{II}}$. The net Hg^0 efflux to the atmosphere E_{ocean} is calculated according to standard equations (Liss, 1983). The mass balance on total Hg in the oceans $O_{Hg}(= O_{Hg^{II}} + O_{Hg^0})$ may be expressed as:

$$\frac{dO_{Hg}}{dt} = D_{ocean} + X_{terra} - E_{ocean} - B_{ocean} \quad (3)$$

G-MCM solves these differential equations (1-3) and others for the ocean interior using a fully implicit solution technique with one-half year timesteps. It was developed for personal computers using Extend™ (Imagine That, San Jose, CA).

3. Model Calibration

Recognizing that the uncertainties in all global Hg budgets are significant, we take MFM as our starting point (Table 1). For each process in the Hg cycle, the rate coefficients are calculated from the modern ratio of its rate to the size of the Hg pool the process draws upon, e.g., $k^D_{ocean} = D_{ocean}/A_{Hg} = 10\ \text{Mmol yr}^{-1}/25\ \text{Mmol} = 0.4\ \text{yr}^{-1}$. We then calibrate G-MCM by forcing our reconstruction of the past to be consistent with the present and with our assumptions about the history of anthropogenic influences on the Hg cycle. Some adjustments to MFM are necessary, however, to account for our different

TABLE I
Modern (*circa* 1990) global Hg cycle fluxes and derived model rate parameters.

	Global Hg Cycle Fluxes (Mmol yr^{-1})			Rate coefficient[a] (yr^{-1})	
Flux/Pool	MFM	Simulation I	Simulation II	Simulation I	Simulation II
D_{ocean}	10	10.0	10.2	0.398	0.398
D_{terra}	15	12.0	13.8	0.482	0.545
$E_{ocean} \approx R$	10	7.5	9.2	0.181[b]	0.218[b]
E_{terra}	5.0	4.7	4.6	0.00094	0.00094
W_{atmo}	—	0.3	0.3	—	—
W_{terra}	—	0.7	0.7	—	—
B_{ocean}	1.0	0.4	0.5	—	—
B_{terra}	—	0.7	0.6	0.000135	0.00012
X_{terra}	1.0	0.8	0.8	0.000165	0.00017
E_{anthro}	10	10	10	—	—
dA_{Hg}/dt	+0.2	+0.4	+0.1	—	—
dO_{Hg}/dt	+0.4	+2.9	+1.2	—	—
dT_{Hg}/dt	+9.4	+6.5	+8.5	—	—

[a] Calculated assuming $A_{Hg} \approx 25$, $O_{Hg^{II}}^{surface} \approx 40$ for 75 m deep surface layer, and $T_{Hg} \approx 5000$.
[b] Parameter shown is k_{ocean}^{R}.

representations of terrestrial and oceanic Hg cycling.

First, MFM did not clearly quantify the inputs of Hg from weathering as required for G-MCM. Fitzgerald (1986) estimated volcanic inputs to the atmosphere W_{atmo} of 0.3 Mmol yr^{-1}. We next assume that Hg from weathering of soils W_{terra} is 0.7 Mmol yr^{-1} in order for weathering to balance MFM's estimate of the current oceanic Hg sedimentation flux. Actual rates of weathering may be 2.5 Mmol yr^{-1} or more (Lindquist, 1991), but adopting this value would require a careful evaluation of geochemical data to determine B_{terra} and B_{ocean}, a task beyond the scope of this paper. Finally, we adjust the relative values of B_{terra} and B_{ocean} in order to obtain unperturbed levels of T_{Hg} that are consistent with modern surface soils, which contain ~5000 Mmol Hg (Lindquist, 1991), and our estimates of cumulative anthropogenic deposition to soils, 900-1000 Mmol.

Our second adjustment involves accounting for mixing into the ocean interior, which is neglected in MFM. We find that dO_{Hg}/dt should be ~3 Mmol yr^{-1} at present given the emissions history assumed below. To accommodate this change in the oceanic Hg budget, we decrease E_{ocean} by 2.5 Mmol yr^{-1} from the MFM budget since D_{ocean} is better constrained by measurements than is E_{ocean} and 10 Mmol yr^{-1} is likely an upper bound on the true D_{ocean} (R. Mason, personal communication). To maintain the atmospheric Hg balance we also decrease D_{terra} by ~3 Mmol yr^{-1}. We refer to the results based on these recalculated parameters as Simulation I (Table 1).

Scavenging by particles is a second process that transports Hg^{II} downward into the ocean interior. MFM estimated a modern flux to the deep ocean (>1000 m depth) of 1 Mmol yr^{-1}. Since the bulk of settling POM has decayed by this depth, the scavenging removal from the surface layer should be considerably larger. If we apply the MFM ratio of Hg:C in oceanic particulate matter (0.6 μg Hg/g C) to current estimates of export production, 10-18 Pg C yr^{-1} (see references in Hudson *et al.*, 1994), a scavenging removal from the surface layer of >30 Mmol yr^{-1} is obtained. Tests with scavenging included in the model indicate that the shape of the Hg concentration profile is sensitive to this process. However, in the presence of mixing, scavenging only causes minor increases in the oceanic Hg uptake rate. Scavenging may become more important when our present representation of the process as an equilibrium sorption reaction is modified to include the kinetics of particle aggregation and settling.

4. Reconstructing Historical Changes in the Global Hg Cycle

Reconstructing historical changes in the global Hg cycle requires that we develop estimates of both the natural, "pretechnological" state of the global Hg cycle and the historical evolution of E_{anthro}. At present, the paleochemical data are too limited to give an independent estimate of the natural conditions. Therefore, in order to estimate the initial state, we assumed that (a) $E_{anthro} = 0$, (b) steady-state conditions prevailed, (c) changes in A_{Hg}, T_{Hg} and O_{Hg} are consistent with model formulations and emissions histories, and (d) modern values of process rate parameters apply throughout the time period, except as discussed below.

For the purposes of this paper, we approximate E_{anthro} as having two components: (1) emissions from gold and silver mining in the Americas and (2) emissions from coal combustion, municipal waste incineration, and other industrial activities (Figure 1). Hg con

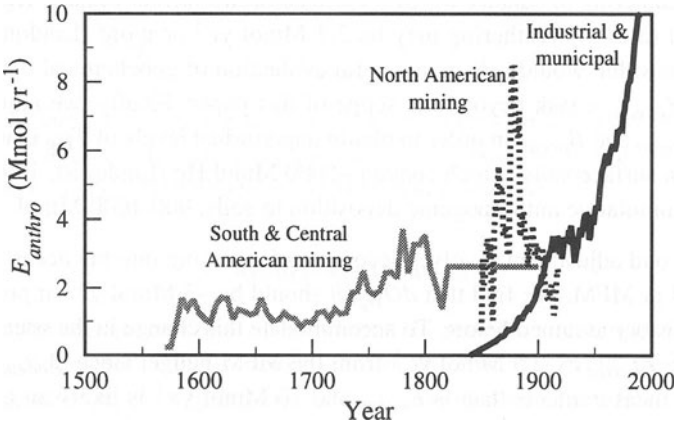

Fig. 1. Historical anthropogenic Hg emissions.

sumption in precious metal mining was substantial from about 1570 to 1920 and about 60 percent of the total amount of Hg consumed in the *patio* process may have been

emitted to the atmosphere (Nriagu, 1994). Since much of the industrial and municipal Hg emissions currently derive from coal combustion (Nriagu, 1989), we approximate their historical evolution by assuming they have increased in constant proportion to global CO_2 emissions from coal combustion (Keeling, 1990; Marland 1990), i.e., 4.17 Mmol-Hg Pg-C^{-1}. The surprising implication is that mining emissions at the height of the North American gold rush, 11 Mmol yr^{-1}, may have been greater than the modern anthropogenic emissions rate of 10 Mmol yr^{-1}

The assumptions of Simulation I imply that the "pretechnological" levels of Hg in the environment were somewhat higher than MFM suggest. Due to mixing into the ocean interior, $O^{surface}_{Hg^{II}}$ increased by only 54% rather than 200% as in MFM, implying that currently about 36% of the oceanic and 60% of the total Hg emissions are anthropogenic in origin. At present, about 44% of the total emissions come directly from anthropogenic activities. The modern D_{terra} is 2.8 times the pretechnological flux, similar to the ratio of 3 proposed by MFM. An important assumption in calibrating G-MCM is the size of the T_{Hg} pool. As represented here, a ~20% increase in E_{terra} is obtained. If terrestrial systems have smaller, more rapidly cycled pools of Hg, a greater terrestrial response to anthropogenic emissions would be expected.

TABLE II

Reconstructed historical global Hg cycle fluxes (Mmol y^{-1}) and pools (Mmol)

	Pre 1890	Pretechnological (*ante* 1570)		Preindustrial (*circa* 1800)[b]	
Flux/Pool	MFM	Simulation I	Simulation II	Simulation I	Simulation II
D_{ocean}	3	3 6	6 1	5 7	9 4
D_{terra}	5	4 3	4 2	6 9	6 4
E_{ocean}	3	4 8	6 2	5 0	8 1
E_{terra}	4 7	3 8	3 7	4 1	3 9
B_{ocean}	0 3	0 5	0 5	0 5	0 5
B_{terra}	0 0	0 6	0 5	0 6	0 5
X_{terra}	0 3	0 67	0 7	0 7	0 7
A_{Hg}	8	9 0	15 3	14 4	23 5
$O^{surface}_{Hg^{II}}$	13 5[a]	25 9	28 4	27 7	37 1
T_{Hg}	—	4070	3980	4320	4190

[a] Value normalized to 75 m deep surface layer, equal to 18 for 100 m as in MFM (1994)

[b] E_{anthro} = 3 5 Mmol y^{-1}

With these extrapolated initial conditions and emissions histories, we use G-MCM to reconstruct the expected evolution of the global Hg cycle and of atmospheric deposition to terrestrial systems D_{terra} (Figure 2). Unlike CO_2, there exist no reliable measurements of atmospheric Hg concentrations prior to the late 1970's nor any paleochemical record of atmospheric Hg concentrations. At present, the best indicators of the historical changes in the Hg cycle consist of the records of deposition over the past few centuries preserved in lake sediments (e.g., Swain *et al.*, 1992) and bogs (Benoit *et al.*, 1994). To facilitate

comparison with the model results, figure 2 also shows the changes in Hg deposition rates relative to the 1800-1850 average inferred from sediment Hg accumulation rates measured in seven lakes in the upper midwest of the United States (Swain *et al.*, 1992). While simulation I does predict the observed generally increasing rates of deposition from pretechnological to modern times, it does not match the details well. Most notably, it predicts modern deposition rates that are 1.8-times "preindustrial" (*circa* 1800), as compared to the observation of 3.7-times higher rates. In addition, the predicted peak due to North American mining centered at about 1880 is too prominent. The ratio of modern/pretechnological values of D_{terra}, 2.7, is closer to the observed modern/preindustrial ratio. The two would be more consistent if the impact of Hg mining emissions during the 1800's was moderated.

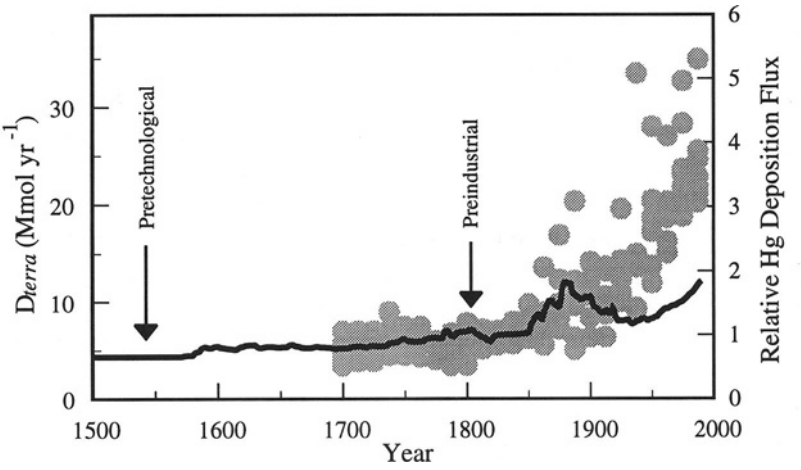

Fig. 2. Simulation I: modeled changes in the global average terrestrial Hg deposition compared to Hg deposition recorded in lake sediments. Historical data are cores from 7 lakes normalized to mean modern/preindustrial ratio for each lake (Swain *et al.*, 1992).

The appropriate way to compare Hg deposition at a particular site to global averages needs to be carefully considered. Variability in deposition rates around the world reflects both the effects of proximity to regional and hemispheric sources as well as the differences in atmospheric chemistry and precipitation volume that influence deposition fluxes. For now, we can only hope that the relative change at a particular site removed from regional sources should compare well to the relative change in global average deposition. (This may not be the case, if as we argue below, changes in atmospheric chemistry may also influence deposition.) This approach has been used by Engstrom *et al.* (1994), who found that modern Hg accumulation rates in the sediments of two Alaskan lakes were 2.5-times the 1800-1850 level and suggested that about one-third of the deposition to the midwest was regional in origin.

The changes in atmospheric chemistry over the past century due to anthropogenic emissions of particles, SO_2, and oxidants also have the potential to influence the global transport of Hg (Munthe and McElroy, 1992). It is likely that these changes have altered

the atmospheric residence time of Hg and possibly the relative rates of deposition to the oceans and to land, where most air pollutants are generated. A detailed consideration of the changes in atmospheric chemistry is beyond the scope of this paper, but we wish to examine how such changes might affect deposition histories. First, we note that changes in the atmospheric residence time will affect A_{Hg}, but not D_{terra} or D_{ocean}, as long as the ratio k^D_{terra}/k^D_{ocean} remains constant. Changes in the relative values of k^D_{terra} and k^D_{ocean} will, however, significantly alter the historical reconstruction since different amounts will accumulate on land and in the oceans.

To examine this question using G-MCM, we hypothesize that k^D_{terra} has increased by a factor of two since 1840, in parallel with coal combustion rates, while k^D_{ocean} has remained nearly constant (Simulation II). In this case, the modern dO_{Hg}/dt is less than for Simulation I (Table I), a change requiring readjustment of the global Hg budget as above. All modern fluxes in Simulation II are close to MFM values. However, pretechnological A_{Hg} and $O^{surface}_{Hg}$ are only 39% and 45% below their respective modern levels and most surprisingly both are within 10% of modern by 1800. About one-third of E_{ocean} and 58% of total emissions is anthropogenic in origin, with E_{anthro} currently accounting for 42%. The modern/pretechnological and modern/preindustrial ratios of D_{terra} are 3.3 and 2.2 respectively, which agree with the sediment records more closely than Simulation I does. Most notably, the overall increase from preindustrial conditions to the present is greater and the maximum at 1880 is lower than current rates of deposition. Although this historical reconstruction does not prove that the hypothesized changes happened, it does suggest that anthropogenic influences on deposition processes should be considered in any historical reconstruction of the global Hg cycle. Changes in k^D_{terra} are likely to vary significantly by region and could contribute to the observed decreases in recent deposition to the upper midwest of the United States (Benoit *et al.*, 1994).

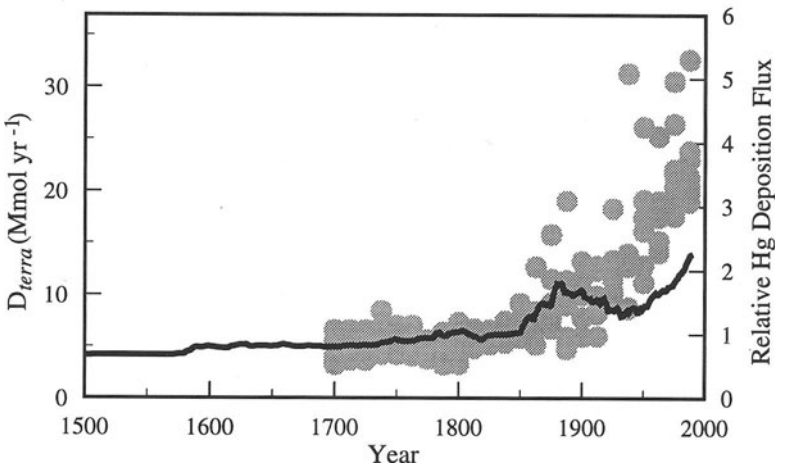

Fig. 3. Simulation II compared to Hg deposition inferred from lake sediments as in Figure 2.

5. Conclusions

We have developed a mechanistic model of the global Hg cycle (G-MCM) and calibrated it using recent estimates of global Hg fluxes and reconstructions of anthropogenic emissions history. Our results suggest the following conclusions:

(a) Global Hg budgets should account for transport of Hg into the ocean's interior. Current transport rates depend on the history of anthropogenic influences on the Hg cycle.

(b) At present, direct anthropogenic emissions account for about 40% of the total Hg input to the atmosphere. An additional 20% results from past anthropogenic emissions being reemitted from oceans and terrestrial systems.

(c) Assuming that changes in Hg emissions alone have caused the observed variations in Hg accumulation rates in lake sediments leads to simulations that do not fit the observations well. An increase in terrestrial relative to oceanic Hg deposition over the period 1850-1990, as might be caused by anthropogenic emissions of SO_2, oxidants, and particles, improves simulations of terrestrial deposition fluxes.

(d) Conversely, a recent decrease in other air pollutants, especially particulate matter, for North America could explain the apparent conflict between increasing atmospheric Hg and apparent decreases in Hg deposition since 1960 (Benoit *et al.*, 1994).

Acknowledgments

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ATMOSPHERIC MERCURY AND TRACE ELEMENTS IN THE REGION OF ALTA FLORESTA IN THE AMAZON BASIN

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Abstract. In the early 1980's the Amazon region in the North of Brazil was the scene of the most intense gold rush in the history of Brazil. Metallic mercury (Hg) in gold mining activities is used to amalgamate particulate gold. The other sources of Hg emissions in Amazonian are tailing deposits and biomass burning of tropical forests and savannas. Total Hg concentrations in the urban area of Alta Floresta ranged from 20 to 5800 ng/m^3. Indoor total Hg concentration in gold shops ranged from 250 to 40600 ng/m^3. Particulate Hg accounts for 5 to 20% of total Hg in Alta Floresta. Through Factor and cluster analysis it was obtained a pattern of relationships between total Hg, fine and coarse mode particulate Hg, Pt, Pb, Ag and several other trace elements associated with the amalgamation process. A clear correlation was also observed with the fine mode biomass burning aerosol and coarse mode soil dust.

1- Introduction

In recent years gold mining and gold prospecting areas in Brazil have become an important issue. Gold mining created a great diversity of problems of an economic, political, social and, above all, environmental nature. In the past 15 years gold mining activities in Amazonia have been responsible for the release of about 1500 t Hg. Metallic Hg in gold mining activities is used to amalgamate particulate gold. During this process, losses of Hg to the environment occur at two distinct stages. Through manipulation of metallic Hg in the separation of gold from gravel, Hg is lost to rivers and soils. Also large emissions occur through amalgam burning. The other source of Hg emissions is the tailing deposits left by gold miners near gold fields areas. Recently, biomass burning in tropical forests also seems to have contributted significantly to Hg release to the atmosphere (Veiga *et al.*, 1994). For the production of each kilogram of gold between 1 and 2 kilos of Hg are emitted into the environment (Pfeiffer and Lacerda, 1988; Pfeiffer *et al.*; 1989, Lacerda and Salomons, 1992). Gold production has been decreasing in Amazonia since 1989. About 70 t Hg are released regionally, contributing to the global burden, and 50 t are lost to the atmosphere (Hacon, 1991; Lacerda and Salomons, 1992).

In the atmosphere more than 95% of Hg occurs in a volatile gaseous form, Hg° (Lindqvist, 1991; Lindqvist and Rhode, 1985). The remaining non-elemental form is associated in aerosol particles and is more water soluble (Schroeder *et al.*, 1991). The residence time for Hg° is long, with current estimates ranging from 0.7 to 2.0 years (Lindqvist, 1991). Estimates of gaseous Hg concentrations in air range from 1 to 50 ng/m^3 in urban areas, and 1 to 5 ng/m^3 in remote rural areas (Fitzgerald, 1986;

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Lindqvist, 1991).

Mercury emissions in Amazonia occur in rural and urban areas. Gold mining generally occurs far from urban areas and the first burning of amalgam almost always takes place where gold is mined. A second amalgam burning (also called "bullion") occurs in general at the gold shops in the urban areas. The Amazon Basin contains the world's largest rain forest, covering an area of about 4 x 10^6 Km^2. This region has intense convective activity, resulting in rapid vertical mixing of biogenic gases and aerosols to high altitudes where they are transported over long distances with a consequent impact on the global tropospheric chemistry (Artaxo *et al.*, 1988, 1990). The biomass burning period lasts from August to the end of September and coincides with the peak period of gold mining activities. The concentration of ozone during this period increases from the background level of 10 to 25 ppbv to values as high as 80 to 120 ppbv (Kaufman *et al.*, 1992). The aerosol particle loading increases from a background value of 10 to 20 $\mu g/m^3$ to values as high as 700 $\mu g/m^3$. A large amount of fine mode aerosol particles (d_p<2μm) are released into the atmosphere, altering the atmosphere chemical composition (Artaxo *et al.*, 1988, 1995). These particles may play an important role in the transport of particulate Hg over long distances since particles between 0.1 and 1 μm (the accumulation mode) have a long atmospheric residence time (Xiao *et al.*, 1991).

The municipality of Alta Floresta in the north of Mato Grosso state in the Amazon Basin was created in 1979. The gold rush of the 1980's replaced rural development with gold mining activities. The urban area of Alta Floresta contains about 25 gold-dealing shops, where 25 t of gold are purified and commercialized annually. The percentage of Hg in the amalgam brought into the gold shops varies between 2 to 10% of the gold mass. Between 0.5 and 2.5 t Hg is emitted annually in the urban area of Alta Floresta. It should be observed that gold dealers in Alta Floresta do not use any kind of air pollution control equipment or any kind of recovery system in the burning process at the gold shops. Figure 1 shows a map of South America with the location of the urban area of Alta Floresta.

Fig. 1 - Map of South America with the location of the Amazon Basin and the urban area of Alta Floresta.

The objective of this work is to characterize total and particulate atmospheric Hg in the urban area of Alta Floresta. Ambient and indoor atmosphere was studied. The association between Hg and particulate sources such as soil dust and biomass burning aerosol particles was also studied. Simultaneous determination of trace element concentrations allows the study of the mechanisms of emission and atmospheric Hg adsorption on existing aerosol particles. The chemical characterization of particles released during the amalgam burning process in gold shops was performed. Indoor Hg and trace elements concentrations were obtained in several gold shops. Through the use of multivariate statistical analysis, it was possible to study the relationship between total and particulate Hg and soil dust and biomass burning components.

2 - Experimental Methods

The atmospheric characterization of Alta Floresta was carried out during two fieldwork campaigns. They occurred in August and September 1992 and 1993, both during the peak of the biomass burning season. This area was chosen because Alta Floresta is one of the most important gold trading centers in Amazonia, and has adequate infrastructure. Alta Floresta suffers strong impact from biomass burning, exposing its inhabitants to high loading of aerosol particles. Important health effects due to the high aerosol concentrations in the region, were observed.

Alta Floresta is located in the Northern part of the Mato Grosso state. Its climate is typical of the Amazon Basin, hot, humid and tropical with temperatures ranging from 23 to 37^0 C, with heavy rainfall during the wet season. The gold production is much higher in the dry season than in the wet season because the heavy rains make it difficult to work along the rivers. The dominant wind direction in the wet season is SE and in the dry season is NW (Farid, 1992).

In this study two sampling programs were carried out in ambient (outdoors) and indoor (at the interior of gold shop dealers). For the establishment of the indoor sampling program, 25 gold shops were surveyed. The survey covers microenvironmental conditions such as internal ventilation, use of adequate exhaust and cowl, existence of chimney, interior building construction, as well as the amount of gold sold daily. Four gold dealers were selected for the sampling program. The gold shops represent a non-point source of Hg emissions, because during the roasting of the amalgam, the Hg emissions are dispersed to the atmosphere through the doors and windows. In the ambient sampling program, three sites were selected taking into account wind direction, the location of the gold dealers and existing infrastructure such as power supply. In both sampling programs, total atmospheric Hg and fine and coarse mode aerosol particles were collected for both indoor and outdoor. The aerosol particles were analyzed for particulate Hg, mass concentration, soot carbon and 25 trace elements.

The sampling campaign of 1992 took place during the first two weeks of September. Three outdoor sites were chosen. The "Gaspar" site is in the middle of the urban area about 500 m from the gold shops. The second site, called "Imperial" is located about 700 m from the gold dealer shops, also near the area of the Hg emissions. The third site is outside downtown and was called "Hotel", about 1500 m from the gold dealer's shops, inside primary jungle. The indoor program in 1992 selected four gold dealers that represent the main characteristics of the gold dealers shops in the urban area. The

samples were collected twice a day for a period of 4 hours each from Monday to Friday. Total Hg and aerosol particles were sampled at a height at least 2.0 m above the ground. The average daytime sampling period was 6 hours and nighttime about 8 hours. During the dry season, relative humidity usually ranged from 70 to 93%, temperatures varying from 25 to 37 °C.

In the 1993 sampling campaign two ambient stations were relocated due to logistic difficulties with power supply. The 1992 "Floresta" site was transferred to the nearby control tower of the airport, 2 km from the gold dealing shops. This 1993 site is called "Airport", and is located at about 500 m from the 1992 "Floresta" site. The 1992 "Imperial" sampling site was discontinued. A new sampling site in the 1993 campaign was located downwind in relation to the gold shops, and is called "Padres" site. This site is outside the urban area, in a primary forest environment, about 3 km downwind from the Hg emissions sources.

In this study, total (total atmospheric Hg includes both particulate and vapor Hg) and particulate Hg were measured. Atmospheric total Hg was sampled in two successive bubble traps containing 5 % $KMnO_4$ in sulfuric acid 2 N (EPA 1983). The flow-rate of about 1 liter per minute was controlled by a rotameter. Trapping efficiency is better than 95%. Acid washed polyethylene vessels were used to store samples. Samples were frozen after sampling. The analysis was performed using cold vapor atomic absorption spectrometry (CVAAS), about one week after sampling. The detection limit of the analytical procedure was 10 ng/m^3 for a period of 4 hours sampling. Accuracy and precision for CVAAS Hg determination was estimated as 10%. Volumes were measured with precision mass flowmeters and calibrated rotameters.

Fine and coarse mode aerosol particles were collected using stacked filter units (SFU). SFU was fitted with an inlet, with a 50% cutoff diameter of 10μm. Samples for total and particulate Hg were collected in parallel. Elemental concentrations were measured by Particle-induced X-ray emission (PIXE) (Artaxo and Orsini, 1987). Elemental concentrations for 25 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Se, Sr, Zr, Pb, Pt, Ag, and Hg) were determined. A nuclear accelerator (LAMFI - Laboratório de Analise de Materiais por Feixes Iônicos) was used for the PIXE analysis. Detection limits are typically 5 ng/m^3 for elements in the range $13<Z<22$ and 0.4 ng/m^3 for elements with $Z>23$. The fine and coarse mode aerosol mass concentrations were obtained through gravimetric analysis of the filters. Black carbon concentration was measured by a reflectance technique using a photometer.

The determination of particulate Hg was performed by PIXE and also by cold vapor atomic absorption spectrometry (CVAAS). The detection limit for CVAAS particulate Hg is 3 ng/m^3. Total Hg was determinated by CVAAS. The 10^{-6} Torr high vacuum in the PIXE chamber allows this method to measure only the non-volatile particulate Hg component. An intercomparison of CVAAS and PIXE was performed, and particulate Hg CVAAS have a very good correlation with the PIXE results. The regression results between the two techniques have a r^2= 0.9998, with a regression equation of Hg(CVAAS)=(2.619±0.009) Hg(PIXE) for n=40 samples.

In order to compare total Hg concentrations at various sites, various statistical tests were performed. The analysis of variance F-Test was used to compare the means and standard deviation at the several sites. Also the Kolmogorov and Cramer-von Mises tests

were used to test the frequency distribution. In order to separate the different components regulating Hg, trace elements and aerosol mass, principal factor analysis (PFA) was used. In order to analyze the relationship between the different samples, hierarchical cluster analysis was used.

3 - RESULTS AND DISCUSSION

It is important to emphasize that this is the first study of atmospheric Hg in the Amazon basin that measures particulate Hg as well as total atmospheric Hg. Also trace elements were measured simultaneously with total and particulate Hg. The high loading of fine particles from biomass burning and coarse soil dust particles makes a large surface area for vapor Hg to condense on. High ozone concentrations, water vapor and solar radiation further enhance the vapor Hg condensation on existing aerosol particles. A large number of samples (249) were analyzed for total Hg during the period 1992-1993. For ambient samples, total Hg results for all sites from the 1992 and 1993 sampling campaigns is presented. For the indoor samples, results for total and particulate Hg, trace elements, soot carbon and aerosol mass concentration are presented.

Table I shows results for total Hg (in ng/m^3) in ambient samples. Using the F-test it is possible to observe that there is not a significant difference between the means for the 1992 measurements of the Gaspar, Imperial and Floresta sites. This rather uniform concentration between the three stations can be explained by the dispersion of Hg vapor and fine mode particles beyond the borders of the urban area. The predominant wind directions during the sampling period were SW, S and SE with a low average wind-speed of 2 m/sec, and long windless periods. However, no correlation was found between total Hg concentrations and meteorological parameters.

Table I - Measurements of total Hg in ambient samples in Alta Floresta, Amazon Basin. Total Hg in ng/m^3. Daytime and nighttime samples included.

Year & Site	N	Arithmetic Mean	Std. Dev.	Geometric Mean	Min.	Max.
1992						
Gaspar	27	882	770	591	60	3090
Imperial	15	677	840	404	30	3560
Floresta	21	640	740	309	10	3050
1993						
Gaspar	30	521	1030	262	20	5790
Padres	31	758	1281	331	20	4850
Aeroporto	29	211	180	163	50	810

(*) N = number of samples.

The values for 1993 are significantly lower than the measurements for 1992 for the Gaspar sampling site. This can be attributed to reduced local gold production in 1993. The Airport station shows statistically significant lower total Hg concentrations compared to the other stations. This can be explained by the wind direction patterns, since the station was upwind for most of the sampling time.

Figure 2 shows the Box-Plots of ambient total Hg for the three sampling sites in 1992, and Figure 3 shows the Box plots for samples collected in 1993. Day and night samples were averaged separately. Median, 5%, 25%, 75% and 95% percentiles are shown. Outlier values were excluded from the plot for a better graphic representation. Using the F-test to compare the means there was no significant difference between nocturnal and diurnal measurements. For the 1993 Gaspar data, nocturnal values are two times higher than diurnal values in terms of geometric mean. This could be caused by variations in the atmospheric inversion layer (mixing layer) over the Amazon Basin, which during the day is about 800 m high and at night time collapses over the forest canopy (Artaxo *et al.*, 1990). It can be observed from Figures 2 and 3 that the two forested sites, 1992 "Hotel" and 1993 "Padres" both shows higher Hg concentrations during daytime. Both sites are located under the forest canopy. The humid forest with a very high leaf index and aerial surface certainly affects the airborne Hg concentrations in unknown ways.

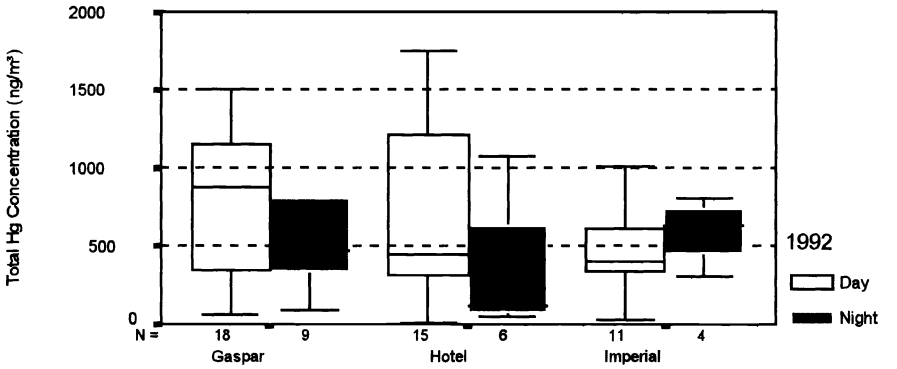

Fig. 2 - Box-Plots of ambient total Hg for the three sampling sites in the 1992 sampling campaign. Day and night samples were averaged separately. Median, 5%, 25%, 75% and 95% percentiles are shown.

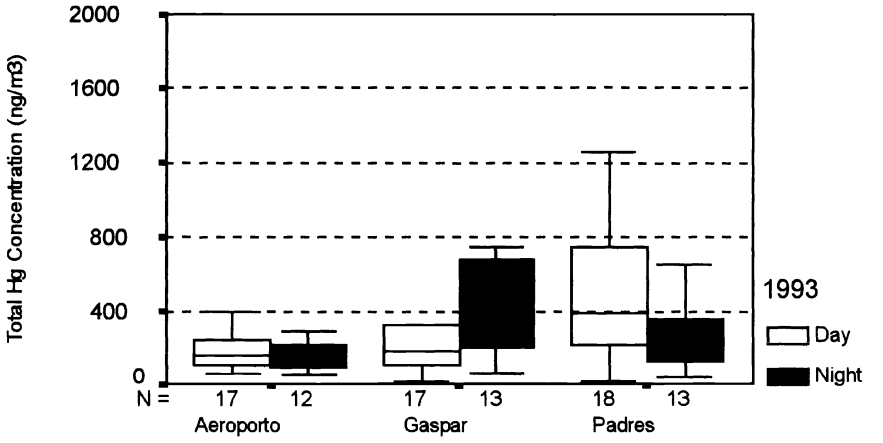

Fig. 3 - Box plots of ambient total Hg for the three sampling sites in the 1993 sampling campaign. Day and night samples were averaged separately.

Total Hg was also measured in the interior of gold dealers' shops. Table II shows data for total Hg measured in four different gold shops. It is important to emphasize that due to the hot climate, these shops have good ventilation, with large and open windows and doors. The amount of Hg present in the gold to be commercialized by each gold shop is directly correlated to the average Hg concentration in each gold dealer shop. The shop coded "D" is the largest gold dealer in the region, showing also the highest total Hg concentrations. The other three shops show similar total Hg concentrations.

The very high airborne particulate concentrations (up to 700 $\mu g/m^3$) facilitate the adsorption of vapor-phase Hg in the surface of existing aerosol particles emitted during biomass burning. These aerosol particle loads also suggest that atmospheric Hg deposition could be related to regional processes due to the practice of burning of the forest. Associated to these biomass burning aerosol particles is high ozone concentrations and non-methane hydrocarbons that are known to enhance the Hg oxidation process (Iverfeldt, 1986).

Table II - Measurements of total Hg in gold dealers shops in Alta Floresta, Amazon Basin. Total Hg in ng/m^3.

Year site (*)	N	Arithmetic Mean	Arithm. Std. Dev.	Geometric mean	Min.	Max.
1992						
A	5	1688	633	1607	1150	2730
B	7	1854	1551	1112	170	4250
C	5	2530	2954	751	70	7280
D	9	19120	8750	17510	10970	32080
1993						
A	16	1133	761	925	250	3050
B	12	4272	3587	3125	780	11040
C	15	3241	3234	1881	560	10420
D	17	7255	10781	3401	990	40590

(*) Sites A, B, C, D, are the four gold shops selected for the indoor measurements. N is the number of samples.

Figure 4 presents the Box-Plots for fine, coarse and inhalable Hg in the particulate phase for the four gold shops selected in 1993 in Alta Floresta. Concentrations of inhalable particulate Hg of about 100 ng/m^3 are observed. In the gold dealers A and C, almost all particulate Hg is present in the coarse mode. For the shops B and D, fine mode particulate Hg accounts for 30 to 50% of inhalable Hg.

Table III shows the elemental composition of particulate matter and total Hg in gold shops in Alta Floresta, in addition to fine mode soot carbon concentration (Soot), FPM (fine mode aerosol mass concentration), CPM (coarse mode aerosol mass concentration), IPM (inhalable aerosol mass concentration). After the symbol for each element, F stands for fine mode and C coarse mode. Very high concentrations of inhalable particles (IPM) were observed, with values up to 951 $\mu g/m^3$. A large amount of coarse mode particles were also present (average of 260 $\mu g/m^3$). In the fine mode, elements associated with

biomass burning particles (S, P, K, Ca, Zn, soot and others) showed high concentrations. In the coarse mode, soil dust related elements (Al, Si, Ti, Mn, Fe) predominates. Coarse mode Fe concentration alone is 17μg/m^3. For both aerosol fractions it is possible to observe a significant presence of elements such as Ag, Pt, and Au. Gold appears in the aerosol phase at concentrations of 50 ng/m^3 in the fraction bellow 10 μm. Pt appears at levels of 56 ng/m^3. Particulate Hg in the fine mode appears as 31 ng/m^3 and in the coarse mode as 72 ng/m^3. These are high values, given that these particulate Hg values were obtained with the PIXE technique, which measures only non-volatile Hg in the particulate phase.

Table III - Elemental composition of particulate matter in gold dealer's shops in Alta Floresta. Concentrations in ng/m^3 (*)

Fine Mode	Arithmetic Mean	Standard Deviation	Coarse Mode	Arithmetic Mean	Standard Deviation
FPM	84100	54000	CPM	260200	180100
Al_F	2342	1628	Al_C	723	597
Si_F	2625	1471	Si_C	4037	2913
P_F	97.4	56.1	P_C	128	46
S_F	930	569	S_C	308	115
Cl_F	221	177	Cl_C	469	502
K_F	1350	945	K_C	1863	1930
Ca_F	345	175	Ca_C	3750	3000
Ti_F	110	64.1	Ti_C	1379	1071
V_F	8.30	3.93	V_C	78.4	79.5
Cr_F	-	-	Cr_C	79.1	50.0
Mn_F	11.10	9.15	Mn_C	42.5	36.3
Fe_F	1217	684	Fe_C	17400	13400
Ni_F	9.50	2.80	Ni_C	32.7	23.6
Cu_F	35.0	34.1	Cu_C	229	208
Zn_F	32.3	21.3	Zn_C	108	95
Se_F	37.3	97.9	Se_C	33.3	41.3
Br_F	36.3	27.6	Br_C	-	-
Rb_F	16.2	11.7	Rb_C	18.6	12.2
Sr_F	4.64	6.36	Sr_C	18.8	11.8
Zr_F	7.72	4.80	Zr_C	54.0	39.5
Ag_F	104	89	Ag_C	-	-
Pt_F	6.15	0.91	Pt_C	49.8	37.7
Au_F	20.9	28.5	Au_C	28.5	17.4
Hg_F	31.2	32.4	Hg_C	72.4	57.5
Pb_F	101	187	Pb_C	55.1	32.1
Soot	12581	6940	-	-	-

(*) See text and footnote of Table IV for description of each variable. After the symbol of each element, F means fine mode aerosol and C means coarse mode. Only values above the detection limits were used in calculating average concentrations.

Table IV shows the factor loading matrix of the factor analysis performed in the fine and coarse mode aerosol samples. From the original 23 variables that were measured in all the samples, five factors were obtained. These five factors explain 85 % of the data variability. The first factor represents soil dust particles with the presence of the coarse fraction Ti, Al, K, Fe, Ca, Si, and CPM. Fine mode iron and titanium are also present in this factor. Coarse mode gold and coarse mode Hg are strongly present in this factor. This indicates that coarse Hg has a component of resuspended contaminated soil. The second factor with high loading for FPM, soot, fine potassium and fine chlorine represents fine mode biomass burning aerosol. Also fine mode Zn contributes to this factor, as expected. The third factor has a high loading for fine mode S, Ca, Fe and Ti, with smaller participation of fine Zn and fine K. This represent a second biomass burning component in the atmosphere of Alta Floresta. The split in different biomass burning components with different elemental composition was also observed in other studies (Artaxo *et al.*, 1990, 1994). The Fourth factor has high loading for fine mode Hg, Pb and Zn. Also in this factor it is possible to observe coarse Hg and coarse Au. Fine Cl is present in this factor. It represents the fine mode Hg component associated with the amalgamation process in the gold dealer shops. The presence of fine Zn and Cl, tracers for biomass burning aerosol suggest the possibility of condensation of vapor of fine Hg particles in the surface of existing biomass burning aerosol particles. The last component has high loading for total Hg, with some participation of fine mode Pb. It is worth stressing the strong relation that Pb has with all the three Hg components: fine, coarse and total. The results in this table point to the relationship between Hg with the two major aerosol sources in the Amazon Basin: biomass burning and soil dust emissions.

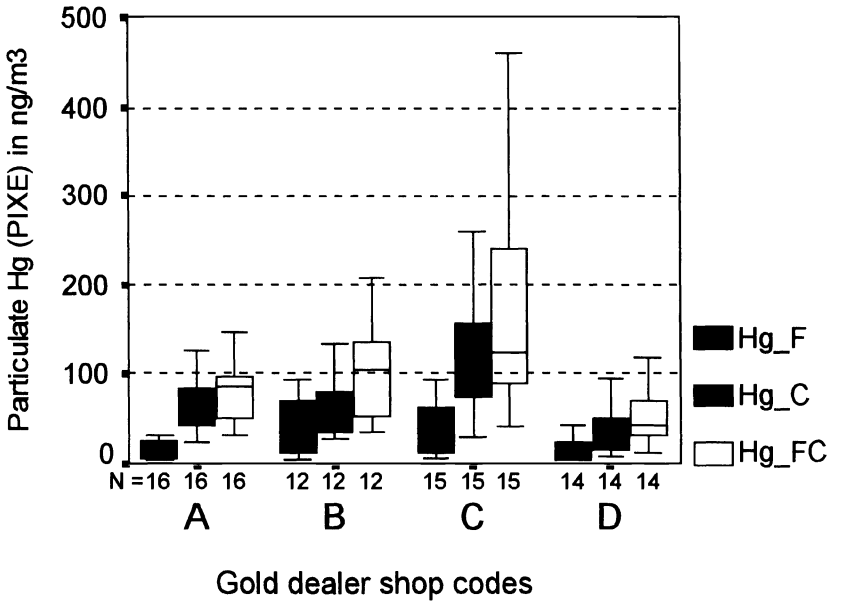

Fig. 4 - Box plots for fine, coarse and inhalable Hg in the particulate phase for the four gold shops selected in 1993 in Alta Floresta. Hg_F is the fine mode particulate Hg, Hg_C is the coarse mode particulate Hg, and Hg_FC is the inhalable particulate Hg concentration.

Table IV - Factor analysis results for Alta Floresta gold dealer's shops. VARIMAX rotated factor loading matrix. Total Hg, aerosol mass, fine and coarse particulate Hg and fine and coarse trace element data were included in the factor analysis. (*)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Coarse Soil Dust	Biomass Burning	Fine Sulfur Calcium	Fine Hg, Zn and Pb	Total Hg
Ti_C	0.96	0.18	-	-	-0.10
Al_C	0.96	0.11	0.11	-	-0.13
K_C	0.95	0.14	-	0.10	-
Fe_C	0.94	0.18	-	-	-0.12
Ca_C	0.94	-	-	0.12	-
Zn_C	0.94	0.13	-	-0.10	-
Si_C	0.86	0.10	0.20	-	-
Pb_C	0.76	0.25	0.27	-	-
Au_C	0.74	0.12	-	0.36	-
CPM	0.71	-	0.20	0.14	-0.28
Hg_C	0.70	0.13	-	0.47	-
FPM	0.28	0.93	-	-	-
Soot	0.16	0.91	0.17	-0.11	-
K_F	0.17	0.89	0.33	-	-
Cl_F	0.14	0.82	-0.15	0.33	-
S_F	-	0.28	0.85	0.16	0.15
Ca_F	0.38	-	0.80	0.15	-
Fe_F	0.59	0.11	0.63	-0.19	-0.29
Ti_F	0.57	0.29	0.57	-0.12	-0.33
Hg_F	0.12	-	-	0.91	-
Zn_F	-	0.49	0.37	0.58	-
Pb_F	-	-	0.18	0.53	0.49
Hg_T	-0.10	-	-	-	0.88

(*) After each element, **F** and **C** mean fine and coarse mode aerosol. Hg_T is the total mercury concentration. Eigenvalues smaller than 0.1 are not showed.

In order to investigate the relationship between Hg and the other elements, cluster analysis was employed. A dendrogram was constructed for the cluster analysis of 57 aerosol samples collected in the interior of gold dealer shops in Alta Floresta. A first group of elements (coarse Ti, Fe, Al, Zn, K, Ca, Si, Pb, CPM, Au, and fine Ti and Fe) was observed to characterize soil dust particles. The presence of coarse Au and Pb in this group shows the association between the soil dust component and the amalgamation process in gold dealer shops. The second group of variables are FPM, soot and fine K and Cl, representing the biomass burning component. A third group shows the presence of total Hg, fine and coarse Hg, fine mode S, Ca, Zn and Pb. This shows that in terms of similarity, the three Hg components are very close to each other. This component also contains biomass burning related elements (fine S, Ca, Zn). Both, factor and cluster analysis indicate the relationship between atmospheric Hg and the two main aerosol components in the Amazon basin: biomass burning and soil dust. Coarse Pb and Au are associated with the coarse soil dust component. In the factor analysis, coarse Hg is also present in this component, as well as in the fine Hg, Pb and Zn factor (factor 5).

4 - CONCLUSIONS

Very high total Hg concentrations of up to 5790 ng/m^3 at ambient sites and up to 40590 ng/m^3 in gold shops were measured The total Hg measurements in Alta Floresta suggest a high environmental exposure for the urban population Mercury present in the coarse mode aerosol particles (2 0<d_p<10μm) accounts for about 70 % of inhalable particulate Hg This coarse mode particulate Hg is associated with soil dust particles The fine mode particulate Hg is associated with the fine mode biomass burning component, probably because of the condensation of vapor Hg in existing fine mode aerosol particles The residence time of this fine mode component is several weeks so that it can be transported over thousands of kilometers outside the Amazon basin

Through factor and cluster analysis it was possible to determine a pattern of relationship between total Hg, fine and coarse mode particulate Hg, Pt, Pb, Ag, and other elements associated with the amalgamation process The very large fine mode aerosol loading from biomass burning, together with high ozone levels, solar radiation and humidity favors the conversion between vapor Hg and particulate Hg in the Amazon basin During the dry season, the soil dust aerosol load in the atmosphere in urban areas in the Amazon basin is very high Soil dust generated near gold shops are contaminated with Hg over the last decade because of dry and wet deposition Due to the high convection mechanisms in tropical regions, this Hg-enriched soil dust can be transported over long distances Further studies on these processes are necessary

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OVERVIEW OF THE FLORIDA ATMOSPHERIC MERCURY STUDY (FAMS)

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Abstract. This manuscript presents a general overview of the Florida Atmospheric Mercury Study (FAMS) its objectives, its spatial design, and its overall methodologies FAMS was initiated in May 1992 with the goal of developing field collection and laboratory analytical protocols for characterizing Hg in rainfall (wet-only and bulk), atmospheric aerosols, and total gaseous Hg (TGM). FAMS now comprises a network of 7 operational stations, with 2 additional stations scheduled to become operational by the end of 1994 Preliminary results for FAMS, which will continue collecting deposition samples through December 1996, are the subjects of other manuscripts in this volume (Gill et al , Landing et al , and Guentzel et al) Results to date suggest that regional deposition in south Florida is driven by large-scale regional or hemispheric processes as opposed to local emission/deposition processes Deposition is seasonally variable, with fluxes 4- to 6-fold higher during April-September compared with October-March The seasonal difference is fluxes is driven both by concentration differences (2- to 3-fold) and differences in rainfall depth

1. Introduction

The discovery of high levels of mercury in Florida largemouth bass over the past several years has sparked considerable interest in Hg contamination of Florida waterways. Recent surveys of Hg concentrations in fish collected in lakes and streams throughout Florida indicate widespread contamination in three fundamentally different types of systems: (1) oligotrophic, softwater seepage lakes with low or no acid neutralizing capacity; (2) riverine systems characterized by high concentrations of DOC, and (3) the Florida Everglades, which is the largest freshwater marsh system in the United States. The occurrence of high concentrations of mercury in fish in the Everglades is particularly striking given its occurrence across a large gradient in hydrologic, trophic, and surface water chemistry conditions.

Depending on the aquatic system affected, a number of different mechanisms may be hypothesized as responsible for the occurrence of mercury in fish in Florida, including (1) a natural consequence of freshwater marshes underlain by organic-rich deposits; (2) altered cycling and release of mercury due to hydrologic alterations; (3) surface and atmospheric releases of mercury related to agricultural practices; (4) relatively unusual surface water geochemistry that may affect mercury cycling, including high SO_4^{2-} concentrations; and (5) altered nutrient cycles. None of these mechanisms is universally applicable to all the affected systems in Florida, and the ubiquitous distribution of high concentrations in fish suggests that atmospheric deposition may be an important source, either through accelerated regional inputs or through local emissions and deposition. The Florida Atmospheric Mercury Study (FAMS) began in May 1992 at a seepage lake in north-central Florida (Lake Barco; Figure 1) with the objective of developing field collection and laboratory analytical protocols for characterizing mercury in wet deposition, bulk deposition, and atmospheric aerosols, as well as measuring concentrations of total gaseous Hg (TGM). Since this relatively modest beginning, FAMS has expanded in scope

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from a single station to a statewide network of nine stations, including a marine background station, with the overall objective of determining regional rates of wet and dry deposition of mercury in Florida and comparing these fluxes with fluxes measured in other continental and marine areas. Other objectives include:

- Evaluating, to the extent possible, the overall contributions of marine, terrestrial, and anthropogenic sources to measured rates of atmospheric deposition of mercury in Florida;
- Determining background contributions to regional rates of mercury deposition, where background sites are defined as locations least likely to be impacted by local anthropogenic inputs; and
- Evaluating the reactivity of mercury in dry deposition and, in particular, atmospheric aerosols.

Finally, although not a specific objective, the experimental design of FAMS should contribute to an examination of the transport pathway between atmospheric mercury and mercury deposition.

In this paper, we present a brief overview of the FAMS program and its basic methodologies. Preliminary results of FAMS are the subject of a series of papers by Gill *et al.*, Landing *et al.*, and Guentzel *et al.* (all this volume).

2. Experimental Design and Methods

2.1. SAMPLING NETWORK

When fully operational by the end of 1994, FAMS will consist of a nine-station network, of which seven are currently operational (Figure 1 and Table 1). The densest portion of the network is in south Florida, where interest in the mercury problem is particularly keen. The network design in south Florida represents a balance between physical and security constraints imposed by the site equipment and the objective of determining spatial variability of atmospheric deposition of mercury in south Florida. The network configuration is designed to help discriminate between regional inputs, including marine contributions, and localized influences on atmospheric deposition of Hg.

2.2. INSTRUMENTATION AND EQUIPMENT

Monitoring for mercury at FAMS sites is performed atop a 14.6 m (48 ft) portable aluminum tower fabricated by UpRight, Inc.[1] to minimize artifacts in sampling induced by collecting entrained particles originating locally. Access to the top of the tower is via an internal staircase. In addition to the sampling tower, each site is equipped with an insulated shed which houses the ground-level equipment, such as the data acquisition system, vacuum pumps, mass flow meters, and the communications equipment. Requisite criteria for selecting candidate study sites include accessibility to direct 120 VAC power.

Continuous meteorological monitoring is performed at each site, including monitoring for wind speed, wind direction, ambient temperature, barometric pressure, and rainfall. Data for each parameter are collected and stored by a data acquisition system as 10-minute averages. Wind speed and wind direction are measured using sensors (Campbell Scientific) which generate frequency (Hertz) and resistance (ohms) to determine the

[1]UpRight, Inc., 1775 Park Street, Selma, CA 93662-0560

respective parameters. The temperature probe is a precision linear thermistor with a direct output. Rainfall, in increments of 0.25 mm, is measured using a tipping bucket rain gage.

A Campbell Scientific CR-10 data acquisition system (DAS) is used to log the meteorological data, mass flow meter measurements, and rainfall events. The DAS also is used to control sampling for total gaseous mercury (TGM) and ambient aerosols. Stored data are downloaded either by modem or onsite with IBM-compatible computer software. Remote access to the data logging system to determine system status is possible via standard phone lines or cellular modem interfaces. Equipment, such as the DAS and cellular phone and modem (which run on 12 VDC power), are driven using a bank of deep-cycle 12 VDC Pb-acid batteries attached to a trickle charger.

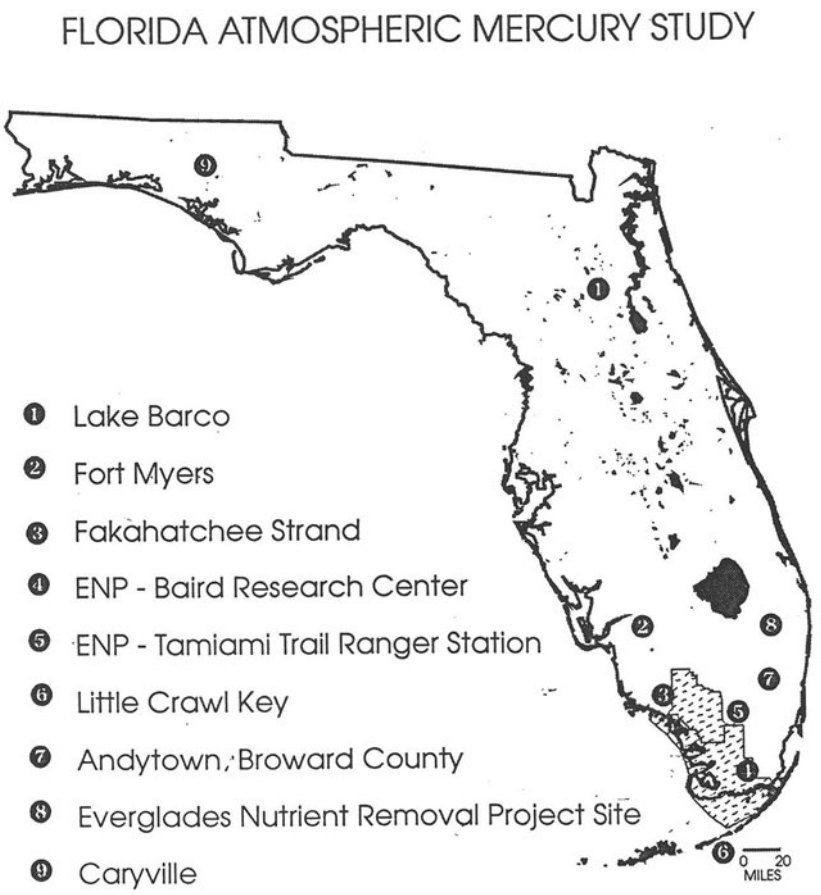

Fig. 1. Location of FAMS mercury deposition monitoring sites in Florida. Site numbers keyed to site descriptions summarized in Table I.

Table I. List of currently operational FAMS sites and sites to be added, and dates when sites became operational

Site	Date Operational	Site Features
	— FAMS Sites Currently Operational —	
(1) Lake Barco	5/92	Acidic (pH = 4 45), low DOC seepage lake study site - well-suited for cycling research to calibrate Mercury Cyling Model
(2) Fort Myers	10/92	Downwind of FP&L Fort Myers Plant and location of proposed Lee County incinerator
(3) Fakahatchee Strand	11/92	West of Everglades protection area Terrestrial background site for South Florida
(4) Everglades National Park - Baird Research Center	5/93	Near southern and eastern edge of Everglades Due west of FP&L Turkey Point Plant
(5) Everglades National Park - Tamiami Trail Ranger Station	5/93	Site most proximal to L-67 Interceptor Canal "hot spot" site of highest fish tissue concentrations of Hg
(6) Little Crawl Key	5/94	Marine background site Located on Little Crawl approximately 100 meters from Atlantic Ocean Site equipped with condensation nucleus counter to discriminate between marine and non-marine air
(7) Andytown, Broward County	5/94	Immediately below Water Conservation Area-2A and downwind of Ft Lauderdale and 2 major incinerators
	— FAMS Sites to be Added —	
(8) Everglades Nutrient Removal Project Site	12/94	Northern Everglades at conjunction of Everglades Agricultural Area (EAA) and Loxahatchee National Wildlife Refuge Site of proposed input-output Hg aquatic research and cycling studies
(9) Caryville	12/94	Florida Panhandle, approximately 25 km south of Florida-Alabama border Site to be used in developing estimates of trans-boundary flux of atmospheric Hg between Florida and northern states

2.3. TYPES OF MEASUREMENTS AND SAMPLING PROTOCOLS

Atmospheric deposition of Hg and other trace metal fluxes is partitioned into estimates of wet and dry deposition through direct measurement of four different types of sample collection:

- Wet Deposition
- Bulk Deposition
- TGM
- Atmospheric aerosols

Sample collection consists of two sampling regimens: integrated, long-term sampling conducted at every site, and short-term, intensive "event" sampling conducted at selected sites three times each year for approximately 1 week. The integrated (long-term) sampling interval is one month.

Wet deposition is measured directly by collecting samples automatically using an Aerochem Metrics® wet/dry deposition sampler modified specifically for mercury sampling. The Aerochem Metrics® collector is configured to sample wet deposition events by an onsite rain sensor. The wet deposition sampler, opened during a rain event, contains three small collection bottles: two serve as replicate Hg samples, and the third is used for other constituent flux determinations including major cations and anions. Total wet deposition for any interval

(*e.g.,* monthly) is simply the product of the volume-weighted mean concentration for Hg in rainfall over the interval and the amount of rainfall deposited. These fluxes are then compared to fluxes of Hg in bulk deposition.

Bulk atmospheric deposition (wet plus dry) samples are collected at each site with a small-diameter (approximately 5 inches) polycarbonate funnel. The funnel is connected to a Teflon receiving bottle via capillary Teflon tubing. The bulk collector is equipped with vertical Teflon spikes to discourage birds from perching on the edge of the funnel, minimizing the associated risk of contamination. The capillary tubing interface is configured with a vapor lock to help prevent evaporative losses of condensate and reduce the introduction of elemental Hg from the ambient air into the sample (Gill and Fitzgerald, 1987). A field collection blank is collected concurrently and consists of the Teflon bottle and tubing with the funnel deployed facing downwards. Sample bottles are changed monthly.

TGM samples are collected by drawing ambient air through a gold (Au) amalgamation collection column (Fitzgerald and Gill, 1979). The collection manifold includes four sets of columns, with each set consisting of three columns connected in series. The first column is the sample column, the second column is used to trap any breakthrough of Hg through the first column and is analyzed as well. The last column is used to prevent any back-diffusion into the sampling train when the sampler is not operational. The gaseous Hg collector is placed next to the particulate Hg collector on top of the sampling tower. A ¼ horsepower, continuous-duty, oilless pump (Pneumotive, Inc.) is used to draw air through the collection columns and is placed at the base of the sampling tower to avoid contamination. The volume of air sampled is determined based on flow rate measurements made with a 0 to 1 liter per minute (LPM) Sierra, Inc. mass flow meter. During onsite sampling, gaseous Hg samples are collected for 12- to 24-hour periods.

Atmospheric aerosols are collected on acid-washed 47 mm polypropylene filters (0.4 μm pore size) mounted in a polypropylene filter holder. The filter holder is placed in a polycarbonate rain shroud mounted on the sampling tower. A ½ horsepower pump, similar to that used for the gaseous Hg sampling, is used to draw air through the filter. Again, the pump is placed at the base of the tower to avoid sample contamination. The volume of air sampled is determined based on flow rates using a 0 to 100 LPM Sierra, Inc. mass flow meter. Field blanks consist of filters placed in holders and within the shroud on top of the tower, but no air is drawn through them.

3. Results and Conclusions

Some of the conclusions that the FAMS program has reached to date include:

- Rainfall Hg in Florida shows a strong seasonal pattern, with 2- to 3-fold higher concentrations and 4- to 6-fold higher fluxes during April-September.

- TGM measurements at Lake Barco averaged 1.49 ±0.31 ng/m^3 for 3- to 5-day integrated samples over approximately a 1-year interval beginning in summer 1992. Initial data from south Florida suggest that similar levels occur. The Lake Barco data also indicate that weak seasonal differences occur, with TGM concentrations higher in the summer compared to the winter (1.55 ±0.30 ng/m^3 *vs.* 1.42 ±0.19 ng/m^3).

- Volume-weighted annual deposition at sites in south Florida do not show any strong east-west trend. Based on only a few very recently collected samples, the mercury concentrations at the marine background (Crawl Key) and "downwind urban" (Andytown) sites are not significantly different from concentrations at the Everglades Baird Research Station site. These results suggest that rainfall mercury

deposition in south Florida is driven by large-scale regional or hemispheric processes as opposed to local emission/deposition processes.

Based on several lines of evidence, aerosol scavenging does not appear to contribute significantly to rainfall mercury deposition in south Florida. This evidence is based on: rain filtration experiments; very low aerosol Hg concentrations; and bulk *vs.* wet deposition agreement. *In toto*, the data support the conclusion that chemical and/or photo-chemical processes in the atmosphere produce the high concentrations of dissolved mercury we find in summertime rainfall. FAMS is investigating options to pursue this question further, including collecting rain samples from clouds using aircraft and sampling from a 550 m transmitting tower in Homestead, FL.

Consistent with the above theory, we find only very weak correlations between rainfall mercury and other trace elements or major ions. Factor analysis yields four significant factors, showing correlations among As, V, and Pb (also Cu, Cd, Ni, and Zn) which may represent anthropogenic sources. As expected from crustal dust input, Al, Fe, and Mn also are well correlated. A relatively weak correlation between Hg and Al may be due to a combination of two processes: enhanced gaseous Hg transformation in the atmosphere during summer months coupled with the summertime peak in the long-range transport of Saharan dust.

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LINKAGES BETWEEN ATMOSPHERIC MERCURY DEPOSITION AND THE METHYLMERCURY CONTENT OF MARINE FISH

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Abstract. Enhanced Hg deposition to productive marine systems may result in concurrent increases in monomethyl Hg (MMHg) concentrations of marine fish. Consequently, it is important to understand what effects an increasing Hg supply may have on the marine food chain. A simple ocean model is employed to estimate the fraction of total Hg inputs which is required to sustain "average" marine fish MMHg concentrations annually. Calculations show that upwelling zones require 20% of total annual Hg inputs, coastal zones 5%, and open-ocean regions only 0.02%. The value for coastal areas is similar to that calculated for the acidified basin of Little Rock Lake, Wisconsin, a small fresh water seepage lake. These calculations point to Hg source strength and rates of particle scavenging as being key factors in controlling the rate of transport to sites of methylation (and subsequent entry into the marine food chain). If biological variables (scavenging rates, primary productivity) remain constant while anthropogenically-derived Hg deposition increases, it is likely that concentrations in marine biota (including fish) will rise in accord.

1. Introduction

The current concern over the biogeochemical cycling and deposition of Hg to terrestrial and aquatic systems is due to the toxicity of monomethyl mercury (MMHg) to humans and its tendency to bioaccumulate. The flux of Hg to the atmosphere (25-38 Mmol) is currently dominated by anthropogenic inputs (50-75% of total; Mason et al., 1994). Swain et al., (1991) has estimated that Hg deposition rates have increased by a factor of 3.7 (since 1850; 2% yr^{-1}) from the analysis of sediment cores of mid-continental lakes. This value agrees well with model predictions (Mason et al., 1994; Hudson et al., 1994), and with an estimate of 1.2-1.5% yr^{-1} made by Slemr and Langer (1992) from studies in the Atlantic Ocean. Since the primary mechanism for the transport and deposition of Hg to surface waters is atmospheric, it is probable that human endeavors are increasing its supply into marine systems. A recent estimate indicates a 3-fold increase in oceanic surface water Hg concentrations relative to pre-industrial periods (Mason et al., 1994). The question of whether Hg is increasing in the atmosphere, however, must be addressed experimentally (Fitzgerald, 1995).

When considering the bioaccumulation of Hg in the marine food chain, one must primarily consider the rates of Hg inputs and transport to the sites of methylation (MMHg is the principal form of Hg in fresh water and marine fish; Grieb et al., 1990). In open-ocean and upwelling environments, MMHg is produced from available substrate in the oxygen minimum region below the thermocline (Mason and Fitzgerald, 1993). The net transport of atmospherically-derived Hg to the oxygen minimum is mediated by the particle flux that descends from the mixed layer. In the northeastern Pacific Ocean, the scavenging of thorium (Th) by particles is a function of the rate of primary productivity, while its rate of transport has been related to the rate of secondary packaging (Bruland and Coale, 1986). These particles typically have sinking rates in the range of hundreds

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of meters per day. As with Th, it is proposed that the incorporation of Hg onto particles is diffusion-limited. Thus, similar mechanisms may be responsible for scavenging and transport of Hg to the site of methylation. It is thought that advective and diffusive transport delivers MMHg to the mixed layer where it has the opportunity to be incorporated into the food web (Mason and Fitzgerald, 1993).

Contemporary studies of mid-continental fresh-water aquatic systems (Fitzgerald and Watras, 1989; Weiner et al., 1990; Gilmour and Henry, 1991; Watras et al., 1994) have focused on processes involving the supply, transport and conversion of Hg species. In the case of Little Rock Lake, WI (an experimentally acidified seepage lake), processes which governed Hg availability (complexation, volatilization) and vertical particle flux were responsible for the transport of atmospherically-derived Hg to the sediments. One expects that a similar relationship would be found along the coasts and estuaries of the world's oceans, where scavenging and transport processes are similar. Here, the sediments appear to be the primary location of MMHg production, and (like fresh water lakes) are likely to be more acutely impacted by anthropogenic inputs than the open ocean.

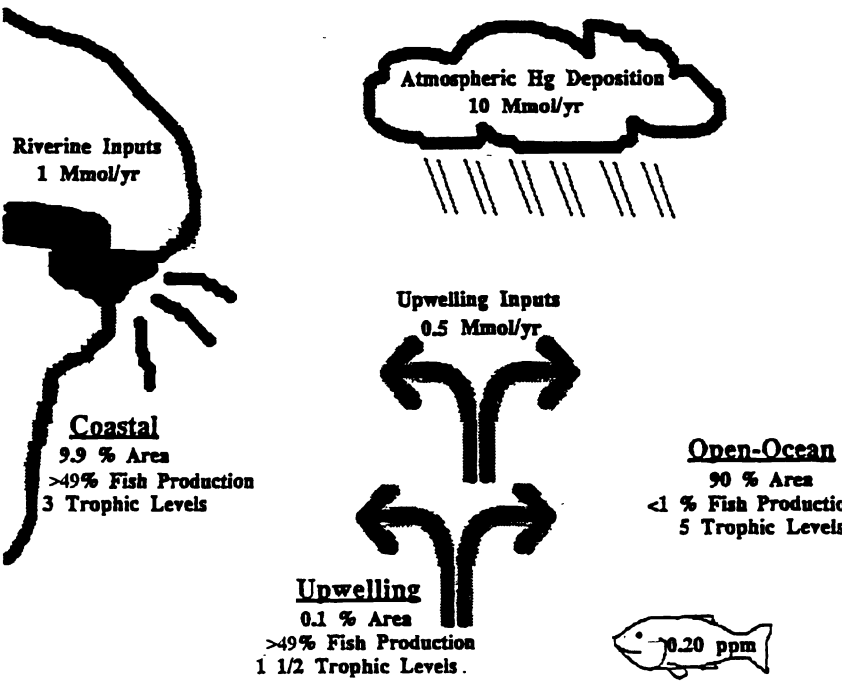

Figure 1. Schematic of the ocean model adapted from Ryther (1969), Mason et al., (1994), Pickard and Emery (1990), and Eisler (1981).

Only a small fraction of total annual Hg inputs to fresh water lakes (from the atmosphere, runoff, and groundwater) is required to account for the Hg which is measured in fish. It is estimated that only 5% of the total Hg deposition to Little Rock Lake is needed to maintain average fish biomass concentrations (assuming a 40% biomass turnover rate; Fitzgerald et al., 1991). This study attempts to estimate a similar value for defined ocean regions, in order to gain a better perspective on the impact of anthropogenic Hg and its subsequent transport on the marine food web.

2. The Model

First-order understanding of the movement of Hg in the marine food chain can be attained by using a simplified ocean model (Figure 1). A three-compartment model was adapted from Ryther (1969) which divides the whole ocean into open-ocean, coastal, and upwelling components. Coastal areas (9.9% of total area) are defined as waters inside of the 180 meter depth contour near continental land masses. The upwelling zone (0.1%) is given as the sum of the combined areas of Peruvian and African upwelling systems, but excludes that of the Antarctic Ocean. The open-ocean (90%) is considered to be the remainder of these areas.

The total production of fish in these areas is difficult to estimate, for there are no proven methods for accurately estimating the standing stock over large areas. Ryther (1969) attempted to estimate total marine fish production in order to gain an understanding of maximum sustainable yield for fisheries. He used an energy budget approach, in which ecological efficiencies determined the transfer of fixed carbon through a pre-determined number of trophic levels. It was argued that open-ocean environments had the most complex food web structure (5 trophic levels), followed by coastal regions (3 levels), and upwelling areas (1 1/2). Fish production is considered to be energy (as fixed carbon) flowing to the highest trophic level of each system. Production values from Ryther (2.21×10^{11} kg yr^{-1}; Table 1) are only first-order estimates; his values do not reliably take in to account productivity in the Antarctic upwelling waters, or the energy sink (more recently discovered) associated with the cycling of bacteria and protozoa (Fenchel, 1988).

TABLE I
Parameters used in the oceanic mixing model.

Parameter	Upwelling	Coastal	Open-Ocean	Cumulative
Area (m^2)	3.60×10^{11}	3.60×10^{13}	3.25×10^{14}	3.61×10^{14}
Avg. Fish Concn. (ppm fresh)	0.20	0.20	0.20	0.20
Fish Production (kg yr^{-1})	1.10×10^{11}	1.10×10^{11}	1.45×10^{9}	2.21×10^{11}
Hg Input Required (mol yr^{-1})	1.10×10^{5}	1.10×10^{5}	1.45×10^{3}	2.21×10^{5}
Sources				
Atmospheric Hg (mol yr^{-1})	1.00×10^{4}	1.00×10^{6}	9.00×10^{6}	1.00×10^{7}
Upwelling Hg (mol yr^{-1})	5.25×10^{5}	0	0	5.25×10^{5}
Riverine Hg (mol yr^{-1})	0	1.00×10^{6}	0	1.00×10^{6}

In order to estimate the "average" Hg concentration in marine fishes, one would need comprehensive data from a large number of important species and locations. Though this is not currently available, a reasonable estimate may be obtained from Eisler (1981), in which literature values (through 1978) of typical concentrations for a broad variety of major marine fish species are given. The average Hg concentration used in this model is derived by weighting the Eisler concentrations with harvest data of the major economically-important species from the Northeast U.S. fishery in 1992 (NOAA, 1992). The result is a total Hg concentration of 0.20 ppm fresh weight, which may represent an upper limit for marine fish, as commercial catches are generally large species.

The sources of Hg to each oceanic category are based upon the current global cycling estimates of Mason et al. (1994). Open-ocean regions are assumed to receive Hg only from the atmosphere, while coastal locations also have a riverine component (Table 1). Upwelling zones receive Hg from the atmosphere and from cooler, deeper waters which are vertically driven by ocean circulation. The average Hg concentration of upwelled water is estimated at 2.0 pM (Mason and Fitzgerald, 1993). An average upwelling rate of 2 m d^{-1} is employed in this region, though rates off of Peru and southwest Africa can increase to 5-10 m d^{-1} during certain periods of the year (Pickard and Emery, 1990). At other times upwelling essentially stops, rendering this as only a crude estimate.

3. Results and Discussion

The model indicates that only small fractions of the total Hg inputs are required to account for maintaining the "average" marine fish concentrations in each ocean zone. The open-ocean region requires only about 0.02% of its total annual Hg sources to be methylated and make its way to the highest trophic levels (consumable fish). Similarly, only 5.4% is required in coastal waters, and 20.3% in upwelling areas (Figure 2). In order to interpret these calculations, we must keep in mind the mechanism proposed for incorporation of Hg into the marine food chain. Away from the coasts, it is thought that methylation occurs in the low-oxygen region (below the thermocline) by the bacterial population (Mason and Fitzgerald, 1993). In coastal and fresh waters, methylation is thought to take place in the surficial sediments and/or the water column near the oxycline (Gilmour and Henry, 1991; Watras et al., 1994; Mason et al., 1993). Upon methylation, Hg must diffuse or advect back into surface waters, where it is incorporated into the lowest levels of the food chain. Mason and Fitzgerald (1993) reported that vertical particle transport was the principal supplier of Hg to the low-O_2 waters in the Equatorial Pacific.

It is argued that the rate of particulate scavenging and subsequent removal from the mixed layer controls the rate at which Hg is removed from the mixed layer and delivered to the low-oxygen region or sediments. Other factors, including the activity and distribution of methylating bacteria (based on temperature, organic carbon availability, and sulfur speciation), will determine the rate at which supplied Hg is converted to MMHg. We must therefore be concerned about the relationship between primary productivity and

Hg source strength for natural waters. Highly productive areas not only provide an enhanced particle transport mechanism to supply Hg to the site of methylation; increased organic loading may support larger populations of remineralizing bacteria, some of which may be responsible for methylation. Mason and Fitzgerald (1993) reported a factor of three difference in new production between two locations in the Equatorial Pacific upwelling region, with a similar relationship in MMHg concentration.

It is interesting to note that marine coastal waters require roughly the same fraction of total Hg inputs as the Little Rock Lake budget (5%; Fitzgerald et al., 1991; Hurley et al., 1991; Watras et al., 1994). This may reflect the similarity of the mechanisms and magnitudes in which Hg is incorporated. Both systems require atmospheric and riverine (watershed) inputs, with methylation taking place in the sediments and/or water column after particle transport and remineralization. The trophic structure in many fresh-water lakes may resemble that of the coastal marine environment. Both systems also experience seasonal temperature variations (formation of a thermocline) which affect the distribution and timing of the methylation process.

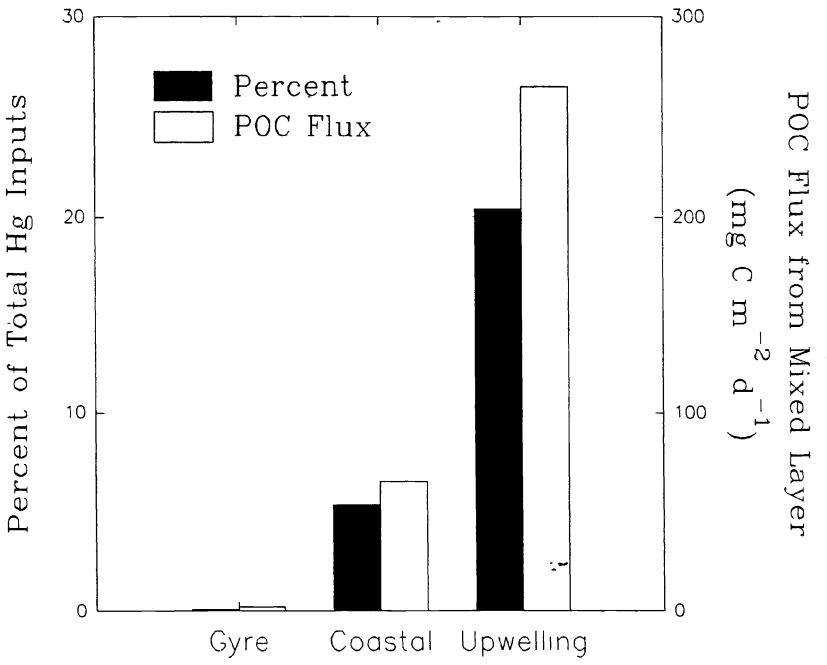

Figure 2. Percentage of total annual Hg inputs required to sustain "average" marine fish concentrations, and particle flux estimates from the surface waters of the oceanic categories (average measurements from the North Pacific gyre, coastal California, and Peruvian upwelling, respectively; Valiela, 1984).

Overall, only 1.9% of Hg inputs to the oceans are required to sustain fish concentrations at 0.20 ppm (fresh wt). This quantity is 22% of the estimated annual flux which is lost from the ocean mixed layer or brought in by riverine sources (~1 Mmol; Mason et al., 1994). This suggests that roughly one-fifth of the Hg which is removed from surface waters is methylated and incorporated into fish tissue. Modelling results indicate that much of the Hg entering the oceans is reduced and recycled (volatilized as Hg^0) to the atmosphere to eventually be deposited in terrestrial soils (Mason et al., 1994). Thus, a large fraction (ca. 22%) of the net input of Hg to the marine environment appears as MMHg in marine fish.

Some may argue that since such small fractions of the total supply are required to account for MMHg in fish (as in open-ocean gyres), an increase in atmospheric deposition would not appreciably affect fish concentrations. Without the mechanisms of Hg removal from the mixed layer (particle scavenging and downward transport), we may theoretically be able to increase Hg loadings to the surface waters without increasing the incorporation of MMHg into the food chain. In reality, we cannot ignore the effects of productivity and transport in supplying the reactant for methylation. Moreover, in aquatic systems, the association of Hg to organic particles will increase in proportion to the reactive Hg concentration. It is expected that increased Hg deposition to the surface mixed layer (primarily the result of elevated anthropogenic emissions) will serve to increase both volatilization and transport of Hg to sites of methylation.

4. Conclusions

The use of a simple ocean model, Hg flux data, and estimates fish production show that small fractions of total annual Hg inputs are needed to maintain concentrations of marine fish at their "average" levels. The open-ocean region required the smallest fraction of Hg (0.02%), followed by coastal waters (5.4%), and upwelling regions (20.3%). This is reflective of differences in their trophic structure, surface area, and rates of productivity. It is emphasized that the relationship between Hg source strength, rate of productivity, and transport will largely determine the extent to which it will be supplied, methylated, and incorporated into the food chain. It is implied that increases in deposition caused principally by anthropogenic emissions will directly result in enhanced food chain bioaccumulation, and higher concentrations in marine fish. The effects of such an increase are far-reaching, as apparent increases in anthropogenic Hg loadings may directly affect a major source of food for humans.

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PART IV

ATMOSPHERIC REACTIONS AND DEPOSITION OF MERCURY

THE GAS PHASE OXIDATION OF ELEMENTAL MERCURY BY OZONE

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Abstract. The gas phase reaction between elemental mercury (Hg^0) and ozone (O_3) has been studied in sunlight, in darkness, at different temperatures, and different surface-to-volume (s/v) ratios. At O_3 concentrations above 20 ppm, a loss of Hg^0 and a simultaneous formation of oxidized mercury (Hg(II)) was observed. The results suggest a partly heterogeneous reaction, with a gas phase rate constant of $3 \pm 2 \times 10^{-20}$ cm^3 $molec.^{-1}$ s^{-1} at 20 °C. This corresponds to an atmospheric Hg half-life of about one year at a mean global O_3 concentration of 30 ppb.

1. Introduction

Atmospheric Hg mainly takes the form of elemental mercury (Hg^0), with concentrations in the range of 1 to 4 ng m^{-3}. Elemental Hg has an average lifetime of 0.5 to 2 years (Seiler *et al.* 1980; Slemr *et al.* 1985; Lindqvist and Rodhe, 1985). Thus, during its lifetime, Hg^0 can be transported and contribute to the Hg load in remote areas. The concentration of Hg in precipitation is usually in the range of 1 to 50 ng L^{-1}. This is several orders of magnitude higher than predicted by the Henry's law distribution coefficient for Hg^0. Hence, Hg^0 must be oxidized either within the aqueous aerosol, or in the gas phase and then adsorbed. One common oxidizer in the atmosphere is ozone (O_3). The background concentration of O_3 is about 20 to 30 ppb but can be as much as several hundred ppb in heavily polluted air (Finlayson-Pitts and Pitts, 1985).

While the aqueous phase reaction of O_3 and Hg^0 is well known (Iverfeldt and Lindqvist, 1986; Munthe, 1992), the corresponding gas phase reaction has not been extensively studied. Data employed in current models were estimated from P'yankov's 1949 research, or from ancillary information in Iverfeldt and Lindqvist (1986). Slemr *et al.* (1985), quote a rate constant of 4.2×10^{-19} cm^3 $molec.^{-1}$ s^{-1} at 20 °C based on the data by P'yankov, while Schroeder *et al.* (1991), using the same data, estimate a value of 4.9×10^{-18} cm^3 $molec.^{-1}$ s^{-1}, *i.e.* almost 10 times faster. The latter also estimate a value of 1.7×10^{-18} cm^3 $molec.^{-1}$ s^{-1} at 20 °C, based on information in the paper by Iverfeldt and Lindqvist. The uncertainties in these numbers reflect the present knowledge of this reaction; which imply a faster oxidation of Hg^0, and hence, a shorter lifetime of Hg^0 than normally predicted. Assuming an O_3 concentration of 30 ppb, the half-life, $t_{1/2}$ ranges from 2 days ($k = 4.9 \times 10^{-18}$ cm^3 $molec.^{-1}$ s^{-1}) to 25 days ($k = 4.2 \times 10^{-19}$ cm^3 $molec.^{-1}$ s^{-1}). Also, oxygen, the allotrope of ozone, does not exhibit any

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significant gas phase reaction with Hg^0. However, in the range of 100 to 300 °C, a heterogeneous reaction occurs in the presence of activated carbon or fly ash (Hall *et al.*, 1994). Because the Hg-O_3 reaction is obviously important to our understanding of atmospheric Hg transport and deposition, this study reexamines the rate, temperature dependence, and other parameters of that reaction.

2. Materials and Methods

Experiments were performed in 0.5, 1 and 2 liter high purity FEP Teflon® reactors. The 0.5 L reactor experiments were then re-run with the reactors filled with 5 mm pieces of 1/4" Teflon® tubing. Surface-to-volume (s/v) ratios were, for the 0.5 L reactor with tubing, 12 cm^{-1}. For the reactors without added tubing, ratios were 0.74 cm^{-1}, 0.58 cm^{-1}, and 0.46 cm^{-1}, respectively. Individual batch reactors were chosen due to the slowness of the Hg-O_3 reaction, and the ability to mass balance every reactor, yielding greater confidence in the inferred reaction mechanism. Other advantages of FEP Teflon® reactors are that they are inert and transparent to solar radiation (>90%). They are also easy to clean between experiments. The main drawback is their relatively high s/v ratio. Consequently, wall loss experiments and experiments at different s/v ratios are an essential part of the study. Reactors were cleaned between experiments using standard methods for trace Hg research (Bloom, 1994). They were equipped with one inlet and one outlet port with stopcocks. A gas mixing system with high purity nitrogen (N_2) as the carrier gas was used to set initial concentrations (Fig. 1). Total pressure was 1 atm at room temperature and followed the gas law at other temperatures. Total gas flow was in the range of 1 to 5 L min^{-1}. Water saturated N_2 was formed by passing N_2 through two bubblers .

Elemental Hg was generated using a Lab-built permeation cell yielding 13 ng min^{-1} at 50 °C. The O_3 was either produced with a commercially-available O_3-generator/analyzer (Dasibi 1003-PC) or through a high voltage electrical discharge instrument (using pure O_2 instead of air to avoid formation of nitric oxides (NO_x)). Thus, in addition to Hg^0, O_3, and N_2, the gas mixture always contains 2 to 10% O_2. The Dasibi instrument has a maximum O_3 output of 1 ppm, while the latter can produce several thousand ppm of O_3. The Hg-generator was calibrated prior to each experiment by adsorption on gold (Au) or platinum (Pt) traps (0.5% platinum on alumina granules, heated to 800 °C) followed by double amalgamation and CVAFS (Cold Vapor Atomic Fluorescence Spectroscopy) detection (Bloom and Fitzgerald, 1989). The O_3-generator was calibrated each time by adsorbing O_3 in 0.1 M potassium chloride (KI) solution followed by iodometric titration with 1 mM sodium thiosulphate ($Na_2S_2O_3$).

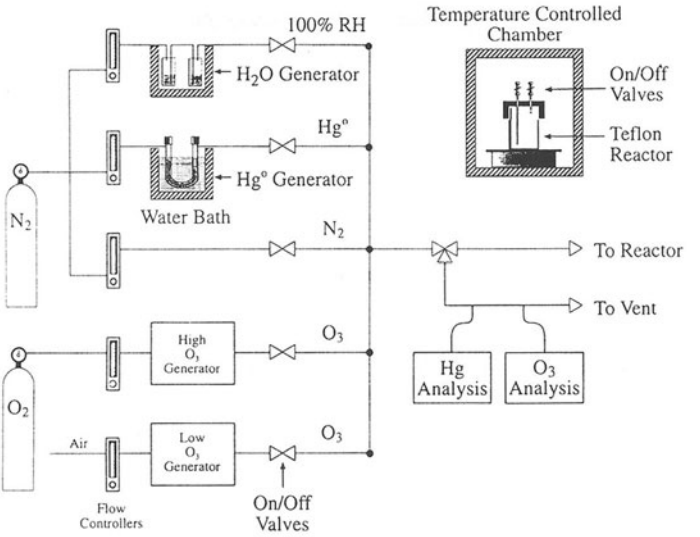

Fig. 1. Experimental set-up.

Experiments were performed with an initial Hg concentration of 1 to 10 μg m^{-3} and an initial O_3 concentration of 0 to 1500 ppm. The reactors were flooded with the preset gas mixture 3 to 5 minutes prior to the experiment. The valves were closed and the reactors stored either in darkness (at temperatures of 22, 50 and 75 °C) or in sunlight, depending on the experiment. After the desired time had elapsed, the reactors were purged with nitrogen (1 L min^{-1}) through a Pt-trap to catch gas phase Hg (the reason for a Pt-trap instead of a Au-trap was that poor recoveries were obtained when sampling Hg + high O_3 (>100 ppm) on Au-traps). The reactors were then rinsed with 100 mL 0.1 M HCl to collect oxidized mercury (Hg(II)) from the walls. The ionic Hg in the rinse solution was determined by stannous chloride ($SnCl_2$) reduction, purging of the Hg^0 to an Au-trap, and CVAFS detection.

Using this analytical protocol, gas phase Hg (Hg^0 + Hg(II)) is collected on the Pt-trap, and adsorbed Hg (Hg(II)) is collected in the rinse solution. Several attempts were made to separate Hg^0 and Hg(II) in the gas phase. Since Hg^0 is oxidized quickly by O_3 in aqueous solution, different solid adsorbers were tried. The use of soda-lime and Dowex have previously been fruitfully used in the separation of Hg species in flue gases (Braun and Metzger, 1987; Bloom, 1993). Other common adsorbers such as Tenax and Chromosorb W were also tested.

Unfortunately, no solid adsorber filled the requirement of adsorbing Hg(II) while letting Hg^0 through unaffected, both with and without O_3. However, a good balance of Hg was obtained by this operative speciation protocol over the entire length of the reactions (>99% conversion of Hg^0 to Hg(II)) suggesting that gaseous Hg can generally be regarded as Hg^0. In experiments with mercuric chloride ($HgCl_2$), more than 99% was adsorbed onto the walls when passing 15 $\mu g\ m^{-3}$ of $HgCl_2(g)$ (flow 0.1 L min^{-1}) through a 1 L Teflon® reactor. It appears therefore that gaseous Hg(II) diffuses to and adsorbs on the reactor wall faster than the formations found in these experiments.

3. Results and Discussion

3.1. WALL LOSSES

Extensive wall loss measurements were made throughout the experiments for both Hg and O_3. It was found that both species exhibited first order loss processes; *i.e.*, the loss was linear over several half-lives when first order plots were performed. However, the loss of O_3 was clearly affected by initial conditions such as how long the reactor had been conditioned with O_3 prior to the experiment. Table I and II summarize the results for Hg^0 and O_3. The collision yields were calculated from experimental wall losses, s/v ratios, and standard gas kinetic considerations as outlined by Grosjean, 1985.

Table I

Wall loss of Hg^0 at different temperatures and conditions. $[Hg^0]$=5 $\mu g\ m^{-3}$.

Condition	s/v (cm^{-1})	k_1 (min^{-1})	Collision Yield
20 °C	0.58	$2.7x10^{-4}$	$2x10^{-9}$
20 °C	12	$20x10^{-4}$	$0.7x10^{-9}$
50 °C	0.58	$10x10^{-4}$	$6x10^{-9}$
70 °C	0.58	$18x10^{-4}$	$10x10^{-9}$
sunlight	0.58	$5.7x10^{-4}$	$4x10^{-9}$

Table II

Wall loss of O_3 at different temperatures and conditions.

Condition	s/v (cm^{-1})	k_2 (min^{-1})	Collision Yields	Collision Yield Literature Value
22 °C	0.58	$0.5\text{-}2.9\times10^{-3}$[a]	$2\text{-}9\times10^{-9}$	$2.6\text{-}17.5\times10^{-9}$ (d,e,f,g)
22 °C	12	2×10^{-3}[b]	0.3×10^{-9}	
50 °C	0.58	$0.65\text{-}5.5\times10^{-3}$	$2\text{-}20\times10^{-9}$	
75 °C	0.58	20×10^{-3}	40×10^{-9}	
Sunlight	0.58	$1.4\text{-}20\times10^{-3}$	—	5.1×10^{-4} min^{-1}

The high rate corresponds to 1 ppm O_3, unconditioned reactor, while the low rate corresponds to 1000 ppm O_3; b. 1000 ppm O_3; c. 1 ppm O_3; d. Grosjean, 1985; e. McMurry and Grosjean, 1985; f. Grosjean et al. 1993[1]; g. Grosjean et al. 1993[2].

3.2. THE Hg + O_3 REACTION

Elemental Hg may react with O_3 to form either HgO(g) or HgO(s) (reaction (1) and (2)).

$$Hg^o(g) + O_3(g) \Rightarrow HgO(g) + O_2(g) \qquad \Delta G^\circ_{298} = -171 \text{ kJ mole}^{-1} \qquad (1)$$

$$Hg^o(g) + O_3(g) \Rightarrow HgO(s) + O_2(g) \qquad \Delta G^\circ_{298} = -254 \text{ kJ mole}^{-1} \qquad (2)$$

Reaction (1) could be a simple bimolecular gas phase reaction, while reaction (2) is more complex. The existence of HgO(g) as a diatomic molecule in the gas phase was established by Grade and Hirschwald, 1980, by means of a high temperature mass spectrometer study, and by Butler *et al.* 1979 in a matrix isolation experiment at 10 K. The large negative Gibbs free energy indicates an almost complete oxidation of Hg^o by O_3 at equilibrium for both reactions (1) and (2). This was confirmed by more than 99% conversion of Hg^o to Hg(II) in some experiments. A loss of Hg^o and a simultaneous formation of Hg(II), either formed or adsorbed onto the walls of the reactor, was observed in all experiments with an O_3 concentration above 20 ppm. A good recovery was obtained in most experiments. Below 20 ppm, the reaction rate was too slow to be measured using this system. At about 1500 ppm, the opposite was true. The rate was found too be too fast to be easily measured with this system, thus giving an O_3 window of a factor of 100 to work within. Figure 2 shows the results from a typical experiment with 190 ppm O_3.

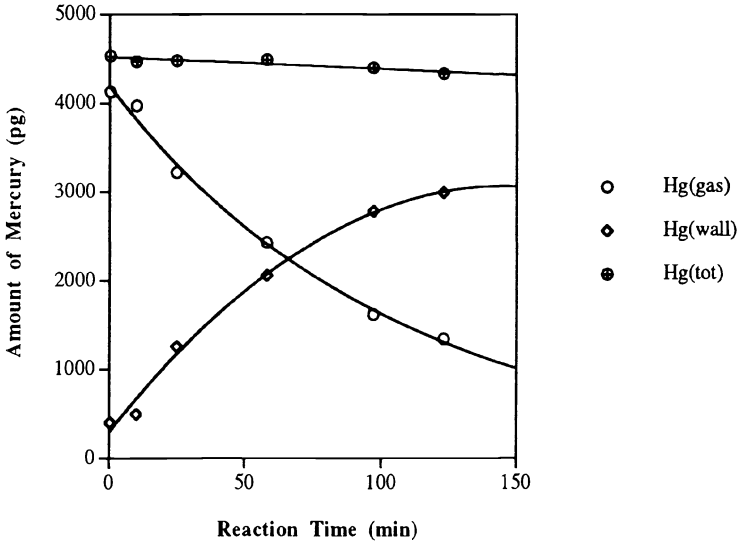

Fig. 2. The results from a typical experiment between Hg and O_3 in 1 L reactors. Initial concentrations of Hg and O_3 were 4.2 μg m^{-3} and 190 ppm, respectively.

The rate constant, k_3, was calculated by comparing the experimental data with a model based on reactions (3) to (5),

$$Hg^o(g) \xrightarrow{k_1} Hg(ads) \quad (3)$$

$$O_3(g) \xrightarrow{k_2} O_3(ads) \quad (4)$$

$$Hg^o(g) + O_3(g) \xrightarrow{k_3} HgO(g,s) + O_2(g) \quad (5)$$

using data for k_1 and k_2 from Table I and II, and the best fit of k_3. The rate constant could, in most cases, also be calculated directly through a pseudo-first-order assumption, since the O_3 concentration normally decreased less than 10% in an experiment.

$$d[Hg]/dt = -k_1 \times [Hg] \quad (a)$$

$$d[Hg]/dt = -k_3 \times [Hg] \times [O_3]^{\beta} \quad (b)$$

combining (a) and (b), and rearranging, gives a simple pseudo-first-order expression:

$$d[Hg]/dt = -k' \times [Hg] \quad (c)$$

with

$$k' = k_3 \times [O_3]^{\beta} + k_1. \quad (d)$$

Figure 3 shows the result from a plot using the data in Figure 2.

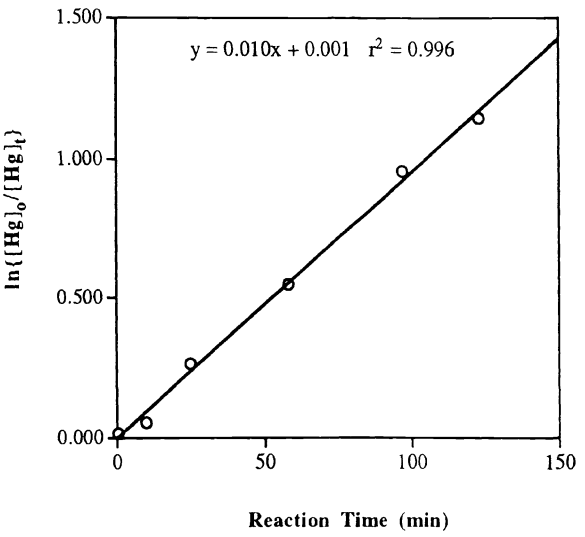

Fig. 3. Pseudo-first -order plot; $\ln\{[Hg]_o/[Hg]_t\}$ *vs.* time.

The linear plot in Figure 3, together with the linear results from other experiments over several more half-lives, suggest that the pseudo-first-order assumption is correct and that the reaction is first-order with respect to Hg^o. The rate constant k_3 can be calculated directly from Equation (d), if k_1 and the order and concentration of O_3 are known, or k' can be plotted against $[O_3]$ with the slope k_3 and intercept, k_1.

3.2.1. The order of reaction with respect to mercury

Pseudo-first-order plots of the observed loss of Hg in the reactor were linear over several half-lives. Neither were there any significant changes in the observed rate when changing, at constant O_3 concentration, the initial Hg concentration by a factor of 10 from 1 to 13 $\mu g\ m^{-3}$. It is therefore suggested that with respect to Hg the reaction is first-order under the conditions employed in this study.

3.2.2. The order of reaction with respect to ozone

The order of reaction with respect to O_3 was calculated using Equation (d) in its logarithmic form.

$$\ln\{k'-k_1\} = \ln k_3 + \beta \ln [O_3]. \qquad (e)$$

Figure 4 shows the results from five experiments with different O_3 concentrations ranging from 20 to 1200 ppm, but otherwise performed under the same conditions.

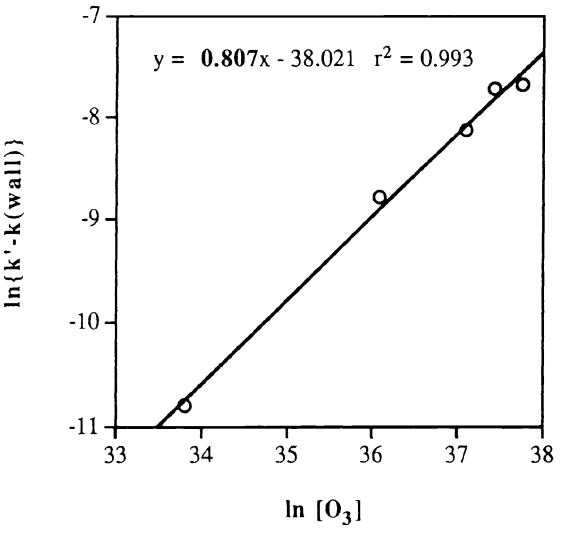

Fig. 4. The order of reaction with respect to O_3. [Hg]= 3$\mu g\ m^{-3}$.

The reaction order is slightly below 1.0 (β=0.81) in these experiments. Analyzing the same data using the initial rate method (Wilkinson, 1980) yields a value of 0.77 (r^2=0.998). The reason for the deviation from one is not yet clear. It could be a true intrinsic property of this reaction, reflecting, for example, the presence of an intermediate species. It appears, more likely, however, that the offset is caused by the adsorption isotherm for O_3 not being directly proportional to the gas phase concentration at high O_3 concentrations, thus suggesting at least a partly heterogeneous reaction. Because the order is relatively close to one, a first order dependence was used in evaluating the rate constant under different conditions *e.g.* temperature and s/v ratios. The main problem appears when the data is extrapolated over several magnitudes of O_3 concentrations, as will be discussed in the conclusion section.

3.2.3. The effect of surface-to-volume ratio (s/v)

Experiments were performed with s/v ratios of 0.46 cm^{-1}, 0.58 cm^{-1}, 0.74 cm^{-1} and 12.3 cm^{-1}, in 2, 1, 0.5 and 0.5 (with added tubing) liter high purity Teflon® reactors. The O_3 concentration was 200 ppm and the Hg concentration 3 $\mu g\ m^{-3}$. The results are shown in Figure 5.

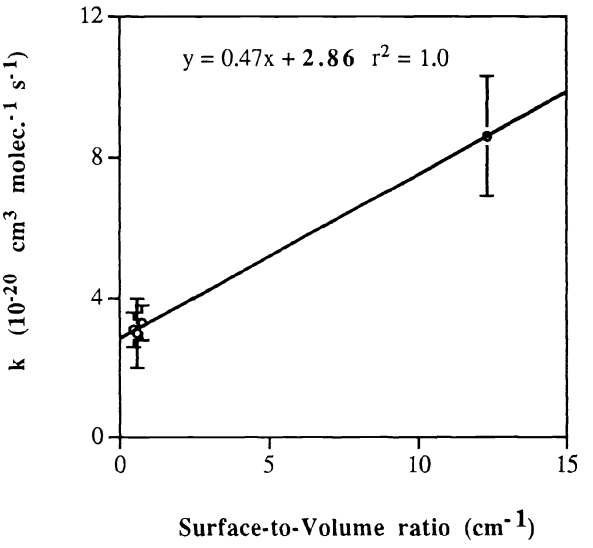

Fig. 5. The effect of increased surface-to-volume ratio.

There is a significant increase in the rate constant with increasing s/v ratio. The increase is, however, much smaller than expected for a heterogeneous reaction. The rate increases by a factor of 3 going from a s/v ratio of 0.47 cm^{-1} to 12.3 cm^{-1}, instead of, as expected for a purely heterogeneous reaction, a factor of 26. This suggests that there is both a gas phase reaction and a heterogeneous gas-solid reaction occurring simultaneously. Extrapolating the data down to a zero s/v ratio, *i.e.*, the intercept with the y-axis, a gas phase rate constant of 2.9×10^{-20} cm^3 $molec.^{-1}$ s^{-1} is obtained. Taking into account existing experimental uncertainties, a conservative value for the gas phase rate constant appears to be $3 \pm 2 \times 10^{-20}$ cm^3 $molec.^{-1}$ s^{-1}.

As seen in Figure 2, the Hg(II) concentration does not go through zero. An even larger deviation from zero was found in experiments with a s/v ratio of 12 cm^{-1}. The explanation probably has to do with the initial purging of the reactor. Assuming that this initial reaction is mainly heterogeneous, it is not difficult to assume that the rate may be much higher when the surface is newly cleaned, and active sites are not deactivated by adsorbed molecules. To study this effect, the amounts of Hg^o(g) and Hg(II)(ads) were measured at different purging times. Table III summarizes the results.

Table III

Results from experiments with different initial purging time in 1 L reactors (s/v=0.58 cm^{-1}). Total flow was 2.5 L min^{-1}; $[O_3]$=360 ppm; $[Hg^o]$=5.6 μg m^{-3}.

Time (min)	Amount of Hg on the Walls (pg)		Calculated Rate Constant (cm^3 $molec.^{-1}$ s^{-1})	
	Run #1	Run #2	Run #1	Run #2
0.5	137	218	9.1×10^{-20}	14.4×10^{-20}
1	293	145	9.7×10^{-20}	4.8×10^{-20}
5	433	655	3.0×10^{-20}	4.3×10^{-20}
10	459	608	1.5×10^{-20}	2.0×10^{-20}
20	553	920	0.9×10^{-20}	1.5×10^{-20}
30	2276	---	2.5×10^{-20}	---
40	-	3052	-	2.5×10^{-20}

The scatter in the data is considerable, but there appears to be a trend of initially higher rates decreasing over time, supporting the idea of a partly heterogeneous reaction deactivated over time. Using the initial concentrations for Hg^o and O_3, a rate constant of 2.5×10^{-20} cm^3 $molec.^{-1}$ s^{-1} is obtained after 30 to 40 min. It is

reassuring that almost the same rate constant is obtained measuring the buildup of Hg(II) on the walls in a flow system as is obtained measuring the decrease in gaseous Hg^0 over time in a closed system.

The intrinsic heterogeneous rate constant is difficult to calculate, since it requires unknown quantities such as the adsorption isotherms for both Hg and O_3 on FEP Teflon®, as well as the correct reaction mechanism. However, an apparent heterogeneous rate constant can be estimated by simply incorporating the surface-to-volume ratio with the rate expression, *i.e.*, the following:

$$d[Hg]/dt = k_{app} \times [Hg] \times [O_3] \times s/v \qquad (e)$$

Using the data in Figure 5, a heterogeneous rate constant, k_{app} of 5×10^{-21} cm^{-4} $molec.^{-1}$ s^{-1} was estimated. This value can probably be regarded as a minimum heterogeneous rate constant, since most surfaces are likely to be more active than Teflon®. It must be remembered, however, that k_{app} contains the equilibrium adsorption constants for either both O_3 and Hg on Teflon®, or only one of them, depending on the correct reaction mechanism.

3.2.4. The effect of temperature

Figure 6 shows the results from experiments performed at 22, 50 and at 75 °C. An activation energy, E_A of approximately 10 kJ/mole and a preexponential factor, A, of 2.1×10^{-18} cm^3 $molec.^{-1}$ s^{-1} were obtained. The activation energy is four times lower than what was estimated by Yarwood and Niki, 1991 (44 kJ $mole^{-1}$) based on the data by P'yankov. However, both activation energies are low, and more typical for a fast radical reaction. This suggests that there must be a large steric factor, in the order of 10^{-7}, to explain why the reaction is so slow. One possibility is that the reaction proceeds through a nonlinear activated complex, before the product, probably HgO(g), is formed.

3.2.5. The effect of relative humidity (RH)

Yarwood and Niki, 1990, calculated based on the data by Iverfeldt and Lindqvist (1986), a rate constant of 1.7×10^{-18} cm^3 $molec.^{-1}$ s^{-1} at a relative humidity of 71%. Experiments were performed at relative humidities of 42 and 87%, but no significant increase in Hg loss was observed in comparison with dry conditions. Thus, a rate 60 times slower than previously predicted was observed. One reason for the disagreement could be the difference in reactor material. Teflon®, as used in this study, is known to be very hydrophobic, and therefore less likely to maintain a water film, while quartz, as used by Iverfeldt and Lindqvist, is much more hydrophilic, and, as a result, will adsorb more water to the walls.

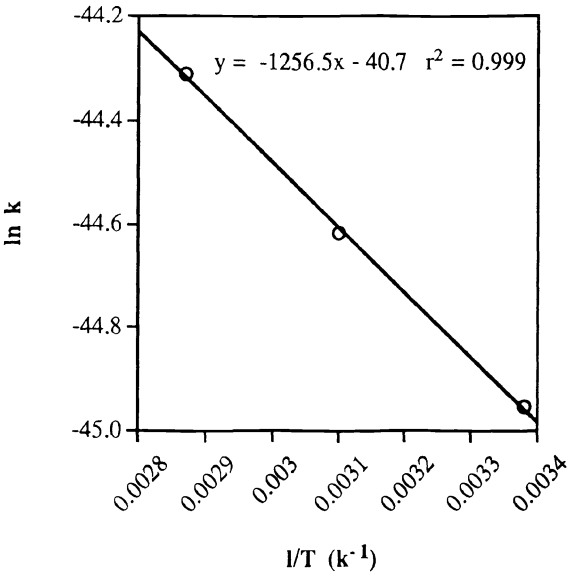

Fig. 6. The temperature dependence of the Hg-O_3 reaction. [Hg]=3 μg m^{-3}; [O_3]=250 ppm.

3.2.6. Photochemical reactions

Sunlight experiments were performed at four different occasions in Seattle, USA. The total solar radiation (direct + diffuse sky radiation) was measured with a pyranometer. In comparison with experiments in darkness, the reaction rate was found to be about six times faster in sunlight. Table IV summaries the results.

Table IV

Summary of results and experimental conditions during solar experiments.

Date	Sun Flux (w m^{-2})	Temp(°C)	[Hg] (μg m^{-3})	[O_3] (ppm)	k (cm^3 molec.$^{-1}$ s^{-1})
940328	750	30	3.4	140	$17.0 \pm 2.4 \times 10^{-20}$
940329	750	30	4.0	260	$10.2 \pm 4.6 \times 10^{-20}$
940506	910	29	5.6	160	$20.0 \pm 3.3 \times 10^{-20}$
940523	950	31	3.4	110	$19.5 \pm 3.3 \times 10^{-20}$

The temperatures shown are the average inside the reactors during the experiment.

The reason for this is not obvious. The photolysis of O_3 produces molecular oxygen (O_2) and atomic oxygen (O), either or both of which may be in excited states, depending on the excitation energy (Finlayson-Pitts and Pitts, 1985);

$$O_3 + h\nu \Rightarrow O_2(X^3\Sigma^-_g, {}^1D_g) + O({}^3P, {}^1D). \quad (6)$$

The oxygen atoms, once formed, will undergo different fates; most will react back with O_2 to form O_3; some will react with water vapor, and some may react with Hg^o or with trace amounts of organic impurities.

According to Yarwood and Niki, 1990, both $O({}^1D)$ and $O({}^3P)$ exhibit a large negative ΔH^o_R for the reaction with Hg^o assuming HgO(g) is the product, reaction (7) and (8).

$$Hg(g) + O({}^1D) \Rightarrow HgO(g) \qquad \Delta H^o_R = -412 \text{ kJ mole}^{-1} \quad (7)$$

$$Hg(g) + O({}^3P) \Rightarrow HgO(g) \qquad \Delta H^o_R = -222 \text{ kJ mole}^{-1}. \quad (8)$$

It is therefore not known if the increased reaction rate observed in sunlight is due to reactions with oxygen atoms, excited oxygen molecules, or activated O_3 molecules. The concentration and distribution of oxygen atoms in these experiments was also not known. This creates difficulty predicting the impact of these results on the atmosphere. However, it is clear that photochemical reactions must be considered in future modeling of Hg, and that the reaction of oxygen atoms with Hg should be studied.

4. Conclusions

The gas phase reaction between Hg and O_3 has been studied in darkness and in sunlight, at different temperatures, relative humidities and s/v ratios. The experimental results suggest that both a homogeneous gas phase reaction and a heterogeneous reaction occur simultaneously. The reaction has a very low activation energy, E_A of 10 kJ $mole^{-1}$ with a preexponential factor of $2x10^{-18}$ cm^3 $molec.^{-1}$ s^{-1}. The reaction order for Hg was found to be 1.0, while the experimental data suggests a reaction order for O_3 of 0.8 instead of, as may be expected, 1.0. It is not clear if this is an intrinsic effect of the reaction or a bias caused by, for example, the adsorption isotherm for O_3 not being directly proportional to the gas phase concentration at high O_3 concentrations and, therefore, not increasing the heterogeneous reaction as much as could be expected. Assuming a true first order O_3 dependence, a gas phase rate constant of $3\pm2 \times 10^{-20}$ cm^3 $molec.^{-1}$ s^{-1} is proposed. This is significantly slower (14 to 163

times) than previously proposed (Slemr, 1985; Schroeder *et al.*, 1991) suggesting that previous results were affected by surface reactions. The reaction was about six times faster in sunlight. No effect from relative humidity was observed. The correct order with respect to O_3 has a large impact on the final conclusion, when extrapolating the results over several orders of magnitude. Table V shows the different results that can be achieved using the same initial data, with a first order dependence, or an order of 0.8 with respect to O_3.

Table V

An example of the different conclusions obtained from a first order or a 0.8 order dependence of $[O_3]$, using the same experimental data.

Order of O_3	Exper. O_3 (molec. cm^{-3})	k' (Exper.)	k_3 (calculated) (cm^3 molec.$^{-1}$ s^{-1})	Atmos. O_3 (molec. cm^{-3})	[Hg] $t_{1/2}$ (Atmos.)
1	$5x10^{-15}$	0.00015	$3.0x10^{-20}$	$7.5x10^{11}$	356 days
0.8	$5x10^{-15}$	0.00015	$4.1x10^{-17}$ *	$7.5x10^{11}$	62 days

* correct unit (cm^3 molec.$^{-1}$)$^{0.8}$ s^{-1}

As seen, a half-life of Hg of about one year is obtained when assuming a first-order dependence, while only 2 months is obtained using an order of 0.8. This, in opposition to the earlier data, corresponds very well with the half-life that most authors have predicted for Hg and suggests that this reaction, even if slow, is important for the transport and transformation of atmospheric Hg in a global perspective. An interesting question is how much does this gas phase reaction contribute to the Hg concentration in rain? A rough estimate may be obtained by using a simple box model (volume: $1x10^{-18}$ cm^3): assuming the concentrations of Hg^o and O_3 to be 3 ng m^{-3} ($9x10^6$ atoms cm^{-3}) and 30 ppb ($7.5x10^{11}$ molec. cm^{-3}), respectively, the oxidation rate is 0.2 molecules of Hg(II) cm^{-3} s^{-1}. Thus, $2x10^{17}$ Hg(II) molecules-per-second are formed in a volume of $1x10^{18}$ cm^3. By further assuming that the air mass contains 2% of water (volume-to-volume) with a half-life of 1 day, and that all Hg(II) formed will be washed out because of its low Henry's law constant, the concentration of Hg(II) in the water will be on the order of 1 ng L^{-1}. This is the low end of what is normally observed, and suggests that other reactions, such as the aqueous phase reaction between Hg and O_3 is usually more important. However, a contribution of 1 ng L^{-1} from this reaction cannot be neglected when considering the origin of oxidized Hg in rain, especially since the O_3 concentration can be much higher than 30 ppb in polluted air.

Before the significance of this reaction can be fully understood, further research must be conducted on the order of reaction with respect to O_3; the effect of heterogeneous reactions on different surfaces such as glass, quartz, salt particles and soot; and on the effect of photolytical reactions

Acknowledgments

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MODELING THE ATMOSPHERIC CHEMISTRY OF MERCURY

- The importance of a detailed description of the chemistry of cloud water.

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Abstract. A model describing the aqueous chemistry and mass transfer processes of atmospheric mercury (Hg) has been used for analyzing the influence of various chemical and physical parameters on aqueous Hg concentrations. The model involves 39 gas phase species in 79 reactions and 32 aqueous species in 93 reactions. Modeled concentrations are in the range 2 to 5 and 5 to 10 ng L^{-1} for dissolved and total Hg, respectively. Accurate descriptions of gas phase as well as aqueous phase chemistry of oxidants, acidifying substances and chlorine chemistry are necessary since there is a complex relationship between a number of species and the aqueous Hg concentrations. Of the physical parameters studied the influence of the assumed fog liquid water content was also found to be of great importance.

1. Introduction

Environmental pollution caused by mercury (Hg) has been a cause of concern for decades since the first adverse effects were reported. Major efforts are now being made to prevent further contamination by decreasing the use of Hg and minimizing emissions.

The environmental cycling of Hg is extremely complicated and involves a multitude of chemical and physical processes that affect its toxicity and mobility. Key species in this environmental cycling are elemental Hg vapor (Hg^0), which is the most commonly occurring form in air, and methylated forms of Hg (MeHg), which is the most toxic species and also the form in which Hg accumulates in biological food chains. Atmospheric deposition is the major source of Hg in areas not affected by direct industrial discharges or geological sources. In remote areas, elevated concentrations of Hg in fish constitutes a potential health hazard which can only be resolved by measures taken to reduce emissions in areas often thousands of kilometers away and sometimes in other countries. In order to be able to motivate such measures, a credible description of the atmospheric transport and deposition processes - a source receptor determination - is necessary. In earlier studies (Petersen *et al.*, 1994) a simplified chemistry was used to describe the oxidation and reduction processes of atmospheric Hg. As our knowledge of the behavior of Hg in the atmosphere increases, models become more complex allowing more detailed descriptions of the transport and transformations occurring in the atmosphere.

This report deals with the chemical and physical processes of atmospheric transformations and deposition of Hg. Hg can be deposited by several different processes, both wet and dry. Here, we focus on the processes involved in converting elemental Hg to water soluble forms in aqueous aerosols (fog droplets). A sensitivity analysis is presented in which the influence of various chemical and physical parameters on Hg concentrations in aqueous aerolsols, are examined.

Water, Air, and Soil Pollution **80**: 317–324, 1995.

2. Model Description

The model used for the calculations, (CAM, Chemistry of Atmospheric Mercury) has been described elsewhere (Pleijel and Munthe, 1994a). The model treats gas phase and aqueous phase chemistry using 90 species in 180 reactions, as well as transport of these species into and out of water droplets. Emissions from the underlying surface are also included in the model formulation, as well as the diurnal variation of sunlight, based on conditions in Sweden. Dry deposition is included for a number of gaseous reactant species except Hg. The calculations were performed by means of the FACSIMILE/CHEKMATE program (Curtis and Sweetenham, 1987).

The model simulates a fog reaching from the ground surface to the top of the mixing layer. In the standard case, a liquid water content of 1 g m^{-3} and an average droplet radius of 10 μm were assumed. As there is no information on Hg levels in clouds full validation of the model is not yet possible. However, typical modeled total Hg concentrations are in the range from about $5 \cdot 10^{-12}$ to $5 \cdot 10^{-11}$ M in relatively good agreement with precipitation collected at monitoring sites on the Swedish west coast where a weighted annual mean of about $5 \cdot 10^{-11}$ M was found during 1993 (Munthe, 1994).

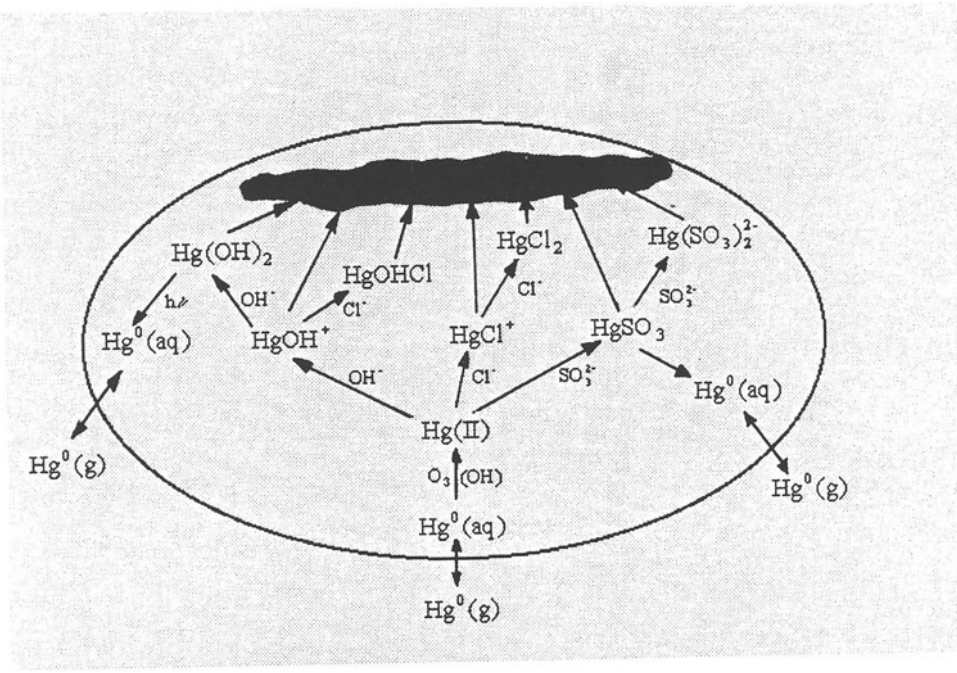

Fig. 1. Outline of the Hg transformation processes covered by the mercury model from (Pleijel and Munthe, 1994a).

Fig. 1 shows the principal transformation processes for Hg included in the model. In the initial oxidation step elemental mercury (Hg^0) is oxidized by ozone to divalent mercury (Hg(II)). Divalent Hg complexes with available ligands and is present in the aqueous phase as $HgSO_3$, $Hg(SO_3)_2^{2-}$, $HgCl^+$, $HgCl_2$, $HgOH^+$, $Hg(OH)_2$ and HgOHCl. Reactions leading to reduction of Hg(II) to Hg^0 indicate ways in which dissolved Hg(II) can be released from the droplet back to the gas phase. Adsorption of Hg(II) by particles within the droplets is treated by means of an empirical relationship derived from field measurements of soot and particulate Hg in precipitation (Petersen, 1992; Petersen *et al.*, 1994). In order to follow the changing concentrations in the droplets, the simulations start with no Hg in the droplets and are allowed to continue for 48 hours. In a real situation, this time period is longer than the expected lifetime of a cloud or fog droplet but this scenario was chosen with the intention of performing sensitivity analysis of the chemistry inside the droplets. A steady-state situation with equal rates of oxidation and reduction of Hg is expected in a cloud after the aqueous Hg concentrations have reached a maximum.

The development of the Hg complexes inside fog droplets, and the simultaneous loss of Hg^0 (g) during 48 hour simulation, is shown in Fig. 2.

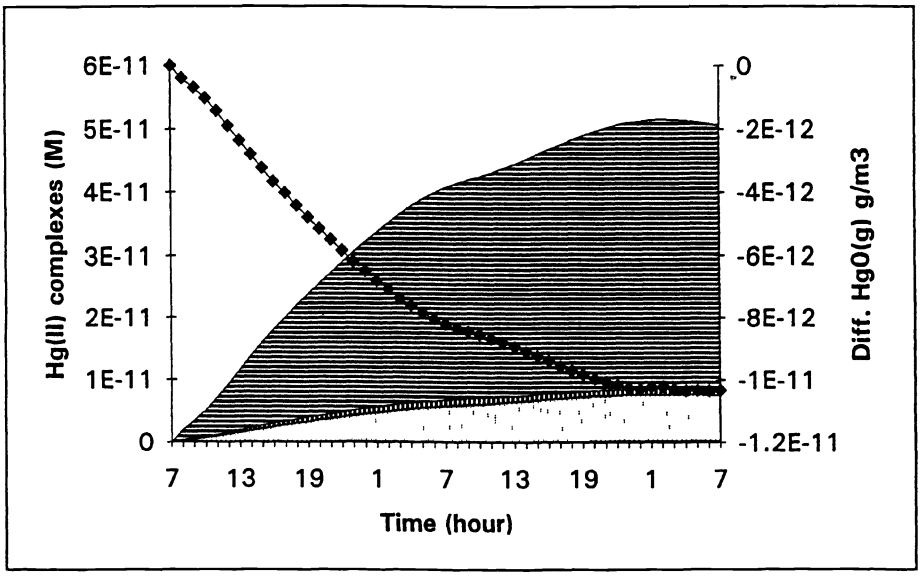

Fig. 2. The development of Hg complexes, Hg(II), in the simulated fog droplets, during 48 hours, starting at 7 a.m. The loss of gaseous elemental Hg is denoted "Diff. Hg^0 (g)", which is the difference between Hg^0 (g) when Hg chemistry is included and Hg^0 (g) when Hg chemistry is excluded from the model calculation.

Hg(II) ads; HgOHCl;
$HgCl_2$; $Hg(SO_3)_2^{2-}$;
Diff. Hg^0.

The change in gas phase Hg^0 concentration is only 0.01 ng m^{-3} out of the 3 ng m^{-3} present at the start of the 48 hours simulation. This is only a very minor fraction and it is clear that for a single cloud of fog event, and, as a consequence, for a rain event, very little of the airborne Hg will be removed.

Within the droplets, Hg adsorbed on particles is the clearly predominant form, under the conditions employed. The most common dissolved species are $HgCl_2$ and HgOHCl. The concentrations of the Hg(II) - S(IV) complexes are almost negligible in comparison to the total Hg concentration but still play a major role in generating Hg^0 and thus for removal of Hg from the droplets.

3. Sensitivity Analysis of the Mercury Model

Mercury is a minor component of the atmosphere, and it is not likely that reactions involving Hg will influence the concentrations of the major atmospheric components related to the formation of acid precipitation and oxidants. Nevertheless, a detailed description of the chemistry of both acid formation, oxidants as well as chlorine needs to be included for accurate predictions of Hg concentrations, since species such as S(IV), O_3 and Cl^- are involved in the reactions leading to mass transfer of Hg between the gas and aqueous phases.

Pleijel and Munthe (1994a) showed that the modeled concentrations of Hg(II) in aqueous droplets increased almost linearly with increasing O_3 concentrations. Moreover, the Hg concentration has a strong inverse non-linear relationship with the gas phase SO_2 concentrations. A more detailed description of the results of the sensitivity tests for the CAM model is shown in Fig. 3.

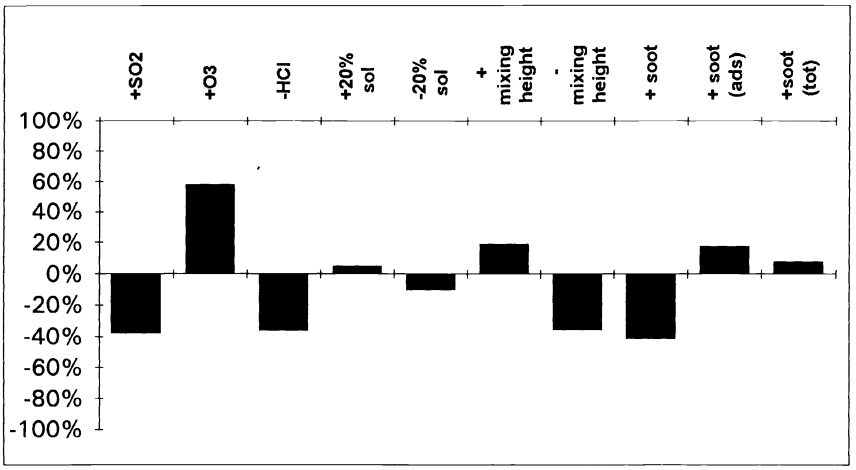

Fig. 3. Sensitivity analysis of various physical and chemical parameters on aqueous Hg(II) concentrations predicted by the CAM model.

The changes in the chemical and physical parameters used as inputs for the different model runs are given in Table 1.

As mentioned above, the O_3 and SO_2 concentrations have an important effect on the concentrations of aqueous Hg species. A higher initial value of SO_2 results in lower concentrations of dissolved Hg(II), as an increase in SO_3^{2-} will favor the complex $HgSO_3$, which is spontaneously reduced to Hg^0. A higher initial value of O_3 causes a higher concentration of dissolved Hg(II), due to an increased oxidation rate of Hg^0.

Table 1.
Parameters used in the sensitivity analysis.

Parameter	Explanation
+ SO_2	Increase of SO_2 from 1.2 to 3.0 ppb
+ O_3	Increase of O_3 from 30 to 50 ppb
- HCl	Decrease of HCl from 1.0 to 0.1 ppb
+ 20 % sol	Increase of solar radiation by 20%
- 20 % sol	Decrease of solar radiation by 20%
+ mixing height	Increase of mixing height from 600 to 800 meters
- mixing height	Decreased of mixing height from 600 to 400 meters
+ soot	Increase of soot from 5 to 10 $\mu g\ m^{-3}$ (effect on dissolved Hg(II)
+ soot (ads)	Increase of soot from 5 to 10 $\mu g\ m^{-3}$ (effect on adsorbed Hg(II)
+ soot (tot)	Increase of soot from 5 to 10 $\mu g\ m^{-3}$ (effect on total Hg(II)

Lowering the HCl concentration markedly reduces the Hg(II) concentration in the droplets since both lowered Cl^- concentration and increased pH favor the formation of Hg-S(IV) complexes and thus the reduction of Hg(II) to Hg^0. Changing the solar radiation intensity has only a small effect caused by an increase in H_2O_2 concentration, which leads to a decrease in pH via oxidation of S(IV).

An increase in the mixing height in relation to the standard case (600 m) gives an increased level of dissolved Hg(II), while a decrease in the mixing height gives the opposite result. In this case, the changes in Hg(II) are caused by dry deposition of gaseous species, which is dependent on the height of the mixing layer. A thin mixing layer can be almost "emptied" of reactant gases owing to dry deposition, while the influence of a higher level mixing layer is more moderate. Dry deposition of gaseous Hg is not included in the model, owing to a lack of data but is expected to be of importance at least for forested areas (Iverfeldt, 1991; Lindberg *et al.*, 1991; Munthe *et al.*, 1994).

The total amount of Hg(II) in the droplets (dissolved Hg(II) in the aqueous phase plus Hg(II) adsorbed to particles) increases with increasing soot concentration in the droplets. The dissolved Hg(II), however, is decreased while the adsorbed Hg(II) fraction increases significantly.

As a first attempt to model the atmospheric chemistry of Hg, the Hg chemistry described schematically in Figure 1, was added to already existing cloud chemistry schemes. The calculations have been presented in detail (Pleijel and Munthe, 1994b). The chemical schemes compared have been presented by Adewuyi (1984), Möller and Mauersberger (1992) and Jacob (1986). The aqueous chemistry covered by the CAM model based on the results of the initial tests performed using these schemes. Key

processes for describing the Hg chemistry were found to be accurate representations of chloride and nitrogen chemistry apart from the descriptions of O_3 and S(IV). Cl^- is directly involved in the chemistry of Hg(II), since it competes with S(IV) to form complexes. Hg(II)-Cl^- complexes are stable whereas complexes involving S(IV) may lead to reduction of Hg(II) and a lowered total concentration in the droplet. NO_x chemistry is of importance, as it will affect the gaseous ozone, which is important in the Hg modeling.

The results from the sensitivity test, using different aqueous chemical schemes are shown in Figure 4.

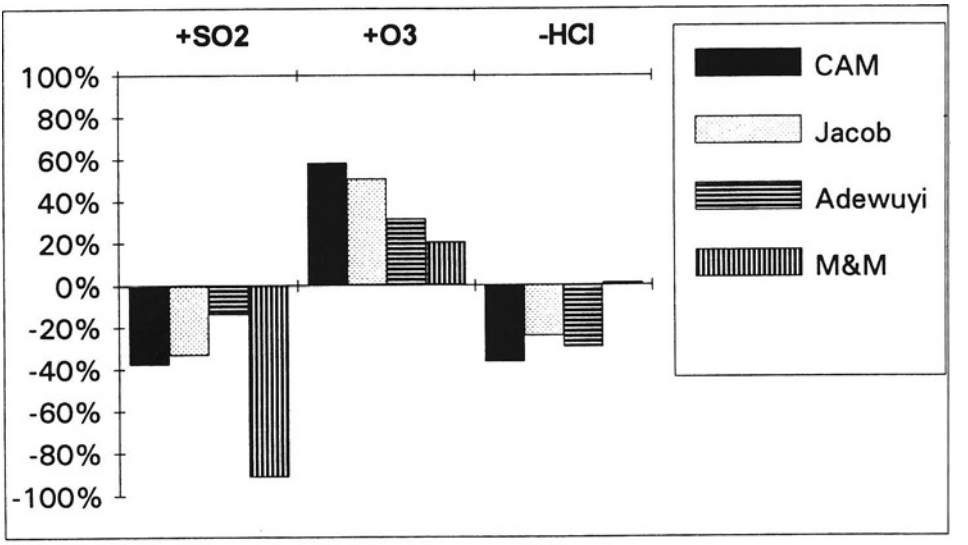

Figure 4. The relative change in dissolved Hg(II) expected with variations in the values for different parameters that define conditions in the aqueous phase. The Hg chemistry is identical in all cases studied, although four different aqueous chemical schemes for the other species involved have been used - CAM (this work), Jacob (1986), Adewuyi (Adewuyi et al., 1984) and M&M (Möller and Mauersberger, 1992).

It is clear that the Hg concentrations calculated using the different chemical schemes vary considerably and that sensitivity to changes in chemical input data is also different. For example, increasing the SO_2 concentration from 1.2 to 3.0 ppb gives different results in the different models. All 4 schemes predict a decrease in aqueous Hg concentrations but the predicted decreases vary from 14% to 91%, for the Adewuyi and M&M schemes, respectively. An inadequate description of the aqueous S(IV) chemistry can lead to errors in the modeling of Hg concentrations. If the rate of oxidation of S(IV) (*e.g.* by O_3 and H_2O_2) is underestimated, a too high S(IV) concentration will be predicted. This, in turn, will lead to an overestimation of the decrease in Hg (in comparison to CAM) since more S(IV) is available for reduction of Hg(II) to Hg^0 which will lower the Hg concentration in the droplets.

The influence of changing the LWC and droplet radius was studied separately. In Fig. 5, the predicted changes in dissolved Hg(II) after a reduction of LWC by a factor of ten and a ten times reduction in radius as well as when the two are combined. A

reduction of LWC leads to a more acid droplet, since more S(IV) is oxidized per unit volume. Since the total amount of water is much smaller in the LWC/10-case, less of the gas phase reactants will be consumed in aqueous reactions. This will lead to a higher rate of oxidation of Hg^0 and the final concentration of Hg will be higher than in the standard case. The lowered pH will favor the $HgCl_2$ complex and prevent reduction of Hg(II) through the Hg(II)-S(IV) reactions which will further increase the aqueous Hg concentration. A decrease in droplet radius has only minor influence on the predicted Hg(II) concentrations.

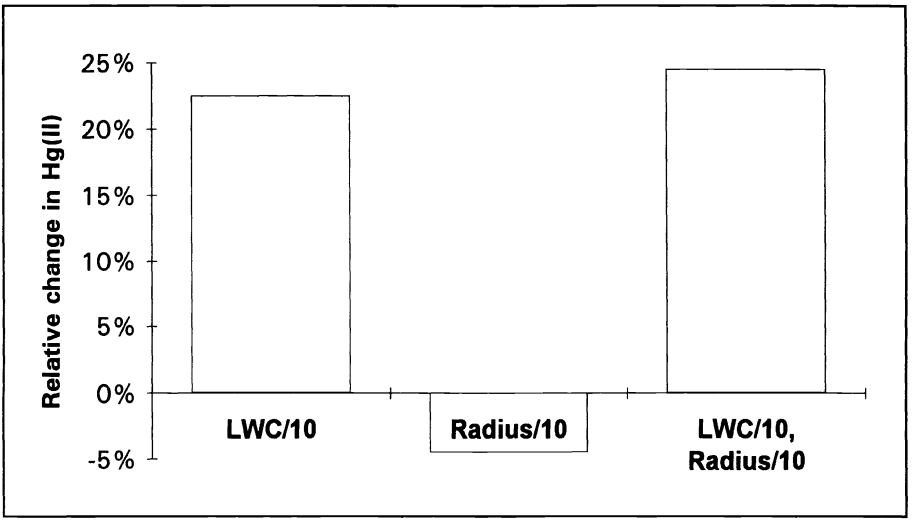

Figure 5. The relative change in dissolved Hg(II) for different radius and liquid water content (LWC).

The influence of a tenfold change in drop radius and liquid water content (LWC) on the sensitivity of the calculated Hg(II) content was tested for some of the cases studied above. The sensitivity of a change in SO_2 is greater than for a change in O_3 concentration when the radius and LWC have been changed. The effect of changing the LWC is much more important than the change of droplet radius and the LWC effect predominates when a combination of radius and LWC reduction is studied. For SO_2, a change of SO_2 from 1.2 to 3.0 ppb gives a decrease in aqueous Hg of about 35 to 40% even if the droplet radius is decreased by a factor of 10. If the LWC is decreased by the same factor, however, the Hg stays constant even after the increase in SO_2. Apparently the reduced pH in the LWC/10 case is sufficient to stabilize the Hg(II).

5. Conclusions

- A detailed description of oxidant and acid precipitation chemistry is essential for accurate predictions of aqueous Hg concentrations. The most critical chemical parameters whose values must be estimated accurately are thus SO_2, O_3, Cl^- and pH.

- Variations in solar intensity only have a minor influence on the predicted Hg concentrations.

- The height of the mixing layer influences the Hg concentration via dry deposition processes of the reactant gases (e.g. O_3 and SO_2).

- Total Hg content (dissolved plus adsorbed Hg(II)) is strongly correlated to soot concentration. At high soot concentrations all Hg(II) is expected to be in the adsorbed form.

- Decreasing the liquid water content of the fog will increase the concentration of Hg(II) due to an increased acidity and oxidation of Hg^0. Decreasing the droplet radius will only have a minor effect.

Acknowledgements.

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DEVELOPMENT AND APPLICATION OF A REACTIVE PLUME MODEL FOR MERCURY EMISSIONS

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Abstract: A reactive plume model that includes atmospheric chemical reactions of mercury was developed. The model simulates advective transport with the mean wind flow; horizontal and vertical turbulent diffusion; gas-phase; aqueous-phase and particulate chemistry; cloud microphysics; wet deposition and dry deposition. The model was applied to the simulation of clear sky, non-precipitating cloud and precipitating cloud scenarios. No significant mercury chemistry occurs in the absence of droplets. In clouds, Hg(II) is reduced to Hg(0) with more reduction taking place in precipitating clouds than in non-precipitating clouds.

Key words: Atmospheric chemistry; mercury; plume model

1. Introduction

Of the several chemicals emitted by sources such as coal-fired power plants and incinerators, mercury has received special attention in the recent years as certain forms of mercury exhibit elevated toxicity and bioconcentrate in vegetation and fish. Consumption of produce and fish containing high mercury concentrations may lead to adverse health effects to humans and predator animals (e.g., Florida panther).

Mercury present in the environment and emitted from industrial facilities may exist in various oxidation states as well as various physical phases. Different forms of mercury may exhibit different behavior in the environment. For example, vapor mercury species would tend to have different deposition velocities than particulate-bound species. Also, various vapor species may have different solubilities in water which would, in turn, lead to different scavenging efficiencies by droplets and, in some cases, different dry deposition rates. Therefore, a comprehensive characterization of the speciation and chemical transformations of mercury is essential for the accurate simulation of its fate and transport.

The complexity of mercury (Hg) behavior, and the need for reliable simulation of the atmospheric fate and transport of Hg emissions call for the development of a reactive plume model for Hg. To that end, an atmospheric chemical kinetic mechanism for Hg was developed and incorporated into a reactive plume model to quantify short- to medium-range (i.e, up to 100 km) transport and deposition of Hg emissions.

In the following sections, we present the formulation of the reactive plume model, a description of the chemical kinetic mechanism of atmospheric Hg and its incorporation into the plume model, and the results of some simulations for fate and transport of Hg from a hypothetical power plant. Finally, concluding remarks and a discussion of knowledge gaps and further research needs are provided.

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2. The Reactive Plume Model

The reactive plume model PARADE was developed under the sponsorship of Electricite de France (EDF) mainly for the purposes of simulating acid deposition due to the emissions of sulfur and nitrogen oxides (SO_x and NO_x) emitted by coal-fired power plants (Joos and Seigneur, 1994). In its original development, the model used as a framework the Reactive Plume Model (RPM) previously developed by Stewart and Liu (1981). Further development and modifications to the model were later performed at various instances (Seigneur, 1982;Joos et al., 1987;Joos and Seigneur, 1994). The current version of the model incorporates seven major modules:

- Transport (advection, updraft and turbulent diffusion)
- Gas-phase chemistry ("dry" atmosphere)
- Aqueous-phase chemistry (clouds and rain)
- Aerosol formation and dynamics
- Dry deposition
- Cloud microphysics
- Wet deposition

We provide next a description of the model's overall framework as well as a brief discussion of the formulation of the individual modules.

2.1. OVERALL MODEL FRAMEWORK

PARADE utilizes a Lagrangian approach to simulate the transport of a power plant plume as it is advected by the mean wind flow. Chemical interactions occurring within the plume, as well as when the plume mixes with background air are also simulated. Transport is performed following a two-dimensional cross-section of the plume as it travels downwind. The cross-section is divided into an array of contiguous cells that are perpendicular to the wind direction and expand horizontally as the plume moves downwind, according to a Gaussian distribution for inert species. The vertical dimension of the cells remains constant for a given simulation. The model can handle up to 10 grid cell layers and up to 10 grid cell columns. Figure 1 presents a schematic description of the PARADE two-dimensional gridded framework.

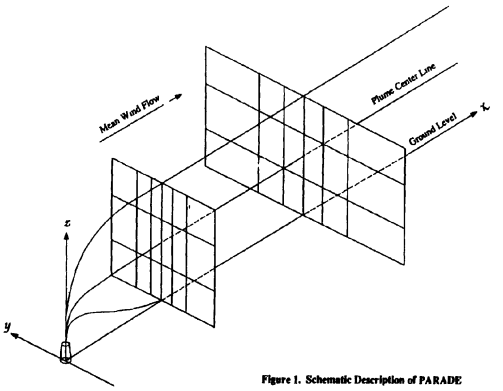

Figure 1. Schematic Description of PARADE

2.2. TRANSPORT PROCESSES

The transport phenomena simulated by PARADE include advection, updraft, and turbulent diffusion. The plume cross-section is advected according to a single wind speed that is allowed to vary with time as the plume moves downwind. In the presence of clouds, an updraft can be incorporated with updraft velocities varying as function of height, if desired. Turbulent diffusion of the chemicals between the grid cells is treated differently in the horizontal and vertical directions. In the horizontal direction, the plume size expands as function of the overall plume dispersion. Reactive species undergo chemical transformations and diffuse between neighboring cells as well as between the cells and the ambient air according to a Fickian diffusion algorithm. In the vertical direction, since the grid layer sizes are fixed, eddy diffusion coefficients are used to characterize inter-layer diffusion. Horizontal and vertical diffusion coefficients are either input directly by the user or calculated according to the atmospheric stability.

2.3. ATMOSPHERIC CHEMISTRY

The gas-phase chemical kinetic mechanism is based on the Carbon-Bond Mechanism (Gery et al., 1989) to simulate the atmospheric chemistry of photochemical oxidant formation. The oxidation of sulfur dioxide (SO_2) to sulfate is also treated. The gas-phase chemistry of mercury is discussed in detail in the next section. The gas-phase chemical mechanism includes nearly 100 reactions among 65 chemical species.

The aqueous-phase chemical kinetic mechanism includes gas-phase/liquid-phase equilibria of volatile/soluble species, ionic and precipitation equilibria, and aqueous-phase irreversible reactions (Seigneur and Saxena, 1988). Several mercury reactions, as discussed below, are included in the aqueous-phase mechanism. The mechanism includes about 70 reactions and equilibria among 65 species. The oxidation of SO_2 taking place in the liquid-phase of atmospheric particles is also treated.

2.4. AEROSOL FORMATION AND DYNAMICS

PARADE allows for a comprehensive treatment of the size-distributed chemical composition of aerosols. Aerosol processes that are simulated include new aerosol formation, condensation of sulfuric acid, nitric acid, ammonia and condensible organics, evaporation of nitrate and ammonium, condensation/evaporation of water, and coagulation. The size distribution is approximated by nine size sections over an aerosol diameter range of 0.01 to 10 μm. At this moment, the model does not simulate the formation/evaporation of particulate mercury.

2.5. DRY DEPOSITION

The simulation of dry deposition of gases and aerosols is based on a resistance approach. It is assumed that dry deposition of atmospheric species to surfaces is limited by a series of three processes that create resistance to deposition. These three resistances are the following:

1. The aerodynamic resistance r_a that is associated with turbulent transport in the lowest atmospheric layer. It is a function of surface roughness, atmospheric stability and wind speed.
2. The surface layer resistance r_s that is associated with Brownian and turbulent transport in the sublayer adjacent to the deposition surface. It is a function of the atmospheric friction velocity and land use.
3. The transfer resistance r_t that is associated with the transfer of the deposited species from the atmosphere to the surface. It is a function of the chemical species and surface type (i.e., land use).

The deposition velocity V_d is then defined as the inverse of the sum of these three resistances, as shown in Equation (1).

$$V_d = 1/(r_a + r_s + r_t) \tag{1}$$

The average dry deposition flux of species i, F_{di}, is calculated as follows.

$$F_{di}(t) = \frac{1}{A(t)} \int_o^t C_i(t)\, V_{di}(t)\, w(t)\, u(t)\, dt \tag{2}$$

where A is the area under the plume from the source to the location reached at time t, C_i is the chemical species concentration in the lowest model layer, V_{di} is the dry deposition velocity for that species, w is the plume width, and u is the wind speed.

2.6. CLOUD MICROPHYSICS AND WET DEPOSITION

PARADE offers a treatment of cloud and rain formation from inputs of meteorological variables such as temperature, pressure and relative humidity profiles. Alternatively, the user can specify the liquid water content in the various model layers and the precipitation rate. The cloud microphysics module simulates the distribution of water among four phases (vapor, cloud droplets, raindrops and ice) as depicted in Figure 2 (Seigneur and Wegrecki, 1990). The raindrop fall velocity is calculated according to the model of Wobus (1971). The precipitation rate is then calculated from the rainwater content and the raindrop fall velocity. The chemical composition of the raindrop is calculated by the aqueous-phase chemistry module.

The average wet deposition flux of species i, F_{wi}, is calculated according to the following equation:

$$F_{wi}(t) = \frac{1}{A(t)} \int_o^t C_i(t) V_r(t) w(t) u(t) dt \tag{3}$$

where A is the area under the plume from the source to the receptor location at time t, C_i is the chemical species concentration in the lowest model layer, V_r is the raindrop fall velocity, w is the plume width, and u is the wind speed.

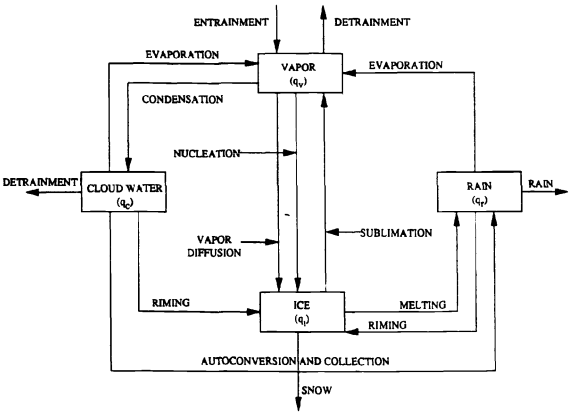

Figure 2. Microphysical Processes Governing Cloud and Rain Water, Water Vapor, and Ice

3. The Mercury Chemical Kinetic Mechanism

The chemical kinetic mechanism of mercury developed by Seigneur et al. (1994) under the sponsorship of the Electric Power Research Institute (EPRI) was included in PARADE. This mechanism is based on a comprehensive review of the literature and most recently available laboratory kinetic data. The gas-phase oxidation kinetics of Hg^0 by O_3 was updated according to the recent data of Hall (1994). The mechanism is presented in Table I. Figure 3 summarizes the major chemical pathways.

TABLE I

Atmospheric Chemical Kinetic Mechanism of Mercury

Reaction	Equilibrium or Reaction Rate Parameter[a]
1 $Hg^0(g) + O_3(g) \rightarrow Hg(II)(g)$	3×10^{-20} cm^3 molec^{-1} s^{-1}
2 $Hg^0(g) + Cl_2(g) \rightarrow HgCl_2(g)$	$\leq 4.1 \times 10^{-16}$ cm^3 molec^{-1} s^{-1}
3 $Hg^0(g) + H_2O_2(g) \rightarrow Hg(OH)_2(g)$	$\leq 4.1 \times 10^{-16}$ cm^3 molec^{-1} s^{-1}
4 $Hg_2^{2+} = Hg^0(aq) + Hg^{2+}$	2.9×10^{-9} M
5 $Hg^{2+} + SO_3^{2-} = HgSO_3(aq)$	5.0×10^{12} M^{-1}
6 $HgSO_3(aq) + SO_3^{2-} = Hg(SO_3)_2^{2-}$	2.5×10^{11} M^{-1}
7 $Hg(SO_3)_2^{2-} \rightarrow Hg^0(aq)$	1×10^{-4} s^{-1}
8 $HgSO_3(aq) \rightarrow Hg^0(aq) + SO_3^{2-}$	0.6 s^{-1}
9 $Hg^0(aq) + O_3(aq) \rightarrow Hg(II)(aq) + O_2(aq)$	4.7×10^7 M^{-1} s^{-1}
10 $Hg(OH)_2(aq) = Hg^{2+} + 2\,OH$	10^{-22} M^2
11 $HgCl_2(aq) = Hg^{2+} + 2\,Cl$	10^{-14} M^2
12 $Hg^0(g) = Hg^0(aq)$	0.11 M/atm
13 $HgCl_2(g) = HgCl_2(aq)$	1.4×10^6 M/atm
14 $Hg(OH)_2(g) = Hg(OH)_2(aq)$	1.2×10^4 M/atm
(a) At 25°C except reaction (1) (22°C) and reaction (12) (20°C)	

There are two dominant oxidation states of mercury in the atmosphere: Hg(0) and Hg(II). Elemental mercury (Hg(0)) is not very soluble. It could be oxidized in the gas phase by oxidants such as chlorine (Cl_2), hydrogen peroxide (H_2O_2) and ozone (O_3). However, significant uncertainties still remain in the kinetics of these reactions and the rates used here for the first two reactions must be seen as upper limits. Hg(0) can also be oxidized fairly rapidly by O_3 in the aqueous phase; however, its low solubility limits the amount of Hg(0) per volume of air that can be converted to Hg(II).

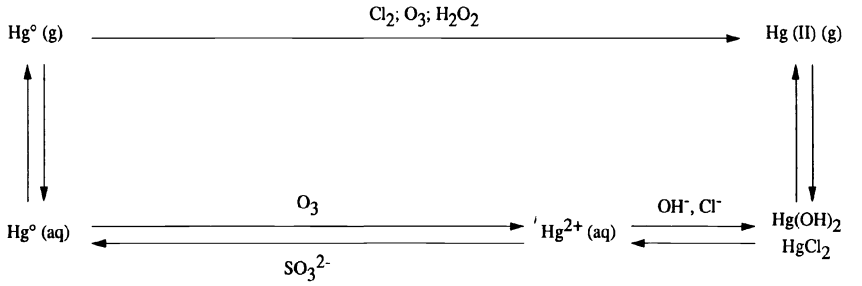

Figure 3. Schematic Description of the Atmospheric Chemistry of Inorganic Mercury

Divalent mercury (Hg(II)) exists in various forms including chloride, hydroxide, oxide and sulfide. Species such as mercury chloride ($HgCl_2$) and mercury hydroxide ($Hg(OH)_2$) are quite soluble, and, therefore, can be removed by precipitation rather effectively. In solution, mercuric ions, Hg^{2+}, can become complexed by sulfite ions (i.e.,dissolved SO_2). The mercury sulfite complexes can then be reduced to Hg(0). Complexes of Hg(II) adsorbed to soot particles can also be photolyzed to produce Hg(0). However, the kinetics of this process is uncertain and this heterogenous chemical reaction was not included in the mechanism.

4. Power Plant Plume Simulations

Model simulations were conducted for a hypothetical power plant plume dispersed into the atmosphere under different meteorological conditions. The characteristics of the power plant emissions are summarized in Table II. The mercury emissions were assumed to consist of 80% Hg(0) and 20% Hg(II) (as $HgCl_2$). Three scenarios were considered.

1. A clear sky scenario with gas-phase chemistry only.
2. A nonprecipitating cloud scenario with both gas-phase and aqueous-phase chemistry.
3. A precipitating cloud scenario with gas-phase and aqueous-phase chemistry.

All cases included dry deposition. Only the third case included wet deposition.

Background concentrations of Hg(0) and Hg(II) were 1.9 ng/m^3 and 0.1 ng/m^3, respectively. The simulations were conducted for 2.5 hours, which corresponds to a downwind distance of 100 km at a wind speed of 11 m/s.

TABLE II

Emission Characteristics of the Hypothetical Power Plant

Chemical	Emission Rate (g/s)	Stack Concentration** (g/m^3)
NO_x	2,000	1.9
SO_2	2,160	2.0
HCl	1.2	1.2×10^{-3}
Hg*	1.4×10^{-3}	1.3×10^{-6}

* Assumed to be 80% Hg(0) and 20% Hg(II)
** At standard temperature and pressure

4.1. CLEAR SKY SCENARIO

In this simulation, no significant transformations took place for mercury. Only a small amount of Hg(0) was converted to Hg(II) by reaction with O_3 and H_2O_2 (concentration of 40 ppb and 0.1 ppb were used for O_3 and H_2O_2, respectively). Moreover, this conversion is likely to be an overestimate since the rate constant of the H_2O_2 reaction is an upper limit. The reaction of Hg(0) with NO_2 was also considered because of its second-order rate with respect to NO_2 and the high NO_2 plume concentrations near the stack. Nevertheless, that reaction did not lead to any significant Hg(0) oxidation. Concentrations of SO_2, NO and NO_2 in the power plant plume are presented as function of downwind distance in Figure 4. Concentrations of Hg(0) and Hg(II) are presented in Figure 5. These plume concentrations decrease as the plume mixes with the background and tend to reach the background concentrations since no significant chemical reactions take place. The evolution of the Hg(II)/Hg(0) ratio is presented in Figure 6. This ratio decreases from the assumed initial stack ratio of 0.25 to the background value of 0.05.

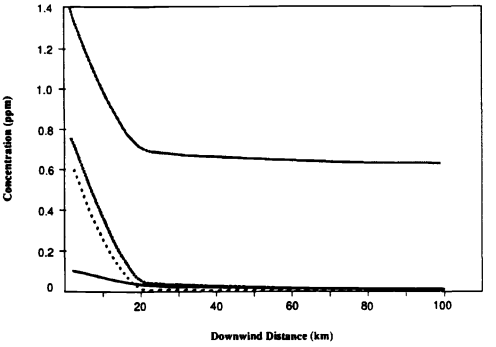

Figure 4. Plume concentrations of SO_2, NO, NO_2 and HCl as a function of downwind distance - clear sky scenario. HCl x 10^3 (——), SO_2 (——), NO (- - - -), NO_2 (——)

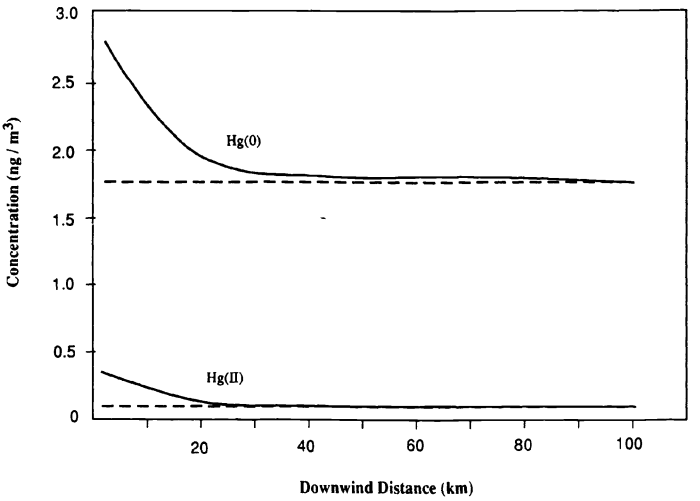

Figure 5. Plume (——) and background (- - -) concentrations of Hg(0) and Hg(II) as a function of downwind distance - clear sky scenario.

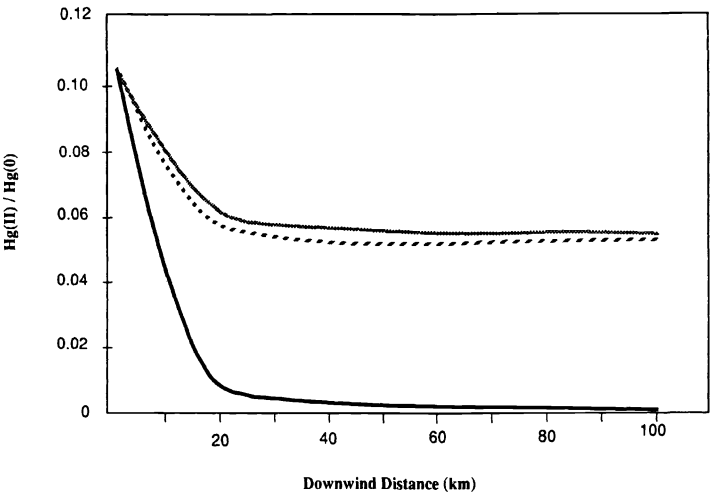

Figure 6. Hg(II) / Hg(0) ratio as a function of downwind distance for various scenarios: clear sky (——); nonprecipitating cloud (- - -); precipitating cloud (——).

The dry deposition velocities for this daytime simulation were 0.005cm/s and 0.5cm/s for Hg(0) and Hg(II), respectively. The dry deposition rates of Hg(0) and Hg(II) are presented in Table III. The contribution of the power plant plume to the total deposition rate is also indicated. It accounts for a small fraction (4%) of the total (i.e., background and power plant plume) deposition.

TABLE III

Calculated Mercury Deposition Rates (g/ha • h)

	Clear Sky Scenario	Precipitating Cloud Scenario	
	Dry Deposition Rate	Dry Deposition Rate	Wet Deposition Rate
Total* Deposition			
Hg(0)	3.1×10^{-6}	3.1×10^{-6}	4.6×10^{-7}
Hg(II)	1.7×10^{-5}	10^{-11}	1.1×10^{-3}
Plant Contribution			
Hg(0)	4.6×10^{-8}	4.7×10^{-8}	5.7×10^{-9}
Hg(II)	7.4×10^{-7}	0	1.9×10^{-5}

* Background and power plant plume

4.2. NON-PRECIPITATING CLOUD SCENARIO

For the non-precipitating cloud scenario, a liquid water content of 0.1 g/m^3 typical of a stratus cloud was assumed. The plume was assumed to be emitted into the cloud layer. Hg(0) and Hg(II) partitioned between the interstitial gas phase and the cloud liquid phase. Because of its solubility, most of Hg(0) was present in the gas phase. On the other hand, 73% of Hg(II) was present, primarily as $HgCl_2$, in the cloud droplets.

The mercury reactions that take place in the aqueous phase include complexation of Hg^{2+} by chloride ions (Cl^- results from dissolution of HCl), complexation of Hg^{2+} by sulfite ions (SO_3^{2-} results from dissolution of SO_2) and subsequent reduction to Hg(0), and oxidation of Hg(0) by dissolved O_3.

The simulation results show some reduction of Hg(II) to Hg(0) in the plume because of the high SO_2 concentrations. Some Hg(II) is complexed by Cl^- as $HgCl_2$ and is not, therefore, available for reduction by dissolved SO_2. As shown in Figure 6, the ratio of Hg(II)/Hg(0) decreased from 0.25 in the emissions (i.e., 20% Hg(II) and 80% Hg(0)) to 0.05 at the end of the simulation, i.e., a value lower than the initial background value.

4.3. PRECIPITATING CLOUD SCENARIO

For the precipitating cloud scenario, a liquid water content of 0.5 g/m^3 was assumed. The precipitation rate was 0.9 mm/h and the raindrop fall velocity was 5 m/s. The plume was emitted into the cloud layer. The partitioning of Hg(0) and Hg(II) between the gas phase and the liquid phase was similar to the previous case except that the higher liquid water content led to more mercury mass to be present in the liquid phase. In this case, nearly 100% of Hg(II) was present in the droplets.

The mercury reactions that took place in this scenario were the same as in the previous scenario; however more Hg(II) was converted to Hg(0). This result is due to the fact that a raining cloud tends to have a higher pH than a nonprecipitating cloud because acidic species such as sulfates, nitrates and chlorides are removed by precipitation faster than less

soluble species such as SO_2 and sulfites. For example, between the downwind distances of 20 and 100 km, the droplet concentration of chloride decreases by 80% whereas the droplet concentration of sulfite decreases only by 50%. As a result, Hg(II) is complexed as $Hg(SO_3)_2^{2-}$ rather than $HgCl_2$ and is thereby reduced faster to Hg(0). As shown in Figure 6, the atmospheric ratio of Hg(II)/Hg(0) in the plume decreased from 0.25 in the emissions to 0.002 at the end of the simulation.

Both dry and wet deposition rates were calculated and are presented in Table III. The wet deposition rate is significantly greater than the dry deposition rate, which is expected during a precipitation event. Clearly, precipitation occurs only a small fraction of the time (1 to 3% in most of the United States) and annual values of mercury wet deposition would, therefore, be lower by about two orders of magnitude (i.e., of the order of 0.1 g/ha·y).

5. Conclusion

The formulation of a reactive plume model that treats emissions of mercury and other chemicals such as nitrogen oxides, sulfur dioxide and hydrogen chloride, was presented. This model includes treatment of advection, convection and dispersion; 170 reactions in the gas phase and the aqueous phase among 130 species; aerosol formation and dynamics; dry deposition, cloud microphysics and wet deposition.

The model was applied to the simulation of a hypothetical power plant plume under various meteorological conditions that included clear skies, non-precipitating stratus clouds, and precipitating clouds.

The model simulation results show dry deposition rates ranging from 3.1×10^{-6} to 2.0×10^{-5} g/ha·h (i.e., 0.03 to 0.18 g/ha·y) for daytime conditions. The lowest value was obtained for the precipitating cloud simulation whereas the highest value was obtained for the clear sky simulation. The nonprecipitating cloud gave dry deposition rates between these two other cases. For the precipitating cloud case, wet deposition was about 0.001 g/ha·h. If one assumes that it rains 1% of the time, annual wet deposition would be of the order 0.1 g/ha·y. The contribution of the power plant emissions to total (i.e., background and power plant contributions) mercury deposition was in the range of 1% to 4% for the downwind distance range considered (i.e., 100 km from the plant).

The model simulations suggest that mercury chemistry in a plume differs in precipitating clouds and non-precipitating clouds. In non-precipitating clouds, Hg(II) tends to be complexed as $HgCl_2$ and therefore, reduction of Hg(II) to Hg(0) is limited by the amount of $HgSO_3$ formed. In precipitating clouds, the chloride ions are removed by rain more rapidly than SO_2 (i.e., SO_3^{2-} ions). Moreover, the higher pH typically associated with a precipitating cloud when acidic species are rained out, favors higher SO_3^{2-} concentrations. As a result, Hg is complexed as $Hg(SO_3)_2^{2-}$ rather than $HgCl_2$, and is rapidly reduced to Hg(0).

These simulation results are commensurate with available experimental data. However, many uncertainties in the atmospheric chemistry and dynamics of mercury species remain. Experimental programs should focus on collecting atmospheric data during precipitation

events to obtain quantitative information on the chemical transformations of mercury that may take place during such conditions. The reactive plume model presented here is an effective conceptual framework that can be used to design such field experiments as well as to analyze the data obtained from the experiments.

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AN EXPERIMENTAL STUDY OF TWO POTENTIAL METHYLATION AGENTS OF MERCURY IN THE ATMOSPHERE: CH_3I AND DMS

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Abstract. Experimental results from a study of the gas and aqueous phase reactions of elemental mercury (Hg^0) with methyl iodide (CH_3I) and dimethyl sulfide (DMS) are presented. In aqueous phase experiments with CH_3I we found no observable increase in methyl mercury (MeHg). A small formation of MeHg, however, was observed in some (but not all) gas phase experiments in sunlight. A loss of Hg^0 and a simultaneous formation of oxidized mercury (Hg(II)) was also observed in these experiments. No reaction, neither methylation or oxidation, was found between Hg^0 and DMS under any conditions investigated. These experiments suggest that a simple homogeneous gas or aqueous phase methylation of Hg^0 by DMS or CH_3I in the atmosphere cannot account for the significant levels of MeHg observed in precipitation.

1. Introduction

Methyl mercury (MeHg) has been observed both in precipitation (0.01-0.5 ng L^{-1}) and in air (0-20 pg m^{-3}) (Bloom and Watras, 1988; Lee and Iverfeldt, 1991; Munthe and Iverfeldt, 1993; Brosset and Lord, 1994), but the source of this atmospheric MeHg is as yet unknown, although it does not appear to be due to direct anthropogenic combustion emissions (Prestbo and Bloom, 1994). The present study investigates the possibility of atmospheric mercury (Hg) methylation by homogeneous gas or aqueous phase reactions between elemental mercury (Hg^0), methyl iodide (CH_3I), and dimethyl sulfide (DMS). Methyl iodide is a well known methylating agent used in organometallic synthetic chemistry, and can be used to produce MeHg by direct methylation (Rochow, 1966; Thayer, 1989). DMS was chosen because of the well known affinity of Hg to sulfur, and DMS's ability to form adducts with Hg salts (Farrager *et al.*, 1929). Methyl iodide is produced by marine periphyton while DMS is produced by phytoplankton in the oceans. Both compounds are subsequently released to the atmosphere where reported concentrations of CH_3I are ~1-4 ppt (Manley and Dastor, 1988) and DMS ~100 ppt (Andreae *et al.*, 1985).

2. Materials and Methods

2.1. GAS PHASE EXPERIMENTS

Gas phase experiments were performed in 1 L ultra-clean Teflon® reactors. A gas mixing system, with nitrogen (N_2) as the carrier gas (0.5-4 L min^{-1}) was used to set initial concentrations. Elemental Hg was generated using a Lab-built diffusion cell, while DMS and CH_3I were generated by VICI Metronics (San Jose, CA) certified diffusion cells. Mercury concentrations were approximately 5 40 μg m^{-3}. CH_3I-to-Hg molar ratios of 2 to 100, and a DMS-to-Hg of 250 were tested. The reactors were flooded with the gas mixture, the

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valves were closed and the reactors stored either in darkness (22 °C or 75 °C) or in sunlight. After a predetermined storage time, the reactors were purged with N_2 (at a flow of 1 L min^{-1}) and the gas phase Hg was either trapped on treated soda-lime (which captures gaseous oxidized mercury (Hg(II)) and MeHg) or on gold-coated sand (which captures total gaseous Hg). Mercury trapped on the reactor walls was recovered by rinsing the reactor with hydrochloric acid (HCl) or with acetic acid (HAc). Samples were analyzed for Hg(II) and MeHg by previously established procedures (Bloom, 1993).

2.2. AQUEOUS PHASE EXPERIMENTS

Aqueous phase experiments were performed in 125 mL Teflon® vessels in both darkness and in sunlight. The experimental solutions were prepared by bubbling the reactants through milli-Q water using the gas mixing system described above. Concentrations were varied over a wide range with CH_3I and DMS-to-Hg ratios of 1 to 1000, with a typical concentration of Hg of $5x10^{-8}$ M. Samples were drawn for MeHg analysis after reaction times ranging from 1 hour to 1 week.

3. Results and Discussion

No measurable MeHg was formed under any conditions in the experiments with DMS. Neither was any methylation observed in darkness (22 °C and 75 °C), or in aqueous experiments with CH_3I. However, in sunlight experiments with CH_3I, Hg^0 was oxidized and a corresponding buildup of Hg(II) was observed on the walls of the reactor (Fig. 1).

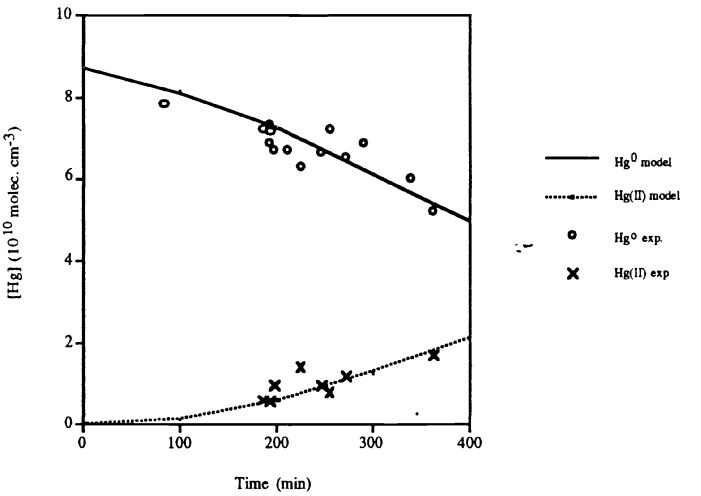

Fig. 1. Comparison of experimental results and model predictions for loss of elemental mercury and formation of oxidized mercury.

In some (but not all) cases a formation of MeHg close to the detection limit was also observed (Table I), whereas gaseous MeHg and Hg(II) levels were not distinguishably above the blanks of the soda-lime traps. The results indicate that the major components in the system are $Hg^0(g)$, adsorbed elemental mercury ($Hg^0(ads)$) and adsorbed oxidized mercury ($Hg^{II}(ads)$). The mass balance was relatively good (96-109%), and it appears that the technique provides accurate and reproducible results.

TABLE I

Results of Hg + CH_3I experiments in 1 liter reactors. CH_3I concentration = 1.1 mg m^{-3}. Experiments were performed Sept. 1 - 30, 1993. The solar flux (J)~700 W m^2.

Run	Time (min)	Hg(tot) (pg L^{-1})	MeHg(w) (pg L^{-1})	Conversion ratio (%)	Formation rate[1]	Rate constant[2]
1	16	17900	1.3	0.007	0.08	$1.5x10^{-20}$
2	151	17900	3.0	0.02	0.02	$3.7x10^{-21}$
3	293	17900	11.0	0.06	0.04	$7.4x10^{-21}$
4	20	20000	0	0	0	0
5	152	20000	0.4	0.002	0.002	$3.3x10^{-22}$
6	290	20000	1.3	0.006	0.004	$6.7x10^{-22}$
7	83	16500	0	0	0	0
8	210	16500	0.5	0.003	0.002	$4.0x10^{-22}$
9	339	16500	1.5	0.009	0.004	$8.1x10^{-22}$
10	310	19500	2.1	0.01	0.007	$1.2x10^{-21}$

The rate constant was calculated assuming a pseudo-first order reaction between Hg^0 and CH_3I.
Unit: 1. pg L^{-1} min^{-1}; 2. cm^3 $molec^{-1}$ s^{-1}

Although the uncertainties are large in Table I, the results provide information about the maximum rate this reaction might have. By using a simple box model (volume: $1x10^{18}$ cm^3), a rough idea of its impact on the environment can be estimated. The rate constants are in the range of $0.3x10^{-21}$ to $15x10^{-21}$ cm^3 $molec^{-1}$ s^{-1}. Assuming the concentration of Hg^0 and CH_3I to be 3 ng m^{-3} ($9x10^6$ atoms cm^{-3}) and 2 ppt ($5x10^7$ molec. cm^{-3}), respectively, the maximum methylation rate is $7x10^{-6}$ molecules of MeHg cm^{-3} s^{-1}. Thus, $7x10^{12}$ MeHg molecules-per-second are formed in a volume of $1x10^{18}$ cm^3. By further assuming that the air mass contains 2% of water (volume-to-volume) with a half life of 1 day, and that all MeHg formed will be washed out because of its low Henry's law constant, the maximum concentration of MeHg in the water will be on the order of $2x10^{-5}$ ng L^{-1}. This is three orders of magnitude lower than is observed in rain water. It appears, therefore, that this reaction is too slow to be significant for the methylation of Hg^0 in the atmosphere, but the limitations of this estimate must be kept in mind. Performing the same calculation for DMS, but using the detection limit as a measure of the maximum rate of formation of MeHg, shows that this reaction is also unlikely to contribute to the observed MeHg in rain.

Using data from Chamedies and Davies (1980) describing the photolytic decomposition of CH_3I, the following model was developed to explain the oxidation of Hg^0 in sunlight by CH_3I.

$$CH_3I(g) + hv \xrightarrow{k_1} CH_3(g) + I(g) \qquad k_1=3x10^{-6}\ s^{-1} \qquad (1)$$

$$I(g) + I(g) + M \xrightarrow{k_2} I_2(g) + M \qquad k_2=3.7x10^{-32}\ cm^6\ molec.^{-2}\ s^{-1} \qquad (2)$$

$$I_2(g) + hv \xrightarrow{k_3} I(g) + I(g) \qquad k_3=0.05\ s^{-1} \qquad (3)$$

$$Hg^o(g) + I_2(g) \xrightarrow{k_4} HgI_2(g) \qquad k_4=?\ (cm^3\ molec.^{-1}\ s^{-1}) \qquad (4)$$

$$Hg^o(g) \xrightarrow{k_5} Hg(ads) \qquad k_5=9.5x10^{-6}\ s^{-1} \qquad (5)$$

$$Hg^o(g) + CH_3I(g) \xrightarrow{k_6} CH_3HgI \qquad k_6=?\ (cm^3\ molec.^{-1}\ s^{-1}) \qquad (6)$$

As seen in Figure 1, there is a fairly good agreement between the model and our laboratory observations with a rate constant of $2.7x10^{-16}$ cm^3 $molec.^{-1}$ s^{-1} for k_4. This is close to the value calculated by Schroeder *et al.* (1991) for the Hg^o + Cl_2 reaction ($4x10^{-16}$ cm^3 $molec.^{-1}$ s^{-1}). However, due to the low concentration of iodine in the atmosphere, this reaction has probably no significant effect on the lifetime of atmospheric Hg^o.

4. Conclusions

Direct methylation of Hg^o by CH_3I or DMS appears not to happen to any significant degree during the experimental conditions employed in this study. It is therefore suggested that the contribution to the atmospheric MeHg load through direct gas or aqueous phase methylation by these compounds is very small. The high levels of MeHg in rain and lack of significant direct anthropogenic inputs suggest, however, that as yet unidentified atmospheric methylation reactions do play a role. A loss of Hg^o and a corresponding buildup of Hg(II), probably HgI_2, was observed in all experiments in sunlight with CH_3I. However, due to the low concentration of iodine in the atmosphere, this reaction probably has no significant effect on the lifetime of atmospheric Hg^o.

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RELATIONSHIPS BETWEEN THE ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS, MAJOR IONS, AND MERCURY IN FLORIDA: THE FAMS PROJECT (1992-1993)

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Abstract. A multiple chemical tracer approach was used in an effort to account for the atmospheric Hg deposition measured throughout Florida as part of the Florida Atmospheric Mercury (FAMS) Study. Samples of bulk deposition and wet-only deposition were analyzed for a suite of major ions and trace elements in addition to Hg. Significant correlations were found between three groups of elements: Al, Mn, and Fe; Ni, Cu, Zn, and Cd; and As, V, and Pb. However, Hg did not correlate strongly with any of the other chemical tracers. Annual bulk deposition fluxes are attributed to sea-salt aerosols (Na, Cl), the delivery of Saharan dust (Al and Fe), the supply of anthropogenic pollutant aerosols (V, Ni, Cu, Zn, As, Cd, Pb), acidic aerosols (nitrate and nss-sulfate), and an unidentified source for Hg.

1. Introduction

The Florida Atmospheric Mercury Study (FAMS) has as its primary goal to quantify the temporal and spatial variability in atmospheric mercury (Hg) deposition across Florida. The organization and rationale for the FAMS project is described by Pollman *et al.* (this volume). Our preliminary data on atmospheric Hg deposition from the five FAMS sites which have been operational for at least 12 months are presented in Guentzel *et al.* (this volume).

The FAMS project goals also include efforts to use a multiple chemical tracer approach in an effort to understand and account for the Hg found in Florida rainfall. A suite of major ions and trace elements was selected for this purpose, including species which reflect input from sea-salt aerosols (sodium-Na, chloride-Cl), aluminosilicate dust (aluminum-Al, manganese-Mn, iron-Fe), acidic aerosols (nitrate, sulfate), and urban atmospheric pollution (vanadium-V, chromium-Cr, nickel-Ni, copper-Cu, zinc-Zn, arsenic-As, selenium-Se, cadmium-Cd, lead-Pb). In this report, we present our preliminary data for major ions and other trace elements measured on the FAMS samples.

2. Materials and Methods

All of the sampling preparation and sample manipulations are performed in a "clean lab" environment at FSU to minimize contamination. Plastic labware is extensively acid washed and checked for the potential of sample contamination. Ultrapure water is provided by a Barnstead NanoPure-II deionization system. Ultrapure HCl (Q-HCl) and HNO_3 (Q-HNO_3) are prepared by sub-boiling distillation in a quartz-glass apparatus. The 6 M HCl is triple-distilled to lower the Hg blank to less than 10 pg/mL.

The rain samples were collected from the five FAMS sites described in detail by Pollman *et al.* (this volume). Lake Barco is located in the Ordway Preserve northeast of

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Gainesville in north-central Florida. The Ft. Myers site is located in the Terry Park recreation complex in central Ft. Myers. The Fakahatchee Strand site is located at the Fakahatchee Strand Ranger Station near the town of Copeland. The Tamiami Trail site is on the grounds of the Tamiami Trail Ranger Station (Everglades National Park), approximately one half of the way across south Florida along US Highway 41. The Everglades Research Center site is located at the Beard Research Center, Everglades National Park, 15 miles southwest of Homestead.

Rainfall samples are collected atop 48-foot tall sampling towers, described by Guentzel *et al.* (this volume). Month-long bulk deposition samples are collected in duplicate using 12.2 cm diameter, 25 cm tall polycarbonate funnels connected via FEP Teflon tubing to 2 liter FEP Teflon receiving bottles which have been pre-charged with 15 mL of 6 M Q-HCl. Wet-only deposition samples are collected using triplicate polycarbonate funnels (9 cm square, 7 cm tall) attached to 1 liter FEP Teflon receiving bottles held in the "wet" bucket side of a modified Aerochem Metrics wet/dry deposition sampler (see Guentzel *et al.*, this volume for details). Two of the bottles are pre-charged with 7.5 mL of 6 M Q-HCl while the unacidified third sample is used for Cl and major ion subsamples.

This sampling strategy has been extensively tested for artifacts such as contamination during sample collection, gaseous Hg uptake during the long deployment, Hg loss during deployment, etc. (Guentzel *et al.*, this volume). Surprisingly, despite the very low pH in the receiving bottles, biological growth (algae?) in the receiving bottles during the deployment can result in trace metal adsorption to the bottle walls. A simple UV oxidation procedure has been developed to eliminate this problem (Guentzel *et al.*, this volume). Samples which exhibit anomalous concentrations due to bird droppings, insects, or other debris in the funnel have been excluded from the data set (this affects less than 5% of the bulk deposition samples and only a few of the wet deposition samples). We have not yet found any evidence for additional artifacts that could affect the quality of the data we are collecting.

Sub-samples for trace element analyses were initially stored in acid washed 125 or 250 mL polyethylene bottles, then prepared for elemental analysis by weighing 100.00 g of sample into a 100 mL PTFE Teflon beaker. The beaker was then placed on a hot plate inside a vertical laminar flow hood located in the clean lab. The hot plate was set on low heat to ensure that the sample was slowly evaporated to dryness, without boiling or frothing. After the evaporation was completed, the residue was redissolved with 10.0 mL of 0.3 M HNO_3 and placed on the hot plate for 10 minutes. The sample was then transferred to an acid washed 15 mL polyethylene bottle and stored for analysis. Trace elements on the pre-concentrated samples were measured using a Perkin-Elmer Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) Elan 5000A, with a sample aspiration rate of 1.0 mL per minute. Peak intensities were corrected using a suite of internal standards (Sc-45, Y-89, In-115, and Tb-159). Mixed-metal check standards were run every 10 samples, with $\pm$2-5% precision.

Background contamination was monitored by including various blanks with each set of evaporations. This includes laboratory reagent blanks, field deployment blanks, and old and new equipment rinse blanks. One reagent blank was taken through the evaporation procedure with each set of 20 samples. Field deployment blanks are collected and analyzed every month, at a rate of 5% of the total sample number. New and old equipment rinse blanks are also collected every month. All blanks and standard solutions

are acidified with 7.5 mL of 6 M Q-HCl per liter of solution, as are all of the samples.

A minimum of 10% of the samples were analyzed in duplicate and/or spiked to determine the recovery efficiency of the procedure. Spike recovery checks were performed by combining 50 grams of sample with 50 grams of a standard in a 100mL PTFE Teflon beaker. This method of spike preparation was chosen in order to ensure that the final concentration of the spiked sample remained within the linear portion of the standard curve. A set of mixed-metal standards was evaporated with each group of samples to monitor the linearity and reproducibility of the measurements. Trace metal recoveries for these procedures are quantitative (± 5 to 10%).

3. Results and Discussion

3.1 Reagent and Field Equipment Blanks

Deployment blanks are quantified by deploying a bulk deposition setup with the funnel pointed downwards. Upon recovery, the funnel is turned upward and rinsed twice with 70 mL of ultrapure acidified (0.045 M Q-HCl) water. The receiving bottle containing 15 mL of 6 M Q-HCl can be recovered either before or after the funnel rinse. New and old equipment blanks are measured by pouring one-half of a 1000 mL bottle of ultrapure acidified water (0.045 M Q-HCl) through the sampling setup (the "B" solution). The remainder of the water is retained as the "A" solution. The equipment blank is reflected in any concentration differences between the A and B solutions. These A/B rinse blanks are collected when new sampling equipment is deployed and also when old equipment is recovered. These various deployment and equipment blanks are not significantly different from the evaporation reagent blanks, and generally represent only 1 to 10% of the sample concentrations. Due to instrumental limitations, the concentrations of Cr and Se are not detectable on most samples and are therefore excluded from the statistical treatment of the data.

3.2 Relationships among Trace Elements and Major Ions

The concentrations of Na and Cl in wet deposition from all five FAMS sites are very well correlated, exhibiting small Cl depletion relative to what one would expect from sea-salt aerosols (Figure 1a). Aerosol washout behavior is exhibited by Na, K, Mg, Ca, and Cl (Cl shown in Figure 1b).

We also observe a strong correlation between nitrate and non sea-salt sulfate (Figure 2a; $R^2=0.62$, 0.5 ± 0.1 gram N per gram S). Savoie *et al.* (1989) reported aerosol N/S mass ratios in Barbados of 0.23 in the summer and 0.92 in the winter, and found significant correlations between nitrate, nss-sulfate, and Saharan dust aerosols. They attributed this relationship to a common westward transport process within the dry Saharan Air Layer (SAL) between 1.5 and 6 km altitude. As we obtain more wet deposition samples from the southern Florida FAMS sites we will see whether we can identify the same or similar processes affecting N and S over south Florida. Alternatively, the data we have thus far may reflect the influence of local, regional, or larger-scale North American processes. The N/S mass ratio of approximately 0.5 is only about half of the North American emissions ratio (N/S = 1.2, data cited in Galloway *et al.*, 1992), suggesting either nitrate depletion or sulfate enrichment in our rain samples.

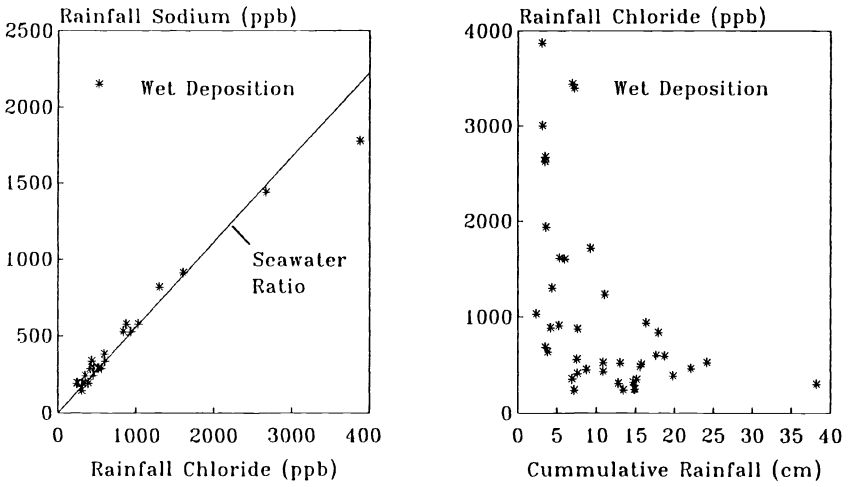

Fig. 1. (a) Na vs. Cl for the FAMS wet deposition samples. The solid line represents the 0.556 Na/Cl mass ratio expected from sea-salt aerosols. (b) Cl vs. monthly integrated rainfall amount illustrating the aerosol washout behavior of Cl.

Because our samples are integrated over a one month period, it is likely that the nitrogen redox speciation in the receiving bottle may have been altered. When we have the equipment in place, we plan to analyze a set of stored samples for total dissolved nitrogen. After subtraction of the measured nitrate+nitrite, this will give us some estimate of the initial ammonia content of the samples. In any event, the nitrate and sulfate in our wet deposition samples also exhibit aerosol washout behavior (nss-sulfate shown in Figure 2b).

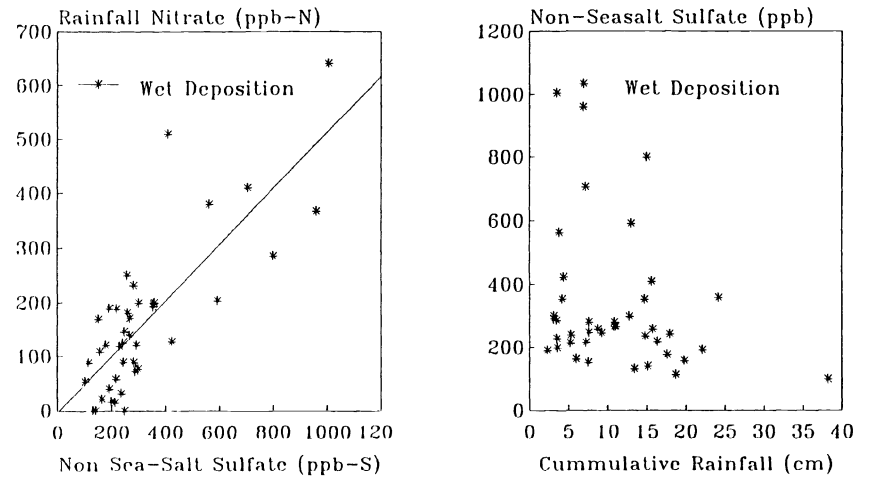

Fig. 2. (a) Nitrate vs. nss-sulfate for the FAMS wet deposition samples. The solid line represents a linear regression of the data (Nitrate-N=0.52±0.06 x nss-sulfate; R^2=0.62; n=41). (b) nss-sulfate vs. monthly integrated rainfall amount illustrating the aerosol washout behavior of nss-sulfate.

Iron and Al are very well correlated (Figure 3a), falling close to the global average crustal abundance ratio (0.61 g Fe per g Al; Taylor, 1964). Manganese correlates less well with Al, and the Mn appears to be enriched about 5-fold relative to average crustal material (Figure 3b). The use of methylcyclopentadienyl manganese tricarbonyl (MMT) to boost octane ratings in unleaded gasoline is a possible source for the excess atmospheric manganese (Abbott, 1987). These elements also exhibit aerosol washout behavior.

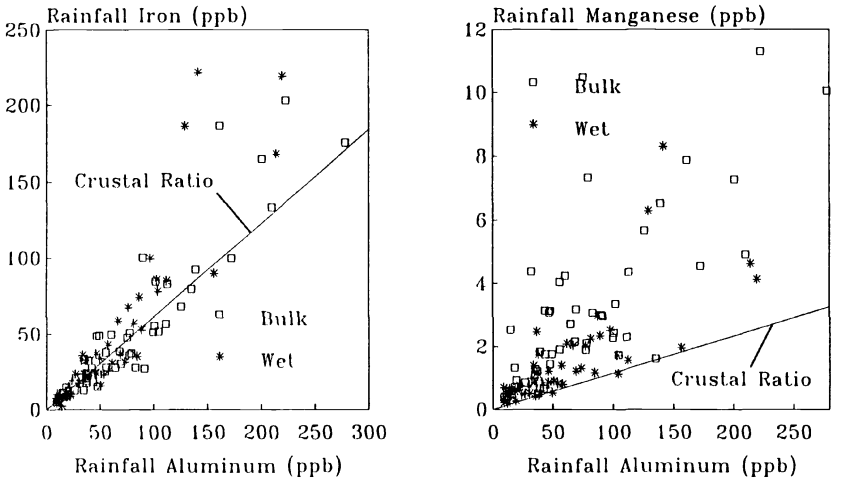

Fig. 3. (a) Fe vs. Al in FAMS bulk and wet deposition samples. The solid line represents the crustal average Fe/Al mass ratio (0.614). (b) Mn vs. Al in the FAMS bulk and wet deposition samples. The solid line represents the crustal average Mn/Al mass ratio (0.0117).

Other strong correlations are observed between Cd, Cu, and Zn (Cd vs. Zn shown in Figure 4a) and between As, V, and Pb (As vs. Pb shown in Figure 4b). The concentrations of these trace metals in the bulk and wet deposition samples are all greatly elevated over what one would predict based on crustal abundance relative to Al. However, the slope of the Cd vs. Zn bulk deposition data is only slightly higher than the crustal average (0.0047 ± 0.0005 g Cd per g Zn observed vs. 0.0029 reported) and the slope of the As vs. Pb data is not significantly different from the crustal average ratio (0.12 ± 0.02 g As per g Pb observed vs. 0.138 reported). The agreement between these ratios and the crustal average ratios is probably fortuitous, since we expect each of these trace elements to have a variety of source terms to the atmosphere.

A recent study of trace metals in aerosols in the Chesapeake Bay region showed a Cd/Zn mass ratio from 2 to 3 times the ratio we observe (Wu *et al.*, 1994). They attribute the bulk of the Cd and Zn in aerosols to municipal waste incinerator emissions. Wu *et al.* (1994) also report a As/Pb mass ratio of 0.13 to 0.15, not especially elevated above the crustal ratio. However they attribute the As to emissions from the steel industry, while motor vehicles and waste incinerators are cited as the dominant sources for the Pb. Church and Scudlark (1992) report a Cd/Zn mass ratio in wet deposition from the Chesapeake Bay region of 0.036, nearly 8 times the ratio we report. They also report an As/Pb mass ratio of 0.09, probably not significantly different from the other ratios

reported of around 0.12 to 0.15. Due to the removal of lead from fuels used in the U.S. and Canada, the levels of atmospheric lead have been declining steadily. As a result, older As/Pb mass ratios as low as 0.03 were reported for Lewes, Delaware and the Mediterranean (Church *et al.*, 1984 and data summarized by Duce *et al.*, 1991).

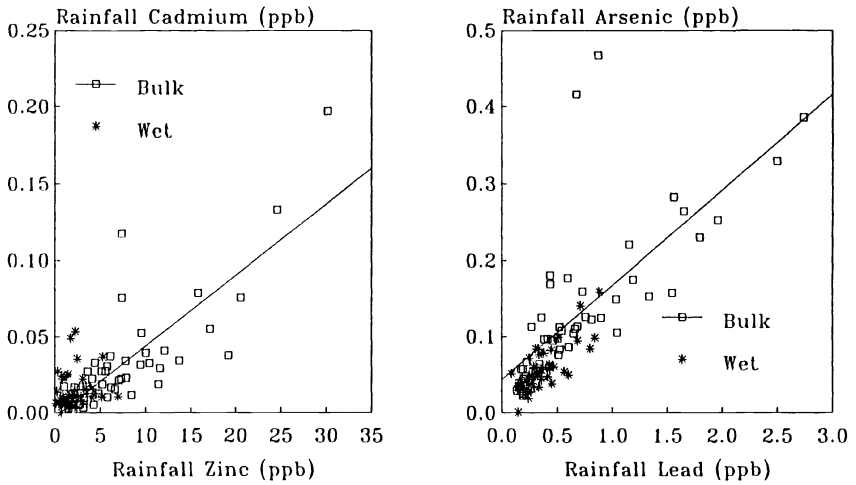

Fig. 4. (a) Cd vs. Zn in the FAMS bulk and wet deposition samples. (b) As vs. Pb in the FAMS bulk and wet deposition samples. The solid line are regression lines for the bulk deposition samples.

While we might expect that the atmosphere in south Florida should be impacted by the emissions from motor vehicles and waste incinerators (among a wide variety of sources), we do not yet have enough data from the marine background site (Little Crawl Key) to demonstrate whether the concentrations and fluxes we find are elevated above the background. Regardless of the sources of these trace elements to the atmosphere in Florida, these "pollutant" tracers clearly exhibit aerosol washout behavior (Figure 5a, 5b).

Somewhat surprisingly, no significant correlations between rainfall Hg and any other of the chemical tracers were observed in the bulk deposition or the wet deposition. The interrelationships among the trace elements were quantified using the multivariate statistical treatment of Principle Component Factor Analysis (PCFA). Using the wet deposition results, the data cluster into five significant factors (Table I).

The first factor explains much of the nitrate, nss-sulfate, As, Pb, and V variance and probably can be interpreted as a pollution component. Jickells *et al.* (1984) also identified a factor in Bermuda rainfall with high weighting for Cd, Cu, Ni, and Zn, attributing it to "a fine neutral aerosol specifically enriched in these trace metals." Factor 2 explains most of the Al, Mn and Fe variance and likely represents the crustal dust component. Factor 3 explains much of the Ni and chloride variance, the remainder of the Cu and Zn variance not explained by factor 1, and probably represents a pollution component although the inclusion of the chloride variance is perhaps surprising. Factor 4 explains most of the Cd variance, contains modest loadings for many of the species in Factor 1, and probably also represents a pollution component. The Hg variance is nearly isolated into Factor 5, with modest loadings for Al and Ni.

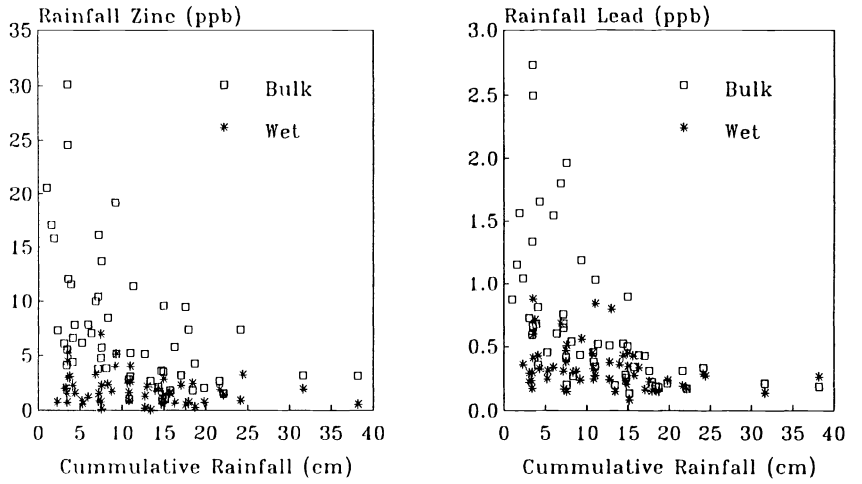

Fig. 5. (a) Zn vs. monthly integrated rainfall for the FAMS bulk and wet deposition samples. (b) Pb vs. monthly integrated rainfall for the FAMS bulk and wet deposition samples. Aerosol washout behavior is exhibited by V, Al, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb.

TABLE I

Varimax Rotated Factor Matrix: Wet Deposition (1993 to 1994; All Sites)

Element	Factor 1 N,S,As,Pb,V	Factor 2 Al,Fe,Mn (Hg)	Factor 3 Ni,Cl (Cu,Zn)	Factor 4 Cd (N,S,As,Zn)	Factor 5 Hg (Al,Ni)
NO_3	0.684	0.112	-0.099	0.403	0.206
nss-SO_4	0.773	-0.002	-0.085	0.372	0.099
As	0.790	0.225	-0.050	0.349	0.024
Pb	0.867	0.142	0.209	0.244	0.034
V	0.923	0.065	-0.033	-0.154	0.038
Cu	0.694	0.131	0.474	-0.013	0.048
Zn	0.612	-0.027	0.504	0.341	-0.076
Al	0.116	0.881	-0.017	0.106	0.320
Fe	0.082	0.975	-0.061	-0.055	0.165
Mn	0.132	0.950	-0.029	0.078	-0.041
Ni	0.205	-0.057	0.829	0.046	0.341
Cl	-0.167	-0.076	0.823	-0.076	-0.265
Hg	0.095	0.338	0.007	-0.022	0.904

A similar treatment of the bulk deposition data yields two "pollution" factors (Cd, Cu, Ni, and Zn; As, Pb, and V), a crustal dust factor (Al, Mn, and Fe), and a Hg factor

with modest loadings for Ni, Al, and V. The remainder of the Hg variance for both treatments falls into the "aluminosilicate" factor (Factor 2) and can be explained as follows. As described by Guentzel *et al.* (this volume), the rainfall rate and the concentrations of Hg in Florida rain increase during the summer months (April to September), combining to yield a significant increase in deposition during the summer. Coincidentally, the delivery of Saharan dust to south Florida also reaches a maximum during the mid-to-late summer (Savoie *et al.*, 1989). The washout of this aerosol material yields very high Al and Fe concentrations during the June-September period, and is especially pronounced at the south Florida sites.

As more data from the FAMS project accumulates, we will have the capability of analyzing the data from each site independently using PCFA (or other multivariate techniques) to evaluate the importance of local *vs* regional or hemispheric emission sources for Hg and other trace elements. Despite the fact that we are lumping data from across Florida and over two years of sampling, strong correlations are still observed between many trace elements, while Hg does not correlate strongly with any of the analytes we have measured thus far.

3.3 ANNUAL DEPOSITION OF TRACE ELEMENTS

The bulk deposition samples collected for the FAMS project are expected to represent 100% of the wet-only deposition. They also contain whatever dry deposition collects in the polycarbonate funnels and is rinsed into the receiving bottles by rainfall during the month-long deployment period and by the pre-recovery rinses with dilute HCl. While we have not investigated the aerodynamic behavior of these funnels with respect to particle trapping, we can use relative difference between sites to reach some quantitative conclusions regarding atmospheric trace element deposition in Florida. The annual bulk deposition of the trace elements is reported in Table II calculated by summing the monthly deposition fluxes. Monthly fluxes are calculated by multiplying the measured chemical concentrations by the monthly rainfall accumulation (measured using a tipping-bucket rain gage on the tower). The errors in these fluxes range from 20 to 30% due to a simple propagation of errors (5 to 10% replicate sample variability per month).

The fluxes of Al and Fe are highest at the Everglades Research Center site and are comparable to those observed in Bermuda, an island in the Sargasso Sea that receives Saharan dust as well (Church *et al.*, 1984; Jickells *et al.*, 1984). The annual Al flux was also reported as 100,000 $\mu g\ m^{-2}yr^{-1}$ at Miami, Florida by Prospero *et al.* (1987), and was dominated by a few rain events carrying Saharan dust. As this aerosol material is washed out by rainfall, the Al and Fe fluxes decrease dramatically across south Florida.

Some evidence of anthropogenic input can be seen in the fluxes of V, Ni, Cu, Zn, and As. The fluxes of these elements are highest at the two sites most likely to be impacted by pollutant aerosols generated by local/regional anthropogenic activity: Everglades Research Center and Ft. Myers. In contrast, the bulk deposition fluxes of Hg are relatively uniform across south Florida (19-28 $\mu g\ m^{-2}yr^{-1}$; Guentzel *et al.*, this volume). In strong contrast to the behavior of the other trace elements and major ions reported here, Hg in rainfall during the Florida summertime does not demonstrate typical washout behavior (Guentzel *et al.*, this volume). Guentzel *et al.* (this volume) present additional evidence that the wet and bulk deposition of Hg in south Florida is not significantly influenced by locally or regionally generated pollutant aerosols. However, it

is important to note that, to date, we have only 12 months of data from the Everglades Research Center and Tamiami Trail Ranger Station sites, 20 months of data from the Fakahatchee Strand and Ft. Myers sites, and 24 months of data from Lake Barco. Year-to-year variations in monthly rainfall amount can be substantial and would dramatically affect these flux calculations. We should eventually have a minimum of 28 months of data from all sites to allow us to more accurately characterize the annual trace element deposition.

TABLE II

FAMS Site Intercomparison: Trace Element Bulk Deposition Fluxes (1993-1994)

Element/Flux	LB	FM	FS	TT	EG	Bermuda[1]
Al $\mu g\ m^{-2}yr^{-1}$	62000	76000	64000	106000	148000	120000
V $\mu g\ m^{-2}yr^{-1}$	900	2930	940	1270	1500	140-160
Mn $\mu g\ m^{-2}yr^{-1}$	2130	1900	3060	2950	4960	300-1500
Fe $\mu g\ m^{-2}yr^{-1}$	32000	48000	37000	74000	104000	72000
Ni $\mu g\ m^{-2}yr^{-1}$	1880	3700	1700	2230	4130	200-300
Cu $\mu g\ m^{-2}yr^{-1}$	430	1400	1080	950	1840	240-1000
Zn $\mu g\ m^{-2}yr^{-1}$	5320	6480	5800	5820	11920	800-2000
As $\mu g\ m^{-2}yr^{-1}$	86	141	104	98	116	20-30[2]
Cd $\mu g\ m^{-2}yr^{-1}$	20	25	16	20	106	90-140
Pb $\mu g\ m^{-2}yr^{-1}$	496	974	403	677	530	1000-1400
Hg $\mu g\ m^{-2}yr^{-1}$	15	23	19	28	20[3]	

1. Church *et al.* (1984); additional Bermuda data courtesy of Tom Church.
2. Cutter (1993).
3. Hg data described in detail by Guentzel *et al.* (this volume)

4. Conclusion

Based on the data we have collected to this point in the FAMS project, we can tentatively describe five "sources" for the chemical species we are measuring in wet and bulk deposition in Florida: (1) Sea-salt aerosols (Na, Cl); (2) Acidic Aerosols (nitrate, nss-sulfate); (3) Soil (Saharan?) dust (Al, Mn, Fe); (4) Heavy metal aerosols (Cd, Cu, Ni, Zn, As, V, Pb); (5) Reactive Hg production in the atmosphere (hypothesized).

The analytes in the first four terms all exhibit classical aerosol scavenging or washout behavior. There are strong correlations among the trace species associated with each source term, and the bulk deposition samples are significantly more concentrated than the wet deposition samples. In contrast, the Hg concentrations do not correlate well with any of the other chemical tracers we have measured, leaving the source of the Hg unidentified at present. The bulk deposition fluxes of V, Mn, Ni, Zn, and As appear to be significantly greater than the background fluxes (as measured in Bermuda), while the fluxes of Al, Fe, Cu, Cd, and Pb are not.

The FAMS network includes two more sites, the "marine background" site on Little Crawl Key, and the Broward County "urban plume" site at the FP&L Andytown

substation (Pollman *et al.*, this volume). Until we have enough data from the marine background site we cannot state conclusively whether any of the fluxes we have calculated are significantly different from the atmospheric flux reaching the area from the oceanic region to the east/southeast. Until then, the lack of strong correlations between Hg and other tracers in rainfall, the apparent unimportance of aerosol washout for Hg, and the relatively uniform Hg rainfall deposition across south Florida (Guentzel *et al.* this volume) suggest that tropospheric oxidation of gaseous elemental Hg may be the dominant source.

Acknowledgements

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WET DEPOSITION OF MERCURY AND AMBIENT MERCURY CONCENTRATIONS AT A SITE IN THE LAKE CHAMPLAIN BASIN

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Abstract. The "Great Waters" program, established in the 1990 Clean Air Act Amendments, mandated that atmospheric deposition of hazardous air pollutants to Lake Champlain (including Hg) be assessed. An assessment of the magnitude and seasonal variation of atmospheric Hg deposition in the Lake Champlain basin was initiated in December 1992 with one year of event precipitation collection, as well as collection of vapor and particle phase Hg in ambient air. Samples were collected at the Vermont Monitoring Cooperative air monitoring site at the Proctor Maple Research Center in Underhill Center, VT. The average volume-weighted concentration for Hg in precipitation was 8.3 ng/L for the sampling year and the average amount of Hg deposited with each precipitation event was 0.069 $\mu g/m^2$. The total amount of Hg deposited through precipitation during 1993 was 9.26 $\mu g/m^2/yr$. A seasonal pattern for Hg in precipitation was evident, with increased concentrations and deposition during spring and summer months. Meteorological analysis indicated the highest levels of Hg in precipitation were associated with regional transport from the south regardless of season, and with transport from the west, southwest and northwest during spring and summer months. Concentrations of ambient vapor phase Hg were typical of rural locations and consistent across seasons. Ambient particulate Hg concentrations averaged 11 pg/m^3 with highest concentrations during the winter months.

Keywords: Mercury, wet deposition, regional transport, particle phase mercury, Lake Champlain

1. Introduction

Lake Champlain, located in the northeastern United States on the border between northern New York state, Vermont and Quebec, has been designated as one of the "Great Waters" by the 1990 Clean Air Act Amendments (CAA). The Great Waters program was established in Section 112(m) of the CAA to identify and assess atmospheric deposition of hazardous air pollutants (HAPs) to the Great Lakes, Chesapeake Bay, Lake Champlain and coastal waters. Mercury (Hg) is one of the 189 HAPs identified in this section of the CAA. Requirements of the Great Waters program include: (a) establishing atmospheric deposition stations to monitor deposition of HAPs within the Lake Champlain watershed, (b) determining the role of atmospheric deposition in the pollutant loading for the lake, and (c) investigating the sources of air pollutants deposited in the watershed.

Mercury concentrations exceeding fish consumption advisory limits have been documented for certain sport fish, and elevated levels of Hg and PCBs have been found in the sediments at many sites within Lake Champlain including those in the deep lake (McIntosh, 1994). This report identified several lake-wide issues for future investigation, including the critical need to better understand how contaminants like Hg and PCBs are entering Lake Champlain.

Atmospheric deposition has been implicated as a primary source of Hg to remote lakes in the Great Lakes region (Swain *et al.*, 1992; Fitzgerald *et al.*, 1991).

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Additionally, atmospheric transport of sulfate and acidic precipitation from the major source regions in the Midwest to New York and New England has been demonstrated (NAPAP, 1991). However, measurements of atmospheric Hg in the Lake Champlain basin have not previously been conducted. Therefore, an assessment of the magnitude and seasonal variation of atmospheric Hg deposition in the Lake Champlain basin was initiated. The scope of the project included one year of event precipitation collection, as well as collection of vapor and particle phase Hg in ambient air.

2. Materials and Methods

An investigation of atmospheric Hg concentrations in the Lake Champlain basin began in December 1992 by the University of Michigan Air Quality Laboratory (UMAQL) in collaboration with the Vermont Monitoring Cooperative. Sampling was conducted at the Vermont Monitoring Cooperative air monitoring site at the Proctor Maple Research Center (PMRC) in Underhill Center, VT. Ongoing monitoring at the PMRC site also includes meteorological measurements and routine trace metal measurements as part of the NESCAUM (North East States for Coordinated Air Use Management) air monitoring network.

The PMRC is located within the Lake Champlain basin between the Adirondack mountains in New York State to the west and the Green mountains in Vermont to the east. Underhill Center is approximately 25 km east of the lake within a forested area on the western side of Mt. Mansfield at approximately 400 m elevation. No major urban or industrial areas exist within about 200 km.

2.1 EVENT PRECIPITATION

Precipitation was collected using an automatic MIC-B collector with a Teflon-coated funnel and glass collection carboy. The protocol used in this study for collection of daily event precipitation for Hg analysis was developed and proven effective in a four site network in Michigan (Hoyer and Keeler, 1994). Precipitation was collected every morning at 8 A.M. if an event had occurred during the previous 24 hours. If precipitation was occurring at 8 A.M. then the sample was collected the following morning. Samples were poured from the collection carboy into acid-cleaned borosilicate glass bottles and shipped to UMAQL for analysis. A Belfort rain gauge was used to record the amount of precipitation from each event at the site.

Samples were processed immediately upon receipt at the UMAQL in a Class 100 ultra-clean laboratory. An aliquot of sample was poured off for analysis of pH and anions and the remaining was oxidized to a 1% BrCl solution and refrigerated overnight. To determine the amount of Hg in a precipitation sample the oxidized Hg was reduced to elemental Hg, bubbled out of solution in a Hg-free nitrogen gas stream, and captured onto a gold-coated sand trap. The Hg was thermally desorbed from the trap in a Hg-free helium gas stream and then quantified by cold vapor atomic fluorescence spectrometry (CVAFS) (Fitzgerald and Gill, 1979). Aqueous Hg standards were used to calibrate the instrument during each day of analysis.

A number of additional analyses were performed on subsets of samples throughout the year. Samples of sufficient volume were analyzed for the operationally-defined reactive Hg species by acidifying an aliquot of sample to a 1% HCl solution. The percent of Hg in the dissolved phase was determined for several samples by filtering through a 0.4 μm pore-size nitrocellulose filter.

2.2 Hg IN AMBIENT AIR

Vapor phase Hg was collected by drawing air at a flow rate of 300 cc/min. into a collection trap containing gold-coated sand. A pre-fired glass-fiber filter was used to remove particles from the air stream prior to reaching the gold sand trap. Samples were collected for 24 hours approximately twice per week: every 6th day on the national network schedule for the U.S. and on Wednesdays to coincide with the NESCAUM network. Collection traps were tested for complete recovery of Hg vapor between every use. Blanked traps were shipped to the site the week prior to sampling and shipped back for analysis after every two sampling days. Vapor phase Hg was quantified directly by thermal desorbtion and CVAFS. Mercury vapor standards were used to calibrate the instrument prior to every day of analysis.

Particulate Hg was collected on a pre-fired glass-fiber filter in an open-face Teflon filter pack at a nominal flow rate of 30 L/min. (Keeler *et al.*, 1995). Samples were collected for 24 hours on the same every 6th day and Wednesday schedule as vapor phase Hg. After sampling, filters were removed from the filter pack using Teflon-coated forceps, placed in an acid-cleaned petri dish, Teflon-taped and shipped to the UMAQL to be stored in a -40°C freezer until analysis. Prior to analysis, the sample filters were transferred to Teflon vials in the ultra-clean laboratory, extracted using a 10% nitric and sulfuric acid solution in Teflon vials, sonicated and oxidized with BrCl (Lamborg *et al.*, 1994). The oxidized Hg in the extraction solution was reduced to elemental Hg, bubbled out of solution onto a gold sand trap and quantified by CVAFS. The instrument was calibrated during each day of analysis using aqueous Hg standard solution applied to glass-fiber filters and extracted as described above for sample filters.

2.3 QUALITY CONTROL AND QUALITY ASSURANCE

Clean technique was used in handling all samples. All equipment and supplies used in sampling were rigorously acid-cleaned in an 11-day cycle (Hoyer and Keeler, 1994). Sample bottles, gold sand traps and glass-fiber filter containers were Teflon-taped and triple-bagged. Particle-free gloves were worn when handling the samples.

For event precipitation, the funnel and collection carboy were rinsed with ultra-pure water after each sample was collected. A newly acid-cleaned collection carboy was installed every two weeks. As a measure of the sampling blank, the funnel and collection carboy were rinsed after two weeks and analyzed for total Hg (Hoyer and Keeler, 1994). The average Hg concentration in 23 precipitation collector blanks was 0.36 ± 0.2 ng/L.

Field blanks were collected regularly for vapor and particle phase Hg samples. For both types of samples, field blanks were taken by assembling the sampling equipment and placing it in the sampling box without drawing air through the system. Field blanks

for vapor phase Hg averaged 0.02 ng Hg on the trap, which corresponds to 0.04 ng/m^3 for a 24-hour sample or 2% of the average vapor phase Hg concentration. Particle phase Hg field blanks averaged 7 pg on the filter, which corresponds to 0.2 pg/m^3 for a 24 hour sample or 1.5% of the particulate Hg typically collected.

For precipitation and particulate samples, a reagent blank was analyzed on each day of analysis. The appropriate amounts of reagents were analyzed to determine the contribution of the reagents to the concentration of Hg obtained for the sample. All samples were blank corrected using the corresponding reagent blank analyzed that day. The current detection limit for Hg in precipitation (calculated as three times the standard deviation of reagent blanks) is 0.15 ng/L.

All particulate samples and 50% of precipitation samples were analyzed in duplicate. Analytical precision calculated from these results were better than 10% for analysis of Hg in both precipitation and particulate samples.

An experiment was performed to confirm that Hg was not being lost from the gold sand traps after sampling, during shipment, or prior to analysis. Gold sand traps were injected with 0.8 ng of elemental Hg vapor (the average amount of Hg collected for a 24-hour sample), shipped to the site, stored for three weeks and returned for analysis. Recovery of the injected Hg from these traps was 100%, indicating no loss of Hg.

A total of 23 precipitation events during 1993 were not analyzed because of insufficient volume. Precipitation events less than 0.08 cm did not produce sufficient volume for analysis using this collector and carboy system. Overall, insufficient volume samples accounted for less than 2% of the annual precipitation at Underhill Center and are evenly distributed over the entire year. Eight precipitation events were not analyzed due to collector problems, operator errors or sample bottle breakage. These samples account for less than 8% of the annual precipitation volume.

3. Results and Discussion

3.1 MERCURY IN PRECIPITATION

Event precipitation sampling began on December 16, 1992. A total of 125 precipitation samples were analyzed for the time period ending December 22, 1993. The average volume-weighted Hg concentration for the sampling year was 8.3 ng/L and the average amount of Hg deposited with each precipitation event was 0.069 μg/m^2 (Table I).

TABLE I
Mercury in event precipitation at Underhill Center, VT (n=125)

	Units	Mean	Range	Median
Vol. Wt. Average Hg Concentration	ng/L	8.3	1.5 - 26	8.0
Precipitation Amount	cm	0.84	0.08 - 4.45	0.5
Wet Deposition of Hg	μg/m^2	0.069	0.002 - 0.398	0.039

The results for Underhill Center, VT are similar to the levels of Hg in precipitation at three sites in Michigan reported by Hoyer *et al.* (1995) for March 1992 to March 1994. Average Hg concentration for precipitation events and wet deposition of Hg at Underhill Center are closest to those for the Pellston site, located in northern Michigan, which had the lowest levels of the three Michigan sites (7.9 ng/L, 0.07 $\mu g/m^2$).

The total amount of Hg deposited by precipitation at the Underhill Center site in 1993 was 9.26 $\mu g/m^2/yr$. The total annual wet deposition of Hg for Underhill Center was substantially higher than the average of the two years at Pellston, but similar to Dexter, and significantly less than South Haven, MI (Table II). The amount of precipitation received at Underhill Center during 1993 is considerably larger than the two year averages for the other locations. A comparison of precipitation amounts at Underhill Center for previous years indicates that 1993 was not significantly different from the climatological average. However, when compared to Burlington, VT, located on the eastern shore of Lake Champlain at the widest part of the lake, Underhill Center received approximately 25% more precipitation during 1993.

This spatial difference in precipitation amounts complicates the calculation of wet deposition of Hg to the lake surface and drainage basin. Using the annual wet deposition of Hg at Underhill Center, an estimated 10.5 kg of Hg was deposited directly to the surface of Lake Champlain (1129 km^2) by precipitation during 1993, and 197.4 kg of Hg was deposited to the drainage basin (21,318 km^2) of the lake. The actual wet deposition of Hg to the lake surface is likely to be less than this estimate due to the spatial variation in precipitation amounts.

The total Hg concentration (ng/L) and amount of Hg deposited ($\mu g/m^2$) for each precipitation event from mid-December 1992 through mid-December 1993 are displayed in Figure 1. A seasonal pattern is evident in these results. Mercury concentrations in precipitation are consistently elevated over the annual mean during the period of April through September. Wet deposition of Hg shows a distinct seasonal trend with several rain events during the months of April through September which had deposition greater than three times the annual mean. Monthly averaged Hg concentrations were highest in June, while average Hg deposition peaked in August along with amount of precipitation.

TABLE II
Comparison of annual wet deposition of mercury

Location	Reference	Annual Wet Deposition ($\mu g/m^2/yr$)	Precipitation Amount (cm/yr)
Underhill Center, VT	This paper	9.26[a]	111.9
Pellston, MI	Hoyer *et al.* (1995)	5.67	71.6
Dexter, MI	"	8.89	87.2
South Haven, MI	"	11.06	102.7

[a] Insufficient volume samples and missed precipitation events included by using amount of precipitation from Belfort gauge and average concentration for month.

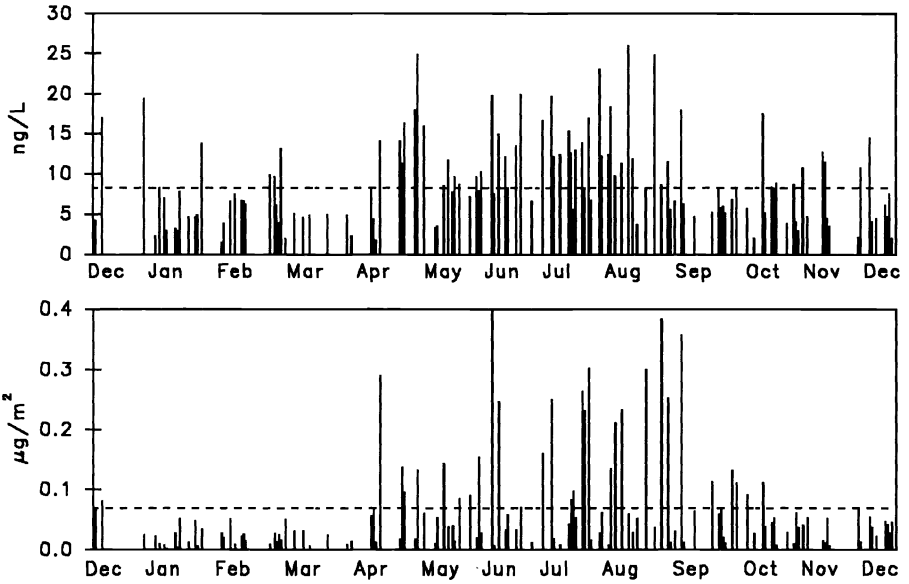

Fig. 1. Hg in event precipitation at Underhill Center, VT during 1993. Top graph is Hg concentration in ng/L, bottom graph is wet deposition of Hg in µg/m² (--- = annual mean).

Seasonal averages of Hg in precipitation further illustrate this trend (Table III). Concentrations of Hg in precipitation were significantly higher during the spring and summer compared to the winter and autumn. Of the 20 highest Hg concentration events, 80% occurred during the spring and summer. The amount of Hg deposited to this site in precipitation was lowest on average during the winter, increased dramatically during the spring, reached a peak during the summer and dropped significantly during autumn.

TABLE III
Seasonal Hg averages and total deposition for precipitation at Underhill Center, VT during 1993

Season	n	Vol. Wt. Average Hg Conc. (ng/L)	Average Wet Deposition (µg/m²)	Average Precip. Amount (cm)	Season Wet Deposition (µg/m²)	Season Precip. Amount (cm)
Winter	26	4.4	0.025	0.56	0.72	16.1
Spring	29	9.9	0.080	0.81	2.59	26.6
Summer	35	11.0	0.115	1.04	4.32	38.8
Autumn	31	6.2	0.055	0.88	1.54	27.6

The seasonal pattern for wet deposition of Hg is not solely due to seasonal differences in precipitation amounts. Higher Hg concentrations and larger amounts of rain combine to produce the summer wet deposition peak. The average amount of precipitation per event during the winter months is about half that for the summer months, while the average deposition of Hg per event during winter is only 20% of that for summer. Wet deposition of Hg for each season is also displayed in Table III. The spring and summer months account for 60% of the annual precipitation. However, 75% of the annual wet deposition of Hg at this site occurs during these months.

The operationally-defined reactive Hg species was quantified for a total of 40 precipitation samples during the period from January through July 1993 (Table IV). The concentration of reactive Hg species in precipitation was generally low (< 3 ng/L). The average percent of total Hg as this reactive species was 15%, but was observed as high as 39%. Concentrations of reactive and total Hg were significantly correlated ($r=0.47$, $p<0.01$). However, the percent reactive Hg was negatively correlated with total Hg concentration ($r=-0.57$, $p<0.0001$). The reactive Hg concentration increased and the percent reactive decreased as total Hg concentration increased, indicating that reactive Hg levels were relatively constant compared to the total Hg in precipitation for this site.

Filtration of precipitation samples with sufficient volume was performed for 5 samples during the spring and for 11 samples during the autumn using a 0.4μm pore size filter. The percent of total Hg in the dissolved phase was greater than 50% on average, and ranged up to nearly 90% (Table IV).

Major ions were quantified for the precipitation samples. Significant correlations between ion and Hg concentrations in precipitation were observed (Table V). The wet deposition of sulfate, nitrate, chloride and acidity correlated strongly with the wet deposition of Hg as well. Also, the concentration of reactive Hg species showed a significant correlation with chloride ion concentration ($r=0.54$, $p<0.001$, $n=40$).

3.2 MERCURY IN AMBIENT AIR

A total of 91 vapor phase and 103 particle phase Hg samples were collected during 1993 (Table VI). The average vapor phase Hg concentration was 2.0 ng/m^3. Similar levels for vapor phase Hg have been observed in other rural locations in the Great Lakes region (Lamborg *et al.*, 1993), and in New York state (Olmez, 1994).

TABLE IV
Reactive and dissolved (< 0.4μm) Hg in precipitation at Underhill Center, VT

	n	Mean	Range	Median
Reactive Hg (ng/L)	40	1.0	0.15 - 2.99	0.8
Percent Reactive Hg	40	15%	2 - 39%	14%
Dissolved Hg (ng/L)	16	5.1	2.0 - 12.5	3.7
Percent Dissolved Hg	16	66%	38 - 89%	68%

TABLE V
Significant correlations for Hg and ions in precipitation at Underhill Center, VT
$p < 0.01$ (n=112)

Ion	Concentration r =	Wet Deposition r =
NO_3^-	0.25	0.73
SO_4^{-2}	0.46	0.88
Cl^-	0.30	0.48
H^+	0.39	0.82

Levels of vapor phase Hg were fairly consistent throughout the sampling year at Underhill Center. Only six samples had elevated vapor phase Hg concentrations (greater than 1 std. dev. above the annual mean). Three of these samples occurred during the winter, however, the three highest vapor phase Hg measurements were in June and July.

For particle phase Hg, the annual average concentration was 11 pg/m^3. A seasonal trend was observed, with elevated particulate Hg concentrations during the winter months, especially in February when all samples were above the annual average (Figure 2). Increasing concentrations in November and December of 1993 provide further support for a seasonal influence on particulate Hg concentrations at this site. A similar increase in the concentration of other metals such as As and Se measured at Underhill Center (NESCAUM data) during the winter months was also observed.

Seasonally averaged particulate Hg concentrations further illustrate this trend. The average for the winter months (16 pg/m^3) is significantly greater than the annual mean concentration (11 pg/m^3), while the averages for the other seasons (9 - 10 pg/m^3) are similar to the annual average.

3.3 CONCURRENT PRECIPITATION AND AMBIENT RESULTS

One of the unique aspects of this project is that concurrent measurements of Hg in precipitation and ambient air were obtained. Simple correlations were calculated between ambient and precipitation concentrations for the sampling days when precipitation occurred during ambient measurements. Some interesting correlations were observed. Ambient particulate Hg was correlated with reactive Hg in precipitation ($r=0.654$, $p<0.02$, n=13). A significant correlation was also found between vapor phase Hg and wet deposition of Hg ($r=0.471$, $p<0.01$, n=33).

TABLE VI
Ambient Hg Concentrations at Underhill Center, VT during 1993

	n	Mean	Range	Median
Vapor phase Hg (ng/m^3)	91	2.0	1.2 - 4.2	1.9
Particle phase Hg (pg/m^3)	103	11	1 - 43	10

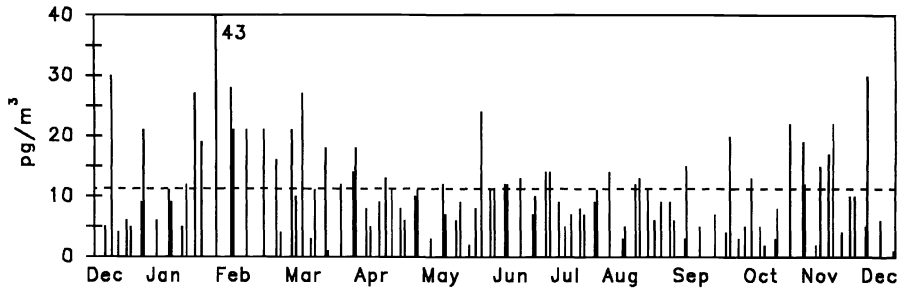

Fig. 2. Ambient particulate Hg concentrations in pg/m³ at Underhill Center, VT during 1993 (--- = annual mean).

Averages calculated for these sampling days did not differ significantly from the annual means for Hg in precipitation or for vapor phase Hg. However, the particulate average was ~20% lower than the annual mean. This may be due to upwind removal of ambient particulate matter by precipitation or simply the result of air mass changes associated with the passage of frontal systems.

3.4 METEOROLOGICAL ANALYSIS

Meteorological influences on atmospheric Hg at Underhill Center were also investigated. The Hybrid Single-Particle Lagrangian Integrated Trajectories Model (Hy-SPLIT) was used with 1993 meteorological input data from the National Meteorological Center's Nested Grid Model (NGM) for the continental US (90 to 180 km every 1 to 2 hr) to plot iso-sigma backward trajectories (Draxler, 1992). Each trajectory plot displays the most probable path of the air mass that arrived at the site on the day and hour specified.

Trajectories for every precipitation event at Underhill Center during 1993 were analyzed and classified by region. Trajectories from southern New England and the eastern half of the mid-Atlantic states were classified as transport from the south. Western New York State and Pennsylvania, and eastern Ohio were considered the southwest region. The upper Midwest and southern Ontario were classified as the west region and the rest of Ontario and western Quebec was considered the northwest region.

Preliminary analysis of these trajectories showed that for the 20 precipitation events with the highest Hg concentrations, 30% were associated with regional transport from the south, 30% from the west and the remaining events were split between the southwest and northwest. Precipitation events with the lowest Hg concentrations generally involved transport with an easterly component.

The elevated Hg concentrations in precipitation associated with transport from the south were distributed throughout the sampling year, indicating this source region is consistently influencing Hg concentrations in precipitation at Underhill Center. However, the 20 precipitation events with the highest concentrations in precipitation that were associated with transport from the west, southwest and northwest were seasonally dependent. Elevated Hg concentrations in precipitation associated with transport from the west occurred only during the summer months. High Hg concentrations associated with transport from the northwest occurred only during the spring, and with transport

from the southwest during both spring and summer. Also interesting to note is that of all the precipitation events during the summer, none were associated with transport from the east, northeast or southeast which typically brought low Hg concentrations in precipitation during the other seasons.

4. Conclusions

Results reported from this first year of atmospheric Hg sampling at Underhill Center, VT indicate that wet deposition of Hg is significant at this site, and therefore, atmospheric deposition is an important source of Hg to the Lake Champlain basin. The seasonal variation observed for Hg in precipitation with higher concentrations in the spring and summer may be influenced by several factors including meteorology, regional transport patterns, source strengths, cloud processes or other atmospheric constituents during the different seasons. Further investigations of how these factors affect atmospheric Hg concentrations are clearly needed.

The significant relationship observed between Hg and major ions in precipitation at Underhill Center may imply a degree of similarity in the sources or mechanisms for atmospheric transport of Hg with that of sulfate and the formation of acidic precipitation.

The observed correlation between the operationally-defined reactive Hg species and Cl^- in precipitation provides support for the speculation that this species may be $HgCl_2$. Also, the correlation observed between ambient particulate Hg and reactive Hg species in precipitation on days when ambient measurements were conducted and precipitation occurred, implies that this species may be associated with particles.

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MECHANISMS OF DEPOSITION OF METHYLMERCURY AND MERCURY TO CONIFEROUS FORESTS

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Abstract. Deposition of methylmercury (MeHg) and mercury (Hg) to a coniferous forest have been investigated using field measurements. Samples of open field (OF) wet deposition, throughfall (TF) and litterfall (LF) have been collected and analyzed for MeHg and Hg during the period November 1991 to April 1994. Average concentrations in TF were 22.8 and 0.38 ng L^{-1}, for Hg and MeHg, respectively. Concentrations in OF precipitation were 11.9 and 0.37 ng L^{-1}, for Hg and MeHg, respectively, during the same period. Considerable differences were found for Hg in TF and OF which was attributed to a dry deposition of Hg. Hg in LF contributes a deposition of equal size as in TF. The relations between OF, TF and total Hg deposition were approximately 1:1.5:3. A decrease in OF Hg was found over the three year period studied. MeHg deposition in OF was also found to decrease during the same period whereas the TF MeHg showed a slight increase. Dry deposition of MeHg is also an important process in a coniferous forest although the flux to the forest floor is not via TF but rather as MeHg in LF.

1. Introduction

Although releases of mercury (Hg) from energy production and other industrial activities is decreasing, the accumulation of Hg in forest soils in Sweden and elsewhere continues to be an environmental problem of great potential magnitude. The amounts of Hg and MeHg present in forests soils are so large that leaching into streams, rivers and lakes will continue for decades or even centuries. Atmospheric deposition of Hg and MeHg to forested catchments remains the major pathway for introducing Hg to terrestrial ecosystems.

Deposition of total Hg in forests has been shown to occur by both wet and dry processes (Iverfeldt, 1991; Lindberg *et al.*, 1991,1992,1994). Possible mechanisms for dry deposition include deposition of particulate matter containing Hg, adsorption onto plant surfaces by gaseous divalent forms (e.g. $HgCl_2$) or *in situ* oxidation of elemental mercury (Hg^0) to forms with lower vapor pressure and higher capability to stick to plant surfaces. Stomatal uptake of Hg^0 also occurs, at least at elevated concentrations of mercury in air (Lindberg *et al.*, 1992).

The knowledge concerning deposition processes of MeHg is comparatively small. Measurements of MeHg in precipitation have been performed both in the US and in Europe (Bloom and Watras, 1989; Lee and Iverfeldt, 1991; Munthe and Iverfeldt, 1993). The overall importance of atmospheric deposition of MeHg has also been discussed. Budget calculations for a small catchment have also been performed where the potential importance of dry deposition of MeHg was recognized (Hultberg *et al.*, 1994).

The results presented here are from a study of the deposition processes for Hg and MeHg. In this presentation, field measurements of Hg and MeHg in OF precipitation, throughfall (TF) and litterfall (LF) are employed.

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2. Materials and methods

The techniques used for sampling and analysis of Hg and MeHg have been extensively described elsewhere and only a short description is given here. Wet deposition (OF and TF) was collected using bulk samplers with a monthly collection period (Lindqvist *et al.*, 1991; Jensen and Iverfeldt, 1994). The collection bottles were pre-acidified with 2.5 mL Suprapur HCl in order to preserve the samples. LF was collected i nylon nets mounted on an aluminium frame.

MeHg was analyzed using aqueous phase ethylation and GC separation followed by pyrolysis and CVAFS detection. All aqueous samples were pretreated by extraction in dichloromethane. Hg was analyzed after BrCl oxidation using $SnCl_2$ reduction, trapping on gold and CVAFS detection (Bloom and Crecelius, 1983; Iverfeldt, 1988,1991)

3. Results and Discussion

Measurements of Hg and MeHg at the Gårdsjön catchments started in the mid eighties. The data presented here are from the period December 1990 to April 1994.

3.1 TOTAL MERCURY IN THROUGHFALL AND OPEN FIELD PRECIPITATION

Measured concentrations of Hg in TF and OF precipitation during this time, are presented in Figure 1.

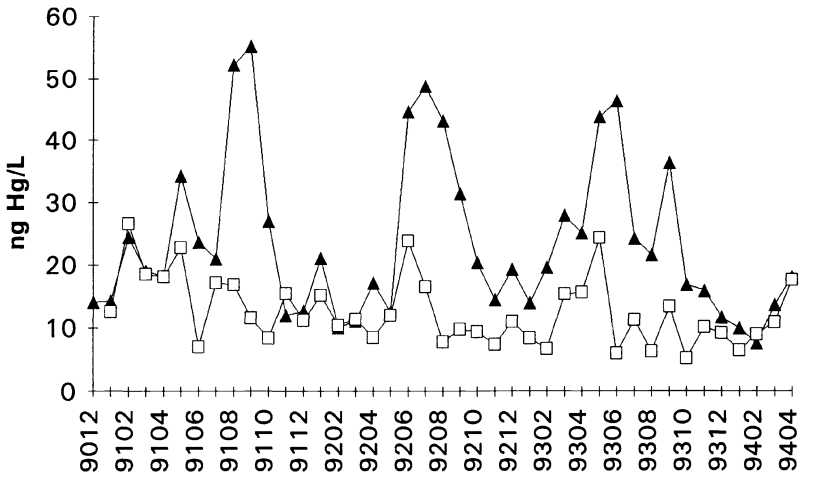

Fig. 1. Concentrations of Hg in TF (▲) and OF precipitation (□) at Gårdsjön, SW Sweden.

A pronounced seasonal variation can be clearly seen for Hg in TF with higher concentrations occurring during the summer months and early fall. During these periods, TF Hg is always higher than the OF Hg sampled simultaneously. The concentration difference decreases or disappears completely during the winter. This behavior is similar to that found in earlier studies at the same location. A somewhat weaker seasonal variation can also be detected for OF Hg. This may be explained by an increase in the oxidizing rate of atmospheric Hg^0 during the summer months, caused by an increased photochemical activity. In this case, the canopy surface seems to provide a reactive surface further increasing the conversion rate.

The increased concentrations of Hg in TF implies that there is a systematic transfer of Hg from the tree surface to the aqueous phase. It is most likely that this Hg originates from dry deposition of airborne Hg during dryer periods, since a root uptake of significant amounts of Hg is not expected. Studies of root-damage on Spruce, exposed for elevated Hg concentrations in nutrient solutions, showed that Hg levels in needles were not related to the concentrations in the nutrient solution (Godbold and Hütterman, 1988).

A continuous decrease in OF Hg concentrations is also evident which in line with observations from other OF Hg sampling stations in Sweden (Iverfeldt *et al.*, 1994; Munthe *et al.*, 1994).

In order to be able to quantify the amounts of Hg dry deposited to the canopy, it is necessary to consider the fluxes of Hg to the forest floor. In Figure 2, the monthly deposition fluxes are depicted.

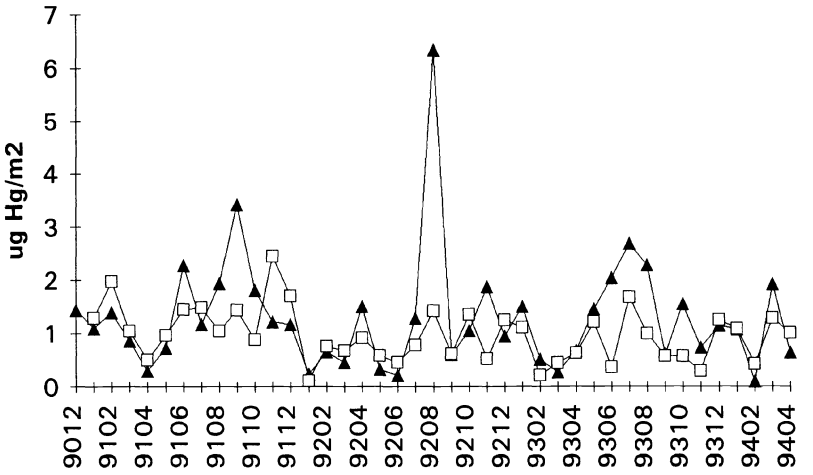

Fig. 2. Deposition of Hg in TF (▲) and OF (□)precipitation.

The difference between TF and OF precipitation if not as pronounced for deposition fluxes as it is for concentrations. For the whole period, average TF concentrations of Hg

are about a factor of two higher than the corresponding OF precipitation concentrations whereas the average deposition is increased by 40% under the canopy. This is due to the difference in precipitation amounts at the two locations which counter-balances the differences in concentration. During the summer months,. an increased evaporation of water in the canopy is expected which leads to enhanced concentration differences in TF compared to OF, but not necessarily an increased deposition. The remaining difference is not accounted for by differences in precipitation and is most likely the result of dry deposition. The average concentrations and wet deposition fluxes for three one-year periods are presented in Table I.

Assuming that the differences between TF and OF precipitation represents dry deposition to the forest canopy, the average contribution via TF to the flux can be calculated to 4.9 $\mu g\ m^{-2}$ per year or about 50% of the OF wet deposition. The differences between OF and TF wet deposition increases markedly from the first year in comparison with the two latter, which is mainly due to the decrease in OF wet deposition. A parallel decrease in TF does not occur and an increased dry deposition is necessary to balance the decrease in OF wet deposition. A possible rationalization is that the mechanisms for generating Hg in OF precipitation are not directly related to the mechanisms yielding dry deposited Hg, which will turn up as Hg in TF. Above it was suggested that the *seasonal* co-variation of Hg in TF and OF was caused by a joint dependence on the oxidizing capacity of the air.

Table I.

Mean concentrations, wet deposition and calculated dry deposition for Hg in the F1 catchment at Gårdsjön, SW Sweden.

	Mean concentration		Wet Deposition		Difference*
Period	Open Field	Troughfall	Open Field	Throughfall	
	$ng\ L^{-1}$		$\mu g\ m^{-2}$		$\mu g\ m^{-2}$.
4/91 - 3/92	13.8	24.9	13.5	15.4	1.9(14%)
4/92 - 3/93	11.4	26.1	9.7	16.5	6.8(70%)
4/93 - 3/94	10.6	22.8	10.4	16.3	5.9(57%)

* Assumed to be dry deposition.

The results presented in this section to some extent disagrees with the previous discussion and suggests that processes and pathways, other than canopy oxidation of Hg^0, may be of equal importance for the total flux of dry deposition.

3.2 TOTAL MERCURY IN LITTERFALL

Data for Hg in LF are not presently available for the whole period. Measured concentrations vary between 33 and 140 ng g^{-1} (dry weight). The fluxes of Hg to the forest floor are of the same order of magnitude as TF fluxes. Fluxes of Hg via LF, TF and open field precipitation for the period March to August 1993 are presented in Table 2.

Table II.
Fluxes of Hg in LF, TF and OF precipitation for the period 3/93 to 8/93.

	Litterfall	Troughfall	Open Field
		$\mu g\ m^{-2}$.	
Hg deposition	10.4	9.4	5.3

The deposition of Hg with LF represents roughly an equal flux of Hg as that depositing via TF. Assuming that this Hg originates from dry deposition, the relation between the different deposition fluxes becomes 1:1.5:3 for OF, TF and total deposition, respectively. This is in line with earlier studies in this area (Iverfeldt, 1991; Driscoll *et al.*, 1994).

3.3 METHYLMERCURY IN THROUGHFALL AND OPEN FIELD PRECIPITATION

Measured concentrations of MeHg in TF and OF precipitation are presented in Figure 3.

For MeHg, the differences in concentrations are not as large as for Hg. The average concentrations for the whole period are 0.383 and 0.371 ng L^{-1}, for TF and OF precipitation, respectively. As for Hg, clear seasonal trends can be found with the highest MeHg concentrations occurring in early spring for both OF and TF (if the two individual peak vales not considered). In contrast to Hg, however, the seasonal variations are slightly less obvious in TF.

A somewhat larger difference between TF and OF can be observed for wet deposition fluxes, in comparison to concentrations. This is mainly due to the decrease in precipitation amounts under the canopy which decreases the deposition via TF. The average annual fluxes for the whole period are 0.203 and 0.337 $\mu g\ m^{-2}$, for TF and OF, respectively. The annual mean concentrations and fluxes are presented in Table 3.

As for Hg, a decreasing trend can be seen for MeHg in OF wet deposition. This is not true for OF mean concentrations which is partly due to the exceptionally high concentration found in September, 1992. TF mean concentrations and wet deposition are more stable over the period which was also observed for Hg (Table I). As for Hg, this suggests that the governing mechanisms for dry and wet deposition of MeHg are not necessarily related (see also Section 3.4 below).

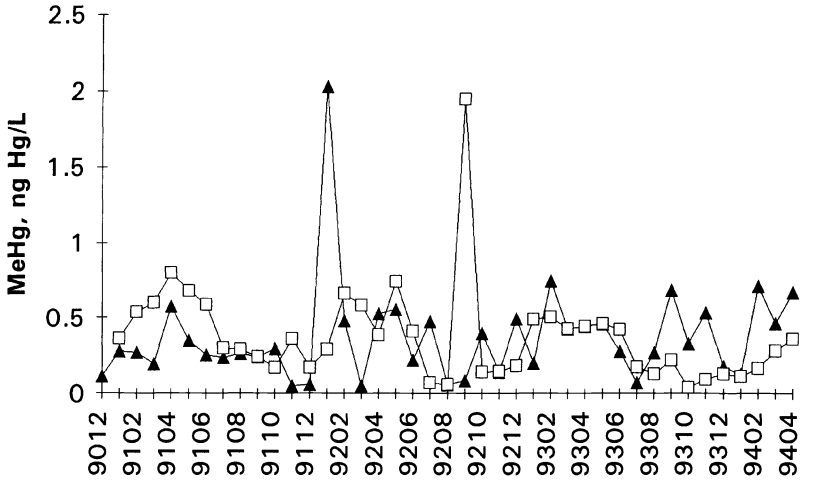

Figure 3. Concentrations of MeHg in TF (▲) and OF precipitation (□).

In Figure 4, the wet deposition fluxes of MeHg in OF and TF are presented.

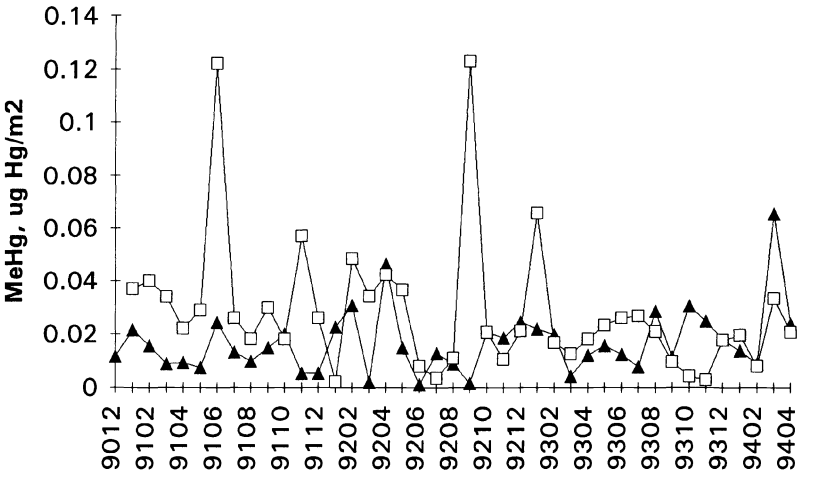

Fig. 4. Wet deposition of MeHg in TF (▲) and OF (□) precipitation.

The difference in annual mean concentrations are not the same for the three years studied. For the first two years the concentrations are very similar with open field precipitation slightly higher (16% on average). A reverse situation is evident the third year with significantly higher concentrations in TF. The average difference in deposition flux is -0.2 $\mu g\ m^{-2}$ with higher deposition in OF precipitation than in TF.

The difference can not only be explained by the different precipitation amounts which suggests that a transfer of MeHg occurs from the aqueous phase to the needles when the precipitation passes through the canopy.

Table III.

Mean concentrations, wet deposition and calculated dry deposition for MeHg in the F1 catchment at Gårdsjön, SW Sweden.

Period	Mean concentration		Wet Deposition		Difference*
	Open Field	Troughfall	Open Field	Throughfall	
	ng L^{-1}		$\mu g\ m^{-2}$.		$\mu g\ m^{-2}$.
4/91 - 3/92	0.43	0.41	0.43	0.16	-0.27
4/92 - 3/93	0.46	0.36	0.37	0.20	-0.17
4/93 - 3/94	0.22	0.38	0.21	0.25	0.04

3.4 METHYLMERCURY IN LITTERFALL

Earlier studies of MeHg in LF have shown that this flux dominates the deposition of MeHg to the forest floor (Hultberg *et al.*, 1994). They reported annual depositions to the forest floor of 0.6 $\mu g\ m^{-2}$ for LF and 0.2 $\mu g\ m^{-2}$ for TF. In the present study, LF concentrations of MeHg varied from 0.29 to 3.9 ng g^{-1}, dry weight. Data are not yet available for a complete flux calculation but samples collected during the six month period April to September 1993 results in a flux of 0.24 $\mu g\ m^{-2}$, slightly less than half the annual flux calculated in the earlier study.

Assuming that the MeHg in LF originates from dry deposition of airborne MeHg, the dry deposition flux to the canopy, and the subsequent flux to the forest floor, is the overall most important source of MeHg to the ecosystem. In Table IV, the fluxes of MeHg in LF, TF and OF precipitation for the period April to September 1993, are presented.

Although this only represents one six-months period, the dominance of LF over TF and OF precipitation is very clear.

If the MeHg in LF all originates from the air or from TF, the adsorption has to be very efficient. Another potentially important process is *in situ* methylation of inorganic Hg in the canopy. The concentration of Hg is in large excess over MeHg and a variety of organic substances are also present in the canopy, either originating in the air or from the needles themselves. No data is presently available on this tentative

process, so this production mechanism must only be regarded as highly speculative at this stage.

Table IV.
Fluxes of MeHg in LF, TF and OF precipitation for the period 4/93 to 9/93.

	Litterfall	Troughfall $\mu g\ m^{-2}$.	Open Field
Hg deposition	0.24	0.09	0.12

4. Conclusions

The data presented in this paper has strengthened the theory that dry deposition processes are important for the flux of Hg and MeHg to forested ecosystems. The relation between deposition of Hg via OF precipitation, TF and total deposition to the forest floor follows the relation 1:1.5:3. Seasonal trends in concentrations and wet deposition of Hg and MeHg were found with maxima for Hg during the summer months and during spring for MeHg.

A clear decreasing trend in concentrations and wet deposition of OF Hg and MeHg was found during the approximately three years of sampling. For TF no decrease is seen. Clearly, different variables are governing for the two types of deposition pathways, *i.e.* wet and dry.

For MeHg the most important dry deposition route is from the air to a relatively stable form in litter. A adsorption of MeHg from TF to the canopy also occurs but this is not of the same importance for the overall flux.

Acknowledgments

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FOLIAR EXCHANGE OF MERCURY VAPOR: EVIDENCE FOR A COMPENSATION POINT

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Abstract. Historical studies for crop and weed species documented elemental Hg vapor (Hg°) deposition to foliage, but they used Hg° concentrations that were orders of magnitude higher than levels now known to occur under background conditions, possibly creating artificially high gradients between the atmosphere and landscape surfaces Measurements of Hg° exchange with white oak (*Quercus alba* L.), red maple (*Acer rubrum* L.), Norway spruce (*Picea abies* L.), and yellow-poplar (*Liriodendron tulipifera* L.) foliage were conducted in an open gas exchange system that allows for simultaneous measurements of CO_2, H_2O and Hg° exchange under controlled environmental conditions When Hg° concentrations were held at 0.5 to 1.5 ng m^{-3}, red maple (*Acer rubrum* L.), Norway spruce (*Picea abies* L.), yellow-poplar (*Liriodendron tulipifera* L.), and white oak (*Quercus alba* L.) foliage exhibited mean Hg° emissions of 5.5, 1.7, 2.7, and 5.3 ng m^{-2} h^{-1}, respectively. At Hg° concentrations between 9 and 20 ng m^{-3} little net exchange of Hg° was observed. However at concentrations between 50 and 70 ng m^{3} the Hg° was deposited to foliage at rates between 22 and 38 ng m^{2} h^{1} These data suggest that dry foliar surfaces in terrestrial forest landscapes may be a dynamic exchange surface that can function as a source or sink dependent on the magnitude of current Hg° concentrations These data provide evidence of species-specific compensation concentrations (or compensation points) for Hg° deposition to seedling foliage in the 10-25 ng m^{3} range

1. Introduction

Mercury (Hg) emissions from the combustion of fossil fuels have been identified as a potential source of Hg accumulating in natural food chains (Lindqvist, 1985; Schroeder et al., 1989) and the problem is of special concern for aquatic systems (Swain et al., 1992). Deposition of elemental Hg vapor (Hg°) to terrestrial forest landscapes may also represent a significant sink within the biogeochemical cycle of Hg (Lindberg et al., 1992), but quantitative data describing rates of exchange with woody plant foliage and other forest landscape surfaces are not available. Forested landscapes are made up of a variety of surfaces with different and often highly variable surface characteristics. Foliar surfaces typically make up 4-8 times the surface area of bare ground, and bark/stem surfaces account for an additional 1.5 ground area equivalents. Because of their stomata and physiologically active mesophyll cells, foliar surfaces represent a diurnally changing sink for many trace gases (Taylor et al., 1988).

Previous studies for crop and weed species documented Hg° deposition to foliage (Du and Fang, 1982; Browne and Fang, 1978), but they used Hg° concentrations that were orders of magnitude higher than levels now known to occur under background conditions (0.5-3 ng m^{-3}), possibly creating artificially high gradients between the atmosphere and landscape surfaces. It is not clear that the mechanisms responsible for Hg° uptake at high concentrations remain active near ambient levels. Other trace gases such as NO and NH_3 are known to exhibit different deposition characteristics as a function of ambient concentrations (Farquhar et al., 1980; Johansson, 1987).

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Du and Fang (1982) determined that Hg° uptake increased with Hg° concentration, increasing temperature, and increased illumination for 7 crop and weed species. They also showed that Hg° uptake was higher in plants exhibiting C_3 rather than C_4 metabolic pathways. Because woody plants characteristic of forest landscapes have C_3 metabolism, we should expect them to show characteristics of Hg° uptake comparable to those reported by Du and Fang (1982) for C_3 crop species. However, it is important to test for these patterns of Hg° uptake because deposition studies for other trace gases have shown substantial differences in deposition characteristics between crop plants and forest tree species (Hanson and Lindberg, 1991). This paper summarizes the results of laboratory measurements of the net exchange of Hg° with hardwood and conifer foliage for a range of atmospheric Hg concentrations and light environments as part of the Electric Power Research Institute's MASE project.

2. Materials and Methods

2.1. Plant materials and culture conditions

Commercially available 1-year-old, bare root red maple (*Acer rubrum* L.), white oak (*Quercus alba* L.), yellow-poplar (*Liriodendron tulipifera* L.) and Norway spruce (*Picea abies* L.) seedlings were potted in a peat-perlite soil mixture (Promix BX) in 16.5 cm diameter plastic pots. The seedlings were grown in a greenhouse under ambient light and temperature conditions and were watered as necessary to maintain pot water contents near field capacity. Environmental conditions in the greenhouse varied diurnally. Photosynthetic photon flux densities reaching the seedlings did not exceed 750 μmol m^{-2} s^{-1} under full sun conditions because of light attenuation by the greenhouse roof. Greenhouse temperatures ranged from 15 to 30 °C depending on the time of day and/or year. Hg concentrations in the greenhouse air were measured to be 8-10 ng m^{-3}.

All plants had been potted for at least 2 months before use, and only mature foliage (i.e., fully expanded) was present on the seedling shoots during measurements. All plants were watered to saturation 24 hours prior to measurements of foliar Hg exchange rates.

2.2. Gas exchange measurements

Measurements of Hg° exchange were conducted in an open gas exchange system designed for foliar trace gas exchange (Hanson et al. 1989). The system isolates the plant shoot from its attached root system and potting media, and it allows for simultaneous measurements of CO_2 and H_2O exchange under controlled conditions of temperature, light, and vapor pressure to ensure the physiological integrity of the plant material. Access ports were added for triplicate sampling of inlet and outlet air streams for the measurement of Hg° from the gas exchange cuvette (Figure 1). Mean cuvette conditions were as follows: photosynthetic photon flux density (PPFD), ~500 μmol m^{-2} s^{-1}; temperature, 29.4 ± 0.5 °C; CO_2 concentration, 345 ± 13 μl l^{-1}. The PPFD level was adequate to open leaf stomata.

Mercury vapor concentrations of inlet and outlet air flows were determined using absorbent cartridges attached to the reaction chamber as shown in Figure 1. The sampling

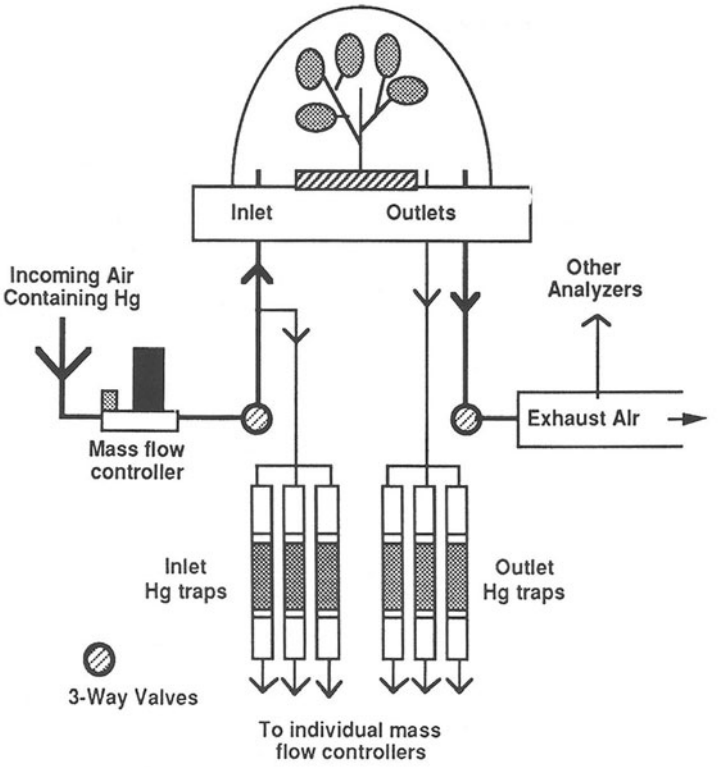

Figure 1. Key features of the trace gas reaction chamber showing the position of the seedling shoot isolated from the pot (not shown), details of the flow pathways, and the replicate Hg° traps for sampling inlet and outlet Hg° concentrations.

cartridges consisted of a quartz glass tube filled with gold coated sand which absorbs total vapor-phase Hg by amalgamation (Fitzgerald and Gill 1979). Air was pulled through each trap at ~0.25 L min^{-1} for fixed time periods and subsequently analyzed for Hg. Flow rates through each trap were determined with a mass flow controller system previously tested for measurements of Hg° in air (Kim and Lindberg, 1994). Mercury determinations were carried out with atomic fluorescence techniques following the procedures of Bloom and Fitzgerald (1988).

Air entering the reaction dome was under positive pressure, ambient reactive trace gases were removed with an AADCO clean air generator, and the resultant clean air was supplemented with Hg° generated from commercial permeation tubes placed in a gas standards generator (Kin-tex, model 570 C). The air mixture was adjusted for temperature, dew point, and CO_2 (~350 µl L^{-1}) prior to entering the exposure chamber.

Water vapor and CO_2 exchange of test plants were monitored to ensure that they retained normal physiological function. Stomatal conductance data for leaves obtained from the water vapor exchange measurement were used to resolve the relative amounts of internal and external deposition, and to document the rate limiting processes responsible

for controlling Hg° deposition to foliage (i.e., stomatal vs. mesophyll resistances to uptake).

Shoot leaf areas for the broadleaf species (one side only) were measured with a leaf area meter (LiCor, model LI-3100), and those for conifers were computed by multiplying total needle length times average needle circumference (determined from ocular micrometer measurements). Petiole and branch area was also present during deposition measurements, but typically accounted for less than 5 % of total shoot area.

2.3. Calculations

The net rates of Hg° exchange (deposition or emission) were calculated as follows:

$$F_s = (Ca\text{-}Ci)*Q*1/A \quad (1)$$

where F_s is flux of Hg° in nmol m^{-2} s^{-1}, (Ca-Ci) is the inlet to outlet concentration differential in nmol m^{-3}, A is the surface's area in m^2, and Q is the flow rate through the reaction dome in m^3 s^{-1}. Throughout this paper negative and positive rates of net Hg° exchange will represent deposition and emission, respectively. The resistance to Hg° was determined according to Taylor et al. (1982):

$$R_m = R_t - (R_b + R_s) \quad (2)$$

where Rm, Rt, Rb, and Rs are the mesophyll, total, boundary layer and stomatal resistances, respectively. All units are s cm^{-1}. Equation 2 assumes no cuticular transport of Hg°. Because conductances (cm s^{-1}) derived from the inverse of the resistances terms are linearly related to gas exchange rates, we present the R_m data as foliar conductance to Hg (K_f). Furthermore, because foliar Hg° exchange may result in net emission or deposition both positive and negative values for K_f are possible.

2.4. System tests

Tests were conducted to determine the exchange of Hg° with surfaces of the empty exposure chamber. For all light levels and Hg° concentrations, we found no significant gradients of emission or deposition from the chamber walls. Therefore, observed inlet to outlet gradients were used without correction in Equation 1.

To test the ability of our system to measure emissions and/or deposition, we monitored exchange rates with known Hg° sinks and sources placed in the reaction chamber. The known Hg° sources were soil cores obtained from a Hg contaminated bottomland hardwood forest stand near Oak Ridge, Tennessee. The forest floor samples were collected as undisturbed cylindrical cores approximately 19 cm in diameter. The forest floor samples were placed in 2500 ml Pyrex evaporating dish for storage and containment during measurements in the gas exchange system. A known sink was created by placing a uniform 5 mm layer of iodized charcoal in a petri dish (64 cm^2 planar exposure area) which was subsequently exposed within the reaction chamber. The measured emission and deposition of Hg° to these prepared sources and sinks are shown in Figure 2.

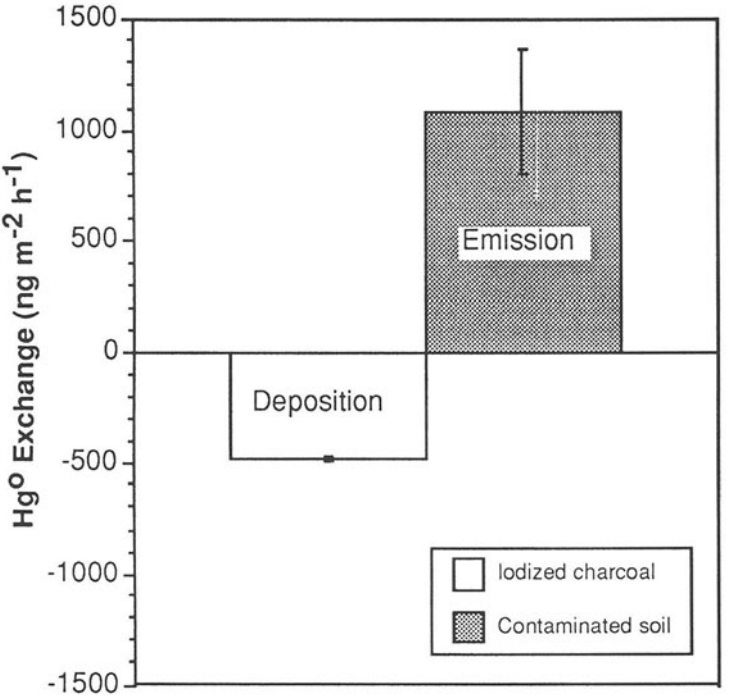

Figure 2. Exchange rates of Hg°(± se) for known sources (contaminated soil) and sinks (iodized charcoal). Note that net deposition and emission are expressed as positive and negative exchange rates, respectively.

2.5. Measurement protocols

Measurements of Hg° exchange with maple, oak and spruce foliage were conducted on 3 to 5 seedlings per species for each of three Hg° concentrations: 0.5-2, 10-20, and 50-70 ng m^{-3}. The yellow-poplar seedlings were only measured at the lowest concentration range. Exact concentrations varied between experiments due to slight changes in the total air flow through the exposure system and the specific foliar conductance of individual plants.

Prior to making measurements on individual plants, they were allowed to equilibrate to the chamber Hg° concentration for a minimum of three hours, and occasionally overnight. Steady-rate Hg° exchange was observed under light and dark conditions to provide data reflecting normal diurnal variability. Because darkness induces gradual stomatal closure, sequential deposition measurements following initiation of darkness allowed us to evaluate the relationship between Hg deposition and foliar conductance. Deposition to leaves having closed stomata is assumed to be sorption to exterior leaf surfaces. However, because the stomata seldom close completely estimates of surface deposition had to be derived from regressions on the data.

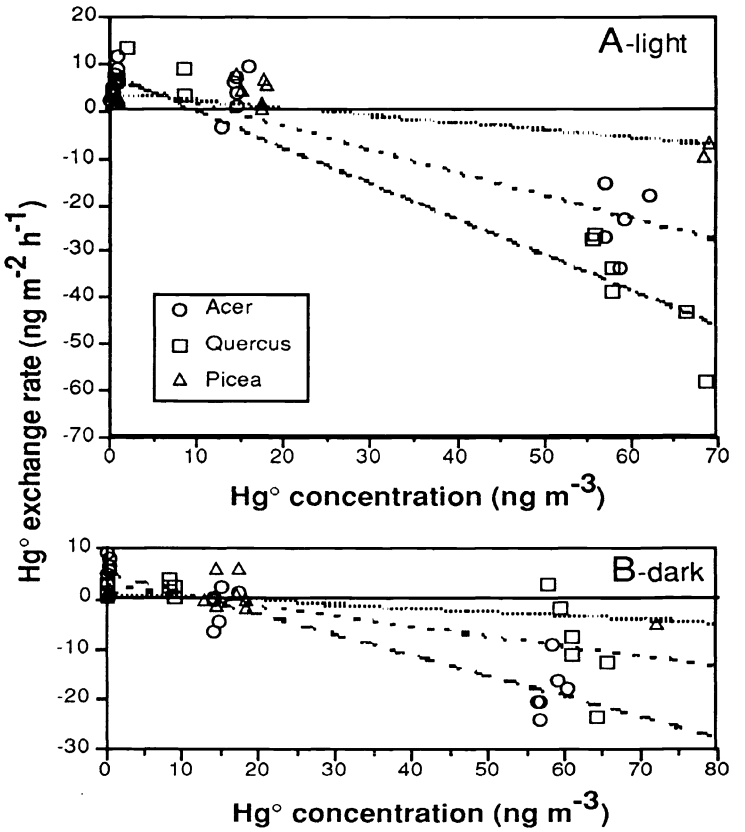

Figure 3. Relationship between Hg° exchange rate and Hg° concentration for *Acer rubrum* L., *Quercus alba* L. and *Picea abies* L. under light (A) versus dark (B) conditions. Each data point represents and individual experimental observation.

3. Results and Discussion

3.1. Net Hg° exchange vs. Hg° concentration

When Hg° concentrations were maintained from 0.5 to 1.5 ng m^{-3}, red maple, Norway spruce, yellow-poplar, and white oak foliage exhibited mean Hg° emissions of 5.5, 1.7, 2.7, and 5.3 ng m^{-2} h^{-1}, respectively. At Hg° concentrations between 9 and 20 ng m^{-3} little net exchange of Hg° was observed. However at concentrations between 50 and 70 ng m^{-3} the Hg° was deposited to hardwood foliage at mean rates between 22 and 38 ng m^{-2} h^{-1} while the mean deposition rate to the Norway spruce needles was lower averaging 9 ng m^{-2} h^{-1}. When these data are evaluated together in Figure 3 they show linear relationships between the Hg° exchange rate and Hg° concentration in air (Table I). The Hg concentration at which no net exchange occurs between the atmosphere and the leaf is termed the compensation concentration (or compensation point). Using the regression coefficients in Table I we estimate compensation points for red maple, white oak, and

Norway spruce to range from 10 to 25 ng m^{-3}.

The relationships between Hg° exchange rates and Hg° concentrations in air documented here suggest that dry foliar surfaces in terrestrial forest landscapes are not always a net sink for atmospheric Hg. They are instead a dynamic exchange surface that may function as a source or sink depending on the magnitude of current Hg° vapor concentrations.

Measurements in the dark exhibited reduced emission and deposition (Figures 3a and 3b), but they had essentially no impact on the compensation concentration (Table I). Du and Fang (1982) and Browne and Fang (1978) showed similar dark-induced reductions in the rate of Hg deposition for a range of crop plants. These authors concluded that the reduced rate of exchange was the result of both reduced stomatal conductance, and light dependent metabolism of the Hg reaching the leaf mesophyll cells. Du and Fang (1983) have documented a close relationship between catalase activity and Hg uptake by foliage. Because our data show significant uptake of Hg° by the leaves in the dark when external Hg° concentrations are sufficiently high, it seems appropriate to conclude that leaf metabolism of Hg° may not be entirely light dependent. Similarly, the presence of significant emission gradients in the dark when atmospheric Hg° concentrations are below the compensation point suggests a non-light dependent source of Hg° within the leaves.

Table I

Regression coefficients (±se) for the linear regressions in Figure 3 relating foliar Hg° exchange rates to external Hg° concentrations Data are provided for measurements conducted under light versus dark environments Significant probabilities (p values) following the regression coefficients reflect a rejection of the null hypothesis that the slope is equal to zero The estimated range of the species-specific compensation concentrations at which no net Hg° exchange takes place are also provided

Species	Linear coefficients				Compensation concentration (ng m-3)
	Slope (m h-1)	Intercept (ng m-2 h-1)	r2	p-value	
Acer rubrum L.					
Light	-0 49±0 05	6 6±1 3	0 83	<0 001	10 - 16
Dark	-0 41±0 04	5 3±1 3	0 88	<0 001	9 - 17
Picea abies L.					
Light	-0 15±0 04	3 8±1 1	0 59	0 001	18 - 33
Dark	-0 07±0 04	1 3±0 8	0 26	0 05	7 - 30
Quercus alba L.					
Light	-0 77±0 06	7 6±2 4	0 93	<0 001	7 - 13
Dark	0 20±0 05	2 7±2 0	0 55	0 002	8 - 23

3.2. Source of the Hg° for the observed biogenic emissions

Our data clearly show emissions of Hg° from the seedling foliage when atmospheric Hg° concentrations are low. What is the source of this Hg°? Equilibration of the plant material at the measurement concentrations prior to measurements eliminated transient solution degassing as a possible cause Analysis of foliar tissues indicated that foliar concentrations of Hg ranged from 0 04-0 06 μg g^{-1} which is similar to levels found in

foliage obtained from background environments (Kothny, 1973; Lindberg et al., 1979; Rasmussen et al., 1991), and the peat-based potting mixture had total Hg levels less than 0.02 ug g^{-1} which is substantially less than other reported soil Hg concentrations from background locations (Lindberg et al., 1979). Therefore we do not believe that the Hg originated from the nursery grown plants or from the peat moss based potting mix. The tap water used to irrigate the plants had mean total Hg and dissolved Hg° levels of 1.1 and 0.4 ng L^{-1}, respectively. Similarly, solution from the pots under well watered conditions had mean total Hg and dissolved Hg° of 3.2 and 0.1 ng L^{-1}, respectively. Although these levels are quite small, they may represent a supply of Hg to support the observed levels of biogenic emissions.

Emissions of elemental Hg° have also been reported from the aquatic vascular plant *Phragmites communis* growing along the shores of a Hg contaminated lake having sediment Hg levels ranging from 3.15 to 10.4 μg g^{-1} (Kozuchowski and Johnson, 1978). Kozuchowski and Johnson related the levels of Hg emissions to the level of soil contamination, the time of day, and leaf temperatures. These authors concluded that Hg emissions were associated with open stomata and the transpiration stream and/or light driven photosynthetic processes. Their reported rates of Hg emissions ranged from 90 to 1750 ng m^{-2} h^{-1} in uncontaminated and highly contaminated soils respectively. These rates from contaminated systems are much higher than we report here for terrestrial plants representative of a clean background environment. Dolar et al., (1971) found that Hg accumulated in watermilfoil (*Myriophyllum spicatum* L.) by physical adsorption and by metabolic uptake and translocation, and they concluded that organic Hg compounds were more likely than inorganic compounds to be translocated. Beauford et al. (1977) studied two terrestrial species (*Pisum sativum* and *Mentha spicata*) and also showed that inorganic $HgCl_2$ could be taken up by plant root systems although the level translocated to the plant shoot was quite small (<5%). Additional information on the emission of Hg° from plants growing on contaminated sediments is available (Siegel et al., 1974, 1981; Siegel and Siegel, 1988). We have also conducted initial experiments which corroborate the transpiration stream as an effective conduit for the transfer of Hg° from the soil solution out through the foliage (data not shown).

Table II

Calculated mean mesophyll conductance of Hg° to foliage of four tree species for low (0.5 to 2 ng m^{-3}) and high (50-70 ng m^{-3}) external Hg° concentrations. Data in parentheses are the range, and negative conductances imply net deposition within the measured foliage. The values shown represent data for foliage under full light at steady-state with open stomata. Resistance terms can be derived from the reciprocals of the Kf data presented. nd = not enough data to estimate.

Species	Mesophyll conductance to Hg° (cm s^{-1})	
	Low [Hg°]	High [Hg°]
Acer rubrum	0.052 (0.034 to 0.08)	-0.016 (-0.007 to -0.03)
Liriodendron tulipifera	0.024 (0.021 to 0.031)	nd
Picea abies	0.013 (0.011 to 0.018)	nd
Quercus alba	0.044 (0.028 to 0.065)	-0.024 (-0.019 to -0.034)

3.3. Internal conductances to Hg° uptake

Mesophyll conductances for biogenic emissions ranged from 0.01 to 0.05 cm s^{-1} and were only slightly greater than the absolute magnitude of the K_f values for deposition conditions (Table II). Although published data on the K_f for Hg° emitting plants were not available, K_f values for deposition in the range from -0.014 to -0.027 cm s-1 have been reported for wheat, oats, and barley (Browne and Fang, 1978; Du and Fang, 1983). Other C4 grasses have been shown to have K_f values for deposition more negative than -0.001 cm s^{-1} (Du and Fang, 1983). The species-specific differences in K_f have often been interpreted as a reflection of variability in the biochemical sink capacity for trace gases (Hanson et al., 1989; Taylor et al., 1982; Taylor and Tingey, 1983). However, Parkhurst (1994) using an analysis of the diffusion of CO_2 within leaves, concludes that tortuous diffusional pathways within the leaves might also contribute to reduced K_f terms for some species. The reduced conductances to Hg for the Norway spruce foliage would likely be partly explained by increased internal diffusion resistances to Hg vapor.

3.4. Implications for Hg° exchange with forested landscapes

State-of-the-art inferential methods for estimating Hg deposition to forest and crop canopies (Lindberg et al., 1992) use a multiple resistance approach that partitions deposition of trace gases into three sequential pathways governed by aerodynamic, boundary layer and receptor surfaces, respectively. Using this approach the deposition of Hg° to forest canopies is predicted to increase proportionately with atmospheric concentrations. The K_f values for the high Hg concentrations in Table II agree with the assumptions made in the Lindberg et al. (1992) model, but our data further suggest that near current ambient levels of Hg° dry foliar surfaces may function as sources of atmospheric Hg vapor. Our work emphasizes that foliage needs to be viewed as a dynamic exchange surface that can function as a source or a sink for Hg dependent on the current concentration of Hg in air. It is likely that variable leaf temperatures, surface conditions (wet vs. dry), and levels of atmospheric oxidants may also affect the net exchange of Hg with foliage. We further anticipate that actual compensation concentrations for any forest species will be a function of Hg levels in soils and soil solutions and the rate of reduction of Hg^{II} to Hg°. Additional experimental observations of Hg° exchange with foliage involving a wider range of species and experimental conditions should be conducted and tested against available models to ensure that the best possible information is available from which to estimate the contribution of foliar Hg exchange to terrestrial Hg cycling processes.

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THE PRECISE MEASUREMENT OF CONCENTRATION GRADIENTS OF MERCURY IN AIR OVER SOILS: A REVIEW OF PAST AND RECENT MEASUREMENTS

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Abstract. Measurements of the atmospheric concentration gradients of mercury (Hg) vapor over soils can be used to determine the direction and magnitude of exchange rates of Hg if certain assumptions are met. However, these gradients are quite small and require highly precise sampling to achieve accurate data. We have developed a sampling and analysis procedure which allows quantification of gradients over background soils. With this procedure we can now measure atmospheric Hg at ambient levels with a precision of ~0.5 to 2% (expressed as relative standard error). This level of precision is well above those published in earlier gradient studies. In our recent studies, gradients measured between 25 and 165 cm above background forest soils at Walker Branch Watershed, Tennessee were quite small, ranging from 0.02 to 0.39 ng/m^3 (expressed as concentration differences). These gradients indicated that Hg emission was about 3 times more frequent than dry deposition. Gradients measured over soils at Lake Gårdsjön, Sweden were generally smaller but also indicated bidirectional fluxes. By comparison, gradients above Hg-contaminated soils in Tennessee were far larger as expected, ranging from 0.12 to 5.60 ng/m^3. These gradients consistently indicated emission of Hg. A number of tests were performed to validate that these gradients were true indications of Hg exchange rates.

1. Introduction

There is now clear evidence that Hg exhibits bidirectional atmospheric fluxes in both terrestrial and aquatic systems, and participants in a recent international workshop agreed that improving the methods for Hg air/surface exchange measurements was a major research need (Lindqvist *et al.*, 1991). Dry deposition has been estimated from throughfall measurements and inferential models (eg. Iverfeldt, 1991; Lindberg *et al.*, 1992), but these methods do not also address upward fluxes. Dynamic chambers have been used to quantify air/surface exchange rates for Hg (Lindberg and Turner, 1977; Xiao *et al.*, 1991). However, chamber methods suffer from their potential to alter the local environment, and are limited to a small surface area (<1 m^2). The use of alternate approaches to measure Hg fluxes, such as the micrometeorological eddy correlation method, has not been attempted because of the absence of fast response (~10 Hz) sensors for Hg.

Micrometeorological gradient techniques for measuring air/surface exchange offer several advantages over chamber systems: 1) the surface is not disrupted because these methods are "in air" techniques; 2) the measurements provide an area-average of the flux; 3) fluxes can readily be determined over large terrestrial and aquatic surfaces; and 4) continuous measurements yield fluxes over a diurnal cycle without concern for problems caused by the extended isolation of the surface from ambient conditions. The gradient methods for trace gases use measurements of vertical profiles of gas concentrations to infer fluxes from simultaneous measurements of turbulent mixing parameters (eg. Denmead, 1983). Since concentration gradients are often quite

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small, very precise data are required. Previous measurements of Hg concentration gradients were done with a single sampler at each level (Johnson and Braman, 1974; Lindberg *et al.*, 1992). This approach is inadequate to differentiate critically very small differences in actual concentrations from differences due to analytical and sampling artifacts (Duyzer *et al.*, 1992) such as may be expected with Hg. Previously published Hg gradients have neither been measured with the precision nor collected with the meteorological data necessary to compute accurate Hg fluxes.

The MASE (Mercury Air/Surface Exchange) project was initiated at ORNL to quantify the deposition and emission of Hg from terrestrial and aquatic ecosystems. A major part of the project involves development and testing of gradient and chamber methods to measure bidirectional area-averaged fluxes of Hg. We review here one aspect of that work, the precise measurement of atmospheric concentration gradients of Hg over soils, and compare our recent data with earlier gradient measurements. Descriptions of our chamber methods for plants and soils are given in companion papers in this volume (Kim and Lindberg, Hanson *et al.*).

2. Research sites and measurement techniques for the MASE project

We measured Hg° vapor concentration gradients near a large area of Hg-contaminated forest soils on the floodplain of East Fork Poplar Creek (EFPC) in Oak Ridge, TN, and over uncontaminated forest soils at Walker Branch Watershed (WBW), ~2.5 km south of EFPC. The EFPC area was contaminated in the 1950's, and recent estimates place the total quantity of Hg in the EFPC soils at ~8×10^4 kg, predominantly as HgS, with a small fraction (~6%) in the elemental form (Revis *et al.*, 1989). Soil Hg concentrations at EFPC range from 50 to 200 $\mu g\ g^{-1}$ (primarily in the uppermost 50 cm), but some soils contain over 1000 $\mu g\ g^{-1}$ of Hg. Soil Hg at the WBW site averaged $0.50 \pm 0.15\ \mu g\ g^{-1}$ based on 10 surface mineral layer samples (~1 to 5 cm) within ~5 to 10 m of our site. Between March and November 1993, we sampled gradients of Hg° vapor between 25 and 165 cm above each of these soils. A limited study was also performed during June 1994 in the boreal forest surrounding Lake Gårdsjön, Sweden where surface soil Hg levels are near $0.10\ \mu g\ g^{-1}$. Further details on each site are available (Lindberg *et al.*, and Kim *et al.*, in press; Iverfeldt, 1991).

We collected gaseous Hg (elemental Hg vapor or Hg°) in air on "standard" gold-coated sand absorbers (gold traps) which were analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) (Bloom and Fitzgerald, 1988). The CVAFS system was calibrated using gas-tight syringe samples of a Hg°-saturated atmosphere maintained in a constant temperature bath (Dumarey *et al.*, 1985), a method which affords very high precision (<0.5% relative standard error based on replicate injections in our laboratory). Our absolute detection limit for Hg° based on gold trap blanks is ~2 pg (compared to typical sample signals of 50 to 200 pg). All handling and analysis of gold traps in our laboratory is done in class 100 laminar flow clean air benches where particulate Hg is < 1 pg/m^3 and typical levels of Hg° are in the range of 5 to 15 ng/m^3. Recent improvements in the CVAFS detection methods for Hg° allow for short term (~1 h) measurements at background levels (sub-pptv, ~1 to 3 ng/m^3) with an accuracy better than 5% (Bloom and Fitzgerald, 1988). This facilitates the application of micrometeorological methods to infer fluxes from measured gradients of Hg° since these approaches require highly precise measurements of small gradients with minimal uncertainty.

We found that the limitation on precise Hg° determination lies largely with sample collection and handling. To overcome problems with earlier gradient measurements, we designed a system

to collect six replicate air samples using a multi-port manifold connected to six separate mass flow controllers and operated by one small vacuum pump (the ORNL MFC system; described in Kim and Lindberg, 1994). Collecting six replicates at each height significantly decreases the uncertainty of the resulting gradients by allowing use of statistical outlier tests and computing of confidence intervals. With this sampling system and our modified CVAFS we can now consistently sample Hg° in air at background levels using a 1 to 2 h sampling period with an overall precision of a few percent or better, an important requirement for gradient studies. Another requirement is that adjacent samplers result in identical concentration data. We extensively tested our MFC samplers for biases between adjacent sampling systems and found no significant bias (Kim and Lindberg, 1994).

The achievement of high precision atmospheric concentration data at ORNL is due to the combined effects of several factors: 1. our MFC sampling system; 2. tightly controlled gold trap blank levels (e.g. generally <1% of the sample signal; the thin gold coating on the sand particles results in a negligible memory effect, and our frequent cleaning and replacement of the trap connectors and plugs has resulted in blanks in the range of <0.5 to 1.5 pg per trap); and 3. modifications to the CVAFS system including: a) mass-flow control of the analytical He gas stream, b) development of a totally inert gas standard injection system, c) accurate and precise control of the temperature of our gas standard, and d) use of peak area for quantification of the CVAFS signal as opposed to peak height. Tests by the authors during May-June 1994 at the IVL in Sweden indicated that high precision data can be achieved with the ORNL sampler in conjunction with a CVAFS system of a different design than that used at ORNL.

The modified Bowen ratio (MBR) method is widely used for inferring fluxes of trace gases from measured concentration gradients (e.g. Duyzer *et al.*, 1992). Our approach involves direct measurements of the gradients and vertical turbulent fluxes of CO_2 or H_2O vapor using eddy correlation with fast-response sensors to derive turbulent mixing coefficients (Baldocchi and Meyers, 1991). The advantages of this approach are discussed in Bartell *et al.*, 1993. Emission and/or dry deposition fluxes of vapor-phase Hg° are then inferred using these mixing coefficients with gradients of Hg° vapor measured over the same height interval (25 to 165 cm). The fluxes and vertical gradients for CO_2 and H_2O vapor were measured simultaneously with Hg° gradients using eddy correlation with fast response instrumentation and infra-red gas analyzers as described in Meyers and Baldocchi (1993). Concurrent with these measurements, routine meteorological data are collected (wind speed and direction, air and soil temperature, humidity, solar radiation, surface wetness, and precipitation). The flux of Hg is computed from its precisely measured gradient and the derived mixing coefficients, assuming similar spatial distributions of sources and sinks for each trace gas (Kim *et al.*, in press). Hence: $F_{Hg} = K_w \times \Delta Hg$, where F_{Hg} is the flux of mercury, ΔHg ($= dHg/dz$) is the vertical concentration gradient of Hg°, and K_w is the turbulent transfer coefficient which was calculated from the ratio of the H_2O vapor flux and its gradient, $K_w = F_{H_2O}/\Delta H_2O$, where $\Delta H_2O = dH_2O/dz$. All concentration gradients are measured over the same height interval and are expressed as concentration differences (i.e. $C_{25\,cm} - C_{165\,cm}$, in units of ng/m^3, understood to be ng/m^3 per 140 cm). As with any such method, certain sampling conditions must be met to assure correct interpretation of the gradients (e.g. steady state exchange, and the absence of in-air reactions or advection of Hg° from local sources; see Denmead 1983).

3. Results and discussion

3.1. A SUMMARY OF RECENTLY MEASURED GRADIENTS IN TENNESSEE AND SWEDEN

Using our sampling system, we consistently achieved high precision air concentration data from multiple replicates. Our mean Hg° concentrations in air showed relative standard errors (RSE) generally in the range 0.5-1.5%, and overall precision rarely exceeded 3% (Fig. 1). As expected, precision was somewhat better at higher air concentrations of Hg° because of the larger sample/blank ratio: the mean RSE for the EFPC data set was 1.1±0.6% where the mean Hg° in air = 3.48 ng/m^3, while that for the background WBW site was 1.4±0.3% (mean Hg° = 2.15 ng/m^3). The limited results from the study at IVL showed a mean RSE of 1.4±0.6%. Table I summarizes the raw concentration data from gradient measurements over EFPC, WBW, and Lake Gårdsjön forest soils showing good examples of the precision of our method and the resulting gradients over both contaminated and clean soils. Based on the 90% confidence intervals computed for the gradients, the overall sampling plus analytical uncertainty in the gradients at the contaminated site is less than 30%, and typically around 10%. As expected the overall uncertainty is higher over background soils, typically around 50%, occasionally as high as 100%, and more than a factor of 2 for the marginally significant gradients.

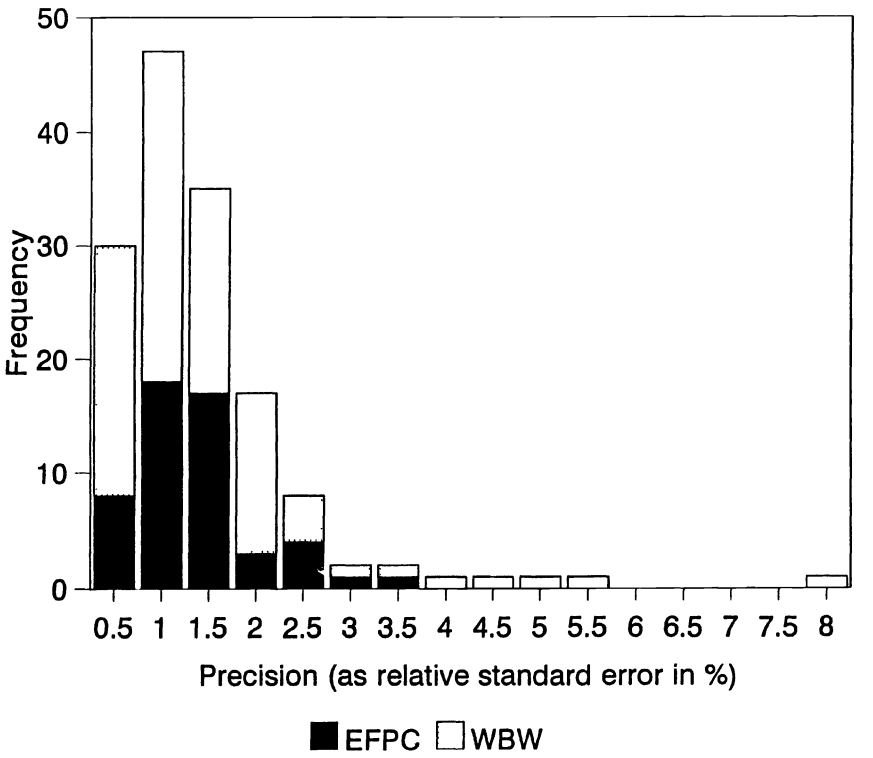

Fig. 1. Frequency plot of the overall sampling plus analytical precision of the concentrations of atmospheric Hg determined with our methods. Precision is given as the relative standard error of the mean (RSE=SE/mean) based on 6 replicate samples.

TABLE I

Replicate Hg air concentration data from gradients measured over contaminated soils (EFPC, 4/23/94) and over background soils in Tennessee (WBW, 6/2/93) and Sweden (LG, 6/6/94) using the ORNL sampler.

Site*	Hgt. (cm)	Hg Concentration in Each Replicate (ng/m³)						Mean
		1	2	3	4	5	6	
EFPC	25	4.14	4.15	4.19	4.17	4.28	outl+	4.19
EFPC	165	3.81	3.85	3.83	3.81	3.83	3.83	3.83
WBW	25	1.93	1.92	outl+	1.93	1.90	1.93	1.92
WBW	165	1.86	1.87	1.85	1.87	1.88	1.84	1.86
LG	25	1.89	1.97	2.00	1.91	2.00	2.01	1.96
LG	150	1.93	1.88	1.96	1.90	2.00	1.85	1.92

		Mean	SE**	RSE(%)**	GRAD.**(ng/m³)	CI**	Sig.**
EFPC	25	4.19	0.02	0.48%			
EFPC	165	3.83	0.01	0.26%	0.36	0.04	p<0.05
WBW	25	1.92	0.01	0.27%			
WBW	165	1.86	0.01	0.30%	0.06	0.02	p<0.05
LG	25	1.96	0.02	0.94%			
LG	150	1.92	0.02	1.10%	0.04	0.09	p<0.10

*Sites: EFPC = East Fork Poplar Creek, TN; WBW = Walker Branch Watershed, TN; LG = Lake Gårdsjön, Sweden. +outl = values identified as statistical outliers and eliminated from the data set (values were 2.92 at EFPC and 2.15 at WBW). Outliers typically resulted from blocked sample traps or unusually high trap blanks.

**SE = standard error; RSE = relative standard error (SE/mean); Grad. = concentration gradient between measurement levels given (as C_{25cm} - C_{165cm}); Ci = 90% confidence interval of the gradient (in ng/m³); Sig. = significance level of the measured gradient.

Figure 2 summarizes the gradient data collected during 1993 in Tennessee, illustrating the absolute concentration differences which must be quantified to use the MBR method. Each of the 26 measurements at the EFPC site (Fig. 2a) yielded a statistically significant ($p<0.05$) concentration gradient of Hg°, with concentrations consistently higher at the 25 cm height than at 165 cm, indicating that only emission of Hg° was occurring from these contaminated soils during our measurements. The resulting Hg° concentration gradients during the spring ranged from 0.12 to 2.88 ng/m³ (mean = 0.75±0.78); during fall the gradients ranged from 0.14 to 5.60 ng/m³ (mean = 1.17±1.70).

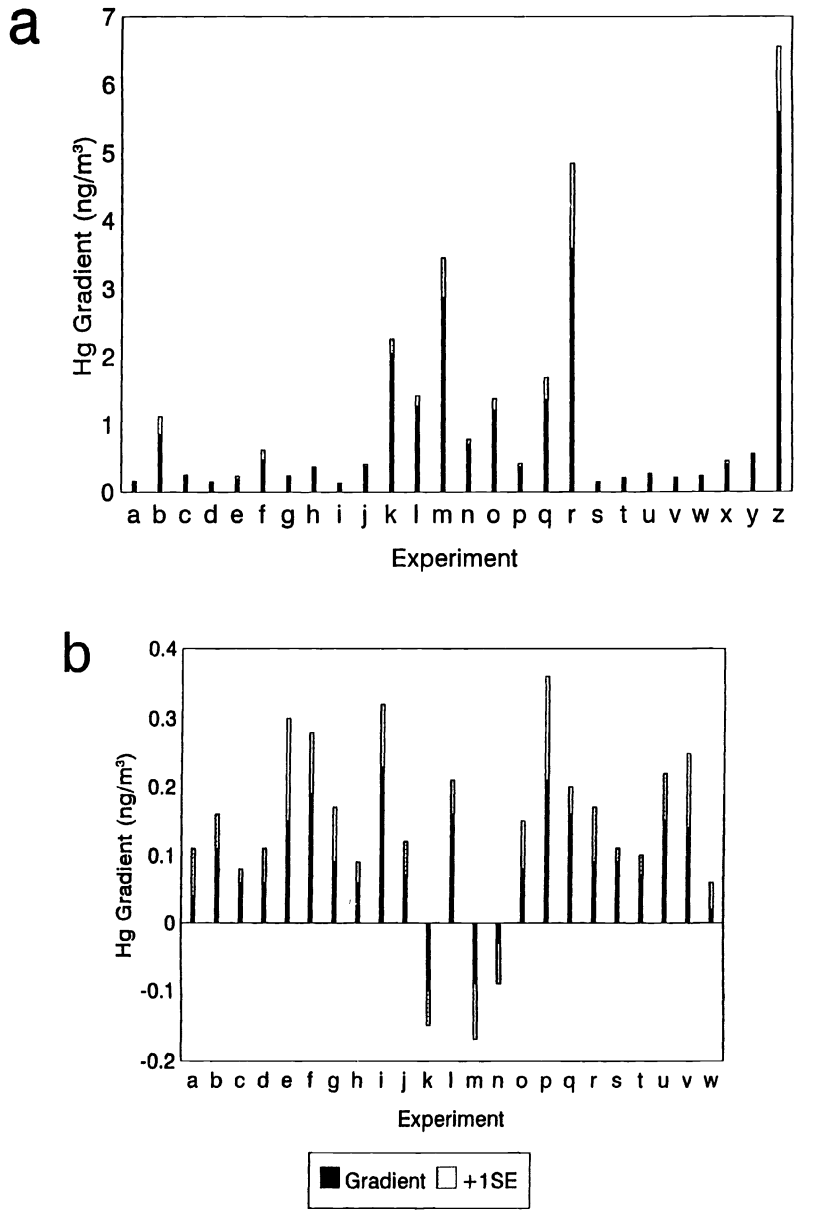

Fig. 2. Gradients of Hg° measured as concentration differences between 25 cm and 165 cm above contaminated soils at EFPC (plot a) and above background soils at WBW (plot b, note different scale) during 1993. The EFPC data were collected during spring (experiments a-o) and fall (p-z), while the WBW data cover spring (a-f), summer (g-r), and fall (s-w). The lower section of each bar represents the computed mean gradients (as C_{25cm}-C_{165cm}) from 6 replicate air concentrations at each level, and the upper section of each bar is the standard error of the mean (SE).

We measured much smaller gradients at the background WBW site (Fig. 2b), as expected. Our method quantified gradients of 0.06 ng/m^3 that were statistically significant at $p<0.05$ and as small as 0.02 ng/m^3 that were significant at $p<0.10$. The bias between our sampling systems is ~0.02 to 0.03 ng/m^3; however, in 20 tests with 12 to 18 replicates each none of the measured biases were significant at $p<0.05$. At WBW only about half of the measured gradients were significant at $p<0.05$ (another 3 gradients were significant at $p<0.10$ and are included in Figure 2). Of the 39 measurements made under ideal conditions, the gradients suggested 30 soil emission events and 9 deposition events. However, sixteen of these events were characterized by non-significant ($p>0.10$) gradients, suggesting near-zero fluxes (10 emission and 6 deposition). Using absolute values for comparison with the EFPC gradients, the significant gradients at the WBW site during the spring/summer ranged from 0.02 to 0.39 ng/m^3; during fall the gradients ranged from 0.07 to 0.15 ng/m^3. Including the non-significant values, the gradients averaged 0.10±0.07 ng/m^3 for emission events and -0.05±0.05 ng/m^3 for deposition events (the means of the significant gradients are nearly identical to these). It is clear that gradients over the WBW soils are much smaller than over the contaminated soils, and that emission gradients are more frequent and larger in magnitude than the deposition gradients. Limited measurements during June 1994 at Lake Gårdsjön in Sweden revealed generally smaller but still quantifiable gradients over soils below a boreal forest during cool weather (range 0.01-0.11 ng/m^3 as both positive and negative gradients).

3.2 PREVIOUS GRADIENT MEASUREMENTS OVER SOILS

The early gradient measurements of Johnson and Braman (1974) suggested bidirectional fluxes of Hg° over a grassy soil in Florida. Of 31 measured gradients between 0.1 and 1.0 m above the ground, 7 suggested deposition but the majority indicated emission of Hg° from the surface. They reported mean concentration differences that fell between 2 to 5 ng/m^3, with some values as large as 8 to 14 ng/m^3 during a plume event. For direct comparisons, we normalized both data sets to the sampling height interval in meters. The mean gradients rank as follows (in absolute value): Florida deposition (4.4±5.0 ng/m^3/m) > Florida emission (2.6±2.1) > EFPC emission (0.66±0.93) > WBW emission (0.071±0.050) > WBW deposition (0.036±0.036). In a study by Schroeder *et al.*, (1989) the sampling height interval was not given, but they reported concentration differences between a lake surface and adjacent land averaging 2.5 ng/m^3.

It is difficult to compare our gradients with those published earlier due to uncertainties in methodology. However, the magnitudes of the earlier gradients seem unreasonable and would suggest very large fluxes, depending on the turbulence intensity during sampling. Both of the early studies emphasized large uncertainties in their data. Schroeder *et al.* stated a "detection limit" for concentration differences of 1.1 ng/m^3, while Johnson and Braman reported their overall precision to be ±10%. The data in Table I and Figure 2 clearly illustrate the levels of precision necessary to accurately quantify Hg° concentration gradients. Based on Hg fluxes over background soils from chamber data (Xiao *et al.*, 1991) and typical turbulence levels below forests, we expect the true gradients over background soils within about 150 cm of the surface to be only a few percent of the mean air concentration (at WBW generally 3 to 7%, median ~5%). However, over contaminated soils they may approach 40 to 50% or larger depending on soil Hg and turbulence levels (at EFPC generally 10 to 30%, median ~20%).

3.3. TESTING THE VALIDITY OF MEASURED GRADIENTS

Although it is now possible to quantify small gradients in atmospheric Hg° with reasonable uncertainty, we need to demonstrate that they yield a meaningful signal. Principles of turbulent exchange suggest simple tests of both the measured gradients and the fluxes computed from them. Because the EFPC soils contain elemental Hg, we expect them to emit Hg° by volatilization. The measured Hg° gradients were consistent with this expectation under a variety of conditions (e.g. Figure 2a). We also expect measured gradients to show a smooth profile between the two sampling heights if the assumptions of the method are met and the concentrations are influenced only by turbulent diffusion. On three occasions under different conditions we measured concentrations of Hg° at intermediate heights and found that the resulting profiles were well behaved (Figure 3). These log-profiles support the application of

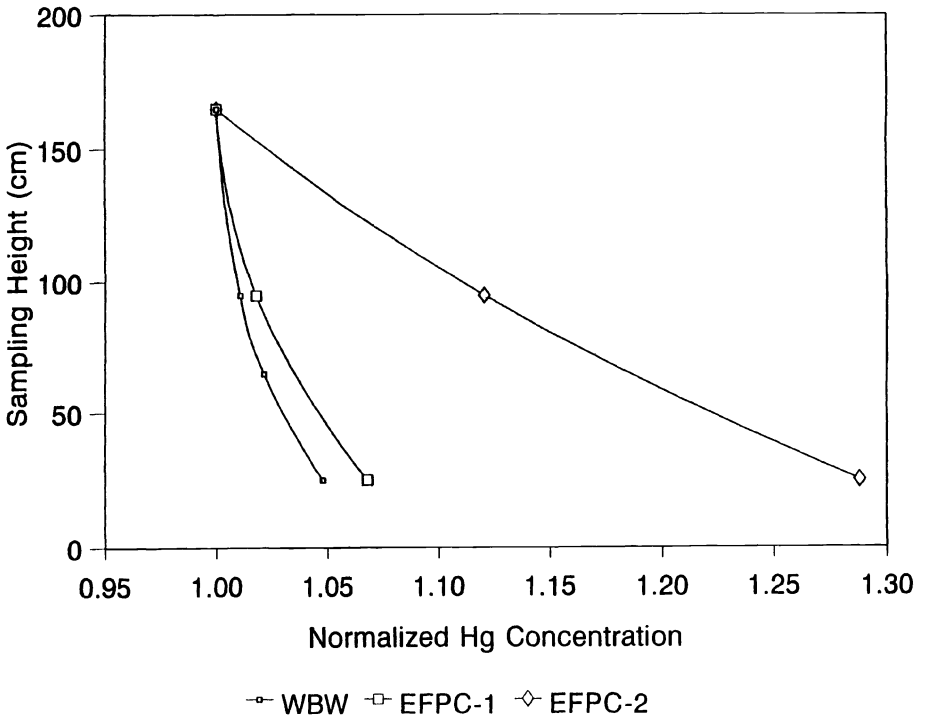

Fig. 3. Multi-height profiles of Hg° measured over background (WBW) and contaminated (EFPC) forest soils in the spring of 1993. The gradients and 90% confidence intervals computed from these data are shown in Fig. 2 (EFPC-1&2 = experiments "g" and "k" in Fig. 2a, WBW = experiment "g" in Fig. 2b).

gradient theory to Hg fluxes over these soils. In addition, because trace gas concentrations measured near a source are diluted by turbulent mixing with background air, we would expect concentration gradients to decrease with increasing atmospheric turbulence. The measured Hg° gradients over both soils exhibited the expected behavior (Lindberg *et al.*, submitted; Kim *et al.*, in press). Finally, the vapor pressure of elemental Hg suggests that Hg° vapor emissions should be strongly influenced by soil temperature. We found significant exponential relationships between temperature and Hg° emission rates from both soils (for log regressions: $r=0.90$ for the EFPC data collected directly downwind of the source area, and $r=0.48$ for WBW data; $n=11$ and 16, $p<0.01$ and $p<0.10$, respectively; Lindberg *et al.*, and Kim *et al.*, in press).

4. Summary and implications

We have developed a multi-replicate, mass-flow-controlled sampler and analytical procedures which meet the extreme precision requirements for application of micrometeorological methods to estimate air/surface exchange rates of elemental Hg vapor from measurements of atmospheric concentration gradients of Hg° over environmental surfaces. During 1993-1994, concentrations of Hg° were measured in profiles over contaminated and background soils with a precision generally around 1%. Our data provided confidence in the method for Hg° because the computed gradients in Hg° behaved as predicted from first principles.

As expected, the gradients over the contaminated soils were significantly larger than those over the background soils and consistently indicated emission of Hg°. Gradients over the background soils indicated both emission and deposition, but emission gradients occurred more frequently and were larger in magnitude than deposition gradients at the WBW site. We used the modified Bowen ratio method to estimate Hg° fluxes from these gradients as reported elsewhere (Lindberg *et al.*, and Kim *et al.*, in press). Emission rates from the contaminated soils averaged 86±72 ng m^{-2} h^{-1}, significantly above fluxes over the background soils at WBW which averaged 7.5±7.0 ng m^{-2} h^{-1} for emission events and -2.2±2.4 ng m^{-2} h^{-1} for deposition events. The preliminary data from Lake Gårdsjön suggested bidirectional fluxes on the order of <1-3 ng m^{-2} h^{-1}.

Precise measurements of Hg° concentration gradients under steady state conditions should be attempted in biogeochemical cycling studies. Even without the micrometeorological capability to compute fluxes, valuable insights can be obtained from gradient data. Given simple estimates of turbulence, semi-quantitative estimates of the magnitude and direction of fluxes can be derived as long as the conditions of the method are met. Successful demonstration of micrometeorological methods for Hg vapor is important because current global estimates of soil emissions of Hg° are based on extremely limited chamber data, and because measurements of dry deposition of Hg° are virtually non-existent. The success of this method over soils supports its utility for measuring bidirectional Hg° fluxes over vegetation and water surfaces, and also for extending its application to other trace gases for which the fast-response sensors needed for eddy correlation are not available (e.g. other vapor phase metals and volatile organics). In addition, our multi-replicate, mass-flow-controlled samplers would also be useful in other studies which require high-precision data. An important research need identified in a recent workshop was to establish a global mercury trends network to quantify small changes in airborne Hg° concentrations at remote sites over time (Lindqvist *et al.*, 1991).

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ATMOSPHERIC DEPOSITION OF MERCURY IN FLORIDA: THE FAMS PROJECT (1992-1994)

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Abstract. The primary goal of the Florida Atmospheric Mercury Study (FAMS) is to quantify the seasonal and geographical variability in the atmospheric deposition of Hg and other trace elements in central and south Florida. Precipitation, aerosol, and gaseous Hg samples have been collected at seven sites in Florida for periods ranging from 3 to 24 months. The summertime wet season in south Florida accounts for 80 to 90% of the annual rainfall Hg deposition. Depositional rates in south Florida are 30 to 50% higher than those from central Florida. Particle phase measurements range from 2 to 18 pg/m^3 Hg at all sites. Measurements of monomethylmercury in precipitation range from <0.005 to 0.020 ng/L.

1. Introduction

A 5-year study focusing on the atmospheric deposition of Hg and other trace elements in central and south Florida has been initiated. The organization and rationale for the FAMS project are described by Pollman *et al.* (this volume). One of the primary objectives of the Florida Atmospheric Mercury Study (FAMS) is to quantify geographical and seasonal variations in atmospheric mercury deposition and to subsequently determine if subregional differences in Hg deposition occur in Florida. Other objectives include quantifying the marine background contribution for Florida, determining the partitioning between wet and dry deposition, investigating the speciation of Hg in precipitation and gaseous Hg, and identifying possible sources of Hg using multiple chemical tracers (Pollman *et al.*, this volume).

The FAMS project presently encompasses the tower-based collection of weekly integrated total gaseous and aerosol mercury samples and monthly integrated bulk and wet deposition samples at seven field locations in north-central and south Florida. The use of ultra-clean protocols during the manual collection of event rain samples for Hg have proven to be extremely successful (Gill and Fitzgerald 1987; Fitzgerald *et al.*, 1991). The establishment of the FAMS monitoring network has been contingent upon the adaptation of these clean collection protocols to automated, tower-based, precipitation sampling. Quantifying the atmospheric deposition of Hg to Florida is a necessary precursor to understanding the mechanisms that govern the partitioning of Hg in Florida's aquatic environments.

2. Materials and Methods

2.1 Site preparation

The FAMS monitoring network presently includes seven sites within Florida (Figure 1). Lake Barco (LB) represents our north-central Florida site. Additional sites are located in

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Ft. Myers (FM), Fakahatchee Strand State Preserve (FS), Tamiami Trail Ranger Station (TT), and Everglades National Park (EG). The marine background; Little Crawl Key (CK) and urban; Andytown (AT) sites were established in April, 1994 (Pollman *et al.*, this volume). The data sets from these two sites are limited, so they will not be discussed in detail. Two new stations will be added in November 1994, at the Everglades nutrient removal project and near Caryville in north Florida. Each station is equipped with a 48' aluminum tower with outboard sampling platforms. The towers are outfitted with a full array of meteorological equipment. A shed at the base of each tower houses pumps, mass-flow systems, meteorological data loggers, and telecommunications equipment. The shed can also serve as a class 100 clean area when necessary (Landing *et al.*, 1993).

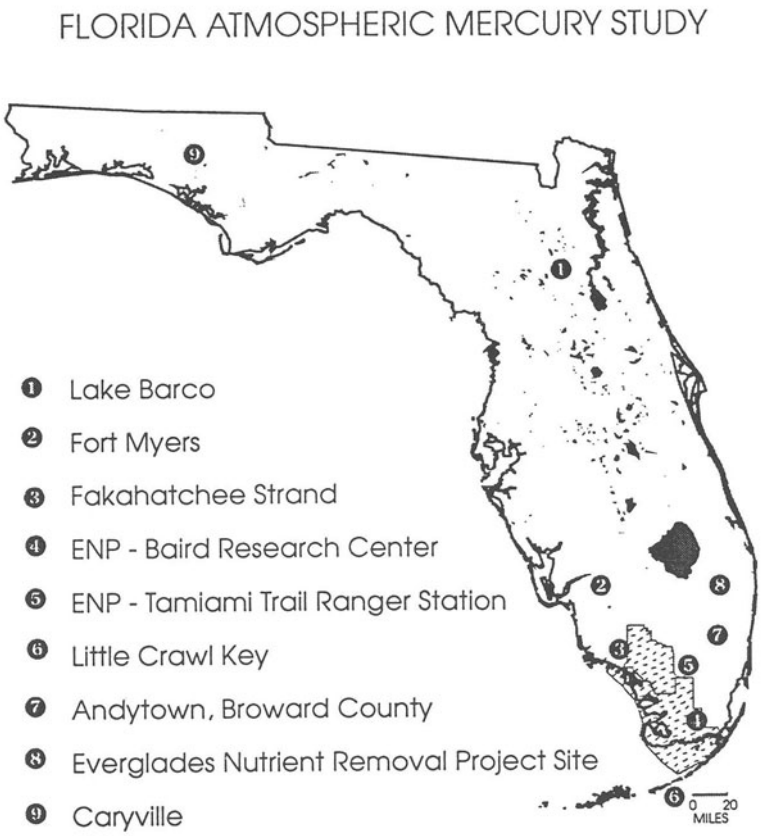

Fig.1. Locations of FAMS monitoring sites.

2.2 SAMPLE COLLECTION

Monthly integrated bulk deposition samples are collected using a modified version of the collectors used by Iverfeldt (1991) and Lindqvist *et al.*(1991). The FAMS sampler consists of a polycarbonate funnel threaded into a PTFE Teflon collar connected to a 90 cm length of 0.64 cm OD FEP Teflon tubing. The tubing is connected to a 2L FEP Teflon receiving bottle threaded into another PTFE Teflon collar. The bottle is precharged with 15 mL 6M triple distilled (3xQ) HCL and is shielded to reduce photochemical reactions. The bulk deposition samplers are deployed in duplicate at each site. Immediately prior to recovery, the walls of the funnels are rinsed into the receiving bottle with two 70 mL aliquots of ultrapure acidified water (0.045M 3xQ-HCl). One of the funnels at one of the sites is turned down for the monthly sampling interval to serve as a field blank.

Wet deposition is collected using a modified version of the Aerochem Metrics wet/dry deposition sampler. The aluminum arms of the sampler are replaced with Teflon-coated arms. The aluminum roof is replaced with a polycarbonate roof equipped with a 6-inch-high Plexiglas rain splash guard. The polyethylene-enclosed foam seal is placed in a FEP Teflon bag. Three 1L teflon receiving bottles are nested inside the wet bucket. The 1-liter bottles are threaded into PTFE Teflon dual collars which also connect to 1L polycarbonate funnels. Two of the Teflon bottles are precharged with 7.5 mL 6M 3xQ-HCl and one is deployed without preservative. The precharged bottles are specifically for mercury, nutrients, and other trace metals, while the unacidified bottle is used to obtain sub-samples for major ions and pH (Landing *et al.*, 1993). The excellent agreement between rain sample and rain gauge volumes ($98 \pm 2\%$, $n = 130$) indicates that the rain events are quantitatively collected with both types of samplers.

Weekly integrated aerosol samples are collected on 47mm 0.4 μm polypropylene membranes (Micron Separations, Inc.) held in open-faced polypropylene filter housings with PTFE Teflon O-rings. Polypropylene membranes were chosen because they can be successfully cleaned for Hg and all of the other trace elements measured in this project. The aerosol filter holders are placed in vented Plexiglas rain shrouds mounted on the outboard platform. Field blanks are placed in identical filter holders within the rain shrouds. The air flow rate through the filters is 50 LPM yielding a 50 cm/s face velocity (Landing *et al.*, 1993). Tests conducted on these filters indicate that they are $>99\%$ efficient at collecting particles >0.4 μm and 96-98% efficient at collecting particles ranging from 0.015 to 0.8 μm (Hal Maring, pers. comm.).

We have determined that a minimum sampling interval of 3-6 days is required to collect a sufficient aerosol sample. The collection of a 24 hour integrated sample does not yield enough particulate Hg to detect accurately. While the possibility of sampling artifacts cannot be ignored during extended sampling periods, several researchers have demonstrated successful collection of weekly integrated aerosol samples, for Hg and trace metals, using 0.4 μm filters in open-faced 47 mm filter holders (Arimoto and Duce 1987; Lindberg *et al.*, 1991). One question to address is loss or gain of Hg from the filters during their deployment. If there were significant loss or gain of Hg during a four week deployment period, them we would expect the filter from the first week to be consistently and significantly lower or higher than the sample from the fourth week. This trend is not observable in the data that we have accumulated thus far.

For cleaning, all Teflonware is rinsed with acetone, cleaned with Micro detergent (Cole-Parmer), leached in conc. reagent grade nitric acid at 55 °C for 7 days, followed by 7 day leaches in 3M HCl, O.5M HCl, and O.5M quartz distilled HCl (1xQ-HCl). Teflon bottles are rinsed with ultrapure water, filled with acidified water (0.045 M 3xQ-HCl), hermetically sealed, double bagged in polyethylene bags and stored in the clean lab until use. Other Teflonware is rinsed with ultrapure water, double bagged in polyethylene bags, and stored in the clean lab. Polycarbonate equipment is Micro washed, leached for 7 days in 3M HCl, 0.5M HCl, 0.5M 1xQ-HCl, rinsed with ultrapure water, double bagged, and stored in the clean lab. Polypropylene aerosol filter holders are washed in Micro after use and are stored in 0.5M 1xQ-HCl between uses. The polypropylene filters are cleaned prior to deployment using sequential 7 day 3M and 0.5M 3xQ-HCL leaches and ultrapure water rinses.

2.3 SAMPLE ANALYSIS

Mercury is measured by dual amalgamation (Fitzgerald and Gill, 1979) using a Brooks-Rand (model 2) cold vapor atomic fluorescence detector. With our instrumental settings, the detector response is linear from 100 to 10,000 pg Hg with a relative standard deviation of $\pm 2\%$ for replicate injections of Hg (yielding an instrumental detection limit of 30 pg Hg). Detector calibration is accomplished using vapor phase additions of a Hg-saturated air standard. The standard is calculated to contain 10.0 ng Hg/cm^3 at 16.7°C (Fitzgerald and Gill, 1979).

Measurements for total mercury are made using a method similar to that described by Gill and Bruland, (1990). The samples are predigested with dilute aqua regia (7.5mL 6M 3xQ-HCl/L and 6mL 7.5M Q-HNO_3/L) and exposed to low wattage UV (730 μW/cm^2; 254 nm) for 48 hours. A solution of 20% hydroxylamine hydrochloride is added to the sample (400 μL/300 mL sample) to quench the free chlorine and the sample is reduced with 25 ml 4% $NaBH_4$ (GFS Chemicals). The analytical detection limit for this procedure, based on three times the standard deviation of the purge blank, is 0.05 ng/L (n=75). Aqueous Hg standards are prepared and analyzed in the HCl/HNO_3 matrix. Standard additions of 1000 pg Hg typically give results of $100 \pm 5\%$. Analytical variability within samples ranges from 0.05 to 1.0 ng/L. Variability between colocated samples ranges from 1 to 5%. An interlaboratory comparison between the FSU (Florida State University) and TAMUG (Texas A&M University at Galveston) labs demonstrates excellent analytical reproducibility. Replicate samples were analyzed in a "blind" intercomparison by Jane Guentzel at FSU and Mary Stordal at TAMUG. The sample concentrations ranged between 0.5 to 2.1 ng/L Hg-total (n=12), with the average absolute deviation between the labs equal to 0.2 ng/L.

The BrCl method (Bloom and Crecelius,1983) and the dilute aqua regia digestion method were compared for their ability to solubilize total Hg in precipitation samples. Duplicate bulk deposition samples were collected, digested with either BrCl or aqua regia, photo-oxidized for 48 hour, neutralized with hydroxylamine HCl, and then analyzed under the same set of conditions, using $NaBH_4$ as the reductant. The average of the aqua regia-to-BrCl ratios was $98 \pm 4\%$ (n=14). This is not significantly different from the routine analytical error ($\pm 5\%$). The comparison between the two methods has been further tested by the participation of FSU in the international intercomparison

exercise (Bloom and Horvat, this volume). The result obtained by Guentzel (1.39 ± 0.06 ng/L, n=2) is not significantly different from the overall result obtained by the primary reference lab (1.27 ± 0.14 ng/L; n=30), and the result obtained by the reference lab using the BrCl/photo-oxidation treatment (1.33 ± 0.12 ng/L; n=6) (Bloom and Horvat, this volume).

Aerosol samples are digested for total mercury and other trace metals using PTFE Teflon digestion bombs (Eggimann and Betzer, 1976). The filters are digested using a mixture of 6M 3xQ-HCl/conc. Q-HNO_3/conc.HF (Ultrex, J.T. Baker). The digest is analyzed for total Hg using $SnCl_2$ reduction (Gill and Fitzgerald, 1987). The procedural detection limit, based on three times the standard deviation of the total (deployment, handling, digestion, and analysis) blank divided by a volume of $300m^3$, is $1.28pg/m^3$ (n=73). Digestions of NIST-2704 standard reference material (Buffalo River Sediment) yield $94 \pm 12\%$ (n=43) for total Hg.

Results and Discussion

3.1 Equipment blanks

Sampling equipment is rotated on a quarterly basis for every station. If the equipment has been fouled by bird droppings or insects it is replaced regardless of the schedule. Equipment blanks for the deployment of new equipment and the recovery of old equipment are quite low relative to the samples. New and old equipment blanks are measured by pouring one-half of a 1000 mL bottle of ultrapure acidified water (0.045 M Q-HCl) through the sampling setup (the "B" solution). The remainder of the water is retained as the "A" solution. The equipment blank is reflected in any differences in Hg concentration between the A and B solutions. New equipment blanks are <20 pg Hg and old equipment blanks are <200 pg Hg. Field blanks for 30 day deployment of bulk and wet deposition are 350 ± 110 pg Hg and 65 ± 21 pg Hg respectively. These blanks are corrected for the initial acid contribution and are negligible relative to the total mass of Hg in the samples (5,000 to 30,000 pg Hg).

3.2 Quality assurance experiments

The integrity and validity of the samples is of paramount importance to this project. Quality assurance tests have been, and continue to be, an integral part of our project. As the project and sampling equipment evolves, so do the QA/QC experiments. The short nature of this paper makes it virtually impossible to address every QA/QC concern. The most important issue to focus on is gain or loss of Hg from the samples during month-long integrated collection periods. Schroeder *et al.*, (1991) state that the principal form of oxidized Hg in the atmospheric environment is $Hg^{2+}$and at pH values less than 5.5, the aqueous phase oxidation of Hg^0 to Hg^{2+} is the dominating reaction. Therefore, loss of Hg from a shielded, acidified sample should be negligible. Gain of Hg through elemental Hg diffusion and oxidation is minimized by the design of the sampling equipment and quantified by collecting field blanks and making the appropriate blank correction.

In addition to measuring blanks, we have attempted to quantify loss or gain of Hg from the samples using aqueous phase Hg standards and actual samples. A 5.0 ng/L Hg(II) standard, acidified to the same level as a bulk deposition sample, was deployed for 30 days. The total Hg measured after recovery of the bottle was not significantly different from the original standard solution: 5.07 vs. 5.04 ng/L respectively. In a 1990 comparison, Iverfeldt and Munthe (1993) demonstrated that there was no significant difference between weekly, biweekly, and monthly collections of bulk precipitation samples. We have also confirmed that there is no significant gain or loss of Hg from bulk deposition samples deployed for a 14 day period. Colocated 24 hour event rain samples and a continuous bulk precipitation sample were collected during a 14 day period. The total mass of Hg in the 14 day integrated sample was 5.1 ng and the volume weighted sum of the event samples was 4.6 ng. The difference between these values is not significantly different from the variability between monthly colocated samples. Similar tests have been successfully completed for the Aerochem Metrics sampler. However, the limited nature of this paper does not allow for a lengthy discussion of QA/QC procedures.

3.3 MERCURY IN PRECIPITATION

The bulk deposition samples contain 100% of the wet deposition and whatever dry deposition collects in the funnels and is rinsed into the receiving bottle. Although we have not fully investigated the aerodynamic behavior of the polycarbonate funnels, if we assume that the bulk deposition funnels collect the majority of any aerosol dry deposition, then we might expect to find differences between bulk and wet deposition proportional to dry deposition. Average volume weighted bulk and wet fluxes and concentrations have been calculated for each FAMS site (Table I). There are no significant differences between bulk and wet flux or concentration at each site. This is direct contrast to the other trace metals. Landing *et al.*, (1994) report that elements such as Al, Cu, Zn, As, and Pb differ significantly between bulk and wet deposition. In Sweden, Iverfeldt and Munthe (1993) also report no significant differences between bulk and wet Hg concentrations or fluxes.

Preliminary calculations suggest that the atmospheric flux of Hg varies seasonally, with the highest fluxes occurring during the summer months (Apr. to Sept.). There does appear to be a slight geographic trend, with the annual volume weighted fluxes being lowest in north-central Florida and increasing towards the southern stations (Table 1). Currently, there does not appear to be a sub-geographical trend within south Florida. Tamiami Trail (TT) is presently the station with the highest annual flux and concentration. These values are accentuated by one month with normal rainfall concentrations and an abnormally high monthly rainfall volume (40 cm). If we substitute a more normal rainfall amount for this month (20 cm), the annual volume weighted flux and concentration would be 20 $\mu g/m^2/yr$ and 21 ng/L, respectively.

TABLE I
Annual Volume Weighted Fluxes ($\mu g/m^2/yr$) and Concentrations (ng/L)

Site	n	Flux (Range) Bulk	Wet	Summer (%)	Winter (%)	Concentration (Range) Bulk	Wet
LB	30	15(11-20)	15(12-20)	64	36	13(9-15)	12(9-15)
FM	24	23(21-25)	24(22-27)	77	23	17(15-20)	18(16-20)
FS	24	19(18-25)	21(20-30)	79	21	15(13-19)	16(14-23)
TT	16	28(25-29)	30(27-31)	86	14	23(19-25)	24(23-26)
EG	16	20(19-23)	21(20-23)	86	14	16(15-17)	18(16-18)

3.4 AEROSOL MERCURY

The average concentrations of particulate mercury at all five sites are given in Table II. These particulate concentrations are lower than previously reported values (Fitzgerald *et al.*, 1991; Iverfeldt, 1991; Lamborg *et al.*, this volume). One possible explanation for these differences is the difference in air mass sources. Florida is a peninsula which receives marine air, while the temperate and subpolar regions are impacted by continental air masses.

TABLE II
Aerosol Mercury (pg/m^3)

Site	n	Mean$\pm$1SD (Range)
LB	40	4.6$\pm$2.0 (1.8-9.1)
FM	32	7.9$\pm$3.5 (4-18)
FS	32	4.5$\pm$1.9 (2.4-12)
TT	32	5.0$\pm$1.9 (2.4-10.7)
EG	32	5.2$\pm$3.8 (1.5-12.8)

Event rain samples collected in northern temperate and sub-polar climates clearly show the affect of particle scavenging of aerosol Hg by rain (Bloom and Watras, 1989; Glass *et al.*, this volume; Iverfeldt, 1991; Lamborg *et al.*, this volume). The data for the monthly wintertime bulk concentrations vs. monthly rainfall volume, when only 14-36% of the annual deposition occurs, show some evidence of particle scavenging (Figure 2a). This graph is similar to the monthly integrated bulk concentration vs. monthly rainfall plot in the nordic regions (Munthe and Iverfeldt, pers. comm.), where particle scavenging is primarily responsible for the Hg found in precipitation year-round (Iverfeldt, 1991). In contrast to this, summertime plots of monthly concentration vs. monthly rainfall do not show evidence of aerosol scavenging (Figure 2b). The relationship between concentration and volume during the summertime is intriguing. High amounts of rainfall coincide with high Hg concentrations suggesting a large and "unlimited" source term for Hg rather than particle washout. For aerosol particles to represent the primary summertime source term for Hg in south Florida rain, a

mechanism which can replace all of the aerosol Hg in the troposphere over south Florida within a few hours would be required. Other elements, such as Al, Cu, Zn, As, and Pb, that do show a large difference between bulk and wet deposition also exhibit classical washout behavior, but correlations between Hg and these other elements are not significant (Landing *et. al.*, this volume).

Another way to evaluate the importance of particulate Hg as a dominant source term is to calculate washout ratios. Washout ratios for the winter (October-March) and summer (April-September) have been calculated for all sites using the equation $w=(Hg_{ppt}(ng/L)*1.2m^3/L)/Hg_{part}\ (ng/m^3)$(Arimoto *et al.*, 1985). Low values between 200 to 2000 are indicative of particle washout, while values above 2000 imply that processes other than aerosol washout contribute to the Hg found in precipitation (Table III).

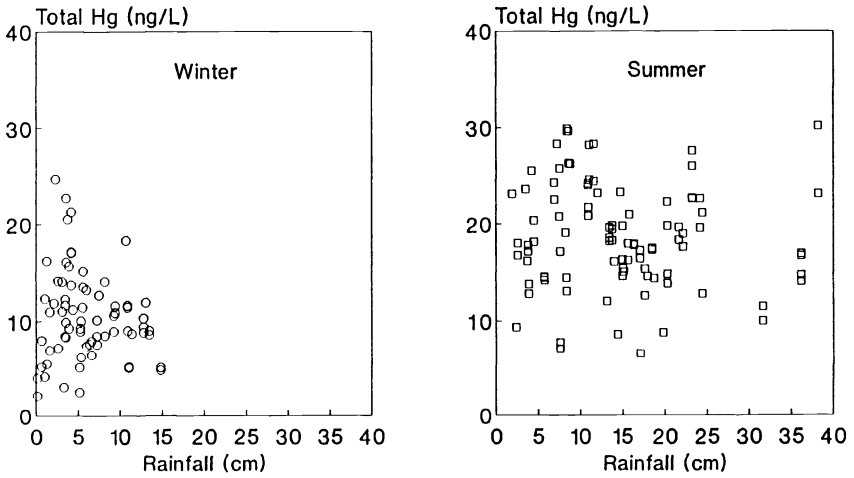

Fig.2. (a) Wintertime integrated Hg concentrations vs. monthly rainfall for 5 sites: October-April; 1992-1994; (b) Summertime integrated Hg concentrations vs. monthly rainfall for 5 sites: May-September; 1992 and 1993.

TABLE III

Aerosol Washout Ratios-Monthly Integrated Samples (Mean±1SD)

Station	Winter	Summer
LB	2350±1100	4300±2250
FM	2000±1050	3000±1200
FS	2500±1110	4200±1800
TT	2900±1450	5900±1900
EG	2400±1200	3900±2500

Wintertime washout ratios range from 2000 to 3000 and suggest that aerosol washout partially contributes to the wintertime deposition, (14-36% of the annual Hg deposition).

Summertime ratios range from 3000 to 6000 and suggest that processes other than particle washout govern summertime deposition, (64-86% of the annual Hg deposition). Washout ratios calculated for event rain samples collected during the summertime range from 5000 to 20000 (Table IV). Despite the large uncertainties, the ratios are 2 to 40 times greater than previously reported values for rainfall Hg (Lamborg *et al.*, this volume; Fitzgerald *et al.*, 1991).

Table IV
Aerosol Washout Ratios-Event Rain Collection

Station	Julian Date	Event Ratio (mean±1SD)
FS (1993)	193	4600±650
	194	4950±700
	195	3700±500
EG (1994)	171	20000±3000
	171	17000±2300
	235	17040±1700
	236	9945±1000

3.5 Monomethyl Mercury in Rain

Measurements of MMHg in summertime event rain samples from south Florida (EG and FS), performed by Frontier Geosciences (Horvat *et al.*, 1993), range from 0.013 to 0.022 ng/L (n=4). Measurements of MMHg from summertime monthly integrated bulk deposition samples (EG, AT, CK) range from 0.020 to <0.005 ng/L (n=7). These measurements are near the analytical detection limit and are an order of magnitude lower than results reported for more temperate environments (Bloom and Watras, 1989; Fitzgerald *et al.*, 1991; Glass *et al.*, this volume). These preliminary values suggest that direct deposition of MMHg may not be a significant source for MMHg in south Florida's aquatic environments.

4. Conclusions

Based on the data we have accumulated thus far, we can make some preliminary conclusions regarding the atmospheric deposition of Hg to Florida and it's possible source terms:

1. The deposition in north-central Florida is 29% lower than in south Florida.
2. There does not appear to be a significant decrease in rainfall Hg deposition from east to west across south Florida.
3. There is generally good agreement between bulk and wet Hg collection, suggesting that dry deposition does not contribute significantly to the total Hg deposition.
4. The unusual concentration to volume relationship and high scavenging ratios suggest that aerosol washout does not appear to be a dominant source term for Hg in south Florida during the summertime.

5. Preliminary measurements of very low MMHg concentrations suggest that direct MMHg deposition may not be significant in south Florida.
6. The regional and seasonal trends in Hg deposition do not appear to be correlated with atmospheric total gaseous Hg concentrations. Future work needs to address the relationship between rainfall Hg deposition and reactive gaseous Hg species in the atmosphere (Gill *et al.*, this volume).

Acknowledgements

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PART V

MERCURY DYNAMICS IN WATERSHEDS

WET DEPOSITION OF METHYL MERCURY IN NORTHWESTERN ONTARIO COMPARED TO OTHER GEOGRAPHIC LOCATIONS[4]

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Abstract. Concentrations of methyl mercury (MeHg) and total mercury (THg) in precipitation were measured at the Experimental Lakes Area (ELA), a remote field station in northwestern Ontario. We found that precipitation was a source of both MeHg and THg to boreal ecosystems, but at lower rates than in industrialized regions of North America and Scandinavia. MeHg concentrations in precipitation ranged from 0.010 to 0.179 ng L^{-1} and were highest when events originated west of the ELA. THg concentrations in precipitation ranged from 0.95 to 9.31 ng L^{-1} and were highest when the events came from the southeast. There was no relationship between THg and MeHg over time in precipitation. Inputs of both MeHg and THg to ecosystems were highest during summer months.

1. Introduction

Contemporary studies show that fish in many lakes have commercially unacceptable concentrations of MeHg in their tissues (> 0.5-1.0 ug g^{-1}). Although in many instances these high concentrations can be attributed to methylation of mercury from industrial discharges (e.g., Rudd *et al.*, 1983) or other anthropogenic activities (e.g., reservoir creation; Hecky *et al.*, 1991), in many remote lakes there is no obvious environmental disturbance. At these remote sites, production of MeHg in sediments and water (Rudd *et al.*, 1983; Parks *et al.*, 1989; Hecky *et al.*, 1991) was thought to be the predominant source of MeHg to fish. Recently, St.Louis *et al.*, (1994a) demonstrated that wetlands at the remote, near pristine, Experimental Lakes Area (ELA) in northwestern Ontario were also important sources of MeHg. This finding explains the high correlation between MeHg in fish and the percent wetlands in the catchment of remote lakes (e.g., Driscoll *et al.*, 1994).

Atmospheric deposition is another possible source of MeHg to lakes and watersheds. Until recently, most studies have concentrated only on estimating atmospheric inputs of THg to ecosystems. Long-term changes in THg deposition are reflected in some cores from lake sediments and peatlands, which clearly show an increase in atmospheric deposition of THg following the Industrial Revolution by about two to five fold (Anonymous, 1994), depending on proximity to industrial areas. Current measurements of THg in modern precipitation also show regional differences (see Discussion).

Very few studies have measured MeHg in atmospheric deposition. However, recent results indicate that precipitation can be an important MeHg input to ecosystems. A study of an upland watershed at the ELA showed that precipitation inputs of MeHg

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were significant when compared to outputs from the watershed (St.Louis *et al.*, 1994a). In southern Sweden, Hultberg *et al.* (1994) concluded that high MeHg in atmospheric deposition was the most probable explanation for high levels of MeHg in fish in drainage lakes. In contrast, in Wisconsin, the lower levels of atmospheric deposition of MeHg were insufficient to account for the amounts of MeHg in biota of seepage lakes (Fitzgerald *et al.*, 1991). Further measurements are needed because MeHg is the most toxic form of mercury and it is not known whether MeHg can be predicted from THg measured in precipitation.

In this study, we show that precipitation is a source of MeHg to ecosystems in a remote area of northwestern Ontario. Concentrations and wet deposition of MeHg were lower than at any other terrestrial sampling site. We also show that MeHg concentrations in precipitation were not related to THg concentrations. Examination of the direction from which the precipitation events originated indicated different sources for MeHg and THg.

2. Materials and Methods

We collected wet deposition samples at the Experimental Lakes Area (ELA) meteorological site (Atmospheric Environment Service designation: Rawson Lake Station), northwestern Ontario. The site is located on a bedrock knoll 500 m northwest of the ELA field camp, 366 m west of Rawson Lake (ELA Lake 239), and at an elevation 43 m above the lake surface. An area of 65 m by 100 m was cleared to accommodate atmospheric sampling equipment. The clearing is surrounded by mixed boreal forest of predominately 4-5 m tall jack pine (*Pinus banksiana*) regenerated after a forest fire in 1980.

Wet deposition samples were collected in wide-mouthed Teflon containers (11 cm diameter, and either 5 cm in height for rain and 15 cm in height for snow) that were first washed in hot HNO_3, filled with a 1% HCl solution, and then stored in two new Ziploc bags. To avoid contamination of the samples, the containers were transported to the field in clean coolers that were placed inside two plastic bags. At the meteorological site, the stringent clean-hands, dirty-hands protocol was used (St.Louis *et al.*, 1994a). Just following the beginning of a precipitation event (usually within 15 minutes), the 1% HCl solution in four containers was drained, and the containers were placed on four acid-washed plexiglass trays secured to wooden posts 1.5 m above the ground. The post were situated in a square approximately 0.6 m apart. Following a precipitation event, samples were transferred to 125 ml Teflon sample bottles that were cleaned as described above. Duplicate MeHg and THg samples were taken when sufficient deposition volume was available. Samples used for THg analyses were acidified with concentrated trace metal grade HCl equal to 2% of the sample volume, while samples used for MeHg analyses were immediately frozen.

On two occasions (16 February 1993 and 24 January 1994) we collected bulk deposition samples by scooping up the upper layer of snow from the centre of the frozen surface of Rawson Lake with the clean Teflon snow collection containers. Snow was allowed to melt in the containers, and then transferred to 125 ml Teflon sample bottles and preserved as above. On a third occasion, we collected lake surface snow (21 March 1994) just following a precipitation event. All previously accumulated snow on the lake surface

had recently melted, and as a result this sample was comparable only to wet deposition.

Unfiltered MeHg samples were analysed by Flett Research Ltd., Winnipeg, Man., and Frontier Geosciences and Brooks Rand, Ltd, both of Seattle, WA, using Bloom's (1989) procedure. The detection limit of this method was 0.01-0.02 ng L^{-1} at a blank level of 0.05-0.1 ng L^{-1}. Flett Research Ltd analysed unfiltered samples for THg using the technique of Bloom and Crecelius (1983). The detection limit of this method is 0.2-0.3 ng L^{-1} at a blank level of 0.3-0.4 ng L^{-1}. The labs analysing all of these samples have recently successfully participated in an international inter-comparison exercise (Bloom and Horvat, this issue).

Input of MeHg and THg (ng ha^{-1}) during each precipitation event was calculated by multiplying the concentration of mercury by the amount of precipitation that fell. Deposition rate was continuously monitored at the ELA meteorological site using an Atmospheric Environmental Service type B standard rain gauge, and snow fall was measured with a Canadian nipher shielded snow gauge.

Annual inputs of MeHg and THg for 1992 and 1993 (years of this study) were estimated by multiplying the volume-weighted mean concentration of mercury in precipitation by the amount of precipitation that fell in the given year. Volume-weighted means of MeHg and THg were calculated for wet deposition by summing inputs (ng ha^{-1}) of all events and dividing by the total deposition volume (L ha^{-1}). The two bulk deposition snow samples collected from the lake surface were omitted from these analyses.

The concentration of THg was compared with the concentration of MeHg measured at a given precipitation event to determine whether THg concentrations were good predictors of MeHg concentrations. We also tested whether concentrations of either THg or MeHg were related to deposition volume. Here we predicted that if there was an initial washout of mercury from the atmosphere, concentrations of mercury would be highest in samples collected during small rain events. Bulk deposition snow samples were not included in these analyses. We used a Pearson's product moment correlation coefficient for the correlation analyses, with *P*-values calculated using randomization tests (1000 iterations; Edgington, 1987).

To determine if the concentration of mercury measured was related to the source of the precipitation event, concentrations of MeHg and THg in precipitation were plotted against the average direction of the five day air parcel back trajectories for storm events. When trajectories made large directional changes during the five day period, only the direction of the final two day approach to the ELA was used in the plot. The five day trajectories for precipitation events that contained high concentrations of MeHg and THg were then superimposed on a map of SO_2 emissions (adapted from Barrie *et al.*, 1992) to determine if air parcels passed over major industrialized zones. Back trajectories beginning at a height of approximately 750 meters (925 hPa) were calculated at the Atmospheric Environment Service using observations of three dimensional wind fields.

3. Results

The volume-weighted mean concentration of MeHg in precipitation was 0.052 ng L^{-1}, ranging between 0.010 ng L^{-1} and 0.179 ng L^{-1} in different events (Table I). Concentrations of MeHg in the two bulk snow samples collected from the lake surface

TABLE I

Concentrations of MeHg and THg, and % of THg that was MeHg, in precipitation sampled at the ELA, northwestern Ontario.

Date of Sample Collection	Precipitation Type	Deposition During Collection Period (mm)	Mean MeHg (ng L^{-1})	Mean THg (ng L^{-1})	% MeHg
7 August 1992	Rain	14.4	0.024	3.65	0.64
22-23 August 1992	Rain	14.9	0.023[1]	7.53	0.31
23 August 1992	Rain	14.8	0.012[1]	5.63[1]	0.20
7 September 1992	Rain	35.0	0.010	1.68	0.57
19-20 October 1992	Snow	10.0	0.179[1]	4.60[1]	3.89
10 November 1992	Snow	2.6	0.028[1]	2.56[1]	1.09
16 February 1993	Lake surface snow		0.008	0.95	0.85
27-28 April 1993	Rain/Snow	21.6	0.023[1]	2.78	0.83
27 May 1993	Rain	9.9	0.037	5.14	0.71
13 June 1993	Rain	18.9	0.026	3.31	0.79
16 June 1993	Rain	11.1	0.074	9.31	0.80
25 July 1993	Rain	3.6	-	5.82[1]	-
26 July 1993	Rain	22.7	0.037[1]	9.78[1]	0.38
8-9 August 1993	Rain	50.4	0.083	2.23	3.71
25-26 August 1993	Rain	24.0	0.152[1]	-	-
29-30 August 1993	Rain	27.3	0.035	2.20	1.60
27-29 October 1993	Rain/Snow	12.2	0.025[1]	3.49	0.70
24 January 1994	Lake surface snow		0.032	1.21	2.60
21 March 1994	Lake surface snow	4.2	0.033	2.71	1.22

[1]Insufficient sample for duplicate analyses.

were low (0.008 and 0.032 ng L^{-1}).

The volume-weighted mean concentration of THg in precipitation was 4.04 ng L^{-1}, ranging between 0.95 ng L^{-1} and 9.31 ng L^{-1} in different events (Table I). One sample taken on 26 August 1993 was omitted from analyses because we believed it was contaminated (43.44 ng L^{-1}). THg concentrations in the two bulk lake surface snow samples were low (0.95 and 1.21 ng L^{-1}).

The proportion of THg in precipitation that was MeHg was not constant, ranging between 0.2% and 3.89% (average calculated from volume-weighted means = 1.28%) (Table I). Over time, concentrations of MeHg were not significantly correlated with concentrations of THg in wet deposition ($r = 0.19$, $P = 0.21$; Figure 1).

The majority of precipitation at the ELA falls as rain, not snow (21 year average of 73%; K. Beaty, pers. comm.), resulting in the bulk of mercury being deposited to watersheds during the ice-free season. This seasonal deposition pattern was further enhanced because the highest concentrations of MeHg and THg were recorded in the summer and fall (Table 1). Input of MeHg during the precipitation

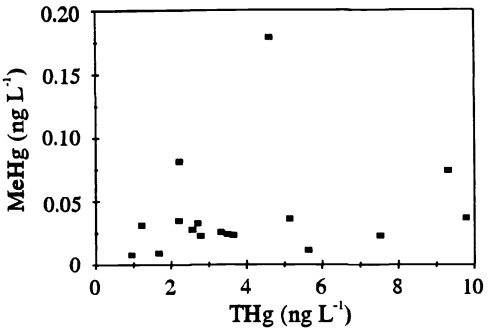

Fig. 1. Relationship between concentrations of THg and concentrations of MeHg in precipitation.

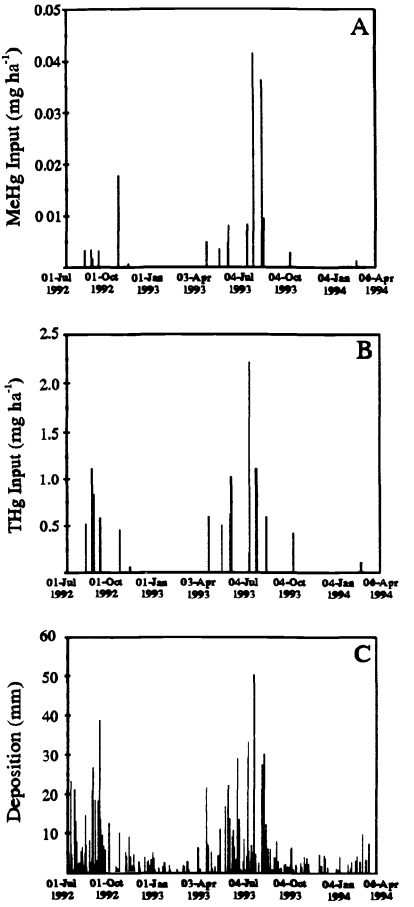

Fig. 2. The first two graphs show calculated inputs (mg ha ^{1}) of MeHg (A) and THg (B) during each sampled event. The bottom graph (C) shows amount of deposition of all precipitation events during the period that we sampled.

events sampled ranged between 0.0007 and 0.04 mg ha^{-1} (Figure 2). Inputs of THg ranged between 0.07 and 2.2 mg ha^{-1} (Figure 2).

Total precipitation at the ELA in 1992 and 1993 was 835.8 mm and 619.6 mm respectively (21 year average ($\pm$S.D.) of 677.3$\pm$123.2 mm; K. Beaty, pers. comm.). Wet deposition of MeHg in these two years was estimated to be 0.43 and 0.32 mg ha^{-1}. Wet deposition of THg was estimated to be 34 and 25 mg ha^{-1}.

There was no significant negative relationship between the amount of precipitation that fell during a given event and MeHg concentration (r = 0.07, P = 0.32; Figure 3) or THg concentration (r = -0.28, P = 0.16; Figure 3) as would be expected if there was an initial "scrubbing" of mercury from the atmosphere.

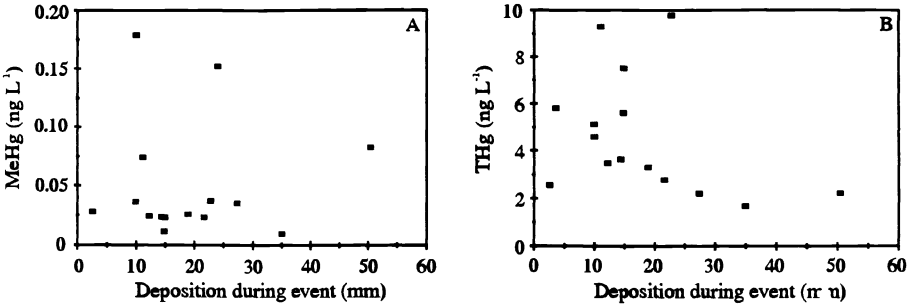

Fig. 3. Relationship between concentrations of MeHg (A) and THg (B) and the amount of precipitation that fell during the sampled event.

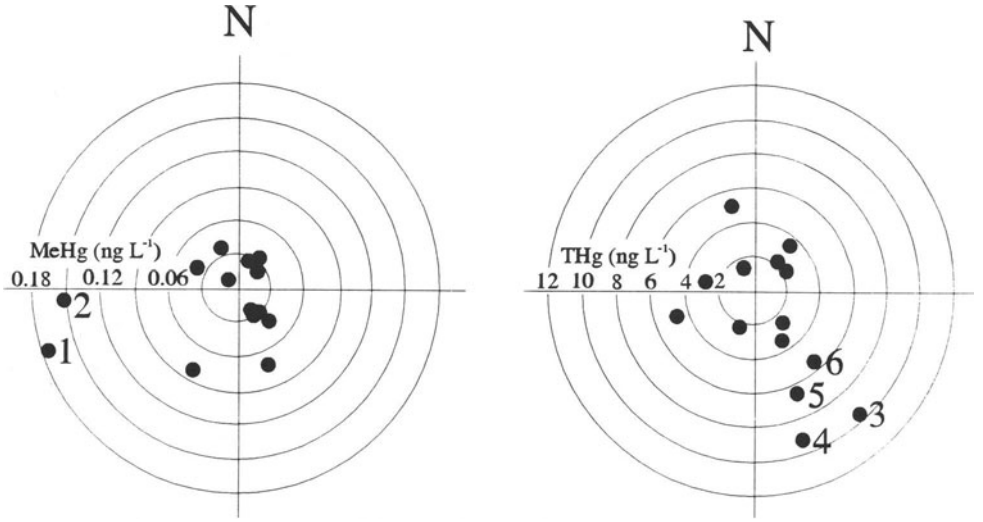

Fig. 4. Concentrations of MeHg and THg in precipitation plotted against the average direction of the five day air parcel back trajectory (750 meters (925 hPa) above the ground) for the event. When trajectories made large directional changes during the five day period, only the direction of the final two day approach to the ELA was used in the plot. Numbered concentrations refer to the five day trajectories plotted in Figure 5.

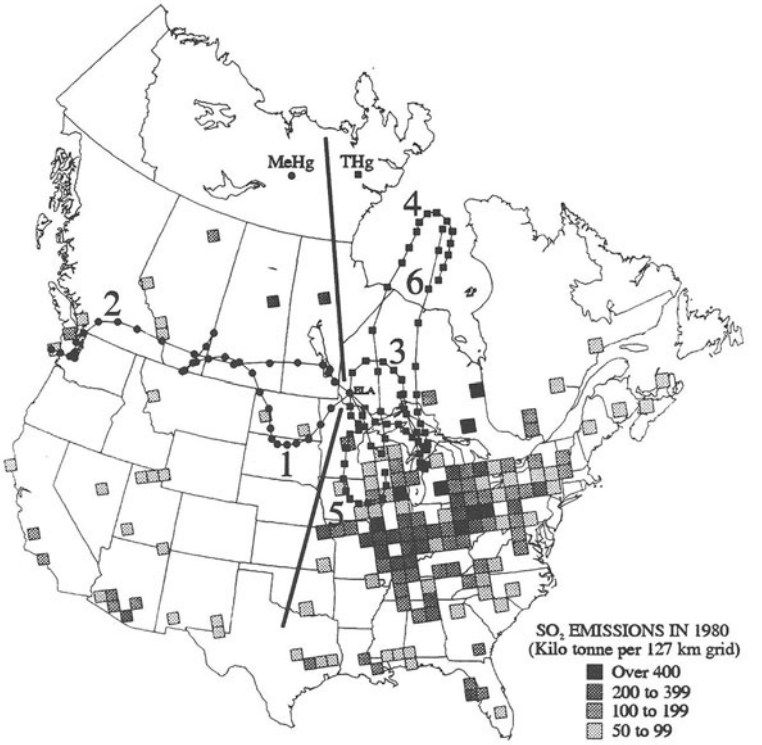

Fig. 5. Five day air parcel trajectories for precipitation events that contained high concentrations of MeHg and THg, superimposed on a map of SO_2 emissions (from Barrie *et al.*, 1992). Trajectory numbers refer to concentrations plotted in Figure 4. The two dark lines visually separate MeHg and THg trajectories.

MeHg concentrations in rain were highest in events that tracked from the west (Figures 4, 5). THg concentrations, however, were highest in precipitation events when the final air parcel approach to the ELA was over industrialized areas to the southeast (Figures 4, 5).

4. Discussion

While concentrations of both MeHg and THg in precipitation at the ELA varied, concentrations were always found above detection limit at this remote location. Only extremely remote locations, such as the equatorial Pacific Ocean and Antarctica, had wet deposition with lower mercury concentrations than at the ELA (Table II). All other terrestrial monitoring sites had higher concentrations and annual inputs (Table II). For example, in southern Scandinavia near areas of heavy industrialization, inputs of MeHg

TABLE II

Mean concentrations of methyl mercury and total mercury in wet deposition and annual inputs of mercury at the Experimental Lakes Area, and at sites in Scandinavia, North America, equatorial Pacific Ocean, and Antarctica Values in parentheses are range of concentrations (when available) taken from the cited references The table is arranged from locations receiving the highest mercury inputs to locations receiving the lowest inputs

Location	Methyl Mercury		Total Mercury		Reference
	Concentration (ng L^{-1})	Input (mg ha^{-1} yr^{-1})	Concentration (ng L^{-1})	Input (mg ha^{-1} yr^{-1})	
Southern Norway			20[1]	350	Iverfeldt, 1991
Southern Sweden	0 05 0 59[2]	1 9-4 1[2]	11 90[2]	100 350[2]	Iverfeldt, 1991, Johanssen *et al* 1991, Lee and Iverfeldt, 1991, Hultberg *et al* 1994, Munthe and Iverfeldt, 1994
Western Sweden		2 9	35[1]	97 270[2]	Iverfeldt, 1991, Munthe and Iverfeldt, 1994, Iverfeldt *et al* , 1994
Denmark			40[1]	170	Iverfeldt, 1991
Dorset			10 2	102	Mierle, 1990
Eastern Sweden		2 0	20[1]	100	Iverfeldt, 1991, Munthe and Iverfeldt, 1994
Central Norway			10[1]	70	Iverfeldt, 1991
Northern Norway			10[1]	50	Iverfeldt, 1991
Southern Finland	(<0 005 0 36)	1 0	5 8	38	M Verta, pers comm
Washington State	0 15 (0 015 0 35)		(2 15)		Bloom and Watras, 1989
Little Rock Lake, Wisconsin	Rain 0 156 (0 059 0 224) Snow 0 058 (0 0 0 08)	Rain and Snow 0 88	Rain 10 5 (3 2 15 2) Snow 6	Rain 45 Snow 47 3	Fitzgerald *et al* 1991
Northern Sweden		0 7			Munthe and Iverfeldt, 1994
ELA	0 052 (0 01 0 179)	0 35 (0 3 0 4)	4 04 (0 95 9 31)	30 (25 34)	This study
Equatorial Pacific Ocean	<0 01		2 9		Mason *et al* , 1992
Antarctica			Snow 0 6		Vandal *et al* 1992

[1]Approximate concentrations taken from Fig 7 in Iverfeldt 1991
[2]Range of mean values taken from the studies cited

and THg to ecosystems were up to ten times higher than at the ELA (Table II).

At the ELA, it appears that there were specific sources of MeHg and THg to precipitation inputs. Plots of back trajectories of storm events suggest that MeHg sources in 1992 and 1993 were predominately west of the ELA, whereas sources of THg were derived from industrialized regions to the southeast. Bloom and Watras (1989) and Fitzgerald *et al.* (1991) also found higher concentrations of MeHg in precipitation in the west (Washington State) than in the southeast (Wisconsin). Concentrations of THg in precipitation were similar, however, at both locations. Because high concentrations of MeHg in precipitation at the ELA originated from different locations than events with high concentrations of THg, it is not surprising that there was no correlation between the two. More research is required to identify sources of both MeHg and THg to the atmosphere.

At the ELA, peak inputs of MeHg and THg occurred during the ice-free season. Although concentrations of mercury in precipitation appear to be related primarily to the direction of storm trajectories (which would include seasonal differences), other factors such as washout of suspended dust during summer precipitation events might result in the high levels of mercury sometimes seen in rain. This pattern is opposite that found in areas where high levels of mercury deposition are thought to result from coal combustion and industrial sources. In Finland, for example, concentrations of MeHg in precipitation were usually much higher in winter snow (0.14 - 0.36 ng L^{-1}) than in summer rain (<0.005-0.09 ng L^{-1}) (M. Verta; pers. comm.). Brosset (1982) also found seasonal variation of total airborne mercury, with maximums in January to March and September to October, that correlated with amounts of soot particles in deposition and seemed partially dependent on wind direction (anthropogenic origin).

Interestingly, in southern Sweden where the amount of MeHg deposition is up to ten times higher than at the ELA, the fate of the MeHg in uplands is similar, with a high percentage of the MeHg being retained or demethylated there (Hultberg and Iverfeldt, 1992; St.Louis *et al.*, 1994a; Rudd, this issue). However, the magnitude of inputs of MeHg to lakes from direct precipitation onto the lake surface and from upland runoff is much greater in Sweden than at the ELA. Unlike the ELA, Hultberg *et al.* (1994) have concluded that atmospheric inputs are the most important sources of MeHg to lakes. At the ELA, where concentrations of MeHg in precipitation were low, runoff from catchments containing wetlands was a more important source of MeHg to lakes than precipitation (St.Louis *et al.*, 1994a; St.Louis *et al.*, 1994b).

More measurements of MeHg in precipitation are needed to evaluate the role of deposition as a source of MeHg to ecosystems in different regions of the world. However, measuring MeHg in precipitation does not address all aspects of atmospheric deposition of MeHg. We need to know the sources of MeHg in deposition. Also, to fully understand the importance of atmospheric inputs of MeHg to ecosystems, future measurements should include contributions from dry deposition, throughfall, and litterfall, which may also be important sources of MeHg to ecosystems (Hultberg *et al.*, 1994).

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CYCLING OF METHYL MERCURY AND MERCURY - RESPONSES IN THE FOREST ROOF CATCHMENT TO THREE YEARS OF DECREASED ATMOSPHERIC DEPOSITION.

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Abstract. Studies of the biogeochemistry of total mercury (Hg) and methyl mercury (MeHg) in the Lake Gårdsjön watershed have shown that the atmosphere is the most important source of Hg and MeHg in the ecosystem. Soils are accumulating most of the deposited Hg and MeHg, but transport of Hg and MeHg from the forested catchments into the lake ecosystems is enough to explain elevated concentrations of MeHg in fish in more than 10 000 Swedish lakes. An experimental roof was constructed to study effects of decreased atmospheric input on an entire forested catchment. The experiment started in April 1991, and decreases in the output of both MeHg and Hg occurred during 1991, 1992 and 1993. Runoff fluxes from the control catchment during the pre-treatment period were related to the experimental catchment using regression analyses. Since April 1991, after three year experiment, predicted compared to measured fluxes showed that Hg output decreased by 32% and MeHg by 28%. The decrease in Hg was most obvious during high water flows in winter/spring while MeHg decreased during all seasons of the year. The decreased input of Hg and MeHg to the Forest Roof Catchment is the most probable explanation to the rapid decrease in output of Hg and MeHg by runoff from the catchment basin.

1. Introduction

Wet and dry deposition of sulphur and nitrogen is a large scale and severe environmental problem in both Europe and North America (Hultberg and Likens, 1992). Hg and MeHg in atmospheric deposition have during recent years, been linked to a large scale environmental problem, the high MeHg content in fish in remote forested lakes.

Atmospheric deposition and biogeochemical cycling of Hg and MeHg in forested catchments has been studied in Lake Gårdsjön watershed for several years (Lee and Hultberg, 1990; Lee and Iverfeldt, 1991; Iverfeldt, 1991; Hultberg *et al.*, 1995; Lee *et al.*, 1995a). 95% of the wet plus dry deposition of Hg in throughfall and Hg in litterfall was retained in organic soil horizons in the catchments (Driscoll *et al.*, 1994). Deposition of MeHg was about 2% of the total Hg deposition to the catchments and 75% of the total MeHg input was retained in the catchment soils. The amount of MeHg retained in the soil corresponded to the input by litterfall, and the amount lost by runoff corresponded to the input by throughfall in the F1 catchment in Gårdsjön (Hultberg *et al.*, 1995). As a result of the higher retention of Hg compared to MeHg in the soil, runoff had a higher proportion (4 - 7%) of MeHg than deposition (2%). Based on measurements of Hg in soil profiles (Lee *et al.*, 1995a) a total pool of 15 to 20 kg/km^2 was found, while the pool of MeHg was only about 0.1 kg/km^2 or 0.5 % to 0.7% of the total pool of Hg (Hultberg *et al.*, 1995).

On the basis of today's input of MeHg by throughfall and litterfall, rough estimates indicate that if this were the only source to the soil pool it would account for about 200 years of input. Based on present day input of Hg by throughfall and litterfall, the pool of

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total Hg in the soil was accumulated during 400 to 500 years. Assuming that the natural Hg deposition was 5 to 10% of today's and that today's deposition had started by 1850, accumulation in the soils may have occurred over a period of 2000 to 3000 years.

The Forest Roof Catchment was designed to test the hypothesis that the Hg stored in the soils is bound strongly owing to low mineralization rates of the organic matter, and that losses by runoff of Hg and MeHg depend on excess atmospheric deposition and catchment characteristics. The roof was intended to decrease the input by throughfall, thereby resulting in a decrease in MeHg and Hg losses by runoff.

2. Material and Methods

The study area is in the vicinity of Lake Gårdsjön on the west coast of Sweden (58°04'N, 12°03'E) (Olsson *et al.*, 1985; Hultberg, 1985). Two catchments were studied; F1 (3.7 ha) was used as a control, and catchment G1 (0.63 ha) was covered with a roof in April, 1991. The experiment was performed to study effects of decreased loading of air pollutants like MeHg, Hg, sulphur, and nitrogen on the biogeochemical turnover and transport of these compounds (Hultberg *et al.*, 1993).

Similarity between the catchments includes mixed coniferous stands dominated by Norway spruce (*Picea abies* (L.) Karst.) and usually a discharge-stream area at the low end with *Sphagnum* spp. vegetation. Similarities in landscape, such as percent forest cover and tree edges result in similar deposition of air pollutants (Olsson *et al.*, 1985; Hultberg, 1985; Hultberg and Grennfelt, 1992). Characteristic features of the roofed catchment are gneiss granodiorite bed-rock and thin podzol soil (average thickness 0.4 m). Small pockets of thicker organic soil/peat occur in the *Sphagnum* dominated valley bottom. Catchment hydrology is characterised by a very high hydraulic conductivity within the upper B horizon determining the water flow pathways. Each catchment was equipped with a water level recorder and V-notch weir for continuous monitoring of the water flow.

Catchment G1, dominated by mature (60 to 110 years old) Norway spruce, was covered with a roof which has an area of 6300 m^2 and was constructed at a height of 2 to 4 m intercepting the throughfall water. The roof consisted of polycarbonate sheets which transmitted 90% of all light with wavelengths greater than 400 mm. About 370 tree trunks penetrated the roof (Hultberg *et al.*, 1993).

For replacement of intercepted throughfall, water was pumped from nearby Lake Gårdsjön and then deionized and dosed with sea water to simulate unpolluted rain typical of this region. For distribution beneath the roof, an irrigation system with some 275 sprinklers having a total capacity of about 3 mm h^{-1} was used. This procedure enabled us to simulate most of the naturally occurring precipitation events. The input of Hg and MeHg with the sprinkling water was insignificant.

Litter falling on the roof was redistributed under the roof. Inputs of Hg and MeHg by litterfall was therefore unchanged compared to pre-treatment conditions.

Precipitation, ground water levels, soil temperatures and discharges were measured continuously at 33 sampling sites inside and outside the covered catchment. The data were logged and transformed automatically by a data base system.

Bulk precipitation and throughfall samples were collected on a monthly basis as integrated samples for the time period. Previous estimates of the Hg load to the forest, as well as to nearby open fields, were also based on monthly precipitation and canopy throughfall samples (Iverfeldt, 1991). In the present investigation, two lines of bulk collectors were operated in catchment F1 during the entire period. The positioning of the collectors was in accordance with the collection strategy previously applied (i.e. fixed distances between the

collectors). MeHg deposition was determined from composite throughfall water samples from the respective lines. In addition, one open field site with three separate bulk collectors was used in the present study. A detailed description of the bulk collectors has been presented elsewhere (Iverfeldt, 1991). Hg samples were preserved by the addition of 2.5 mL HCl (Merck, suprapur) to the collection bottle (0.5 L) before the start of the sampling period. The collection of litterfall for MeHg and Hg analysis was performed using previously reported methods (Iverfeldt, 1991). In brief, nets were located in parallel with the monthly throughfall collectors. Samples were frozen immediately after collection and were stored frozen in triple plastic bags until analysed.

Surface runoff water samples were collected at the catchment weir in teflon bottles at a frequency of one to two samples per month. MeHg and Hg levels were always determined in each sample. Concentrations of MeHg in water samples and litterfall were determined by GC-CVAFS with aqueous phase ethylation using extraction/distillation as a pre-separation step (Bloom, 1989; Horvat *et al.*, 1988).

Monthly fluxes of Hg and MeHg were calculated using daily water flows and linear interpolation of the chemical analyses between sampling occasions. Regression analyses of the monthly Hg and MeHg fluxes from the control catchment and the roof catchment were performed for the pre-treatment period. These regressions were used to calculate predicted fluxes of Hg and MeHg, respectively, using the measured post-treatment fluxes from the control catchment. The predicted fluxes were compared to the measurements in the experimental catchment, and the differences were used to quantify the effects of the decreased input on catchment output from the roof catchment.

3. Results and Discussion

3.1 The Hg and MeHg concentrations in runoff

The monitoring of Hg and MeHg concentrations in runoff from catchment F1 represents one of the longest records of these chemical species. Analyses of MeHg started in the autumn of 1986, and except for a period during 1988/89, continues through June 1994 (Fig. 1). Hg analyses started in 1987 and still continues. In the roofed catchment (G1) sampling started in 1989 and continues through June 1994. Monitoring in both catchments is planned to continue over the next few years to evaluate the effects of the decreased atmospheric input to the roof atchment.

Hg concentrations typically ranged between 2 and 6 ng/L in both catchments. The concentrations in F1 increased from 1987 to the end of 1991, and a significant decrease occurred in 1992 and 1993. The concentrations were lowest in the cold winter of 1993/94. The Hg concentrations have increased during the spring 1994 but are still low compared to earlier years. The Hg concentrations in the roof catchment G1 have shown similar changes (Fig. 2), and a decline occurred after the start of the experiment in April, 1991.

The MeHg concentrations are generally less than 1 ng/L, and typically range between 0.1 and 0.4 ng/L, or about 6% of the Hg concentrations in both catchments. MeHg showed a seasonal variation in concentration in both catchments (Fig. 3). In the spring and summer the concentrations regularly exceeded 0.2 ng/L while most winters had a period with concentrations less than 0.1 ng/L. Decreased concentrations of MeHg were recorded in both catchments in 1993. During 5 months of the cold winter of 1993/94 low concentrations were observed during the whole period. The control catchment F1 had a sharp increase in MeHg during May whereas the roof catchment still remained at low concentrations.

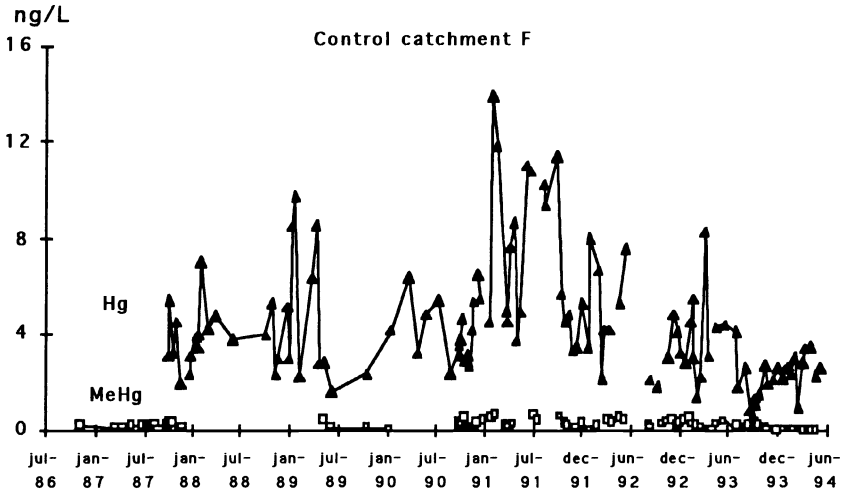

Fig. 1. Hg and MeHg concentrations in runoff from control catchment F1 during the years 1986 to 1994.

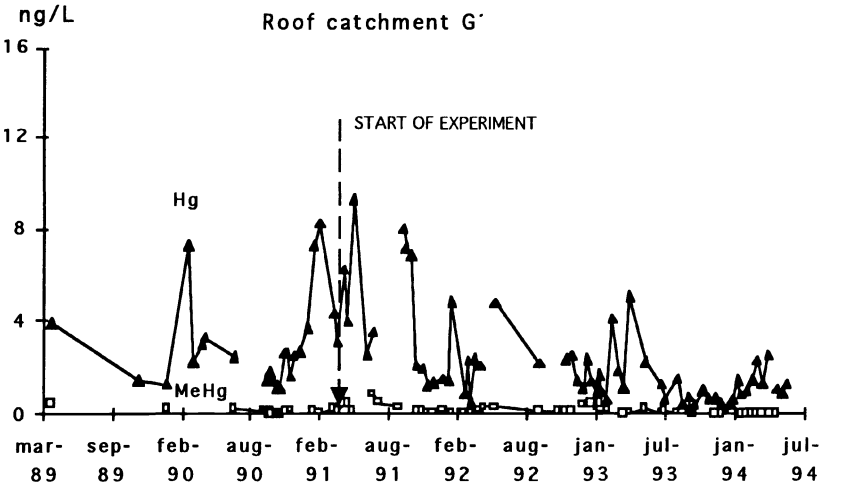

Fig. 2. Hg and MeHg concentrations in runoff from the roof catchment G1 during the years 1989 to 1994.

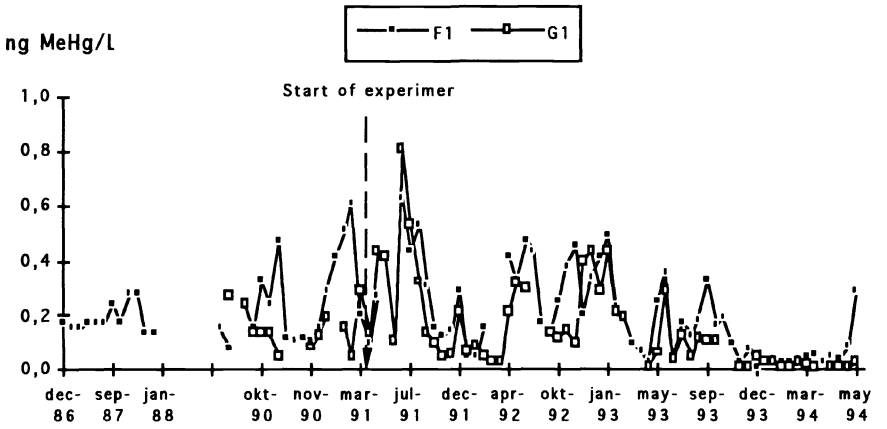

Fig. 3. MeHg concentrations in runoff from the roof catchment G1 and the control catchment F1 during the years 1986 to 1994.

The increase in Hg from 1987 to 1990/91 and the following decrease during 1992 and 1993 may be related to temporal variations in climatic conditions as well as changing inputs to the catchments. 1987 was an unusually wet year and 1989, 1990 and 1991 were drier. Figure 4 shows that 1990/91 had the lowest yearly water flow of the seven years 1987/88 to 1993/94. Water flows increased during 1992 and 1993: This corresponds to decreasing concentrations in Hg as well as MeHg. The winter of 1993/94 was the first cold winter in 6 years, with deep frozen soils during several months, resulting in deeper water flows within the catchments. The deep soil water had low concentrations of Hg (Lee *et al.*, 1995a), resulting in low concentrations in the runoff. The increase in MeHg in runoff from the control catchment in May 1994 resulted from water transported through upper soil horizons during high flow which occured after a drought in March 1994 (Fig. 4).

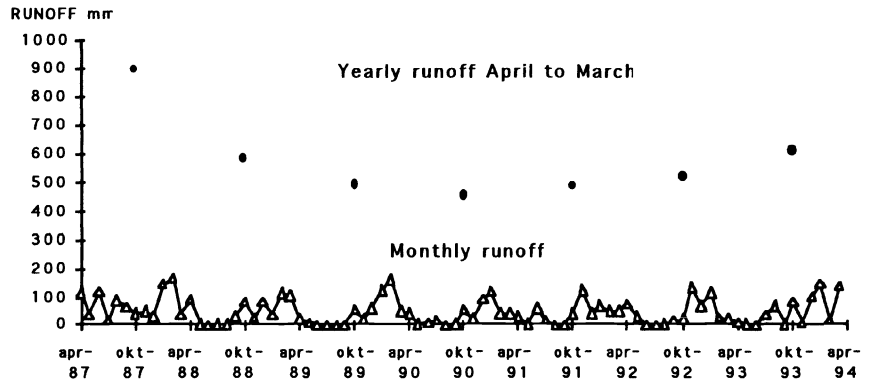

Figure 4. Yearly (April to March) and monthly water fluxes in mm by runoff from the control catchment F1.

3.2 Input/output fluxes in precipitation, throughfall, litterfall and runoff

Input/output fluxes of Hg for the control catchment F1 in the Gårdsjön watershed (Iverfeldt and Johansson 1988; Iverfeldt, 1991; Driscoll *et al.*, 1994) and for MeHg (Lee and Hultberg, 1990; Lee *et al.*, 1995a; Hultberg *et al.*, 1995) have been presented earlier. Yearly fluxes for April to March recalculated from earlier presented data as well as input /output fluxes from 1992/93 and 1993/94 are summarised in Table I together with fluxes from the roof catchment G1.

Hg input by throughfall to the catchments was about 40 - 70% higher than open field precipitation, and input by litterfall was 85 - 100% higher than open field deposition . The total deposition to a forested catchment (throughfall plus litterfall) was almost three times higher than open field deposition. In the control catchment Hg output by runoff was only 6% of the total input in 1991/92 and 3% in 1993/94. When compared to input by throughfall, output was 6% and 17% during the two years. Hg output from the roof catchment G1 was about 60% of the output from F1 before start of the experiment in April 1991 but decreased to about 20% during 1993/94, three years after start of the experiment.

TABLE I.

Yearly input /output fluxes in g/km^2 during April to March of Hg and MeHg in the control and roof catchments in the Gårdsjön watershed in Southwest Sweden

	g/km^2						Runoff		Hg		MeHg		%MeHg	
Year	Open field		Throughfall		Litterfall									
	Hg	MeHg	Hg	MeHg	Hg	MeHg			F1	G1	F1	G1	F1	G1
90/91									2.6	1.5	0.16	0.07	6	5
91/92	13.5	0.43	15.3	0.16	25	0.6			2.9	1.0	0.12	0.07	4	7
92/93	9.7	0.37	16.5	0.19					2.0	1.1	0.18	0.09	9	8
93/94	10.4	0.21	16.3	0.25	21*	0.5*			1.3	0.3	0.04	0.015	3	4

* 6 month data multiplied by 2 (data from Munthe *et al.*, 1995)

Input of MeHg by throughfall was (unlike Hg) lower than input to open field, with the exception of 1993/94, when inputs by throughfall and open field were similar. Input of MeHg to the forested catchments by litterfall was generally much higher (200 - 375%) compared to input by throughfall. Tree canopies seem to be efficient scavengers of MeHg from the atmosphere, or else MeHg may be formed from Hg in the needles.

At the start of the roof experiment runoff fluxes of Hg and MeHg showed similar relations between the two catchments, with about 50% lower output from G1 compared to the control catchment F1. During the third year after the start of the roof experiment, output of Hg and MeHg from G1 were 23% and 37%, respectively, of that in the control catchment. The amount of MeHg was between 3 - 9% of Hg, and there was remarkable similarity between the two catchments in this regard. In both catchments, MeHg in runoff was 6% of Hg during the four years of the study.

The yearly input/output measurements showed a sharp decrease in output by runoff for both Hg and MeHg during the third year of the experiment. The decrease, however, was large in both catchments, making an evaluation of experimental versus natural climatic effects hard to interpret. From the yearly data (Table I), however, it is clear that a larger decrease in output of Hg and possibly MeHg has occurred from the roof catchment compared to the control. To quantify the experimental effects and separate them from effects of other causes, a regression analysis was performed with monthly pre-treatment output fluxes of Hg and MeHg from F1 and G1 as variables. The method has earlier been presented by Hultberg *et al.*, 1990. The calculated regressions are shown below:

$$Hg_{G1} = Hg_{F1} * 0.54 + 0.08 \text{ ; with } r = 0.98\text{; standard error } 0.42\text{; } p<0.005$$

$$MeHg_{G1} = MeHg_{F1} * 0.53 + 0.02 \text{ ; with } r = 0.76\text{; standard error } 0.05\text{; } p<0.005$$

The regressions were used to predict the fluxes in the experimental catchment, using the measured runoff fluxes from the control catchment for the three years after the start of treatments. The predicted monthly output fluxes from the roof catchment derived from the regression were compared to the measured outputs using accumulated monthly data.

Figure 5 shows the accumulated predicted and measured output fluxes from the roof catchment during three years. From this detailed picture of the quantitative experimental effect that has occurred, it is clear that a decrease in Hg began two months after the experiment started. The effects were largest during late winter and spring 1992, 1993 and 1994 (Fig. 6), when the most pronounced decreases in Hg occurred. By April 1994, the output of Hg in runoff from the roof catchment decreased by 32%. The decrease occurred during the spring high flow period with generally high water table in the catchments in the Gårdsjön watershed.

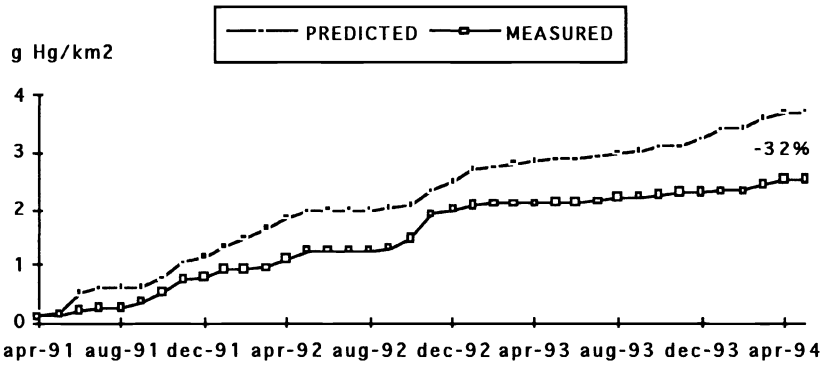

Fig. 5. Predicted and measured accumulated Hg after start of the roof experiment in Gårdsjön, southwest Sweden.

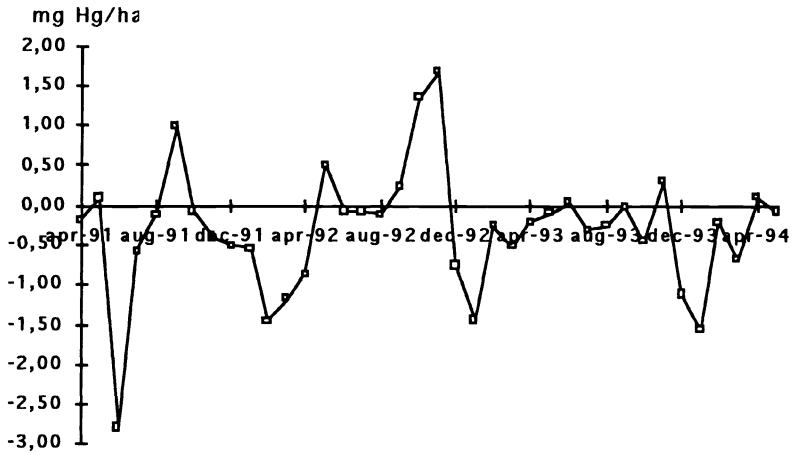

Fig. 6. Monthly changes in runoff fluxes of Hg after start of the roof experiment in Gårdsjön.

In contrast to Hg, MeHg showed no decrease during the first seven months, and less than a 10% decrease occurred over the first two years 1991 and 1992 (Fig. 7).

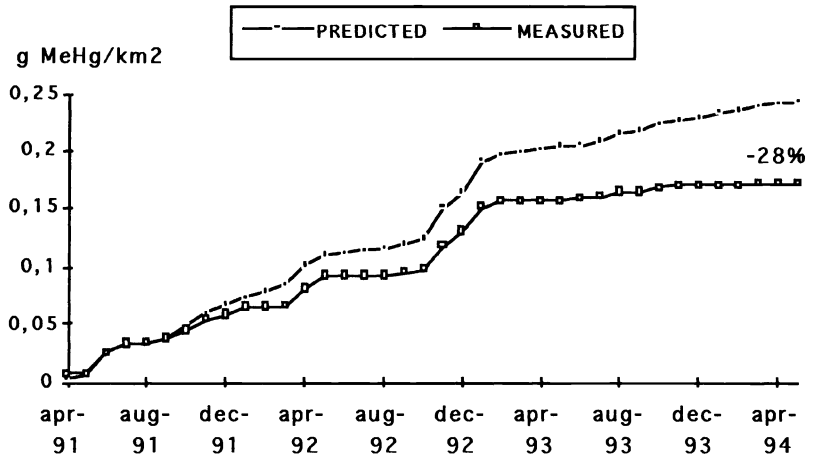

Figure 7. Predicted and measured output by runoff of MeHg after start of the roof experiment in Gårdsjön.

From the winter of 1992/93 and during the following 18 months a steady decrease by 20% occurred. By April 1994, the accumulated decrease in output of MeHg was 28% during the three year experimental period.

4. Conclusions

The principal result of the three years of experiment in the Forest Roof Project is that significant decreases occurred in surface runoff concentrations and output fluxes of both Hg and MeHg after the atmospheric input was excluded by a roof. The large soil pools of Hg and MeHg result in a reduced transport of Hg and MeHg from the catchment after three years. The MeHg transport by runoff decreased in a more steady way than Hg, which was more strongly controlled by hydrologic factors. Presumably the behaviour of MeHg was due to interactions with the catchment soils (Lee *et al.*, 1995b). The Hg transport decreased during periods with water saturated soils and shorter retention time of water in the catchment. The behaviour of Hg was similar to observations of nitrate losses from forested catchments in the NITREX-project where, at sites with low atmospheric deposition of ammonium and nitrate; nitrate typically only appears in runoff during winter/spring when its time of contact with the soil is short (Hultberg *et al.*, 1994). The decrease in Hg and MeHg in runoff was similar to the decrease in sulphur (40% by October 1993) in the same experiment (Hultberg *et al.*, 1993).

The decreased atmospheric input of Hg and MeHg to the roof catchments resulted in a faster and larger decrease in runoff of both Hg and MeHg than was expected before the start of the experiment in Gårdsjön. A critical load concept not to exceed the health standards for MeHg in fish was presented in an earlier study (Hultberg *et al.*, 1995). The atmospheric deposition of MeHg presented for Gårdsjön in Table I was estimated to exceed the critical load for MeHg over large areas in Sweden. If the results from the roof experiment at Gårdsjön are valid for other areas with lakes and streams sensitive to atmospheric deposition of Hg and MeHg, control measures for Hg and MeHg emissions may give fast responses to the input of Hg and MeHg to lakes from the atmosphere as well as from the surrounding catchment.

Acknowledgements

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Mercury Cycling in the Allequash Creek Watershed, Northern Wisconsin

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Abstract. Although there have been recent significant gains in our understanding of mercury (Hg) cycling in aquatic environments, few studies have addressed Hg cycling on a watershed scale. In particular, attention to Hg species transfer between watershed components (upland soils, groundwater, wetlands, streams, and lakes) has been lacking. This study describes spatial and temporal distributions of total Hg and MeHg among watershed components of the Allequash Creek watershed (northern Wisconsin, USA). Substantial increases in total Hg and MeHg were observed as groundwater discharged through peat to form springs that flow into the stream, or rivulets that drain across the surface of the wetland. This increase was concomitant with increases in DOC. During fall, when the Allequash Creek wetland released a substantial amount of DOC to the stream, a 2-3 fold increase in total Hg concentrations was observed along the entire length of the stream. Methylmercury, however, did not show a similar response. Substantial variability was observed in total Hg (0.9 to 6.3) and MeHg (<0.02 to 0.33) concentrations during synoptic surveys of the entire creek. For the Allequash Creek watershed, the contributing groundwater basin is about 50% larger than the topographic drainage basin. Total Hg concentrations in groundwater, the area of the groundwater basin, and annual stream flow data give a watershed-yield rate of 1.2 mg/km^2/d, which equates to a retention rate of 96%. The calculated MeHg yield rate for the wetland area is 0.6 to 1.5 mg/km^2/d, a value that is 3-6 fold greater than the atmospheric deposition rate.

1. Introduction

Recent development of ultra-clean sampling techniques coupled with sub-ng L^{-1} quantification limits for total mercury (Hg_T) and methylmercury (MeHg) in aqueous samples has allowed scientists to quantify standing pools, identify major transport routes, and estimate important process rates in freshwater aquatic systems (Lindqvist *et al.*, 1991; Watras and Huckabee, 1994). Because of concerns over contamination of sport-fish populations, most of the advances in aquatic Hg research have been part of lake studies. There is increasing information that points to post-depositional transport of Hg from upland areas to lakes and reservoirs by subsurface or stream flows (Mierle, 1990; Aastrup et a., 1991; Krabbenhoft and Babiarz, 1992; Swain *et al.*, 1992) as important vectors for the delivery of Hg to aquatic systems. To date, there have been very few efforts to

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examine Hg cycling on the watershed scale, and to examine the role of various components of watersheds in the aquatic Hg cycle.

Wetlands components of watersheds may be important in Hg cycling because of 1) their proximity with steams, lakes, and reservoirs, and 2) their high organic carbon content (for which trace metals have a strong affinity). Studies in Canada (St. Louis *et al.*, 1994) and Wisconsin (Hurley *et al.*, 1994a) have shown that the net export rate of Hg_T and MeHg from watersheds is related to the areal extent of wetlands in a catchment. The exact mechanisms resulting in this observation are not well known. The purpose of this paper is to examine the role of wetlands in the cycling of aqueous Hg (Hg_T and MeHg) in a remote watershed of northern Wisconsin.

2. Study Area

The 21.8 km^2 Allequash Creek watershed (Figure 1) is part of the Wisconsin Lake District, which has an area of about 15,000 km^2 and contains over 3000 lakes. About 80 percent of the land area in the Lake District, and the entire Allequash Creek watershed, lie within two state forests. The physical hydrology of the Lake District can be described as a mosaic of small basins, which generally contain several lakes, wetlands, one or more streams, and upland forests. Within the Allequash Creek watershed land types are divided among forests, lakes and streams, and wetlands in about a 50:30:20 ratio. Upland areas are forested with a mixture of coniferous and deciduous species, while sphagnum moss, leatherleaf, tussocks sedge, and black spruce predominate in wetlands.

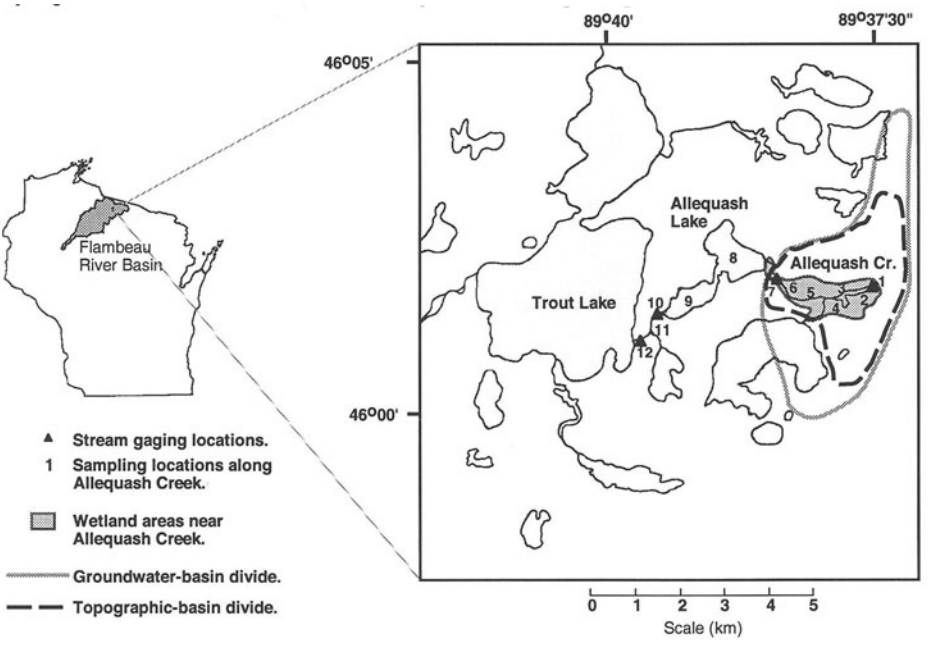

Fig. 1. Site location map for the Allequash Creek watershed in northern Wisconsin.

Geological features of the area are dominated by 30 to 50 m of sandy outwash deposits (kettle holes, kames, crevasse fills) overlying Precambrian igneous and metamorphic bedrock. Overall relief in the area is low, although many of the hillslopes are at or near the angle of repose for sandy soils. This results in sharply defined boundaries between forests, wetlands, and lakes and streams. The outwash deposits are hydraulically conductive (average $K \approx 1x10^{-5}$ m/s; Krabbenhoft, 1988), which promotes effective exchange of water and solutes between watershed components. The predominant forest soils are poorly developed, with 10 to 15 cm of a humic A horizon overlying sand.

Allequash Creek originates as a small (about 10 ha) pond in an area known locally as "The Springs", because of the numerous point discharges of groundwater at the bases of hillslopes and near-shore areas of the pond. Flow out of the pond is limited by a beaver dam at site 4. As water flows out of the pond it channels and flows through a 1.6 km^2 wetland. Water drains over the surface of the wetland to the stream by numerous small channels, or rivulets (about 20 to 30 cm wide x 5 to 10 cm deep). The rivulets are hydraulically similar to springs, in that their flow is sustained by groundwater that has seeped through peat. At the outlet of the wetland (site 7, Figure 1), the channel narrows (about 3 m wide), and the wetland is limited to a riparian zone about 3 m wide on either side of the channel. The creek then flows about 0.5 km and discharges to Allequash Lake. Allequash Lake has two distinct basins; the inlet basin is seasonally stratified and has average and maximum depths of 4.5 and 7 m, respectively, compared to 1.5 and 3 m, respectively, for the non-stratified outlet basin. From the outlet of Allequash Lake, the creek flows about 1 km to Trout Lake, the discharge point for the watershed.

The Allequash Creek watershed has been the focus of the North Temperate Lakes-Water, Energy, and Biogeochemical Budgets (NTL-WEBB) project for the past three years. Three hillslope-hydrology research sites (sites 1, 7, and 10 along Allequash Creek, Figure 1) are intensively monitored with hydrologic instruments, and the flow is continuously gaged at these three locations and the outlet of the watershed (site 12). Basic water chemistry parameters are monitored on about a bi-monthly basis at 10 locations along the creek transect.

3. Methods

Ultra-clean sampling protocols were used in all aspects of the field-sampling program. Samples were collected using stringently cleaned (sub-boiling concentrated nitric acid) Teflon[1] tubing, in-line filter holders, and bottles. Samples were filtered using pre-ashed, quartz-fiber filters (nominal 0.7 μm poresize). Total-Hg samples were acidified with 6N HCl (10 ml acid per 500 ml sample) soon after acquiring the sample, while MeHg samples were generally put on dry ice in the field, or in a few cases kept in a

[1] Any use of trade, product or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

cooler at 4°C and immediately frozen upon return from the field. Stream samples were taken upstream from a fiberglass canoe by field personnel wearing lint-free suits and arm-length plastic gloves.

To assess the mechanisms by which Hg is transferred through the Allequash Creek watershed, a variety of water samples were collected, including: stream, groundwater, springs, interstitial water from near-surface peat, and the rivulets draining the wetland. Synoptic samplings of the entire length of Allequash Creek were conducted in July, August, and September 1992. During these sampling periods, stream and spring water samples for Hg_T and MeHg were not filtered. Filtered and unfiltered samples were collected in 1993 and 1994. During the synoptic samplings, stream water was collected at 11 locations (sites 2-12, Figure 1). Groundwater samples were taken from shallow (3 m) minipiezometers at two locations (sites 1 and 7, Figure 1) that were constructed of polyethylene and flow continuously due to strong, upward hydraulic gradients. Springs located near site 1 were sampled by carefully positioning a Teflon sampling line in the flowing water to minimize suspension of sediment. Samples were collected 5 to 10 minutes after the sample line had been positioned, to allow equilibration of the sampling area. Interstitial porewater samples from the wetland were taken near site 6, as close as possible to the wetland/stream interface (about 2 m). Samples were taken using the same methodology as Krabbenhoft and Babiarz (1992) by incising a small hole into the surface of the peat (about 10 cm wide by 10 cm deep) and slowly pumping water from the hole. Rivulets were sampled near site 6 using the same methods described above for sampling springs.

Total-Hg samples were analyzed at the Water Chemistry Program, University of Wisconsin-Madison, using BrCl oxidation, SnCl reduction, dual gold amalgamation, and detection by cold-vapor atomic fluorescence (Bloom and Fitzgerald, 1988). Methylmercury determinations were performed using the ethylation and distillation technique of Horvat *et al.* (1993). Quantification limits for Hg_T and MeHg were 0.06 and 0.02 ng L^{-1}, respectively.

4. Results and Discussion

4.1. SPATIAL AND TEMPORAL DISTRIBUTIONS OF Hg_T AND MeHg

Results of the synoptic stream sampling of 1992 show considerable variability in Hg_T and MeHg concentrations (Figure 2). Substantial increases in Hg_T and MeHg result as groundwater from below discharges through the peat and becomes spring flow (compare groundwater and spring samples in Figure 2). Total-Hg concentrations in groundwater are very similar to those observed previously at nearby Pallette and Little Rock Lakes (Krabbenhoft and Babiarz, 1992), and range from 1 to 2 ng L^{-1}. Spring samples show a 2 to 4 fold increase in Hg_T, indicating a substantial release rate from peat. Although groundwater dissolved organic carbon (DOC) concentrations are quite variable in this watershed, at site 1 DOC ranges from 1 to 2 mg L^{-1}, whereas spring water ranges from 10 to 15 mg L^{-1} (Table I). This observation suggests a strong association between

DOC generation and Hg release from the peat. Methylmercury shows an even more dramatic increase in concentration between groundwater and springs. In fact, during the entire study, groundwater samples were always below our detection level for MeHg (0.02 ng L^{-1}). Spring samples, on the other hand, ranged from 0.2 to 1.2 ng L^{-1} MeHg during the study (Table I). If the only source of MeHg in spring samples was from atmospheric deposition to the forest soils, with subsequent mobilization by upward discharging groundwater, by mass-balance considerations the MeHg concentrations in spring samples would be much less. Using the MeHg atmospheric deposition rate estimated by Fitzgerald *et al.* (1991) of 90 mg/km^2/y, the groundwater discharge rate would have to be limited to 0.18 m/y to give an average MeHg concentration in spring water of 0.5 ng L^{-1}. This discharge velocity is about 2 to 20 times less than other estimates of specific discharge in these outwash sediments (0.3 to 3.0 m/y). Thus, because there is far more MeHg in spring water than what can be accounted for by simple flushing of MeHg derived from atmospheric deposition, net methylation of inorganic Hg within the peat is likely the dominant source of MeHg in spring water at Allequash Creek. Near-surface, interstitial water from the wetland is much lower than spring water in MeHg content, with an average concentration of 0.13 ng L^{-1}. This observation points to the very near surface peat as the important site of production and transfer of MeHg to springs, and ultimately to points lower in the watershed.

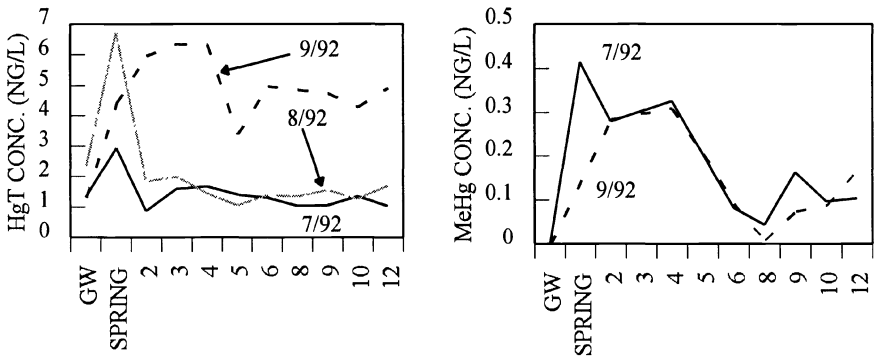

Fig. 2. Results of the 1992 synoptic sampling of Allequash Creek for Hg_T and MeHg. Sampling site numbers correspond to the locations on Figure 1, groundwater (GW) and spring samples were collected at sites 1. 6, and 7.

Methylmercury concentrations in the wetland pond (sites 2-4) are intermediate between groundwater and spring water (Table I). The observed small range of concentrations (0.21 to 0.33 ng L^{-1}) reflect the observed MeHg concentrations in the sources of water to the pond, namely spring water and groundwater. Under quiescent conditions, release of Hg_T and MeHg from the sediment/water interface may occur much like that observed in the hypolimnion of lakes (Hurley *et al.*, 1994b; Andren *et al.*, 1994). Below the dam (sites 5 and 6) MeHg concentrations are lower than the pond, perhaps due to dilution by groundwater that is low in MeHg, demethylation, or particle scavenging.

An increase in stream flow by a factor of about 3 from site 4 (the beaver dam) to site 7 (wetland outlet) argues for groundwater dilution.

The minimum observed MeHg concentration was at the deep basin of Allequash Lake during the July and September, 1992 synoptic samplings. This suggests that the deep lake basin is a primary sink for MeHg produced and transported anywhere above this point in the watershed. Particle settling in stratified lakes is known to be a very effective mechanism for transport of MeHg in northern Wisconsin Lakes (Hurley *et al.*, 1994c), and is likely the most important removal mechanism of MeHg from the water column. Filtered and unfiltered sample replicates of spring, pond, and stream water, however, showed a maximum of only 18% of the MeHg in the particulate phase. Aqueous-phase transport (as operationally defined by our filtering method) appears to be the dominant MeHg-transport vector of in the Allequash Creek watershed.

Total-Hg concentrations showed a dramatic increase in September along the entire stream transect. It is interesting to note, however, that MeHg concentrations did not show any apparent increase at this time. During early fall wetland plants become senescent, typically resulting in a release of DOC. Water samples collected at the outlet of the wetland (site 7) show a substantial increase in DOC in September for 1992 and 1993 (Figure 3). Total-Hg concentrations appear to be associated with this source of released carbon, while MeHg does not.

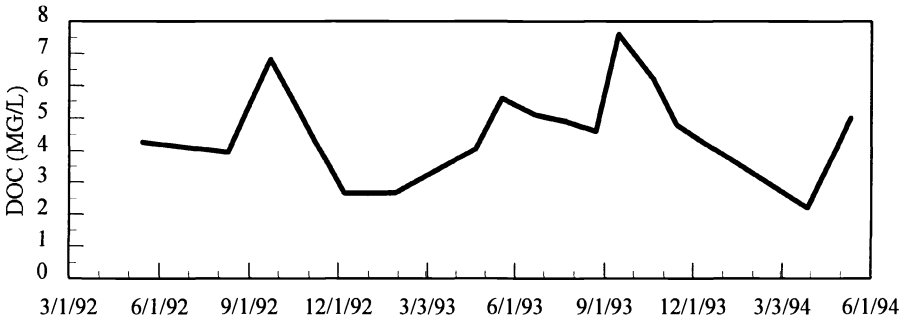

Fig. 3. 1992-1993 DOC sampling results at the outlet of the Allequash Creek wetland (site 7, Figure 1).

Table I summarizes the Hg_T and MeHg, and DOC data collected during this study (1992-1994). Starting at the top of the catchment, groundwater showed moderate Hg_T concentrations, no detectable MeHg, and low DOC levels. Springs (including the rivulets draining the wetland) consistently showed elevated concentrations of Hg_T, MeHg, and DOC. Interstitial porewaters from the wetland surface had Hg_T concentrations similar to groundwater, and elevated concentrations of MeHg and DOC, although not nearly as high as spring-water samples. Stream water had intermediate concentrations of all these constituents (with the exception of one sample which had a concentration of 0.5 ng L^{-1} Hg_T), which is somewhat surprising considering the likelihood of in-stream processes (e.g. particle scavenging) that should greatly influence aqueous concentrations (Hurley *et al.*, 1994c).

TABLE I

Sampling results (1992-1994) for Hg_T, MeHg, and DOC for various components of the Allequash Creek watershed.

Watershed component	Hg_T (ng L^{-1})	MeHg (ng L^{-1})	DOC (mg L^{-1})
Groundwater	1.1 - 3.3	<0.02	0.6 - 2.2
Spring water	3.0 - 6.8	0.15 - 1.22	10.0 - 15.6
Wetland interstitial water	3.9	0.09 - 0.17	1.7 - 2.9
Wetland pond water (sites 2-4, Figure 1)	0.9 - 6.3	0.21 - 0.33	3.7 - 11.0
Wetland stream water (sites 5-7, Figure 1)	0.9 - 5.9	0.08 - 0.21	2.8 - 7.8
Allequash Lake (sites 8 and 9, Figure 1)	1.1 - 5.1	<0.02 - .16	4.2 - 7.2
Lower basin streams (sites 10-12, Figure 1)	0.5 - 5.5	0.09 - 0.17	4.1 - 7.4

4.2 WATERSHED YIELD RATES

Watershed yield rates for Hg are commonly used to differentiate retention abilities among varying land types. Several authors have shown that there is an inverse relation between percentage of wetland and retention ability of watersheds (Mierle, 1990; St. Louis *et al.*, 1994; Hurley *et al.*, 1994a). By sampling various components of the Allequash Creek watershed, our study sheds new light on the reasons for this observation. In addition, by compartmentalizing our study watershed, Hg yield rates for individual compartments can be calculated.

A basic requirement for calculating watershed yield rates is estimating the area of the land surface which contributes water to stream flow. This is especially important for Hg, where it is generally assumed that atmospheric deposition is the primary source (Krabbenhoft and Babiarz, 1992). Most often, the area of the contributing basin is estimated using topographic maps, and assuming that surface drainage divides coincide with groundwater divides. This assumption only holds, however, when vertical relief is high and the aquifer is relatively homogeneous. Anderson and Hunt (1994) constructed a numerical, groundwater-flow model for the region around the Allequash Creek watershed, and with this model can predict the groundwater contributing area for any lake, stream, or specific stream segment. For our study, the model was used to estimate the groundwater contributing area above the wetland outlet (site 7). The model estimated the area of the groundwater shed above site 7 to be 15.0 km^2, which is about 50% greater than that estimated by topographic divides (9.9 km^2). By dividing the total annual flow (4.38 $x10^6$ m^3) for 1993 from the wetland outlet by these two areas, two estimates of groundwater recharge result: 0.29 m y^{-1}(groundwater shed), 0.44 m y^{-1} (surface-water shed). Previous studies in northern Wisconsin indicate the average recharge rate is about 0.25 m y^{-1} (Anderson and Munter, 1981; Krabbenhoft *et al.*, 1990), which lends credence to our use of the groundwater-shed area in yield rate calculations.

By using an average Hg_T stream concentration of 2.9 ng L^{-1}, we calculate whole-watershed yield rates of 2.3 mg km^{-2} d^{-1} (groundwater shed), which is similar to values calculated previously for Wisconsin and Ontario (Mierle, 1990; St. Louis *et al.*, 1994, Hurley *et al.*, 1994a). A value 50% too large would be estimated if the area of the

surface-drainage divides was used (3.5 mg km^{-2} d^{-1}), If we assume an atmospheric deposition rate for Hg_T of 27.4 mg km^{-2} d^{-1}(wet and dry, Fitzgerald, 1991), 92% of the annually deposited Hg is being retained in the watershed. Noting that the average groundwater-Hg concentration (1.5 ng L^{-1}) is about half that of the stream, a yield rate of 1.2 mg km^{-2} $d^{-1}$for the upland soils results. In this case, the upland areas in the groundwater shed are estimated to retain about 96% of the atmospheric-Hg burden, which agrees well with the value calculated by Krabbenhoft and Babiarz (1992). This retention rate is considerably higher than those reported previously, but it is based on groundwater concentrations and does not include effects of wetlands or sediment/water exchange processes that are inherently included into whole-watershed yield rates. All of the groundwater samples collected for this study were below our detection limit for MeHg. This apparently high retention rate may indicate net demethylation in upland soils and/or along groundwater flowpaths in the Allequash Creek watershed.

By comparing Hg_T and MeHg concentrations in samples from the creek, springs, and groundwater, we can calculate the yield and retention rates of the wetland. Given a wetland surface area of 1.7 km^2, and the observation that the average stream-water concentration of Hg_T is 1.1 ng L^{-1} greater at the wetland outlet than the average groundwater concentration, we calculate a yield rate of 7.7 mg km^{-2} d^{-1}, or a 70% retention rate for the wetland. For MeHg, if we use a concentration range of 0.08 to 0.21 ng L^{-1} in stream water, we calculate a yield rate of 0.6 to 1.5 mg km^{-2} d^{-1}, which is similar to values calculated by St. Louis *et al.* (1994) for wetland areas alone. If we subtract the MeHg contributed by atmospheric deposition (0.24 mg km^{-2} d^{-1}), we estimate the net methylation rate of this wetland to be about 0.3 to 1.2 mg km^{-2} d^{-1}.

5. Conclusions

Studies of Hg cycling at Allequash Creek show that important processes occur at the groundwater/wetland/surface water interfaces. Both Hg_T and MeHg revealed marked increases in concentrations as groundwater discharges through peat into the wetland or as spring flow to surface water. The increase in Hg species concentrations is concomitant with increases in DOC. A substantial increase in Hg_T was observed in stream water during fall, and was coincident with the seasonal release of DOC from the wetland. Methylmercury, however, did not show this same seasonal response. There was considerable variability in Hg_T and MeHg concentrations during synoptic surveys along the entire length of Allequash Creek; thus, sampling of many locations was necessary to infer interactions among watershed components. The groundwater basin is 50% larger than the topographic-surface divide for the Allequash Creek watershed; watershed yield rates based on the area of the surface-drainage divide would be correspondingly 50% too large. Isolation and sampling of specific components of the watershed allowed for more detailed calculation of transfer (yield) rates of Hg_T and MeHg, and to identify important watershed Hg-cycling processes.

Acknowledgments

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Terrestrial Sources of Methylmercury in Surface Waters: The Importance of the Riparian Zone on the Svartberget Catchment

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Abstract. The runoff of methylmercury (MeHg) from forested catchments to surface waters has been identified as a potentially significant input of MeHg to the aquatic ecosystem. Little, however, is known of the processes which control the transfer of MeHg from soils to surface waters. This study investigated the potential terrestrial sources of MeHg in runoff by sampling profiles of soil solution chemistry and determining the flux of water through those profiles into two tributaries on the Svartberget Catchment in northern Sweden. One study profile was from the podzol soil that covers most of the catchment area. The other profiles were taken in the riparian zone of each of the two tributaries. Soil solution was extracted from the soils by centrifugation.

High catchment soil solution concentrations of MeHg (>1 ng l^{-1}) occur in the surface layers of the soil, but overland flow on the catchment is rare. MeHg concentrations in the podzol profile dropped to less than 0.2 ng l^{-1} in the mineral soil just 5 cm below the mor layer. In the riparian soil profiles sampled in October, MeHg concentrations were higher (ca. 0.4 ng l^{-1}), but in a July sampling the concentrations in the riparian profiles were comparable to those in the podzol (i.e. < 0.2 ng l^{-1}). Very high concentrations of MeHg were found in the streambank sphagnum mosses (>2 ng l^{-1}) partially submerged within the stream.

The concentrations of MeHg observed under the podzol soil were insufficient to sustain the concentration of MeHg in runoff from the forested subcatchments where podzol profiles cover more than 70% of the surface area. The only sources of additional MeHg that lie along major runoff flow pathways are the riparian soils and mosses on the streambanks. It is therefore hypothesized that output of MeHg from the forest areas of the catchment is controlled by the biogeochemical processes in the riparian zone.

1. Introduction

In the past decade, mercury (Hg) contamination has been recognized as a major problem in Swedish surface waters. More than 10,000 of Sweden's 83,000 lakes are estimated to have fish with Hg levels that are unacceptable for human consumption (Håkansson *et al.*, 1990). Many of these "blacklisted" lakes are located in rural and northerly areas that have been less effected by other forms of air pollution.

Methylmercury (MeHg) is the principal species of Hg responsible for Hg accumulation in the aquatic food chain (Boudou and Ribeyre, 1990). Few budget studies of MeHg transfers from soils to surface waters are currently available, but the one study done previously in Sweden indicated that stream runoff could account for half of the MeHg in lake water (Iverfeldt and Johansson, 1988; Lee and Iverfeldt, 1991). Most of that runoff moves through the soils where a large portion of atmospheric Hg/MeHg deposition has accumulated. The accumulation in superficial soil layers has saved the aquatic environment from the full effects of Hg deposition, but at the same time the accumulation has created a terrestrial store of Hg that is a classic example of a so-called "chemical time bomb".

As an initial step towards understanding what controls the output of MeHg from soils to stream water, this paper seeks to identify the catchment origins of the MeHg and associated chemical species (e.g. total organic carbon [TOC] and total mercury [Hg-tot])

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in runoff from the forested Svartberget Catchment in northern Sweden. The study catchment lies just a few km from a lake black-listed for Hg contamination.

Previous work on the origins of TOC and acidity in the study area (Bishop *et al.*, 1990, 1994; Bishop, 1991a) has indicated the importance of the riparian zone for stream chemistry. Those findings provided the basis for the experimental plan to investigate the origins of MeHg, with particular attention paid to riparian soils and even the mosses growing on the stream bank. The approach taken by this study was to sample soil solution from profiles where the lateral flow pathways and rates of water flux are well characterized. One of these profiles is located in the mineral soil at some distance from the stream channel, and the other two profiles are from the organic-rich riparian soils The patterns of hydrological flux in the profiles are then compared to the chemistry of runoff entering the stream from the soil at the time the profiles were sampled.

2. Study Area

The 50 ha Svartberget Catchment is located in northern Sweden (64° 14' N, 19° 46' E). The catchment is afforested with mature Scots Pine (*Pinus sylvestris*) on higher ground and Norway Spruce (*Picea abies*) in low-lying areas. Understory vegetation is a mix of lichens and berries (mostly *Vaccinium myrtillus*, *Vacc. vitis-idaea* and *Deschampsia flexuosa*) on the hillslopes, changing into moss (*Sphagnum spp.* and *Polytrichum spp*) near the streams.

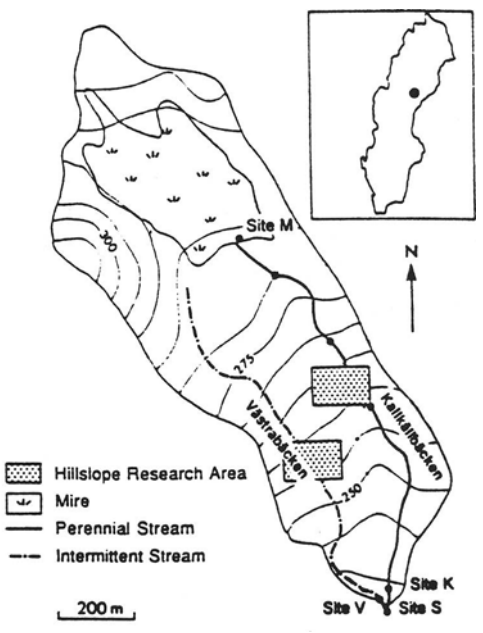


Fig. 1. The Svartberget Catchment showing the hillslope research areas where the study transects are located, and the stream sampling points from which runoff chemistry was calculated

The catchment is drained by two tributaries, Västrabäcken and Kallkällbäcken (Figure 1). The latter has its source in the outlet of an 8 ha mire. Both tributaries were deepened and straightened in the 1930's. The forest soils are predominantly well-developed iron podzols which have developed upon up to several meters a locally derived glacial till overlying gneissic bedrock. In the vicinity of the tributaries, however, there is a band of riparian peats which has been shown to influence stream chemistry (Bishop *et al.*, 1990, 1993; Bishop 1991a). Differences in the chemistry of the two tributaries have been linked to the greater depth of the organic-rich soil horizons alongside Kallkällbacken where the depth of peat 12 m from the stream is twice as likely to be greater than 40 cm deep (Bishop, 1994, Bishop *et al.*, 1994).

Aluminum speciation in catchment soil profiles has shown low proportions of inorganic monomeric Al below the A horizon (Bishop *et al.*, 1993). The pH and Al in the soil and stream runoff are therefore believed to have been relatively unaffected by acidification despite the presence of anthropogenic sulfate in precipitation (Bishop, 1991b).

3. Methods

This paper seeks to relate the interaction of flow pathways and soil solution chemistry to MeHg concentrations in runoff from the forested portions of the catchment. This was done by sampling soil solution in profiles located along transects parallel to the direction of lateral water flow to the stream as estimated from local topography. Opposing pairs of hillslope transects on both Västrabäcken and Kallkällbäcken were used (Figure 2). Measurements of groundwater level at fixed distances along these transects have been complemented by measurements of tensiometers and piezometers to determine the flow regime. For purposes of this study, the relationship between water table and runoff was used to estimate the flux of water through 5-cm thick, horizontal layers in the study soil profiles given different rates of runoff. This analysis assumed a constant lateral gradient of hydraulic potential, and that all lateral flow occurred according to Darcy's Law in the saturated portion of the upper meter of the soil. It was furthermore assumed that both sides of each tributary contributed equally to flow and that there was a decrease in lateral flux moving away from the stream proportional to the decrease in upslope area.

Soil solution chemistry was measured in three profiles along these transects at up to five levels on each profile. One study profile (PDZ) was chosen to be representative of the mineral soils which cover the majority of the catchment. This profile was located in the hillslope research area, 40 m west of Kallkällbäcken in a well-developed iron podzol profile (Figure 1). The other two profiles were in riparian peat soils. One (Profile RIK) was 5 m west of Kallkällbäcken on the same transect as the PDZ Profile. The other riparian profile (Profile RIV) was located 5 m east of Västrabäcken (Figure 2). Sampling levels were selected to coincide with specific horizons on each soil profile (Table I).

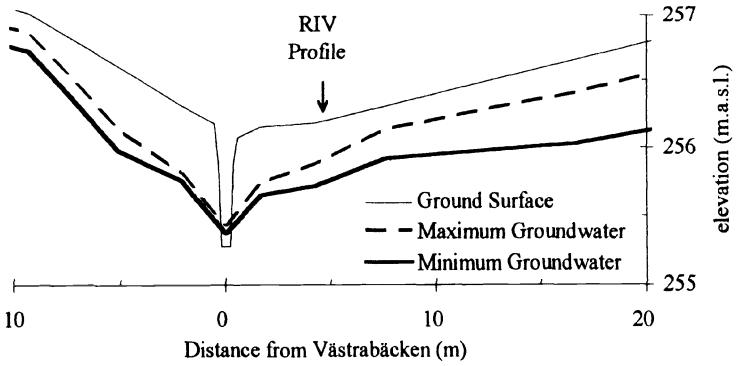


Fig. 2. A portion of the transect along which the riparian soil profile (RIV) near Västrabäcken was located. The minimum and maximum water levels during the snow-free period of 1993 are indicated.

Table I

Soil Profile Samples

Sample Level	Podzol Profile		Riparian Profiles		
	Description	Depth	Description	Depth	
		PDZ Profile		RIK Profile	RIV Profile
1	Mor	-7 - 0	Living Mosses	-10 - 0	-10 - 0
2	A horizon	0 - 7	Top of peat	0 - 10	0 - 10
3	Bs horizon	7 - 14	Bottom of Peat	35 - 40	15 - 25
4	B horizon	30 - 40	Organic-rich mineral soil	40 - 50	25 - 35
5	B/C Transition	60 - 70	"clean" mineral soil	65 - 75	40 - 50

Soil samples were collected from the desired levels on the face of a pit that was refilled after sampling. Subsequent samples at a site were made by excavating a fresh face 30 cm upslope. The chemistry of the mosses growing on the streambank and extending into the stream was characterized by samples divided into up to three layers, KS-1 were the living mosses in Kallkällbäcken. KS-2 was from the dead mat underlying the living moss, and KS-3 was the mineral soil upon which the mat rested.

At least 300 ml of solution were extracted from each sample by centrifuging 100 g portions of mineral soil in a polyethylene holder for 1 hour using the free drainage method described by Giesler and Lundström (1993). Smaller portions and a 20 min. centrifuge cycle were used for extracting water from mor, peat and streambank mosses. Centrifuged soil solution and streamwater were not filtered in order to avoid contamination or adsorption by the filters. Centrifugation has an advantage over lysimeter methods in that there is less risk for alteration of the sample through contact with the lysimeter surface or during storage in the lysimeter. The concentration of TOC in centrifuged soil solution, however, is higher than that recovered by lysimeters (Zabowski and Ugolini, 1990).

Soil samples were stored in closed polyethylene bags at 4° C until they were centrifuged. The centrifugation of peat and moss samples was completed within 24 hours of sample collection. Mineral soil sample centrifugation was completed within a week. The sampling, storage and analysis protocols for the Hg-tot/MeHg water samples are described in Lee *et al.* (1995b).

The polyethylene centrifuge containers could not be washed with the trace-metal free protocols used for other plasticware, so contamination experiments were performed with distilled water and DOC-rich stream water. A 1 hour centrifuge cycle changed the content of MeHg by only a few percent. Thus it was assumed that the centrifugation method did not alter the MeHg concentration in the samples. A similar test has yet to be done for Hg-tot. Since the centrifugation technique took several days to complete for mineral soil, the effect of soil storage is a concern. This was investigated by taking one set of samples that were extracted within 48 hours. A portion of those soil samples was then stored for 1 month at 4° C before centrifugation. The variations in MeHg after storage indicated the danger of alteration during storage. (Table II). After storage there was a large increase in MeHg in the living moss sample, and decreases in the other samples.

Table II

Effect of Soil Sample Storage on MeHg in Soil Solution

Sample	RIV - 1 Living Mosses	RIV - 2 Top of Peat	RIV - 4 Organic-rich Mineral Soil
Centrifugation within 48 hours (ng l^{-1})	0.77	0.45	0.40
Centrifugation after 1 month (ng l^{-1})	2.56	0.35	0.18

Water flow was measured with V-notch weirs at Sites M, V and S (Figure 1). The flow at Site K was calculated from these values. Water chemistry was sampled at Sites M, V and K. The chemistry of runoff water leaving Subcatchment V at the time of soil sampling was assumed to be equal to the water chemistry at Site V. The chemistry of water leaving the forested subcatchment of Kallkällbäcken below the mire (Subcatchment MK) was calculated from the difference in flow and chemistry at sites M and K.

4. Results

Some of the soil profiles were sampled on October 22, 1992 and October 28, 1993. All of the profiles were sampled on July 23, 1993. These samplings occurred during periods of low flow (< 1 mm d^{-1}). The 1992 soil sampling was performed under a half-meter of fresh snow. Streambank mosses were sampled October 23, 1992, July 28, 1993 and October 26, 1993. A runoff event intervened between the July 23 sampling of soil and the July 28 sampling of streambank mosses. The Hg-tot/MeHg dynamics of that storm are described in Bishop *et al.* (1995).

Analysis of the water level and runoff relationship on the study transects indicated that the water level in each sampling site was between 60 and 75 cm depth at the time of sampling. (Figure 3). Flow is essentially vertically downwards above the water table in the catchment. During the rain event subsequent to the July 23 soil sampling, the water level rose 25 to 35 cm, with most of the stormflow moving through this 25 to 35 cm thick layer of temporarily saturated soil. The lateral flux across the RIK profile is several times that across the RIV profile.

The pH in soil solution from all soil profiles was lowest in the mor or moss at the soil surface sample (3.5-3.8, data not shown). The pH increased with depth to between 5.0 and 6.5 towards the bottom of the soil profiles. The pH in the tributaries (Sites V and K) was between 4.8 at 5.5 at the time of the soil samplings. The pH dropped to ca. 4.3 during the July 25 runoff episode which occurred just after the July 23 soil sampling.

Concentrations of TOC in soil solution were over 100 mg l^{-1} in all of the superficial samples, but dropped to less than 100 mg l^{-1} below the soil surface. (Figure 5a). The TOC in the PDZ Profile decreased to less than 5 mg l^{-1} in the illuviated B horizon and below. The TOC levels in the riparian peats were higher throughout the RIV profile in the October samples than in the July 1993 sample. Such a "seasonal" variation was not seen in the PDZ Profile.

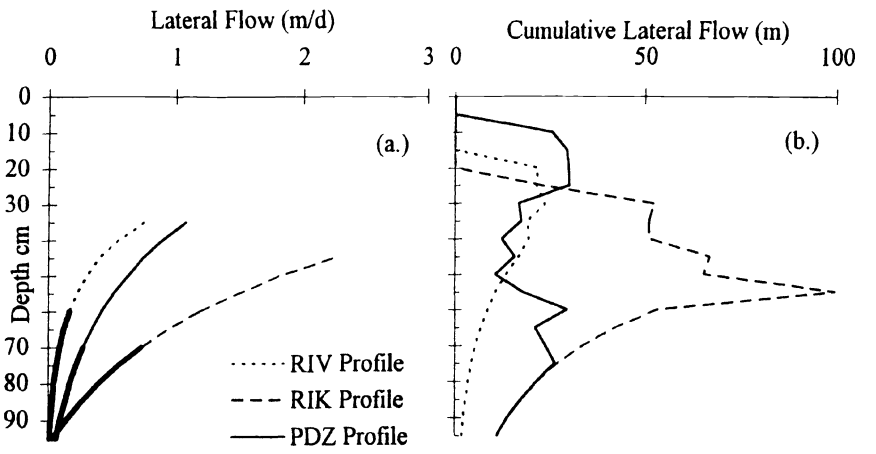


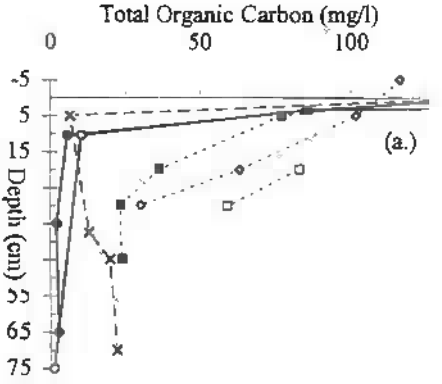
Fig. 3. The daily lateral flux of water across different levels in the soil profile under the low flow conditions at which soil profiles were sampled (thick lines), and at peak flow during the July 25, 1993 rain-driven runoff episode (thin lines).

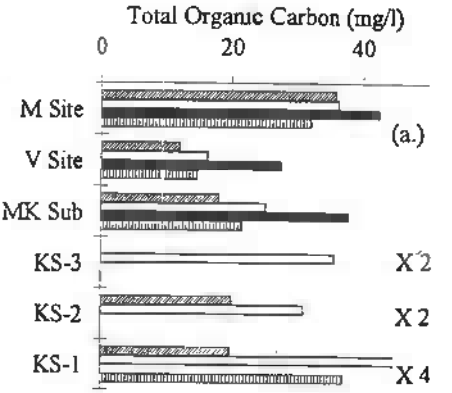
Fig. 4. The cumulative lateral flux across different levels in the soil profiles during the snow-free portion of 1993 (June 1 - November 31)

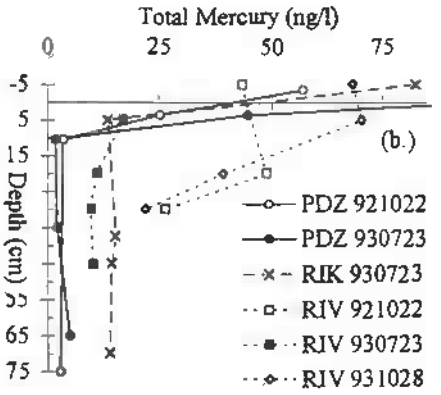
The TOC in runoff from the forest soils was ca. 15 mg l^{-1} from the Västrabäcken tributary and 18-25 mg l^{-1} from Kallkällbäcken below the mire at the time of the soil samplings (Figure 6a). Total organic carbon concentrations in the bank moss centrifugate were always much higher than in the stream, with the concentrations from the living sphagnum (KS-1) being especially high. During the July 25 rain event subsequent to the July 23, 1993 soil sampling, TOC concentration in runoff rose by over 50% in both tributaries (Bishop *et al.*, this volume).

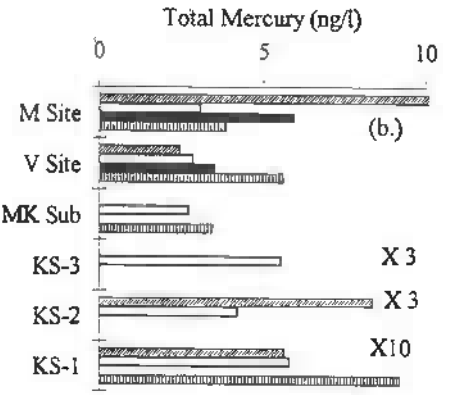
The Hg-tot concentrations were over 40 ng l^{-1} in the water centrifuged from the organic matter at the top of the soil profile. Total mercury concentrations dropped in concentration with depth on all profiles (Figure 5b). The concentration was lowest (< 5 ng l^{-1}) in the B horizon of the PDZ Profile and below. The October 1992 and 1993 RIV profiles had the highest subsurface Hg-tot values (20-60 ng l^{-1}). The July 1993 RIK and RIV samples had somewhat lower concentrations below the soil surface (10-20 ng l^{-1}). The Hg-tot concentration in Västrabäcken ranged from 2.5 to over 5 ng l^{-1} (Figure 6b). The calculated concentration in runoff from Subcatchment MK was around 3 ng l^{-1} during the 1993 soil samplings, but was apparently a sink for Hg-tot coming out of the mire in both October 1992 and during the July 25 runoff episode. The Hg-tot in the living sphagnum was an order of magnitude higher than that observed in runoff (>50 ng l^{-1}). Even the dead mat of bank mosses and the mineral stream bank material had Hg-tot concentrations several times those in the stream.

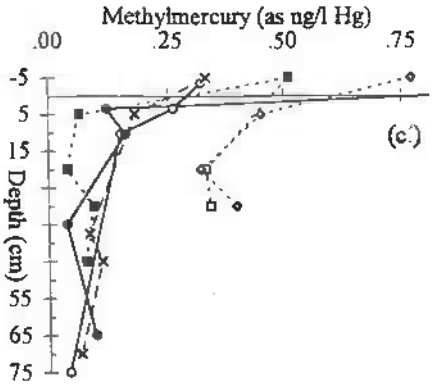
Methylmercury concentrations were also highest (0.3 - 1.5) ng l^{-1} in the surface layer of each soil profile, but dropped to below the 0.2 ng l^{-1} at depths greater than 10 cm in the PDZ profile during both the July and October samplings (Figure 5c). In the July 1993 sampling, the subsurface soil solutions in the riparian soil profiles RIV and RIK were also below 0.2 ng l^{-1}, and often below 0.1 ng l^{-1}. In the October samplings, though, the MeHg concentrations remained at ca. 0.4 ng l^{-1} between 10 and 40 cm depth.











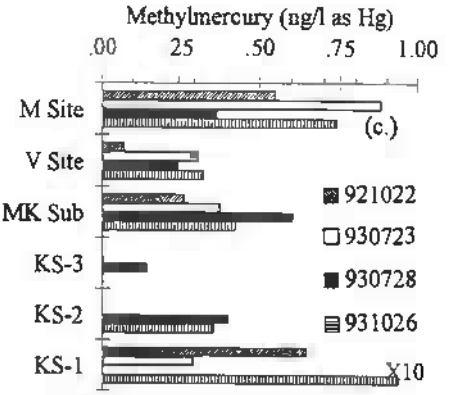


Fig. 5. Chemistry of the soil solution centrifuged from the soil profiles. (a). TOC, (b) Hg-tot and (c) MeHg

Fig. 6 Chemistry of the runoff from the forested V and MK transects as well as the streambank moss samples, (a) TOC, (b) Hg-tot and (c) MeHg. The July 25, 1993 flow peak followed sampling of stream and soils on July 23 under low flow conditions.

Methylmercury in the living stream sphagnum was many times more than in streamwater and hillslope runoff (Figure 6c). The dead mat of moss on Kallkällbäcken had values comparable to that in the MK Subcatchment runoff.

Methylmercury in runoff during the soil sampling ranged from 0.25 to 0.42 ng l^{-1} from Subcatchment MK, and 0.08 to 0.32 ng l^{-1} on Västrabäcken. After the July 25 runoff event, MeHg calculated in runoff from Subcatchment MK peaked at 0.6 ng l^{-1}, while the output concentration from Subcatchment V decreased slightly to 0.25 ng l^{-1}. The increase in calculated Subcatchment MK concentration results from a strong decrease in output from the mire (Site M) while concentration downstream at Site K did not decrease commensurately (Bishop *et al.*, 1995).

5. Discussion and Conclusions

The general pattern of water flow through the catchment starts in the upslope podzols with vertical infiltration of precipitation down through the mor, A horizon, and portions of the B horizon to the water table at a depth of several decimeters. Lateral flow dominates from that point, with the greatest flux immediately below the water table. Changes in flow rate result largely from rainfall inputs raising the water table. This increases the transmissivity of the soil profile, and most of the increased runoff moves in the transiently saturated soil layers. When the lateral flow reaches the last 10-20 m before the stream, it moves under and through a zone of organic-rich soils in the riparian zone (Bishop, 1991a). The water table actually shifts to a deeper level in the soil profile within a few meters of the stream, and overland flow is rarely observed. Over 75% of rain event runoff is usually pre-event water displaced from the catchment, and this pattern was followed by the July 25, 1993 rain episode (Bishop *et al.*, 1995). The total lateral flux and its distribution in the soil profile differ considerably. Using the relationship between lateral flux and water table (Figure 3), the total flux during the snow free period between June 1 and November 31 1993 was calculated (Figure 4). The RIK profile had the highest lateral flux, but that flux was concentrated below 40 cm depth.

The lowest soil level sampled in each profile by this study was located near the water table at the time of sampling, i.e. in the soil layers contributing most to lateral flux across the profile. The increase in water table during the July 25 runoff episode intersected the next sampling location further up in the soil profile.

The concentration of TOC below the A horizon in the podzol (PDZ) soil profile was much lower than the TOC concentration in runoff. The TOC levels at the top of the saturated portion of the riparian zone were comparable to the levels seen in the stream, and the streambank mosses provided a potential source to complement the TOC leaving the soil. Hg-tot throughout the riparian soil profiles was in excess of that reaching the stream. Nonetheless, during both the October 22, 1992 and July 23, 1993 samplings, the stream channel (or atmosphere) was a sink for some of the Hg-tot which left the mire at Site M, but did not reach Site K 1000 m downstream.

In contrast to the Hg-tot, and to a lesser extent TOC, MeHg concentrations in the saturated zone of lateral flow were almost always less than half of the concentration in runoff during the July sampling (Figures 5c and 6c). The streambank mosses are deemed

to be the most likely source of the additional MeHg needed to reach the concentrations in the July 23 runoff. During the October sampling, the increased MeHg levels in the soil solution from the riparian zone of Västrabäcken were sufficient to generate the runoff concentrations of MeHg. No such difference between the October and July MeHg concentrations was observed in the podzol (PDZ) soil profile.

Although MeHg, Hg-tot and TOC output from the V and MK subcatchments differed during the year, no clear differences in the chemistry of soil solution in the riparian peat profiles (RIV and RIK) were apparent in the July 23 sampling, despite the greater lateral flux and depth of the peat in the Kallkällbäcken riparian zone.

The large capacity of the streambank mosses to hold and release TOC, MeHg and Hg-tot may serve not only as a source of these elements, but also as a buffer which can modify the chemistry of the water entering the stream. For example, neither the increase in Hg-tot from the mire (Site M) nor the decrease in MeHg output from the mire during the July event was manifested downstream at Site K where over a third of the water is from the mire (Bishop *et al.*, 1995). The bank mosses could have counteracted the changes in mire runoff chemistry by absorbing Hg-tot and releasing MeHg, thus keeping the stream at Site K close to the MeHg/Hg-tot concentrations that obtained prior to the episode.

The central question in this study about MeHg output from catchments is the extent to which contemporary atmospheric deposition of MeHg is related to output. The majority of the catchment, and over 70% of the forested MK and V subcatchments are covered by podzol soils. The concentration of MeHg leaving these areas (as represented by the PDZ profile) is too small to account for the output from the MK and V subcatchments at the time of sampling.

Extrapolating these observations to the annual budget reveals a similar shortfall. Assuming that the concentrations of MeHg in the PDZ profiles from October 1992 and July 1993 are approximately the average concentrations under the podzol soils, and that the distribution of total annual lateral flux is similar to that determined for the summer half of the year (Figure 4), then the mean concentration of MeHg moving laterally under the podzols in 0.12 ng l^{-1}. The volume-weighted mean annual concentration in runoff from the MK Subcatchment, on the other hand, was 0.3 ng l^{-1}, while the average concentration from the V Subcatchment was 0.22 ng l^{-1} (Lee *et al.*, 1995). Thus another source of MeHg is required to account for the concentrations of MeHg in runoff.

Given that extractions of soil solution by centrifugation and measurement of MeHg in unfiltered samples are apt to err on the side of overestimating the concentration in soil solution moving across the profile, the shortage of MeHg coming from the podzol soils may be greater than estimated. The only potential source of MeHg lying along the flow pathways between the podzol soils and the stream are the organic-rich riparian soils and the stream bank mosses. The balance of the MeHg needed to achieve the concentrations in runoff is thus hypothesized to arise in the riparian zone.

The extent of this zone is limited, so the net MeHg output per unit area is higher than that for the podzol soils. Assuming that the riparian zone extends 10 m to either side of the stream and that the concentration of MeHg in water leaving the upslope podzols is 0.12 ng l^{-1}, then, during 1993, 0.5 mg $ha^{-1}yr^{-1}$ would come from the podzols, while 8.9 mg $ha^{-1}yr^{-1}$ would leave the 2 ha of riparian zone on the MK Subcatchment. 2.1 mg $ha^{-1}yr^{-1}$ would leave the 2 ha riparian zone on the V catchment. The output from

the M Subcatchment (only half of which is mire) was 1.65 mg $ha^{-1}yr^{-1}$ (Lee *et al.*, 1995b).

The preliminary atmospheric input for this catchment is 3 mg $ha^{-1}yr^{-1}$ (Lee *et al.*, 1995a). This could be a significant input to the soil solution even in the riparian zone, but the high concentrations in the superficial soil layers make it unclear that the concentration of MeHg in water infiltrating into the soil is a function of the contemporary atmospheric deposition. Net methylation of contemporary Hg deposition or mobilization of the large MeHg/Hg pools in the soil are both potential sources of MeHg in runoff that are alternatives to contemporary MeHg deposition.

Regardless, however, of the proximal source of the MeHg which enters runoff in the riparian zone, it is the processes located in the riparian zone that have a central role in determining the amount of MeHg reaching surface waters from the forested subcatchments. Stream bank mosses may also play a major role, either as an area of net MeHg production, or as a store that can buffer changes in stream chemistry.

Acknowledgments

The authors would like to thank Magnus Edström, Sam Bishop and Agnetha Plamboeck for their assistance with the fieldwork, as well as Emma Lord for her painstaking care with the Hg-tot/MeHg analyses. The long-standing support of the Svartberget Forest Research Station is also gratefully acknowledged. This research was made possible by a grant from the Swedish Environmental Protection Agency.

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Methylmercury Output from the Svartberget Catchment in Northern Sweden During Spring Flood

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Abstract. The problem of mercury (Hg) accumulation in the aquatic food chain is widespread in Sweden. The methylmercury (MeHg) in runoff from catchments may be an important component of the MeHg load in surface waters. The spring flood in northern Sweden constitutes a major portion of the annual catchment runoff. This brief, but large event, therefore, may be of significance for the annual output of MeHg from soils to surface waters in this region.

Methylmercury, total mercury (Hg-tot) and other chemical parameters were measured in spring flood runoff during April and May 1993 from two tributaries as well as the headwater mire of the 50 ha Svartberget Catchment. Snow cores from April 1993 and April 1994 prior to the onset of spring snowmelt were also analyzed. Stable isotope techniques were used to estimate the proportion of snowmelt in runoff.

During the spring flood, Hg-tot and TOC were diluted in output from the headwater mire compared to the concentrations observed prior to the flood. Over half of the runoff from the mire was snowmelt according to the isotope hydrograph separation. In runoff from the two forested tributaries, however, TOC and Hg-tot concentrations increased. About a third of this runoff was snowmelt. MeHg concentrations in the spring flood declined at all locations to the lowest levels recorded during 1993 (<0.2 ng l^{-1}). The runoff concentrations of MeHg were less than the average snow core concentration of 0.34 +/- 0.17 ng l^{-1}. The differences in MeHg dynamics in comparison to TOC or Hg-tot suggest that there are factors independent of the availability of Hg-tot or TOC, and even contemporary MeHg deposition (in this case the snowpack MeHg concentrations) which determine the concentrations and output of MeHg during spring flood.

1. Introduction

Mercury (Hg) contamination of surface waters is widespread in Sweden (Håkansson *et al.*, 1990). This makes it of interest to locate the sources of the Hg in the aquatic food chain. Of primary importance is the source of methylmercury (MeHg), which is the species of Hg most prone to accumulation in fish (Boudou and Ribeyre, 1990). Potential sources of Hg/MeHg are direct inputs from the atmosphere, release from sediments or runoff from the terrestrial environment. More budget studies are needed to determine the relative contributions of such sources to the MeHg loading of the aquatic ecosystem. A budget study from southern Sweden, however, suggests that as much as half of the MeHg loading could originate in runoff from the surrounding catchment (Iverfeldt and Johansson, 1988; Lee and Iverfeldt, 1991). The positive correlation between the catchment/lake area ratio and Hg content in fish that has been found in Sweden (Nilsson and Håkansson, 1992) may also be related to the importance of terrestrial outputs. Since a large store of anthropogenic Hg has already accumulated in the soils (Aastrup *et al.*, 1991), the terrestrial storage is a classic example of a so-called "chemical time-bomb" since even a small alteration in the mobility of this pool could have major repercussions for Hg accumulation in the aquatic food chain.

The transfer of Hg/MeHg from soils to surface waters is associated with the output of water from the soil. In the boreal region where unacceptable levels of Hg in fish are

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disturbingly widespread, the output of water from the catchment during the spring flood is of special significance. Much of the annual precipitation comes as snow, much of which melts during a few weeks in the spring. This generates a flood hydrograph which accounts for a large proportion of annual runoff. The chemistry of runoff during this period is often of interest because of the presence of sensitive developmental stages for many aquatic species. In the case of MeHg inputs to surface waters, though, it is the large potential for transfers of MeHg from the terrestrial to the aquatic ecosystem during spring flood that is of particular importance.

In this study, the outputs of total mercury (Hg-tot) and MeHg from two tributaries and a headwater mire on the forested Svartberget catchment in northern Sweden during spring snowmelt were quantified. The results are evaluated in relation to other chemical parameters and the annual subcatchment output budgets presented by Lee *et al.* (1995a,b), as well as a rain-driven episode which occurred during July 1993 (Bishop *et al.*, 1995).

2. Study Site

The 50 ha Svartberget catchment is located in northern Sweden (64° 14' N, 19° 46' E) where the average annual temperature is 0° C. The catchment is afforested with Norway Spruce (*Picea abies*) in low-lying areas and Scots Pine (*Pinus sylvestris*) on higher ground. There is an 8 ha mire at the upper end of the catchment. This mire drains into Kallkällbäcken, which is one of two tributaries on the catchment (Figure 1). The other tributary is Västrabäcken.

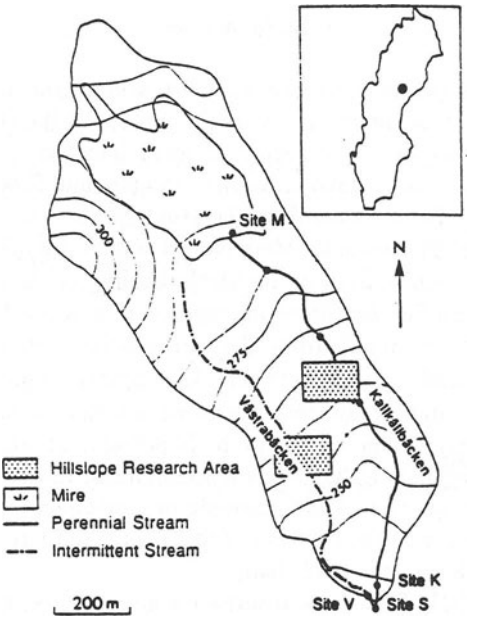

Fig. 1. The Svartberget Catchment showing the location of the sites where flow and chemistry were measured or calculated.

The catchment is covered by several meters of glacial till upon which podzol soils have developed (Grip and Bishop, 1990). These podzol soils give way to riparian peats in the vicinity of the tributaries. Both tributaries were straightened and deepened to a depth of approximately 1 m during the 1930's. A complete description of the site may be found in Bishop (1991).

Ten years of data on precipitation and runoff at the outlet of the catchment are available. The annual average precipitation over that period has been 718 mm, about a third of which fell as snow. The annual runoff has averaged 325 mm, with the difference (393 mm) attributed to evapotranspiration. Half of the runoff has occurred between June 1 and November 31, which corresponds roughly to the snow-free half of the year. One-third of the annual runoff occurs in the three weeks of highest flow during spring flood in April and/or May.

3. Methods

Hourly runoff over a 90° V-notch weir was measured at Site M where the 8 ha mire and an additional 7 ha of surrounding till soils drain into Kallkällbäcken; Site V just above where the Västrabäcken tributary joins Kallkällbäcken, and at Site S which is the outlet for the whole catchment (Figure 1, Table I). Flows at Site K on Kallkällbäcken just above its confluence with Västrabäcken were calculated from the difference in flow at Sites V and S. Subcatchment areas were calculated on the assumption that output per unit area from each subcatchment was the same over the course of the year. Site S is a year-round monitoring station which uses a siphon to shunt streamflow into a heated enclosure where the weir is located. During the 1993 spring flood reported here, automatic flow measurements began at Sites V and M on April 23.

Stream chemistry was sampled at sites M, V and K. The water was not filtered, so as to avoid a potential source of sample alteration. The difference between the total organic carbon (TOC) in unfiltered samples and dissolved organic carbon (DOC) after filtration with a 0.45 μm filter is typically less than 10% at Svartberget. Separate Hg-tot and MeHg samples were collected in 100 ml Teflon or Pyrex flasks which had been cleaned according to trace-metal free protocols. The Hg-tot samples were preserved immediately with 1 ml of suprapure HCl in each 100 ml sample. The MeHg samples were preserved by the Swedish Environmental Research Institute (SERI) at Gothenburg within 72 hours of sampling. Both Hg-tot and MeHg concentrations were measured at SERI using analytical methods described in Lee, *et al.*, (1995b).

The amount and chemistry of runoff from the forest soils on Kallkällbäcken below the mire were estimated from the differences in flow and chemistry at Sites M and K (referred to as Subcatchment MK, Table I). This calculation assumed that the chemical constituents of runoff were neither lost to nor gained from the streambank or atmosphere.

Methylmercury measurements were made in the snowpack at three sites: one was an open field, the second was in a pine stand, and the third was in a spruce stand. A snow core was taken from each site and allowed to melt in an open plastic bag that had been rinsed in a weak acid solution. The melted snow cores were then transferred to acid-washed bottles for storage until analysis.

To assess the proportion of runoff that was fresh snowmelt, oxygen isotope ratios were measured weekly in the snow pack and in the streamwater in conjunction with Hg-tot/MeHg sampling. Isotope hydrograph separation was used to determine the amount of snowmelt in runoff (X) using Equation (1).

$$X = 1 - \left(\frac{C_r - C_s}{C_p - C_s} \right) \tag{1}$$

C_p is the oxygen isotope ratio of the "pre-event" water stored within the soil prior to the spring flood, C_s is the isotope ratio of the snowmelt and C_r is the isotope ratio in runoff, which is treated as a mixture of snowmelt and pre-event water. The value of C_p was set equal to the isotope ratio of streamwater during low flow prior to spring flood, and C_s was estimated from the snowpack samples. A description of the theory behind this hydrograph separation and the separation of several spring floods in Sweden may be found in Rodhe (1981, 1987).

4. Results

The spring flood commenced on April 23, 1993 and proceeded without interruption into mid-May. In this study, the elemental output budgets for spring flood were calculated for the three-week period between April 23 and May 14, 1993.

There was a strong diurnal variation in runoff which is not apparent in figures for daily flow (c.f. Figure 2 with average daily flows and Figure 3 with hourly flows). Water samples were taken in the afternoon near the peak of each day's flow. The amount of runoff from the catchment during the three weeks of spring flood was 99 mm, or 27% of the 1993 runoff (Table I). This was lower than the 14 year average spring flood of 116 mm, or 36% of annual runoff). The peak proportion of snowmelt water in runoff indicated by IHS was 60% from the mire and 40% from the forested parts of the catchment (Figure 2). The mire runoff also comes earlier than that from the other subcatchments.

Table I

Relative Contribution of Spring Flood to the Catchment Output Budget[1]

Subcatchment	Area	Spring Flood as a Percentage of Annual Output			
	(ha)	Water	TOC	Hg-tot	MeHg
M (Mire)	14.8	31	20	29	8
V (Västrabäcken)	8.6	29	33	37	10
MK (Kallkällbäcken below the mire)	26.2	23	22	36	16
S (whole catchment)	49.6	27	22	34	12

[1] Annual output values are from Lee *et al.* (1995b)

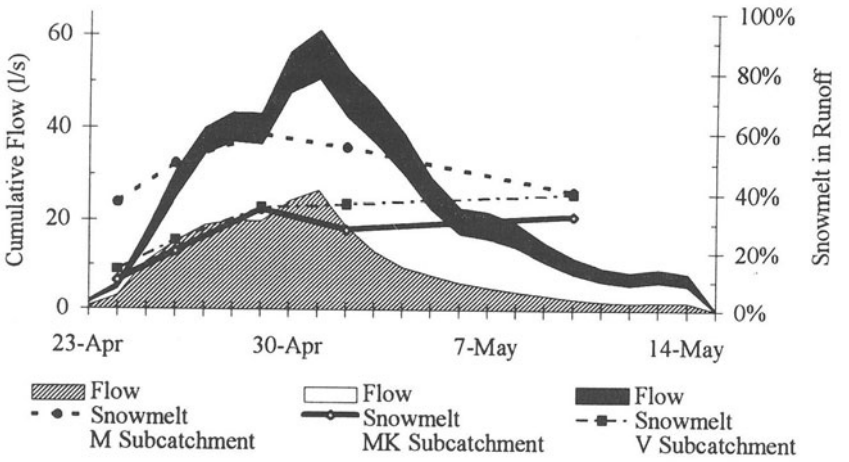

Fig. 2. Daily average runoff from the different subcatchments during the spring flood (shaded areas on diagram with vertical axis to the left) and the percentage of snowmelt in runoff as estimated from isotope hydrograph separation (lines on diagram with vertical axis to the right).

With the onset of spring snowmelt, pH fell from above 5.5 at sites A and V to 4.2 at A and 4.5 at V during the peak of spring flood (data not shown). By late May, pH at these sites had returned to ca. 5. At Site E, pH was lower prior to snowmelt (4.7) and fell to 4.0 during the flood peak before climbing to 4.5 in late May.

The measured equivalence of cations (Mg^{2+}, Ca^{2+}, Na^{+1}, K^{+1}, H^{+1}, $NH4^{+1}$ but excluding Al and Fe) exceeded the measured equivalence of anions (Cl^{-1}, $NO3^{-1}$, $SO4^{2-}$) by more than 100 ueq/l at all three sampling sites both prior to, during and after spring flood. That measured anion deficit was at least a third of the total negative equivalence in the stream water. That difference is attributed to organic ions (Bishop, *et al.*, 1990, Grip and Bishop, 1990). This is one indication of the importance of TOC for the chemistry of surface waters at Svartberget and northern Sweden in general (Kullberg *et al.*, 1993). The estimated concentration of dissociated organic functional groups per mg TOC during April and May in the streamwater samples varied between 6 and 8.

The pattern of TOC in runoff from the forested V and MK subcatchments differed from that in the mire runoff during the spring flood (Figure 3a). Prior to the spring flood, and thereafter, TOC concentration was highest in the output from the mire at Site M (over 30 mg l^{-1} in early April), but after a small initial increase TOC declined at Site M during spring flood to a minimum under 15 mg l^{-1}. Runoff from subcatchments V and MK, on the other hand, increased in TOC concentration during spring snowmelt relative to the concentrations at low flow both prior to spring flood and after the spring flood. The concentrations of TOC in runoff from the MK and V subcatchments were similar during the spring flood itself, climbing to a peak of 30 mg l^{-1} during the onset of the flood, tapering off to 25 mg l^{-1} at the peak flow, and then continuing that gradual decline through the falling limb of the spring flood hydrograph.

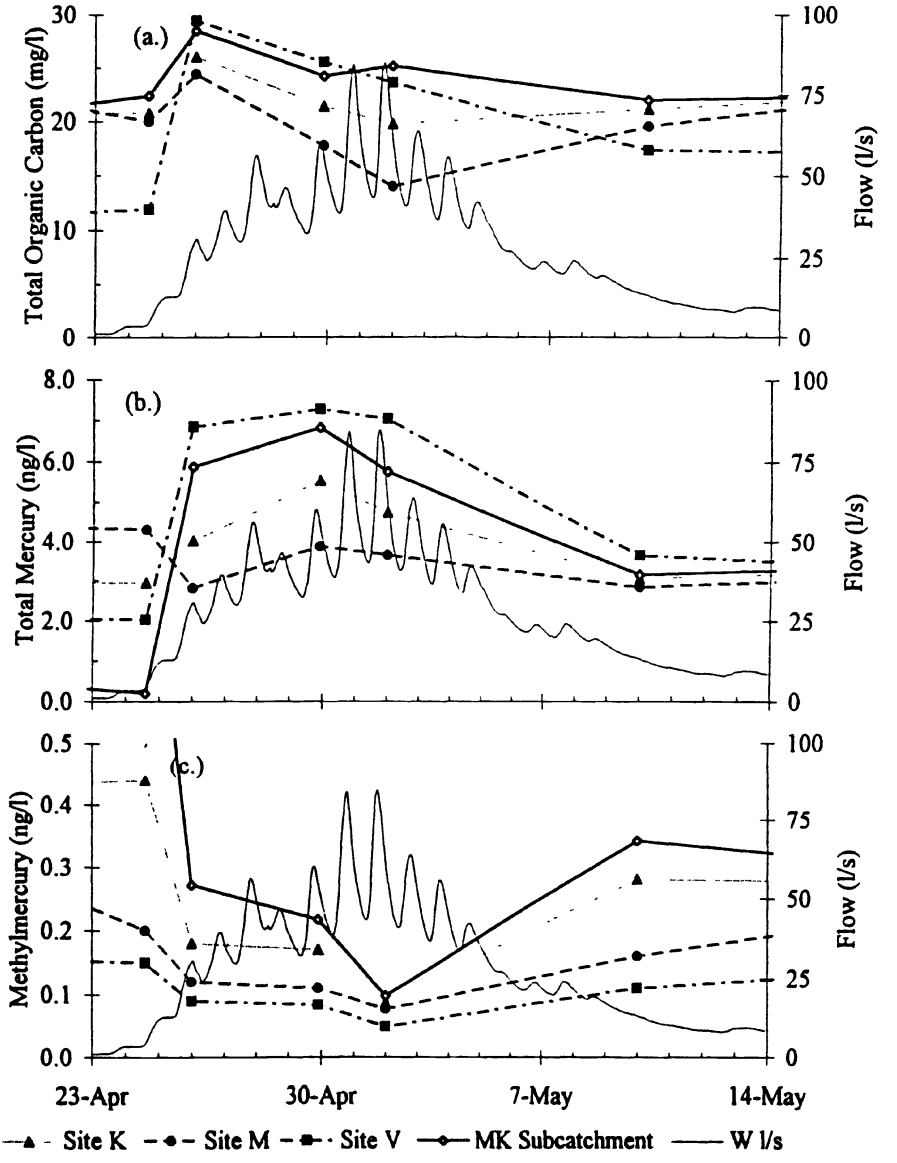

Fig. 3. Measured and calculated concentrations in the different subcatchments during the spring flood (a.) TOC, (b.) Hg-tot and (c.) MeHg. Hourly runoff from the catchment at Site S is included on each plot for reference.

Total mercury concentrations also increased in the runoff from the forested subcatchments during snowmelt (Figure 3b). The Hg-tot concentration increased from below 2 mg l^{-1} in the MK and V subcatchments to a peak of over 6 ng l^{-1} during the early part of the spring flood before receding to between 3 and 4 ng l^{-1} by the end of the flood. The output from the mire declined somewhat from just above 4 ng l^{-1} prior to the spring flood to under 3 ng l^{-1} on the falling limb of the flood hydrograph.

Methylmercury concentrations, unlike those of TOC and Hg-tot, declined at all sites (Figure 3c). The lowest concentrations in streamwater during 1993 were observed just after the peak of spring runoff (< 0.1 ng l^{-1}). Concentrations increased to between 0.1 and 0.4 ng l^{-1} at different sites by the end of the spring flood. The concentrations in mid-May on the MK Subcatchment were similar to the annual mean, volume weighted subcatchment runoff concentration of 0.30 ng l^{-1}. At the same time, concentrations from the V and M subcatchments were still well below the volume-weighted annual means of 0.22 ng l^{-1} for the V Subcatchment and 0.42 ng l^{-1} for the M Subcatchment (Lee *et al.*, 1995b).

The MeHg in the snow pack was sampled on April 7, 1993 and April 25, 1994 prior to the onset of spring snowmelt (Table II). The concentrations varied from 0.11 to 0.58 ng l^{-1} with an average value of 0.34 +/- 0.17 ng l^{-1}.

Table II

MeHg Concentrations in Snowpack

	MeHg (as ng l^{-1} Hg)		
Date	Open Field	Pine Stand	Spruce Stand
April 7, 1993	0.37	0.15	0.54
April 25, 1994	0.11	0.41	0.46

5. Discussion

The amount, timing and major ion chemistry of the 1993 spring flood were within the range of what has been observed during spring floods in the preceding eight years at Svartberget.

The decrease of MeHg concentration with flow at all locations throughout the spring flood suggests a limitation of MeHg available for transport. The decrease in MeHg occurred despite the presence of MeHg concentrations in snowpack well above the concentrations seen in runoff and a large proportion of snowmelt in the runoff.

A similar dilution of MeHg with flow occurred during the July episode (Figure 4). The concentrations during the July episode, however, remained higher than those at similar runoff levels during spring flood. (Bishop *et al.*, 1995). This results from what appears to be a seasonal influence on MeHg concentrations in runoff upon which flow related changes in MeHg concentration are superimposed. There was, though, more variation in the response among the subcatchments during the July episode and the rain-driven episode generated considerably less runoff than spring flood.

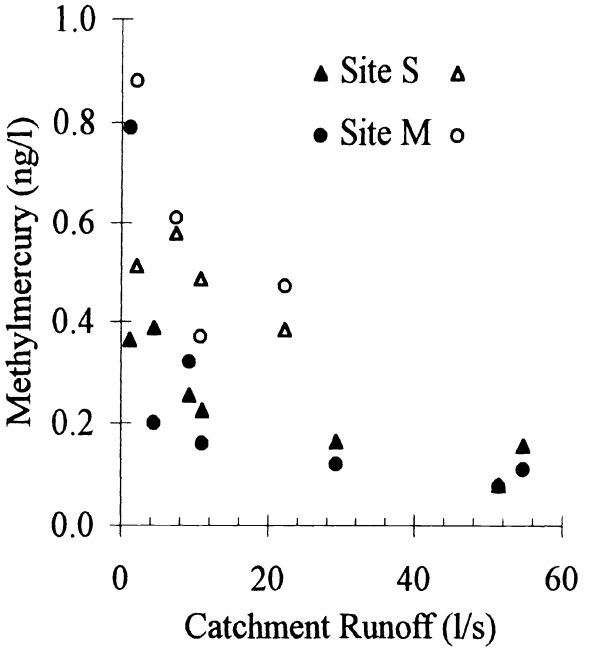

Fig. 4. Relationship between flow and MeHg concentration during spring flood (filled symbols) and the July rain episode (open symbols) described in Bishop *et al.*, (1995).

Decreases in concentration are common for many mineral elements during spring flood (Ca concentrations, for example, decreased by 50% during the 1993 spring flood.). Such source limitations, however were not apparent in runoff from the forested V and MK subcatchments for TOC or, to a lesser extent Hg-tot. Concentrations of both these substances were greater during the spring flood than during the low flow prior to the flood. The mire, on the other hand, had lower concentrations of TOC and Hg-tot in the spring flood relative to the elevated concentrations observed prior to the spring flood. The decrease in concentration of these elements from the mire may have been related to the larger throughput of snow which had negligible amounts of TOC, while more of the runoff from the forested subcatchment was displaced from the soil.

The negative covariation of MeHg with flow during spring snowmelt and a positive correlation for TOC led to a decline in the ratio of MeHg per mg TOC during spring flood to under 0.01 ng MeHg per mg TOC. During the rest of the year the ratio varied from 0.01 to 0.04 (Pettersson *et al.*, 1995).

The contribution of spring flood to the annual output of MeHg from the catchment as a whole (12%) is smaller than the contribution of spring flood to the output of water (26%) (Table I). The output from the mire (M) subcatchment is even lower, with under 10% of the annual output occurring during the spring flood. The relative output of TOC and Hg-tot is higher in the runoff, with 34% of the annual Hg-tot output from the catchment occurring during spring flood. The catchment output of TOC was comparable

to that for water (23%). The proportion of TOC output varied within the catchment from over 30% of the V output occurring during spring flood to 20% of the mire output.

Monthly Hg-tot output from the catchment peaked during the spring flood. As a result of the negative covariation between MeHg and flow during spring flood, though, MeHg output did not peak in the spring (Lee *et al.*, 1995b). The concentration and output of MeHg in runoff subsequently increased during the summer with catchment output reaching a monthly maximum in August. Even though MeHg output during the spring flood at this site was relatively small, however, the large flux of water will amplify the effect of concentration changes on MeHg output to surface waters. Thus even modest increases in the concentration of MeHg during this period would be of significance to the annual MeHg output budget.

6. Conclusions

The spring flood is of singular importance for the output of water and its constituents in the boreal region. Thus the dynamics of Hg-tot and MeHg concentrations during this period exert a large influence on the total amount of Hg-tot/MeHg reaching surface waters from boreal catchments.

Despite the high runoff rate, TOC and Hg-tot concentrations in runoff from the forested subcatchments of the Svartberget Catchment actually increased during the spring flood. This resulted in a large proportion of the TOC and Hg-tot output coming during the spring snowmelt. An important exception to that general pattern was a decrease in the concentration of TOC in water leaving the headwater mire. During the spring snowmelt period, the concentration of TOC in the mire runoff was lower than from the other two forested subcatchments, even though the mire runoff had the highest average annual TOC concentrations.

Methylmercury concentrations, by contrast, were sharply reduced during spring snowmelt at all sites. The decrease in MeHg concentrations occurred despite indications that the concentrations of MeHg in snowmelt were higher than the concentrations in runoff. Even in the mire, where some 60% of the peak flow was snowmelt, the runoff concentrations of MeHg were lower than the values measured in the snowpack. More comprehensive measurements of snowpack MeHg concentrations, however, would be desirable to strengthen that conclusion.

The differences in MeHg dynamics in comparison to TOC or Hg-tot suggest that there are factors independent of the availability of Hg-tot or TOC, and even contemporary MeHg deposition (in this case the snowpack MeHg concentrations) which determine the concentrations and output of MeHg during spring flood. Furthermore, the rate of those processes which make MeHg available for hydrological transport out of the soil are too slow during the spring to maintain, much less increase MeHg concentration during spring snowmelt. This is the case even though the principal flow pathways followed by spring runoff are most likely superficial and rich in both Hg-tot and TOC.

Acknowledgments

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SUBCATCHMENT OUTPUT OF MERCURY AND METHYLMERCURY AT SVARTBERGET IN NORTHERN SWEDEN

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ABSTRACT. The subcatchments of two tributaries and the headwater mire of the 50 ha Swartberget catchment were studied Monthly sampling was conducted during 1993 on the two tributaries and at the outlet of a mire This was complemented by more intensive sampling during spring flood and a rain-driven episode at the end of July Samples were analyzed for total methylmercury (MeHg), total mercury (Hg-tot) and TOC The MeHg and TOC content of water were also fractionated into humic and non-humic components Outputs budgets based on continuous flow monitoring and monthly volume weighted average concentrations of MeHg/ Hg were calculated for the subcatchments of the two tributaries and the mire There was a pronounced decline in MeHg concentrations at all sampling locations during the spring flood A clear pattern of the seasonal variation in the MeHg outputs was evident at all three sampling locations Minimum MeHg concentrations occurred during spring flood and increased during the summer to peak levels in the autumn before tapering off during the winter (except for at the mire) The mire had larger increases in MeHg concentrations during the summer and did not decline during the winter The warmth and increased soil humidity may promote the biogeochemical processes, including methylation, demethylation which make MeHg available for export by runoff from the soil Variations in Hg-tot concentrations were differed from MeHg in streams that there were increases in Hg-tot concentrations with flow during both spring flood and the July rain event in runoff from the forested tributaries

The highest outputs of both humic and non-humic MeHg occurred during summer from all subcatchments Those high outputs extended into the autumn at the mire The largest monthly output of Hg-tot was during the spring flood period and the next largest was during the period of summer rainfall Despite the similarity in mineralogy and atmospheric deposition on the two tributary subcatchments, there was ca 30% larger ouput of MeHg per unit area from the tributary which had deeper riparian peats The output of Hg-tot, however, was higher on the catchment with the shallower riparian peats The difference in the geometry of the riparian zone may contribute to these differences in output The annual output concentrations at the mire outlet of MeHg was 0 65 ng /L and of Hg-tot was 4 04 ng/L In the main tributary MeHg was 0 42 ng/L and Hg-tot was 3 64 ng/L In the Vastrabäcken tributary, the mean MeHg concerntration was 0 25 ng/L and the Hg-tot concerntration was 4 02 ng/L Among the three subcatchments the largest annual output fluxes of MeHg were from the mire, 0 16 g/km2*yr, the next from Kallkällbäcken below the mire, 0 12 g/km2*yr, and the lowest from Västrabäcken, 0 08 g/km2*yr

1. Introduction

A small percentage of the total mercury (Hg-tot) (<0.02%) and methylmercury (MeHg) (<0.2 %) in soil is transported annually in runoff from forest soil to surface water (Lee *et al.*, 1994a; Hultberg *et al.*, 1994; Aastrup*et al.*; 1991). Nevertheless, this terrestrial output via runoff water to drainage lakes has been recognized as an important source of MeHg and total Hg in remote lakes in Sweden (Iverfeldt and Johansson, 1988; Lee and Hultberg, 1990; Lee and Iverfeldt, 1991). The dissolved natural organic substances (DOC) are important factors regulating the concentrations of MeHg and total Hg in runoff water (Iverfeldt and Johansson, 1988; Lee and Hultberg, 1990; Lee and Iverfeldt, 1991). Other factors such as limestone treatment of soil, acidification of soils and waters, and extensive peatlands in a catchment seem to be of less importance (Johansson *et al.*, 1991) in

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regulating the transport of Hg from the drainage area. Little is, however, known about the factors controlling the transfer/transport of MeHg and total Hg from soil to runoff, especially the hydrological factors and catchment characteristics such as the extent of peatland and character of the riparian zone. Research at the Svartberget Research Catchment has demonstrated how important the interplay between DOC source areas and the hydrological transport is to the distinct seasonal and flow-related changes in DOC concentration and character (Bishop *et al.*, 1994).

This paper analyzes the subcatchment MeHg/Hg-tot output dynamics in streamwaters over the course of a year. Companion papers in this volume consider in more detail the influence of the riparian zone geometry on subcatchment output (Bishop*et al.*, 1995a), the dynamics of spring flood (Bishop*et al.*, 1995b), and a rain driven episode (Bishop *et al.*, 1995c), as well as the relationship between TOC and MeHg in runoff (Pettersson *et al.*, 1995).

2. Study Site and Methods

2.1. SITE DESCRIPTION

The study was conducted in the 50 ha Svartberget catchment (Figure.1) in northern Sweden (64 14' N,10 46'E.). The catchment is forested with mature Norway spruce in the lower parts and Scots pine at higher elevations on podzol soil. Slopes range from 5 to 10 %, and the soils have developed on a till overburden that is several meters thick. Mean annual temperature in the area is 0°C with an average annual precipatation of 720 mm, of which roughly half is snow. Annual runoff from the catchment is 330 mm, with a mean pH of 4.4.

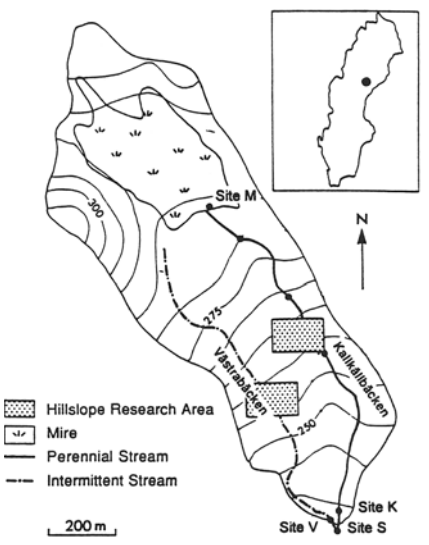

Figure 1 The Svartberget Catchmeht showing the location of the sites where flow amd chemistry were measured

There are two tributaries, Kallkällbäcken and Västrabäcken. The Kallkällbäcken tributary starts at the outlet of a mire. The area of the mire (8 ha) and including the surrounding subcatchment is 15 ha. The Kallkällbäcken subcatchment below the mire is 26 ha in area, and the Västrabäcken tributary is 8 ha in area. The demarcation of the boundary between these two forested catchments was based on the analysis of runoff from each subcatchment using the assumption that runoff per unit area was the same. This assumption is based on the similarities in physiography, vegetation and soil parent material in the two subcatchments.

Much of the riparian zone along the length of both tributaries is covered by peat 20 to 80 cm in depth overlaying a mineral soil enriched in DOC. The riparian zone along Kallkällbäcken consisted of deep peat (40 to 80 cm in depth 12 m away from the stream) twice as much as along Västrabäcken. Both streams were ditched to about the same depth (ca. 1 m) during 1930's. The deep peat profiles create streambanks consisting almost completely of peat, wheras the shallow peat profiles (20 to 40 cm in depth) have mineral soil on the lower sections of the streambank.

2.2. SAMPLING AND ANALYSIS

Hourly runoff was measured with a pressure transducer behind a 90° V-notch weir at Site M, V, K and S (Site S is the outlet for the whole catchment). Output of flow and chemistry from the forest soils on Kallkällbäck below the mire (refered to as Subcatchment Mk, Table I) were estimated from the differences in flow and chemistry at Site M and K.

Table I

Subcatchment Areas*

Subcatchment	M	K	V	MK
Area (ha)	14.8	41.0	8.6	26.2

* The area of the whole catchment (Site S) is 49.6 ha.

Sampling was performed monthly for MeHg and Hg-tot and weekly for TOC at Sites K and V on the the two tirbutaries, as well as at the mire outlet (Site M) during the period January 1 to December 31, 1993. More intensive sampling was conducted during the spring flood (April 4 to May 9) and a rain storm episode (July 23 to 28). The humic fraction of TOC was isolated on a weak anion-exchange resin, diethylaminoethyl-sephadax-A25 (Pharmacia Fine Chemical) in a batch procedure (Pettersson *et al.*,1993). After a contact time of 20 minutes the supernatant was decanted and collected. This supernatant is considered to be the non-humic fraction of the sample. Due to the problems usually connected to an ultra-low Hg level (picogram amounts) and arising from the high content of humic substances in water samples, care was taken to choose an appropriate and validated pretreatment procedure to isolate MeHg from the sample matrix as well as a sensitive detection system (Lee *et al.*,1994b, 1994c). The GC-CVAFS technique with aqueous phase ethylation and using distillation preseparation steps (Bloom, 1989; Horvat *et al.*, 1988) were used to determine the concentrations of MeHg and non-humic MeHg (MeHg in non-humic fraction of TOC) in water samples. Verification of the analytical procedures was performed using analysis of certified reference materials and the method of standard addition. The concentration of humic MeHg (MeHg in humic fraction of TOC) was calculated by substraction of non-humic MeHg from the total MeHg. The extensive cleaning procedure, which is part of the water sample collection and analytical method for Hg-tot used in the present study, has been described previously (Bloom and Crecelius, 1983; Iverfeldt, 1991) TOC was analysed with a Shimadzu TOC-5000 analyzer utilizing catalytic combustion and absorbance at 254 nm was measured with a Beckman

DU-8 spectrophotometer. The absorbance measured at 254 nm gives a measure of the content of humic substances in the water.

3. Results and Discussion

3.1. AVERAGE CONCENTRATIONS OF MeHg , HUMIC MeHg AND Hg-tot IN RUNOFF

In the study period from January to December 1993, the mire outlet had highest average concentrations of MeHg. The Västrabäcken tributary had lowest MeHg and MeHg in the humic fraction of TOC among the sampling locations, but the Västrabäcken tributary had a Hg-tot value that was almost as high as that from the mire (Table II).

Table II

Average volume-weighted concentrations of MeHg and Hg-tot, and the percentages of MeHg in humic fraction of TOC in the runoffs as well as the range of the measureed concentrations.

Runoff	MeHg, ng/L (range of meas conc.)	Hg-tot, ng/L (range of meas. conc.)	MeHg in humic fraction, (%)
Mire outlet	0.65 (0.1-1.4)	4.04 (2.1-6.0)	63
Kallkällbäcken	0.42 (0.1-0.6)	3.64 (1.3-5.5)	67
Västrabäcken	0.25 (0.1-0.4)	4.02 (1.3-7.3)	44
Kallkällbäcken below the mire	0.30	3.49	70

3.2. SEASONAL VARIATION IN CONCENTRATIONS AND OUTPUT FLUXES

The concentrations at all three sampling locations had similar trends in the variation of MeHg and Hg-tot concentration though the amplitude of that variation differed (Figure 2).There were flow related changes in the episode MeHg and Hg-tot data (Bishop *et al.*1995b; 1995c) as well as a strong seasonal trend in the MeHg and humic fraction of MeHg which started from a minimum during spring flood and increased throughout the summer. That increase in concentration was largest and continued longest into the autumn at Site M, the mire outlet. The maximum values observed on December/Januaray at the mire outlet, during the July rain event in the Kallkällbäcken tributary and on August/September in the Västrabäcken tributary. The minimum Hg-tot value observed during the July rain event at the mire outlet and in the Västrabäcken tributary, and at the end of August on the Kallkällbäcken tributary. The maxiumum concentrations of Hg-tot occurred during the high flow at the begining of the June on all runoffs (Figure 2).

The monthly average concentration increase during the summer, which occurred despite large amounts of runoff, particularly in August, contributed to a progressive increase in the amount of MeHg exported per unit area from each subcatchment (Table III). This is in contrast to the spring flood where large runoff amounts were coupled with decreasing concentrations. This suggest that the availability of MeHg for export in runoff is seaonally variable. During spring flood there was a limitation of MeHg available for

transport. July and August are usually the warmest months in every year, and were also the wettest months during 1993. These conditions may promote the biogeochemical processes, including transferring MeHg/Hg from soil to soil water and methylation /demethylation, which control the net production of MeHg in soil/soil water and that, combined with runoff, lead to high rates of MeHg transfer from soil to streams. A similar seasonal variation in the MeHg outputs in runoff was also observerd from other forested catchment in Sweden (Lee and Hultberg, 1990; Hultberg *et al.*, 1994).

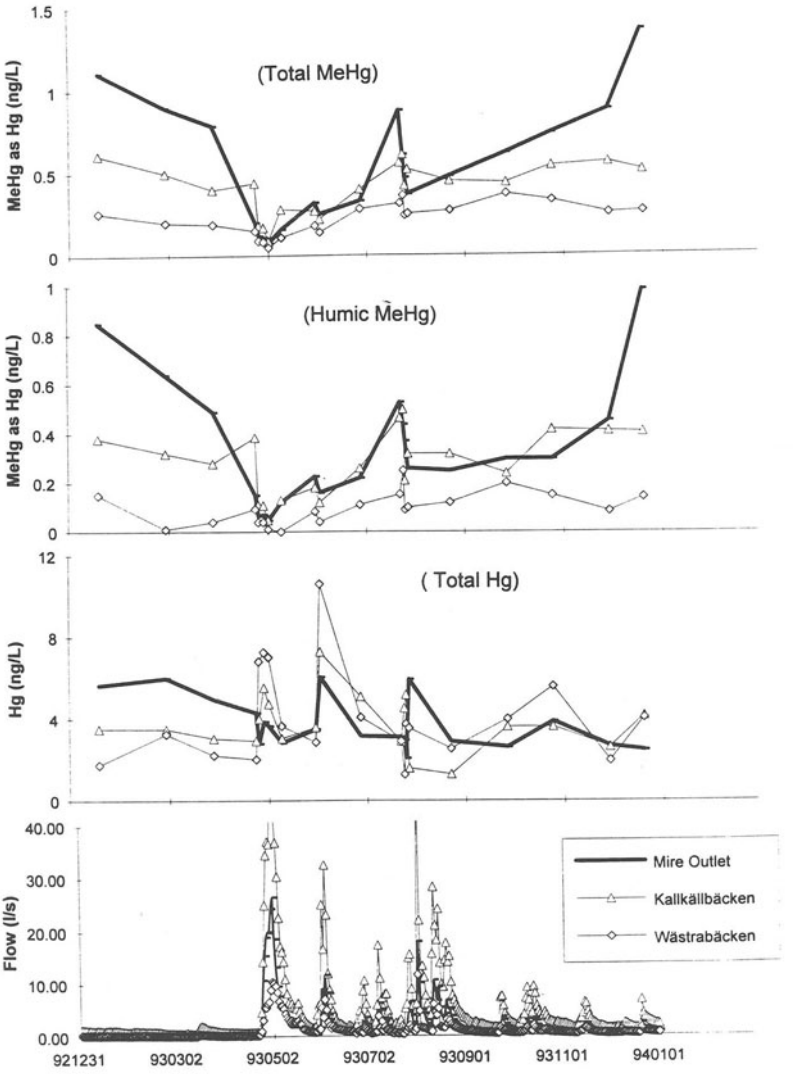

Figure 2 Seasonal variation of measured concentrations of MeHg, Humic MeHg, and Hg-tot in the different subcatchments Daily mean runoff from the catchment is included for reference

Table III

Monthly output (mg/km^2* month) of MeHg, Humic MeHg and Hg-tot in the different subcatchments
Monthly average concentrations of MeHg, Hg-tot and runoff from the catchment are also included

	Monthly flow (kilo liter/month)			MeHg (mg/km^2*month)			MeHg-hum (mg/km^2*month)		
	V	M	MK	V	M	MK	V	M	MK
Jan	693	1168	2090	2 0	8 6	2 6	1 1	6 6	0 9
Feb	475	802	1435	1 2	5 3	1 6	0 3	3 9	0 7
Mar	596	1005	1797	1 3	5 6	1 5	0 2	3 7	1 1
Apr	3513	10308	8607	3 8	9 6	9 2	1 6	6 0	6 6
May	9107	10484	18435	9 5	8 8	14 6	1 2	6 0	6 7
Jun	4249	6429	11060	8 7	12 2	11 6	2 7	7 9	6 9
Jul	2480	5592	9040	7 9	20 1	15 6	3 5	13 2	11 4
Aug	6291	12366	21594	25 6	36 1	28 3	14 7	21 3	15 8
Sep	1582	2737	4466	7 0	10 7	4 6	4 0	5 3	2 8
Oct	1954	3716	6894	7 5	17 4	10 4	3 5	7 5	9 9
Nov	1370	2311	4134	4 3	12 8	6 3	1 6	6 1	6 7
Dec	1261	2128	3805	3 6	17 8	1 6	1 7	12 4	2 2

	Hg-tot (mg/km^2*month)			Monthly average conc MeHg (ng/L)			Monthly average conc Hg-tot (ng/L)		
	V	M	MK	V	M	MK	V	M	MK
Jan	15	45	18	0 26	1 10	0 33	1 85	5 69	2 31
Feb	15	32	12	0 22	0 98	0 3	2 70	5 88	2 19
Mar	18	36	14	0 19	0 83	0 22	2 64	5 38	2 03
Apr	254	248	194	0 1	0 14	0 28	6 28	3 58	5 93
May	527	241	311	0 09	0 12	0 21	5 04	3 42	4 45
Jun	390	213	293	0 18	0 28	0 28	7 98	4 94	7 00
Jul	97	134	129	0 29	0 54	0 45	3 39	3 58	3 77
Aug	216	349	0	0 37	0 43	0 35	2 98	4 20	0
Sep	64	50	52	0 40	0 58	0 27	3 5	2 7	3 08
Oct	112	85	98	0 34	0 7	0 4	4 97	3 4	3 74
Nov	54	49	46	0 28	0 82	0 4	3 42	3 16	2 94
Dec	50	36	64	0 25	1 25	0 11	3 46	2 54	4 42

The seasonal effects leading to the progressing increase in concentration did not appear in the seasonal variation of Hg-tot monthly average concentrations. In the spring flood Hg-tot concentration variations increased with flow from the forest V and MK subcatchments, but decreased with flow from the M subcatchment (Figure 2 and Table III). The largest catchment outputs of Hg-tot per unit area came with the spring flood, and thus came earlier than the maxium MeHg outputs. This may explaine that a pronounced decline in the ratios of MeHg to Hg-tot occurred during the spring flood episode on the tributaries.

The proportion of non-humic MeHg also increased during the summer. The highest outputs of both humic and non-humic MeHg occurred during summer from all subcatchments. Those high outputs of non-humic MeHg decreased slightly in the autumn at the mire, but decreased largely in runoff from MK subcatchment (Figure 3).

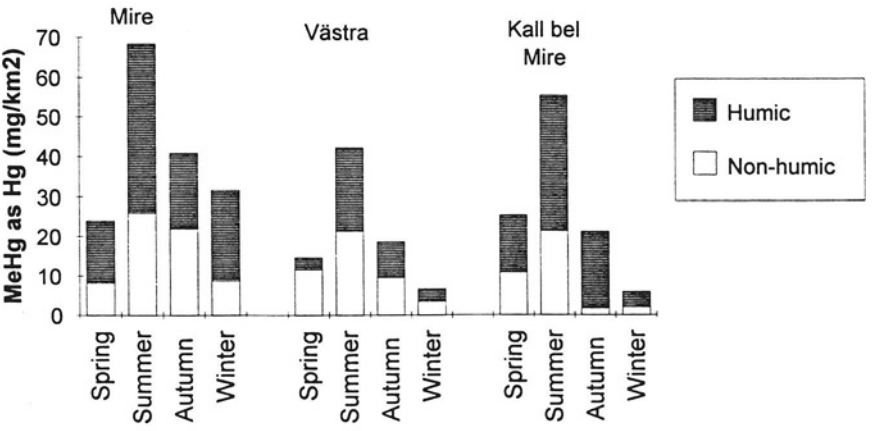

Figure 3. The seasonal output (mg/km^2) of humic and non-humic MeHg in the different subcatchments.

3.3. OUTPUT FLUXES OF MeHg, HUMIC MeHg AND Hg-tot FROM SUBCATCHMENTS

The low monthly outputs of MeHg and humic MeHg during winter and spring (before snowmelt) result from the low discharge. Outputs of MeHg began to increase with the spring flood even though concentrations decreased during the spring flood. The increase in monthly outputs continued over the summer, to reach maximum values in August when both discharge and concentrations were high (Table III). In contrast to MeHg the largest monthly output of Hg-tot occurred during the spring flood except in the mire where output peaked in August. Västrabäcken had the highest Hg-tot outputs among three subcatchments during summer period despite having the lowest MeHg output.

Among the three subcatchments the largest annual output fluxes of MeHg from the mire, the next from Kallkällbäcken below the mire and the least from Västrabäcken (Table IV). For the entire catchment the mire contributed almost 41 % of MeHg output and 47 % from the Kallkällbäcken below the mire and 12 % from the Västrabäcken which was similar to the area of each subcatchment, which were 30 %, 53 % and 17 %, respectively, of the total subcatchment.

Despite the similarity in mineralogy and atmospheric deposition of the two forested subcatchments V and MK, that MK had a ca. 30 % higher outputs of MeHg per unit area with deep riparian peat than the Västrabäcken , on the other hand, had a 39 % higher output of Hg-tot per unit area. The subcatcatchments differ in the depth of their riparian peats, with Kallkällbäcken having twice as much deep peat (great than 40 cm depth 12 m from the stream). The lateral flux of water through the riparian peat on Kallkällbäcken is also three times hgher than on Västrabäcken (Bishop *et al.,* 1995b, 1995c). These differences in the riparian zone may contribute to the differences in outputs on MeHg and Hg-tot. Among three subcatchments the mire had the highest output flux of MeHg and also highest ratio of MeHg to Hg-tot in output. The results also show that Västrabäcken had a low ratio (0.44) of humic MeHg to total MeHg compared to the ratio in th MK subcatchment (0.65) and the mire (0.61). Västrabäcken also had a lower ratio of MeHg to Hg-tot in outputs (0.55) as opposed to 0.09 in runoff from MK and the Mire (0.11).

Table IV

Annual output fluxes of MeHg and Hg-tot from subcatchment as well as the ratio of the MeHg to Hg-tot and the ratio of MeHg in humic fractions of TOC to total MeHg.

Subcatchment	MeHg	Hg-tot	MeHg/Hg-tot	MeHg-hum/MeHg
	$g/km^2 * yr$		ratio	ratio
M	0.17	1.5	0.11	0.61
MK	0.11	1.2	0.09	0.65
V	0.08	1.8	0.05	0.44
Whole catchment	0.12	1.4		

Comparing the output of MeHg and Hg-tot from these subcatchments with the Gårdsjön catchment in the southwestern part of Sweden having 0.12 $g/km^2 * yr$ of MeHg and 2.3 to 3.5 $g/km^2 * yr$ of Hg-tot, the subcatchments M and MK had similar output of MeHg but lower output of Hg-tot (Lee and Hultberg, 1990; Hultberg*et al.*, 1994) despite having much higher mean MeHg concentration and also TOC concentration. The much lower annual runoff from the Svartberget catchment, about 60 % of that from the Gårdsjön catchment, is the main explanation. The outputs of Hg-tot from the subcatchments were much lower than that from catchment in the southern areas of Sweden (Iverfeldt and Johansson, 1988), but in the same level as that from nothern areas. Catchments without lakes and with very little peatland were often found having high runoff amouts and higher output of Hg-tot, and catchment with extensive peatlands may reduce the Hg-tot output from the drainage area (Verta *et al.*,1986; Iverfeldt and Johansson, 1988).

3.4. MeHg/HUMIC MeHg IN RELATION TO TOTAL ORGANIC CARBON AND HUMIC SUBSTANCES

A positive correlation between MeHg and the content of humic substances in water was previously observed in different swedish streams (Lee and Iverfeldt, 1991; Lee and Hultberg, 1990) This suggests that the transfer/transport of MeHg from soil to runoff was closely related to the transfer/transport of organic substances. Similar relations were also found in the present study. It is interesting to note that the humic MeHg at all sampling locations showed a clear response to the content of humic substances in water. The total MeHg concentration, however, was only positively correlated to the content of humic substances in the mire outlet, but not in the Västrabäcken (Pettersson*et al.* 1995). That results from more than 50% of total MeHg occurring in the non-humic fraction of MeHg in the Västrabäcken (Table II). It suggests that when examining the relationship between MeHg and TOC, one should distinguish between the humic and non-humic fractions. The fraction of humic MeHg of total MeHg was about 0.70±0.1 and not correlated to the content of humic substances in the mire outlet and the main tributary (Figure 4). The fractions was, though, positively correlated in the Västrabäcken. The possible explanation is that both the concentration and the strength of complexation of humic substances/non-humic substances to MeHg are important factors for the final equilibrium concentrations of humic and non-humic MeHg. Due to high concentration of humic substances (20 to 40

mg/L) present in the mire outlet and the main tributary it provided a strong complexation with MeHg and did not result in strong correlation to the content of humic substances. While in the Västrabäcken not only the ratio of humic MeHg to total MeHg was correlated to the content of substances, but also at same concentration of humic substances (at same adsorbance at 254 nm) a lower ratio of humic MeHg to total MeHg was observed compared to the other two sampling locations. It suggested that the complexation of non-humic fraction of TOC with MeHg must be very strong , despite the low concentration of non-humic fraction of TOC (1 to 5 mg/L). The another evidence to support the hypothesis of the strong complexation of non-humic fraction of TOC with MeHg is that in all runoffs the amount of MeHg (ng) per mg TOC in the non-humic fraction is 10 to 20 times that in the humic fraction. That also suggests that a small change in non-humic TOC could have a disproportionately large effect on the MeHg output.

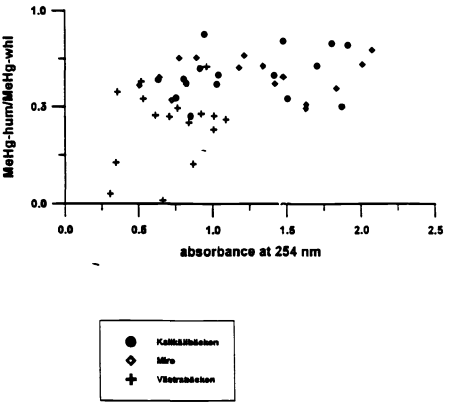

Figure 4. The fraction of humic MeHg of total MeHg (MeHg-hum/MeHg-whl) against absorbance at 254 nm in the subcatchments.

4. Conclusions

The subcatchments M and MK had similar output of MeHg as that from Gårdsjön catchment in the southwestern area of Sweden despite having much higher mean MeHg concentration and also TOC concentration. The much lower annual runoff from the Svartberget catchment, about 60 % of that from Gårdsjön catchment, is the main explanation. The outputs of Hg-tot from the subcatchments were much lower than that from the catchment in southern Sweden, but in the same level as that from other nothern areas.

The contribution of the entire catchment output of MeHg from the mire (15 ha) is large (40%). While the contribution from the forested V and MK subcatchments (35 ha) is (60 %) still important. Also there is a tendency for the output of MeHg and Hg-tot from the mire to decrease during runoff events.

Output varied among the forested subcatchments despite similarities. Subcatchment MK had a ca. 30 % higher outputs of MeHg per km^2*yr than the subcatchment V, on the other hand, which had a 39 % higher output of Hg-tot per km^2*yr. These differences may be related to the differences in the riparian zone, differing in the depth of their riparian peats with subcatchment MK having twice as much deep peat (Bishop et al, 1995a)

Methylmercury and Hg-tot also had different relationships to flow during the critical spring flood period with Hg-tot showing a positive relation to flow, while MeHg was negatively related.

Biogeochemical processes sensitive to temperature and soil moisture are likely to be factors responsible for the seasonal variation.

Methylmercury in the humic fraction was larger than in non-humic fraction, but the amount of non-humic MeHg per mg humic TOC was several times that of the humic MeHg per mg humic TOC. Thus alteration in the non-humic TOC fraction could have a greater impact on MeHg output.

We hope these data sufficient to use as a basis for a modelling attempt, though similar studies will be needed in other areas, as well as continuation of this one.

Acknowledgements

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ANTHROPOGENIC MERCURY ENRICHMENT IN REMOTE LAKES OF NORTHERN QUÉBEC (CANADA)

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Abstract. In a sub-Arctic region of the province of Québec, at sites situated 200 to 1400 km away from the closest industrial centers, we find the ubiquitous presence of anthropogenic Hg, reflected by steadily increasing concentrations of this metal in lake sediments, since about 1940, to rates averaging 2.3 times the preindustrial levels. Mercury concentrations in lake sediments were found to be proportional to the amounts of terrestrial organic carbon from the catchment area. It would, therefore, be misleading to derive continental-scale gradients of this pollutant based on Hg concentrations in oligotrophic lake sediments, unless they are normalized to their organic carbon content. Our normalized data for sediments of remote lakes along a 1200 km transect (45 to 55°N) clearly indicate that the distribution pattern of long-range Hg contamination is independent of the latitude over the boreal forest domain. This uniform contamination contrasts with that of Pb, which decreases towards the north over the same latitudinal span, away from the industrial centers of the St Lawrence Valley and the U.S. Mid-West.

1. Introduction

The deleterious effects of mercury (Hg) resulting from long range atmospheric transport (Verta *et al.*, 1989; Iverfeldt, 1991; Swain *et al.*, 1992) are a cause of concern, as a growing number of aquatic systems in the northern hemisphere have been reported to bear high mercury burdens (Hakanson *et al.*, 1988; McMurtry *et al.*, 1989; Lindqvist, 1991; Meili, 1991; Lathrop *et al.*, 1991; Wren *et al.* 1991). The presence of mercury may either be predominantly a reflection of local anthropogenic sources (Iverfeldt, 1991; Lathrop *et al.*, 1991; Johansson *et al.*, 1991; Nater and Grigal; 1992) or of more global scale processes (Steinnes and Andersson, 1991; Slemr and Langer, 1992 Swain *et al.*, 1992) and therefore uniformly distributed over large continental areas. In Canada, substantial increase in sediment mercury loadings have been reported in lakes situated in south-eastern Canada (Speyer, 1980; Evans, 1986; Rybak *et al.*, 1989). Because of their geographic positions, all these lakes were under the direct influence of westerlies carrying mercury from industrial centers in their paths (Delisle *et al.* 1979; Ouellet and Jones, 1982; Mierle, 1990). In more septentrional regions of the Canadian boreal forest domain, the history of mercury atmospheric contamination remains to be elucidated.

Following its release into the atmosphere, particulate Hg is deposited locally or

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regionally within a few weeks (Iverfeldt, 1991; Slemr and Langer, 1992). In contrast, the residence time of gazeous Hg^0 or Hg^{II} fixed on aerosol size particles is estimated to be about one year, and may therefore be transported over thousands of kilometers from its source before being deposited (Glass *et al.*, 1986; Slemr and Langer, 1992). Mapping the extent of Hg transport, however, is an elusive quest because the direct determination of Hg in precipitation is hampered by temporal variability and low concentrations (Iverfeldt, 1991). Alternatively, lake sediment records can provide time-averaged patterns of Hg deposition, as demonstrated in northern Minnesota and Wisconsin, where modern fluxes of Hg were shown to reach 3.7 times the pre-industrial levels (Swain *et al.*, 1992). Resolving the controversy concerning widespread as opposed to regional contamination by anthropogenic Hg is of special interest in Québec where the development of hydroelectric reservoirs results in Hg release from flooded soils and subsequent bioaccumulation through the food chain (Verdon *et al.*, 1991). The present study was undertaken to evaluate the level of mercury contamination of the Québec boreal forest domain. Inspired by the findings reported for the north central U.S. (Nater and Grigal, 1992), we hypothesized that Hg concentrations in lake sediments would show a clear pattern of distribution with increasing distance away from urban and industrial sources (from 200 km for the southernmost sampling sites to 1400 km for the northernmost). Furthermore, our initial hypothesis was influenced by an earlier report (Ouellet and Jones, 1982) of the existence of a strong gradient in wet sulphate deposition in our study area. In parallel, we analysed Pb concentrations in lake sediments because the spatial distribution of this element in the environment is also governed by atmospheric transport (Evans and Rigler, 1985; Johansson, 1989; Sturges and Barrie, 1989).

2. Materials and Methods

The sediments were collected with either a remotely-triggered stainless steel box corer or a 15 cm diameter core tube manually inserted by divers, in the deepest part of ten remote lakes, distributed along a 10^o of latitude transect on the Canadian Shield, extending from southwestern Québec to eastern Hudson Bay (Figure 1). Minimal disturbance of flocculent surface sediments was achieved by these coring methods. The lakes were chosen on the basis of their size (small lakes: ~ 0.04 to ~ 6 km^2), maximum depth (6 to 13 m), pH (6.0 to 7.3) and oligotrophic characteristics. To complement the pristine environments, we collected cores from four lakes whose respective water levels were raised through impoundment of hydroelectric reservoirs (LG-2 and Cabonga, impounded 14 and 65 years ago, respectively). All sediments were subsampled at one centimeter intervals.

The Hg content of the sediments was determined by atomic fluorescence following acid digestion, employing recent analytical developments (Bloom, 1989; Pichet *et al.*, 1994)). Analyses for Pb were conducted on the Hg digests by graphite furnace atomic absorption spectrophotometry. Sedimentation rates were determined from the decay of excess ^{210}Pb below the mixed surface layer and average rates were corrected for

porosity change with core depth. Organic carbon concentrations were measured with a Carlo Erba CHN amlyser. Stable C isotope ratios ($^{13}C/^{12}C$) of particulate organic C were determined with a PRISM mass spectrometer following the standard combustion in presence of cupric oxide. The results are reported as $\delta^{13}C$ (‰) values relative to the Pee Dee Belemnite limestone standard (PDB).

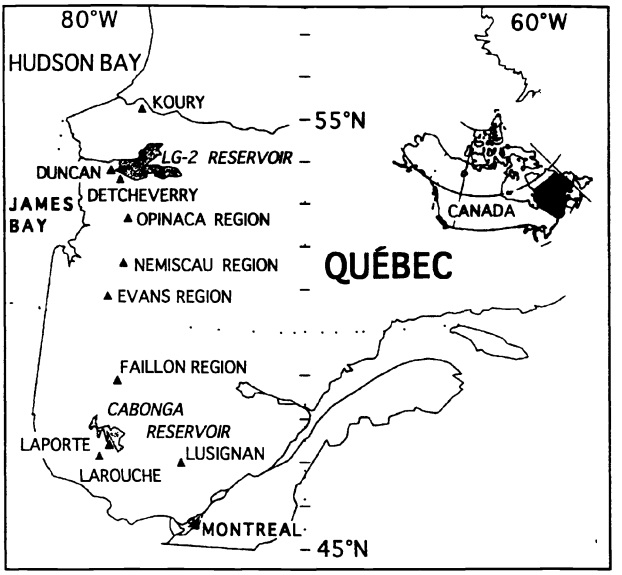

Fig. 1. Sample locations

3. Results and Discussion

For all sampled lakes, sedimentation rates fall within a narrow range of 0.1 to 0.3 cm/yr (Table I). Bioturbation by chironomids is responsible for sediment mixing in the top 2 to 6 cm. All Hg and Pb profiles are characterized by constant concentrations at depth (Figure 2). In the top 10-20 cm, Hg and Pb profiles follow the same trend and clearly show a dramatic increase in the flux of these metals to the sediment (Figure 2 & Table I). Both Hg and Pb are only weakly susceptible to diagenetic remobilization in lake sediments, being strongly bound to refractory organic matter (Rybak *et al.*, 1989; Verta *et al.*, 1989; Dominik *et al.*, 1991; Louchouarn *et al.*, 1993) Thus, the departure in Hg and Pb concentrations above background values may be interpreted as the record of the airborne contamination of the pristine lacustrine systems. In each sedimentary profiles, the age of the onset of contamination was calculated after subtracting the time required for the deposition of one mixed layer. We estimate that the uncertainty in the historical reconstructions of local contamination does not exceed ten years. Variations in absolute Hg and Pb baseline concentrations between lakes reflect dissimilar pre-industrial inputs of these metals from their respective drainage basins. The ratios of the surface to baseline

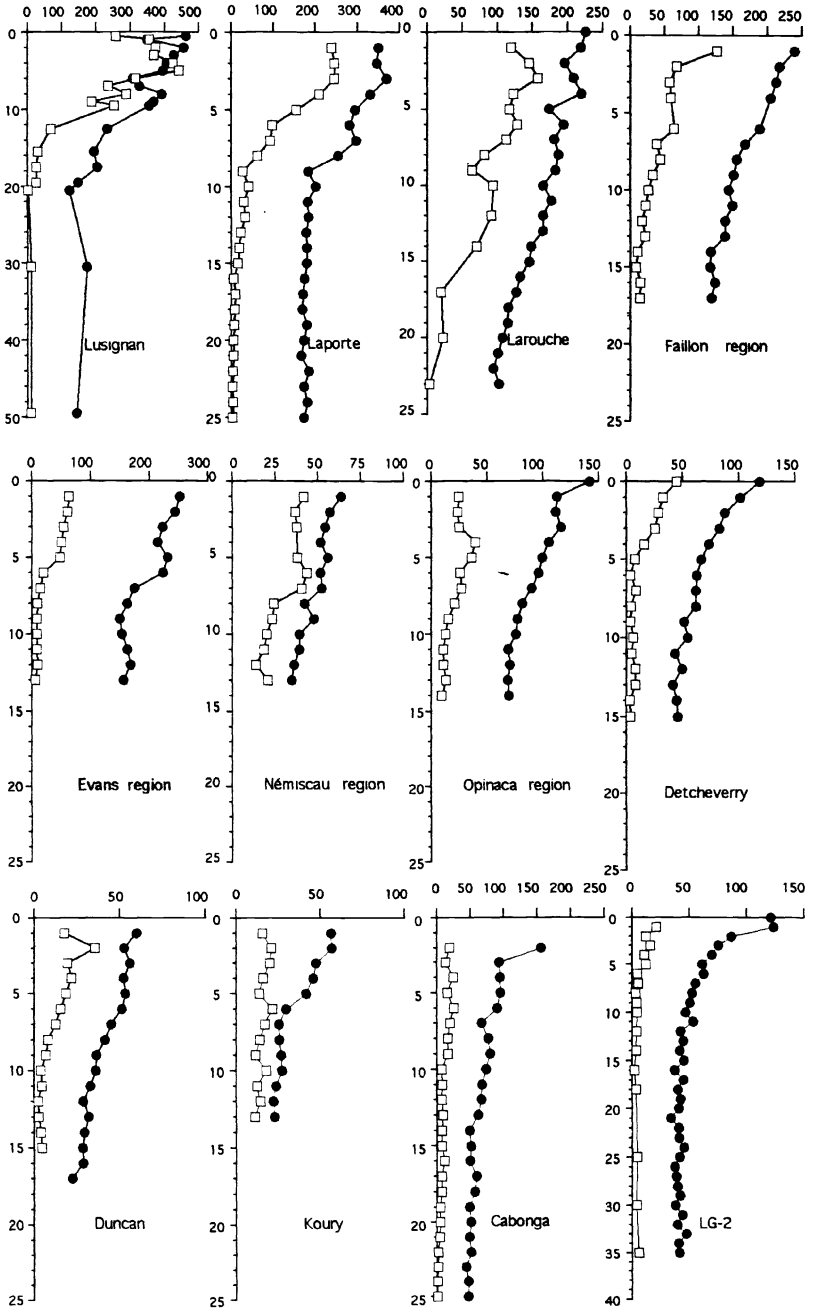

Fig. 2. Mercury (•, ng/g) and lead (□, μg/g) profiles in the sediments of 10 natural lakes and 2 flooded lakes.

Hg concentrations (Anthropogenic Sedimentary Enrichment Factor, ASEF) average 2.3 for all sampled lakes and are independent of latitude. In contrast, variations in the organic carbon content in any given lake sediment core are negligible, indicating that fairly stable sedimentary conditions prevailed over the period represented by the sampled interval.

TABLE I

Location, chemical and sedimentological characteristics of the lakes investigated, including the Hg and Pb anthropic sedimentary enrichment factor (ASEF) and the time elapsed since the beginning of significant Hg enrichment in the lake sediments (n.r.: baseline concentration not reached.; * mean values over the length of the core, with a standard deviation smaller than 0.8).

Site	Latitude North	$C_{surface}$ (%)	C_{deep} (%)	$\delta^{13}C$ (PDB) (‰)*	Hg ASEF	Pb ASEF	Sedimentation (cm/year)	Record of Hg enrichment (years)
Natural lakes								
Lusignan	46°41'	24.8	25.8	-28.5	3.5	147	0.24	80
Laporte	47°12'	17.9	19.7	-28.6	2.0	62	0.135	55
Larouche	47°12'	11.3	11.9	-28.9	2.2	40	0.30	57
Faillon region	48°22'	14.1	13.6	-27.9	2.0	13	0.20	57
Evans region	50°36'	17.4	17.7	-28.7	1.6	11	0.075	66
Némiscau region	51°36'	3.9	3.1	-27.5	1.8	3	0.20	50
Opinaca region	52°40'	8.5	6.6	-27.6	2.0	4	0.16	50
Detcheverry	53°27'	8.3	8.7		1.7	10	0.19	53
Detcheverry	53°27'	9.5	8.9		2.8	7.5		
Duncan	53°29'	4.1	2.8		2.6	7		
Koury	55°07'	2.8	1.5	-27.8	2.5	1.5		
Flooded lakes								
Cabonga	47°17'	4.6	3.9	-27.5	2.1	13		
Cabonga	47°17'	7.2	7.8	-26.4			0.12	n.r.
Cabonga	47°17'	4.4	4.4	-27.6	1.5			
LG-2	53°29'	9.4	5.7	-27.6	2.3	10	0.17	53
LG-2	53°29'	9.4	5.7		2.3	1.3	0.26	50
LG-2	53°31'	9.8	13.0	-26.6	3.0	3.5		
LG-2	53°32'	8	3.8	-27.1	6.2	6		

The sharp rise in the Hg deposition rate above background levels occurred, for all lakes situated north of 47° latitude, in the early 1940's irrespective of latitude (Table I). This observation is consistent with what was reported for Hg and other metals in the sediments of undisturbed lakes of southern Québec (Ouellet and Jones, 1982), and for one headwater lake in Newfoundland (Rybak *et al.*, 1989). The only exception to our recorded mid-1940's increase in Hg concentration was observed in the southernmost lake, Lake

Lusignan. It corresponds to a change initiated ca. 1910 and may be attributed to the local influence of a small copper mine. In comparison, Hg accumulation records from the industrialized regions of Minnesota and Wisconsin show that the increased fluxes of Hg date back nearly 140 years (Swain *et al.*, 1992). Mercury concentrations in Finnish lake sediments (Verta *et al.*, 1989) and peat bogs of southern Sweden (Jensen and Jensen, 1991) also started to rise dramatically at the turn of this century, as opposed to the 1960's for peat bogs of northwestern Norway (Jensen and Jensen, 1991). Thus, anthropogenic Hg seems to have reached northern sites of North America and Europe at a later date. The reason for this variation may be attributed to their remoteness from industrial centers and their lack of exposure to short range fallout of particulate Hg.

Although surface sediments in the two latitudinally extreme lakes contain the lowest and highest recorded Hg concentrations, neither the absolute Hg maximum surface concentrations, nor the Hg ASEF appear to be correlated with latitude (Table I). The influence of large regional inputs, such as from the mining area of Abitibi, between 48 and 49 ^{o}N, could not be resolved either. The most noticeable difference between the sampled lake sediments is their organic matter content, C_{org}, which ranges from 3 to 25 % dry weight (Table 1). Our ^{13}C measurements (Table 1) indicate that the C_{org} in the sampled lake sediments of southwestern Québec is composed mainly of terrestrial material (LaZerte, 1983; Meili *et al.*, 1993). This observation attests to the oligotrophic nature of the 10 sampled lakes.

The surficial sediment Hg anthropogenic enrichment concentrations (EHg, surface minus baseline concentrations) are directly proportional to their C_{org} (EHg = 12.3xC -23.8, r^2 = 0.932; Fig. 3). These variables and the residuals from the least squares fits (7% of EHg) are strongly of latitude. It is well documented that Hg forms stable complexes with organic matter (Lindqvist, 1991). As a matter of fact, several authors hypothesized that most Hg present in the water column (Ivefeldt and Johansson, 1998; Mierle, 1990; Mierle and Ingram, 1991; Meili, 1991; Lee and Iverfeldt, 1991) or buried in the sediments (Evans, 1986; Meili, 1991; Swain *et al.*, 1992) of various natural lakes could be transported by surface runoff along with the outwash of terrestrial organic matter, in both dissolved and particulate forms. The strong relationship reported here between the allochthonous C_{org} concentration and the sediment EHg concentrations of the 10 oligotrophic lakes confirm the latter hypothesis. Sediment focussing in the deeper parts of a lake, however, would only help to amplify this relationship. The external loading of fine grained particles, including organic matter, to a lake is dependent upon the physiography (slope, drainage area : lake surface ratio) and the composition of the catchment (vegetation type, acidity of runoff) (Meili, 1991; Nelson and Campbell, 1991; Rowan *et al.*, 1992). The local flux of carbon is then modulated by in-lake depositional processes.

Our data reinforce previous findings (Swain *et al.*, 1992) from which it was postulated that the quantity of Hg brought to a lake is directly proportional to the amount of carbon leached from the surrounding soils, regardless of soil type. Calculated

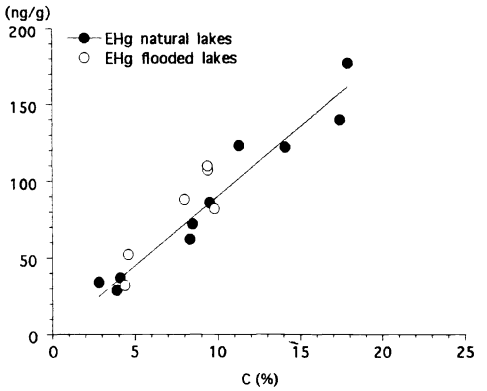

Fig. 3. The Hg surficial sediment anthropic enrichment (EHg) as a function of the organic carbon content for the natural lake sediments sampled along the North-South transect.

sedimentary fluxes of Hg range from 35 to 76 $\mu g/m^2/yr$, for all cored sites, which is systematically 3 to 5 times higher than the direct atmospheric Hg deposition rates presently proposed for central North America (Glass *et al.*, 1986; Mierle, 1990; Fitzgerald *et al.*, 1991; Swain *et al.*, 1992). As indicated above, our estimated sedimentary fluxes may be overestimated because of particle focussing in the deeper parts of the lake where we sampled. Nevertheless, these high values corroborate our conclusions that most Hg found in these lake sediments must have been brought by the outwash of terrestrial organic matter.

The relationship between EHg and C_{org} also holds true for sediment samples of lakes presently incorporated into the LG-2 and Cabonga hydroelectric reservoirs, where, respectively, 2-3 cm and ≈ 20 cm of sediment has accumulated since impoundment. Thus, Hg inputs are directly related to the accumulation of organic matter, even if the latter has varied through time in response to a major change in the sedimentary regime following impoundment.

In contrast to the Hg distribution patterns reported for the central U.S. (Nater and Grigal, 1992), southern Ontario (Lathrop *et al.* 1991) and southern Scandinavia (Iverfeldt, 1991; Johansson *et al.* 1991), our data display no clear regional gradient in Hg ASEF or in sedimentary Hg concentrations once they are normalized to C_{org} (Figure 4). We can assume that, unlike previously cited reports of local or regional contamination, most of the anthropogenic Hg burden in sediments of our study area must have accumulated from gaseous Hg^0 or submicron aerosols which remain in the atmosphere for long periods of time, since it was deposited far from the direct influence of heavily industrialized regions. Thus, we propose that, away from major emission sources, Hg is deposited evenly over large continental expanses. Our results concur, but on a much wider latitudinal scale, with previous observations by Swain *et al.* (1992) who reported nearly uniform Hg atmospheric deposition over northern Minnesota and Wisconsin. They also imply that the

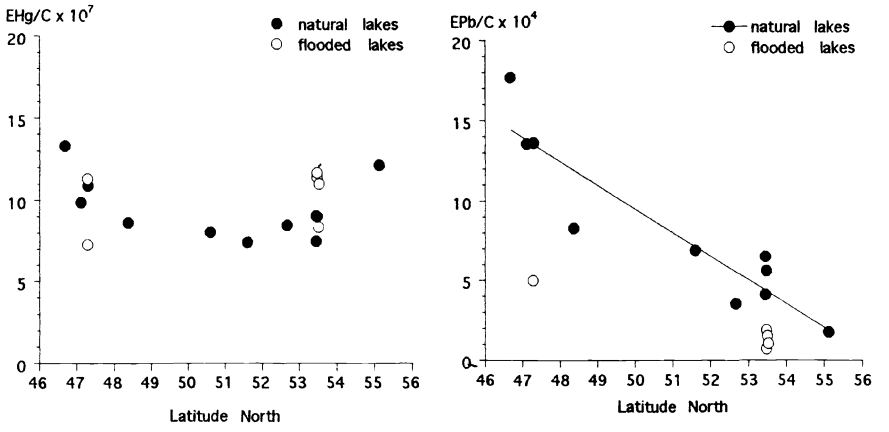

Fig. 4. The Hg and Pb surficial sediment anthropic enrichments normalized to the organic carbon content (EHg/C and EPb/C) as a function of the latitude for the lake sediments sampled along the North-South transect.

anthropic origin of the airborne Hg in remote regions of northern Québec cannot be clearly traced.

As suggested by previous observations in Québec and Ontario (Rowan and Kalff, 1993), and like for Hg, most of the Pb found in lake sediments should also have been transported with the leaching of the terrestrial organic matter. The EPb values in the sampled lake sediments are indeed linearly correlated to the C_{org} content yet more poorly than for EHg values, particularly when data from the hydroelectric reservoirs are included (r^2 = 0.897). One can also observe that, in contrast to Hg, the EPb concentrations normalized with respect to Corg decrease linearly with increasing latitude (Figure 4). Likewise, Pb-ASEF values decrease by more than one order of magnitude from the southernmost stations northward (Table 1). This suggests that, in contrast to Hg, the atmospheric transport of anthropogenic Pb over remote areas of northern Québec involves a particulate phase which is preferentially deposited close to the heavily industrialized regions south of the 46th parallel in North America. A similar decreasing gradient of anthropogenic Pb deposition away from industrialized regions was reported for southeastern Canada (Evans and Rigler, 1985) and Sweden (Johansson, 1989).

4. Conclusion

Over time, the spatially uniform and still increasing deposition rates of anthropogenic Hg over the boreal forest domain may lead to a generalized contamination of all natural aquatic ecosystems. So far, Hg contamination is most acute to organisms living in newly impounded hydroelectric reservoirs of northern Québec as mercury transfer to the food chain is promoted by intense microbial and benthic activity in the Hg-laden flooded soils (Verdon *et al.*, 1991; Louchouarn *et al.*, 1993). We can only assume that a fraction of the mercury released in this manner is anthropogenic, and has slowly accumulated in the soils over the last half century. In addition, the return to pre-impoundment Hg concentrations in aquatic organisms will be delayed by the continuous deposition of atmospheric Hg over the reservoirs and their watersheds.

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OUTPUT OF METHYLMERCURY FROM A CATCHMENT IN NORTHERN SWEDEN

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ABSTRACT. The runoff output of methylmercury (MeHg) from the 50 ha Svartberget Catchment in northern Sweden was studied during 1993. These outputs are compared to those from the Gårdsjön Catchment in the southwestern part of Sweden. Although the wet deposition of MeHg is several times higher in southern Sweden the output of MeHg per unit area from the two catchments was comparable (0.12 g /km^2*yr). Furthermore, the concentration of MeHg (0.4 ng/L) in the Svartberget Catchment was more than twice that from the Gårdsjön Catchment. These results suggest that the contemporary wet deposition of MeHg in itself is not a good indicator of runoff concentration or output per unit area. DOC transport and catchment characteristics such as wetland area, or possibly other forms of contemporary atmospheric deposition may all be more important for explaining MeHg output from the terrestrial ecosystem.

1. Introduction

The atmospheric deposition of mercury (Hg) and methylmercury (MeHg) on forest soil is very effectively immobilized by humic substances and accumulates in the mor layer and superficial soil horizons (Andersson, 1979; Lee *et. al.*, 1994a; Aastrup *et al.*, 1991; Hultberg *et al.*, 1994). A small fraction of the soil store of the MeHg/Hg-tot predominately bound to organic substances in the soil can be transfered together with DOC from soil to a deeper soil layer (B- and C-horizon) and to surface water (Lee and Hultberg, 1990; Lee *et al.*, 1994a; Aastrup *et al.*, 1991). The main factors regulating the runoff of Hg in the different regions of Sweden have been related to the humic content in water. However, the direct influence on the MeHg/Hg output of atmospheric deposition of Hg is not completely resolved. The critical load was previously assessed by linking the atmospheric deposition of Hg to the Hg content in fish, with fluxes and pools of Hg in soil/ water ecosystems as the basis for the mass balance model (Johansson *et al.*, 1991).

The small watershed approach can facilitate the understanding of the transport and cycling of MeHg/Hg in the forest ecosystem. Very few studies on the transport and biogeochemical cycle of MeHg in the forested catchment have been published (Lee and Hultberg, 1990; Aastrup *et al.*, 1991; Lee *et al.*, 1994a, Hultberg *et al.*, 1994). This study documents the annual output of MeHg from a rural catchment in northern Sweden. Those results are then compared to the outputs from a forest ecosystem in southern Sweden and discussed in relation to regional deposition patterns of MeHg in Sweden.

2. Study site and Methods

2.1. SITE DESCRIPTION

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The study was conducted on the 50 ha Svartberget Catchment (Figure 1) in northern Sweden (64° 14' N,10° 46' E.). The catchment is forested with mature Norway spruce in the lower lying areas and Scots pine at higher elevations on podzol soils. The forest soils are predominantly well-developed on iron podzols which have developed on a locally derived glacial till overlying gneissic bedrock. The mean annual temperature in the area is 0°C, with an average annual precipatation of 720 mm, of which roughly a third is snow. The annual runoff from the catchment is 330 mm, with a mean pH of 4.4. The catchment is drained by two tributaries, Västrabäcken and Kallkällbäcken. The laterstarts at the outlet of a mire. Both streamswere ditched to about the same depth (ca. 1 m) during the 1930's.

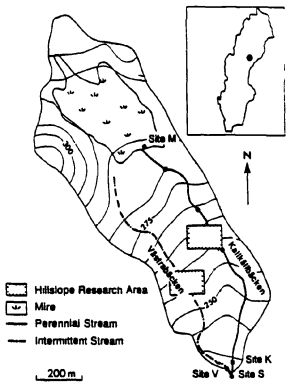

Figure 1. The Svartberget Catchmeht showing the location of the sites where flow amd chemistry were measured.

2.2. SAMPLING AND ANALYSIS

The volume-weighted concentrations and outputs of MeHg from the Svartberget catchment are based on continuous flow monitoring and the monthly chemistry sampling at Sites K and V (Kallkällbäcken and Västrabäcken, respectively). 83% of the catchment drains through Site K and the remaining 17% drains through Site V. More intensive sampling was conducted during the spring flood (April 4 to May 9) and during a rain storm episode (July 23 to 28).

Due to the problems usually connected to an ultra-low Hg level (picogram amounts) and those specific to the high content of humic substances in water samples, care was taken to choose an appropriate and validated pretreatment procedure to isolate MeHg from the sample matrix as well as a sensitive detection system (Lee *et al.*, 1994b, 1994c). Concentration of MeHg in water samples was determined using a GC-CVAFS technique with aqueous phase ethylation with distillation preseparation steps (Bloom, 1989; Horvat *et al.*, 1993). The extensive cleaning procedure, which is part of the water sample collection and analytical method for Hg-tot used in the present study, has been described previously (Bloom and Crecelius, 1983; Iverfeldt, 1991).

3. Results and discussion

3.1. RUNOFF CONCENTRATIONS AND OUTPUTS OF METHYLMERCURY.

In the study period from January to December 1993, there was a strong seasonal trend in the MeHg concentrations which started from a minimum during spring flood and increased throughout the summer (Figure 2a). This concentration increase during the summer occurred despite large amounts of runoff, particularly in August (Figure 2b).

This is in contrast to the spring flood where large runoff amounts were coupled with decreasing concentrations (Bishop *et al.*,1995b). This suggest that the availability of MeHg for export in runoff is seasonably variable. July and August are usually the warmest months in every year, and were also the wettest months during 1993. These conditions may promote the biogeochemical processes that, combined with runoff, and lead to high rates of MeHg transfer from soil to streams. A similar seasonal variation in the MeHg outputs in runoff was also observered from a another forested catchment in Sweden (Lee and Hultberg, 1990; Hultberg *et al.*, 1994).

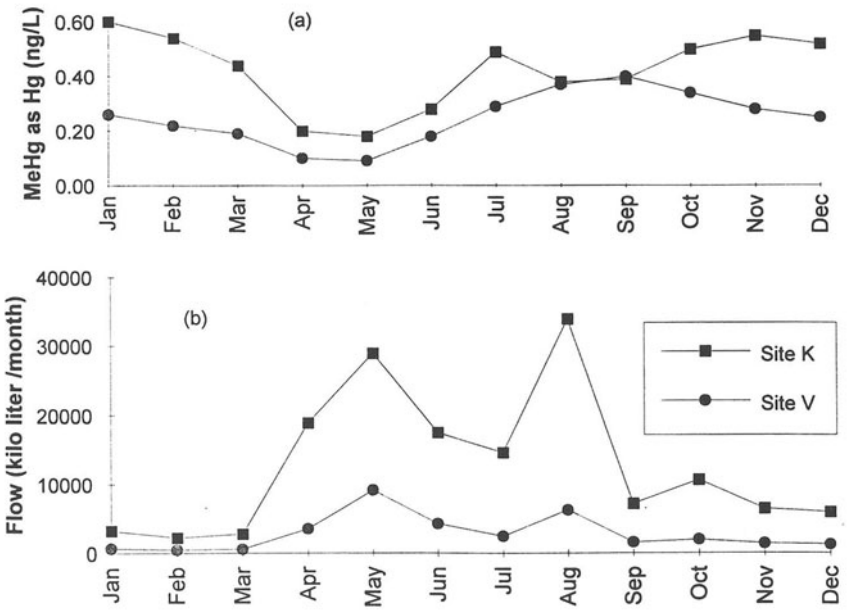

Figure 2. (a) The monthly average volume-weighted concentration of MeHg in two tributaries. (b) Monthly mean runoff from the subcatchment.

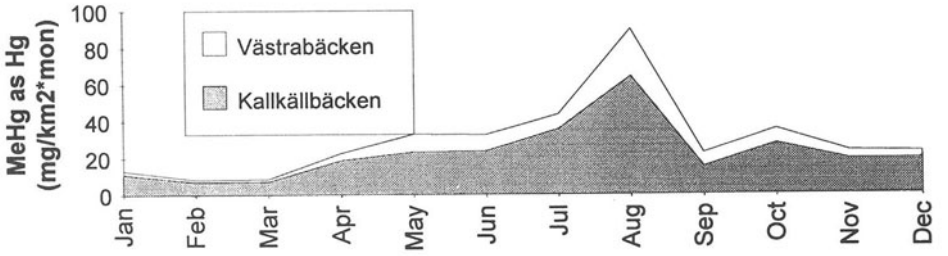

Figure 3. The monthly output (mg/km^2* month) of MeHg from the subcatchments and the entire catchment (= Kallkällbäcken + Västrabäcken).

The low monthly outputs of MeHg during the winter and spring periods (before snowmelt) were mainly due to low discharge (Figure 3). The progressively increasing monthly outputs of MeHg began from April/May, and reached the maximum value in

August. During August the discharge was not only greatest of the year, but also the concentrations of MeHg was high.

The yearly output flux of MeHg from the entire catchment was 0.12 g/km^2*yr with an average concentration in runoff of 0.40 ng /L.(Table I). A four year time series of outputs from the Gårdsjön Catchment indicated a similar annual output per unit area. This occurs despite regional estimates of MeHg deposition that show Svartberget having a wet deposition that is less than a third of the deposition in the Gårdsjön area (Munthe and Iverfeldt, 1993). Furthermore, the concentration of MeHg in runoff at Svartbeget is almost twice that at Gårdsjön (0.2 ng /L) (Hultberg *et al.*, 1995).

These results suggest that the contemporary wet deposition of MeHg in itself is not a good indicator of runoff concentration or output per unit area. DOC transport and catchment characteristics such as wetland area, or possibly other forms of contemporary atmospheric deposition may all be more important for explaining MeHg output from the terrestrial ecosystem.

Table I
Mean Annual Outputs

	Precipitation mm	Runoff mm	Flux g /km^2*yr	Concentration ng/L	DOC mg C/L
Svartberget	720	330	0.12	0.4	15 *
Gårdsjön	1112	586	0.12	0.2	7.8**

*Bishop *et al.* 1994.
**Measureed between 1979-81 (Broberg and Persson, 1984).

Acknowledgements

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EFFECT OF pH AND IODIDE ON THE ADSORPTION OF MERCURY(II) BY ILLITE

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Abstract. The effect of I^- concentration on the mobility of Hg(II) in clay suspensions was studied over an environmentally-significant pH range. The addition of I^- decreased the adsorption of Hg(II), except at very low (50 μg/L) I^- concentrations. In suspensions of greater I^- concentration (1.5 and 50 mg/L), Hg(II) adsorption was independant of pH; at low concentrations, Hg(II) adsorption decreased with increasing pH, presumably due to competition from hydroxycomplexes for surface adsorption sites. I was an effective extractant for Hg, outperforming all other halides in extraction efficiency.

1. Introduction

The effect of complex formation on the transport and fate of inorganic mercury(II) has been thoroughly reviewed (Gilmour, 1971; Elliott and Huang, 1979; Schuster, 1991). It is generally accepted that chloride is the most significant inorganic ligand responsible for increasing the mobility of Hg, due in part to the abundance, mobility and persistance of Cl^- and in part to the low affinity of Hg-Cl complexes for the soil surface (Farrah and Pickering, 1978). Hahne and Kroontje (1973a, b) considered Cl^- concentration to be as important a parameter as pH in determining the mobility of Hg. Experimental results of several researchers qualitatively confirm these results (Newton *et al.*, 1976; Feick *et al.*, 1972; Barrow and Cox, 1992 a, b). Due to the abundance of Cl^-, little research on the effect of other, less prevalent ligands has been performed. It is possible that other ligands, particularly other halides, could also cause a significant increase in Hg mobility at concentrations much lower than those required of Cl^- (Hepler and Olofsson, 1975).

A lixiviant composed of I^- and I_2 is currently under investigation for use in the removal of Hg from contaminated soil and sediments (Faust, 1993; Shoesmith *et al.*, 1994). Initial tests indicate that this lixiviant effectively removes Hg from contaminated soils; however, the potential for more widespread Hg contamination exists if soils with residual I^- are returned to their original sites or disposed of in unlined landfills, or if the lixiviant is used *in situ*. The residual I^- in treated soils has the potential to complex residual Hg; if this residual I^- escapes from the treated soil or disposal site, it may also complex down-gradient Hg. No information exists on the interactions of Hg and I^- in soils; the aim of this research is to assess the impact of low concentrations of I^- on the adsorption of Hg. The clay mineral illite was chosen as a substrate due to its abundance in the soils of Eastern Tennessee.

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2. Materials and Methods

Fithian illite was ground with a mortar and pestle to recover the < 32 μm fraction, and then was saturated with potassium by repeatedly suspending and centrifuging in 0.01 M KNO_3. Twelve, 100-mL stock suspensions of 1 g/L were prepared in 0.01 M KNO_3 and stored in polypropylene bottles. Appropriate volumes of 0.01 N HNO_3 and 0.01 N NaOH were added to produce stock suspensions with pH values in the range of 4 to 10. Ten-milliliter subsamples of each stock suspension were transfered into 14-mL polypropylene culture tubes and spiked with solutions of $^{203}Hg(NO_3)_2$ and NaI to achieve initial suspension concentrations of 0 and 200 μg/L Hg, and 0 and 50 mg/L I^-. After the completion of a one day equilibration period, a 1-mL aliquot was drawn from each of the suspensions, transfered to a 7-mL vial, and preserved in 1 mL of 4 N HNO_3. These samples were analyzed to determine the equilibrium Hg concentration (C_{eq}) in the suspension. A separate 3-mL aliquot of the suspension was filtered through a 0.2 μm polycarbonate membrane. The filter containing the solids was transferred into a 7-mL vial and analyzed to determine Hg adsorbed (C_{ads}). A 1-mL aliquot of the filtrate was transferred into a 7-mL vial, preserved in 1 mL of 4 N HNO_3, and analyzed to determine aqueous Hg concentration (C_{aq}). The pH of each sample was measured and recorded. Samples were analyzed for a period of 2 to 15 minutes using a 3" x 3" Bicron NaI deep-well crystal and a Nuclear Data Accuspec gamma spectrometer. Mass balance was checked by comparing aqueous and solids Hg concentrations to initial Hg concentrations. Adsorption percentages were determined from the measured solids and suspension phase concentrations:

$$\% \text{ adsorption} = C_{ads}\ (\mu g/g) \div C_{eq}\ (\mu g/L) \times \text{illite concentration in suspension (g/L)}.$$

3. Results and Discussion

3.1 EFFECT OF IODIDE AND pH ON Hg ADSORPTION BY ILLITE

Hg was lost from some samples during equilibration, especially at higher pH and lower I^- concentrations. Hg losses were approximately 20% to 30% when $I^- = 0$ and 50 μg/L, but losses were less than 5% when $I^- \geq 1.5$ mg/L. The poor mass balance for suspensions of lower I^- concentration resulted in greater scatter in data. We concluded that these losses were due to Hg adsorption to container walls; similar observations have been made by Newton and Ellis (1974). We used the equilibrium activity (C_{eq}) as the total Hg concentration, and reported concentrations as μg/L or μg/g of clay in suspension.

Typical results for the adsorption of Hg by illite (1 g/L) in the presence of I^- (0 - 50 mg/L) are presented in Figure 1. The maximum adsorption of Hg in the absence of I^- and at low I^- concentrations (< 50 μg/L) was in the range of 80 to 85%. Adsorption decreased slightly with increasing pH up to a pH of 9; for pH values above 9, adsorption decreased sharply, due to competition between hydroxide ions and Hg complexes for adsorption sites (Elliott and Huang, 1979). At greater I^- concentrations, adsorption significantly decreased to 25% for $I^- = 1.5$ mg/L and less than 20% at $I^- = 50$ mg/L. While maximum adsorption occurred at low pH (pH < 4) for suspensions with little or no iodide, adsorption in suspensions of $I^- = 1.5$ mg/L and $I^- = 50$ mg/L appeared to be relatively independant of pH.

The effect of increasing I^- concentration on Hg adsorption is further illustrated in Figure 2. Clearly, concentrations of I^- greater than 50 μg/L significantly altered the

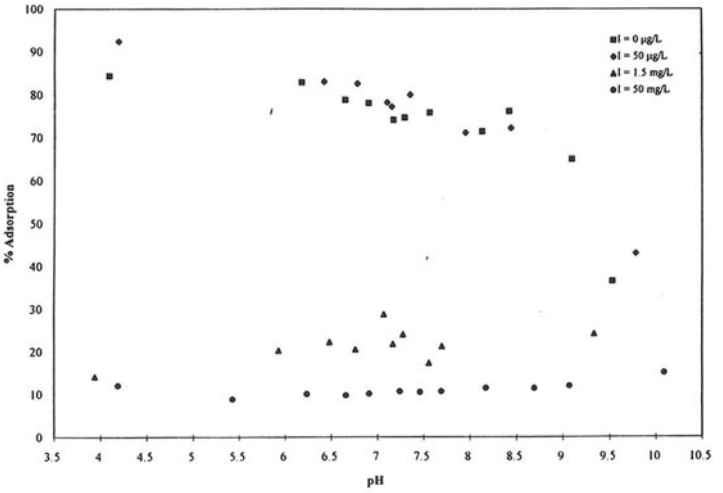

Fig. 1. Effect of varying NaI concentration on the adsorption of Hg(II) by illite as a function of pH

adsorptive behavior of Hg, and the effect of pH was relatively insignificant.

3.2 DESORPTION OF Hg FROM SOIL

The ability of I^- to desorb Hg from contaminated soils was also investigated. Soils from a Hg-contaminated floodplain in Oak Ridge, Tennessee were treated with three concentrations of halide salt solutions to assess their ability to remove Hg. The results are tabulated in Table I. Clearly, I^- was the most effective desorbing agent. The smallest I^- concentration tested (0.001 M) performed better than the other halides at the highest concentration tested, with the exception of 0.1 M F^-. In addition, I^- was the only halide that removed a noticable fraction of Hg from the soils. Even at 0.1 M, F^-, Cl^-, and Br^- extracted little Hg; on the other hand, I^- removed almost 6% of the adsorbed Hg.

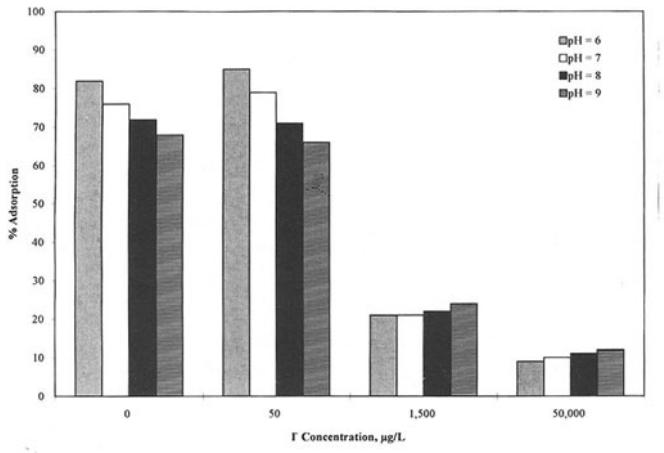

Fig. 2. Adsorption of Hg(II) by illite as a function of I concentration (initial Hg = 40 µg/L)

TABLE I
Efficiency of different halide solutions at extracting Hg from contaminated soils

Solution Concentration (M)	Percent Desorbed (%)			
	F^-	Cl^-	Br^-	I^-
0.001	0.0056	0.0073	0.013	0.041
0.01	0.010	0.012	0.023	1.1
0.1	0.12	0.017	0.040	5.9

4. Conclusions

Hg adsorption by illite decreased at high I^- concentrations ($\geq$ 1.5 mg/L). I^- also desorbed significant concentrations of Hg from contaminated soils, especially when large (0.1 M) concentrations were used. The ability of I^- to both decrease adsorption and cause desorption of Hg may influence the use of I^- as a lixiviant in soil decontamination.

Acknowledgements

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PART VI

LAKE AND RESERVOIR MERCURY

MODELING THE TRANSPORT AND FATE OF MERCURY IN AN URBAN LAKE (ONONDAGA LAKE, NY)

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Abstract. A mass balance model was developed to simulate mercury (Hg) cycling in Onondaga Lake, New York. MERC4, a U.S. Environmental Protection Agency model of the physical and biogeochemical transport and transformation of Hg, was modified by the addition of input from two supporting models (Fish Bioenergetics Model 2 and a lake eutrophication model) to model the transport of Hg into and out of plankton and fish. The model calculates the concentrations of total Hg, methylmercury, elemental Hg, and ionic Hg in both dissolved and particulate forms in the water column. The model was calibrated to an extensive data set of temporally and spatially variable Hg concentrations in Onondaga Lake in 1992. In addition to standard transport processes of advection and dispersion included in MERC4, the Onondaga Lake Mercury Model includes remineralization to simulate release of Hg from settling particulates before incorporation into sediment. The model provides an analytical framework for understanding and predicting the behavior of Hg in Onondaga Lake and has potential use in evaluating the relative impact of different source control and remedial alternatives.

1. Introduction

As the understanding of mercury (Hg) cycling in the environment has evolved, several attempts have been made to model these dynamic processes. For example, Harris (1991) developed a model that follows Hg cycling in aquatic systems and the Electric Power Research Institute developed the Mercury Cycling Model (Tetra Tech, 1992; Hudson *et al.*, 1992) to examine Hg cycling in Wisconsin seepage lakes. Both models are dynamic, mechanistic, mass balance models. Recently, the kinetic subroutine pertinent to Hg from the Mercury Cycling Model was incorporated into WASP4 (Water Quality Analysis Simulation Program; U.S. EPA, 1991). The resulting model, MERC4 (AScI, 1992), can simulate Hg cycling (but not bioaccumulation) in a variety of aquatic systems (e.g., rivers, lakes, estuaries).

The Onondaga Lake Mercury Model (OLMM) was developed as part of a large remedial investigation and feasibility study of Onondaga Lake, New York, a slightly alkaline, hypereutrophic lake which received historical discharges of Hg from two Hg-cell chloralkali plants. One purpose of the OLMM was to provide an analytical framework for understanding and predicting the behavior of Hg in Onondaga Lake. MERC4, the principal model in the OLMM, was modified to be supported by the Fish Bioenergetics Model 2 (FBM2) (Hewett and Johnson, 1991) to track Hg in fishes, and a lake eutrophication model (HydroQual, 1994) to estimate phytoplankton populations and settling rates.

This paper describes construction of the OLMM and results of its calibration to an extensive data set from the 1992 Onondaga Lake field investigation (Henry *et al.*, 1995; Jacobs *et al.*, 1995). Bioaccumulation is only briefly described because final calibration is incomplete. Bioaccumulation in the OLMM will be described in more detail in a later publication.

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2. General Components of the Onondaga Lake Mercury Model

2.1. MERC4

MERC4 is implemented as a kinetic subroutine for Hg transformations that is linked with the transport modeling routines of the WASP4 model (U.S. EPA, 1991). The kinetics add the ability to represent sorption of Hg to solids and complexation of Hg with dissolved organic carbon, transformations among Hg species (e.g., reduction, methylation), and complexation of Hg with other water quality constituents (e.g., hydroxide, chloride, sulfide). For the purpose of modeling Onondaga Lake, the transport modeling capabilities of MERC4 were extended to include remineralization of Hg species (i.e., release of Hg from particles in the water column), and the MERC4 kinetic routines were extended to include accumulation and release of Hg by plankton and fish. Figure 1 illustrates the conceptual framework for the OLMM.

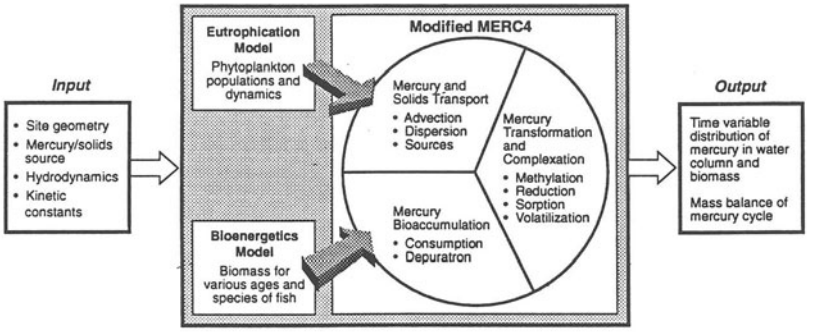

Fig 1. Conceptualization of the Onondaga Lake Mercury Model

2.2. FBM2

FBM2 is a set of mathematical equations that describe individual fish consumption, respiration, specific dynamic action, egestion, excretion, and reproduction, and that balance the energy requirements of these processes to determine individual growth. These processes, on a population basis, are used in the modified kinetics of MERC4 to model accumulation and depuration of Hg in fish.

2.3. Eutrophication Model

The eutrophication model of Onondaga Lake is implemented as a kinetic expression that utilizes environmental conditions (i.e., nutrients, sunlight, and temperature) to simulate the dynamics of phytoplankton biomass. Biomass dynamics, such as growth, respiration, and settling, are provided to MERC4 as input.

3. Development of the Onondaga Lake Mercury Model

3.1. SEGMENTATION

Onondaga Lake was conceptually divided into 3 segments to represent different water column regimes. These regimes are 1) the littoral zone (i.e., the nearshore epilimnion in contact with lake-bottom sediments, 2) the pelagic zone (i.e., the epilimnion underlain by the hypolimnion), and 3) the profundal zone (i.e., the hypolimnion underlain by profundal sediments). Environmental conditions and Hg transformation rates may differ in each of these segments.

3.2. TRANSPORT

3.2.1. *Advection*

A water balance for Onondaga Lake was computed using the weekly averages of measured tributary inflows (Henry *et al.*, 1995), estimated evaporation, measured precipitation in Syracuse (NOAA, 1992), estimated groundwater inflow, and estimated changes in the lake volume based on the surface area of the lake and the elevation of the lake recorded by the U.S. Geological Survey (USGS, 1993). Groundwater contributed 0.3 percent of total water inflow and was omitted from the water balance. The excess water was assigned as outflow to the Seneca River. All outflows were calculated to be positive.

Surface water inflows, with the exception of Ninemile Creek, enter the littoral segment and mix with the pelagic segment. Because of its high chloride content and resulting elevated density (HydroQual, 1994), flow from Ninemile Creek is specified to enter the lake by way of the profundal segment to simulate plunging. The lake outflow leaves through the littoral segment.

3.2.2. *Dispersion*

Dispersive mixing between the profundal and pelagic segments in the OLMM is used to simulate spring and fall turnover and summer stratification. Increased mixing coefficients are specified during turnover to nearly homogenize the epilimnion and hypolimnion. Decreased mixing is specified during stratification to reduce mixing across the thermocline. As a result, the concentration of Hg increases in the profundal segment simulating the concentration increase in the hypolimnion observed in the 1992 data (Jacobs *et al.*, 1995).

3.2.3. *Settling*

The settling and deposition of three types of particles are specified in the OLMM. These particles represent inorganic (fluvial) solids, phytoplankton, and detritus. No estimates of resuspension were available; therefore, a net settling term was used based on data from sediment traps deployed in both the pelagic and profundal zones of the lake (Henry *et al.*, 1995). Settling rates of inorganic particles were estimated from mass accumulation rates in sediment traps and total suspended solids concentrations in the overlying water. The estimated settling rates of phytoplankton and detritus were provided by the eutrophication model of Onondaga Lake (HydroQual, 1994). Final settling rates were adjusted during calibration.

3.2.4. *Remineralization*

Remineralization is defined in the OLMM as the release of Hg from settling particles in profundal water close to the sediment-water interface. Hurley *et al.* (1994) have described this process for Little Rock Lake, Wisconsin. Remineralization of Hg in Onondaga Lake is supported by the

comparison of gross and net Hg sedimentation as discussed in Henry *et al.* (1995). Resuspension of bottom sediments can also result in greater gross than sedimentation; however, resuspension was considered insignificant in the profundal waters of Onondaga Lake where the water column is quiescent in this region. A temporally variable recycling fraction is applied to each type of particle. Recycling fractions were adjusted during calibration.

3.3. Loads

Tributaries, sediments, groundwater, and atmospheric deposition all contribute Hg to Onondaga Lake. The contribution of each was calculated from field data, experimental data, and literature (Henry *et al.*, 1995). All Hg loads, except dissolved flux from sediment, were specified as fixed inputs. Although Hg release from the sediment is likely to be dependent upon factors that affect the rate of Hg methylation (e.g., dissolved oxygen concentration), there are insufficient data from Onondaga Lake to characterize this functional relationship. As a result, fluxes of Hg from sediment were adjusted during calibration.

3.4. Mercury Kinetics

MERC4 recognizes four types of Hg (i.e., elemental, methyl-, ionic, and inert) to model Hg cycling. However, the distinction between ionic (i.e., reactive) and inert (i.e., non-reactive) Hg is highly dependent on the analytical technique used to make the measurement (Bloom, 1994). In addition, the implications of this distinction on Hg transformation processes in the environment are unknown. Therefore, the "reactive" and "non-reactive" fractions (both available from the Onondaga Lake data set) were combined into a single Hg type (hereafter referred to as ionic Hg) for the modeling effort. In this paper, ionic Hg refers to all Hg species, with the exception of elemental Hg, CH_3Hg, and dimethylmercury [$(CH_3)_2Hg$] which can be measured directly. The values for inion Hg were derived as follows:

$$Hg_{ionic} = Hg_{total} - [\text{elemental Hg} + CH_3Hg + (CH_3)_2Hg]$$

The Hg cycle used in the application of MERC4 to Onondaga Lake is presented in Figure 2. Three Hg species (i.e., elemental, methyl-, and ionic) are modeled. The model includes two transformations between species (net methylation and reduction), sorption to three particle types (fluvial, phytoplankton, and detritus), and volatilization. Because there are no site-specific data on the concentrations or equilibrium constants for Hg complexes (e.g., with chloride, sulfide, hydroxide) and little information on the participation of these complexes in transformation reactions or sorption equilibria, each Hg species is considered as a pool of various complexes. All members of a pool are presumed to participate equally in any transformation or sorption/desorption processes.

3.4.1. *Transformation*

Two transformations between Hg species are explicitly modeled. The concomitant processes of Hg methylation and methylmercury (CH_3Hg) demethylation were combined as net Hg methylation. While the two processes can be differentiated analytically (Furutani and Rudd, 1980; Ramlal *et al.*, 1986), the current method of choice for measuring methylation rates (Gilmour, 1995), which was used in Onondaga Lake (Henry *et al.*, 1995), yields an estimate of net CH_3Hg production. Based on the literature (Winfrey and Rudd, 1990; Gilmour and Henry, 1991) and experimental data (Henry

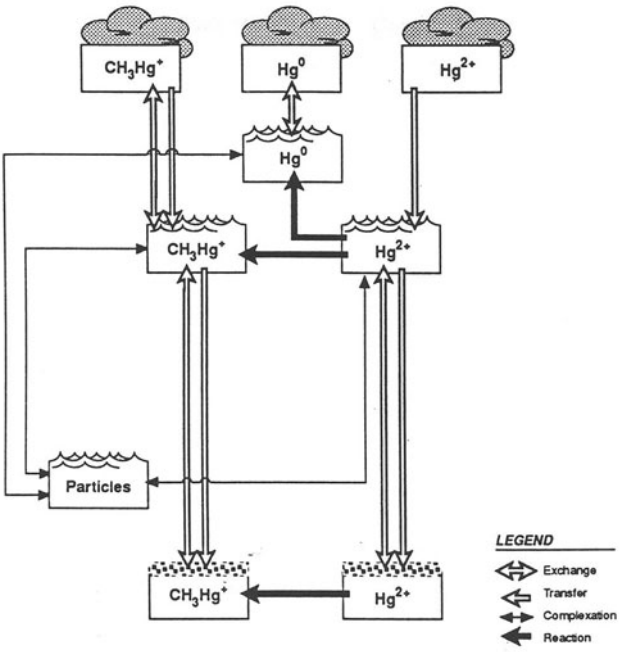

Fig 2. Simplified mercury cycling in the Onondaga Lake Mercury Model

et al., 1995), net methylation is modeled as increasing with temperature and occurring at low dissolved oxygen concentrations (in the hypolimnion). The rate of methylation of ionic Hg was adjusted during calibration until model calculations of methylation on a volumetric basis compared well with experimental observations made in Onondaga Lake during 1992 (Henry *et al.*, 1995).

Reduction of ionic Hg to elemental Hg is modeled as increasing with temperature and occurring under oxic conditions (in the epilimnion). The rate of reduction was adjusted during calibration so that calculated concentrations of elemental Hg most effectively simulated observed elemental Hg concentrations.

Other environmental characteristics in Onondaga Lake that may influence methylation and reduction rates in the water column (e.g., pH, organic carbon, ionic Hg speciation) were not included in the water-column methylation reaction. Insufficient site-specific or literature data were available to distinguish the form of the functional relationship (if any) between these parameters and the rate of CH_3Hg production in Onondaga Lake.

3.4.2. *Sorption*

A site-specific partition coefficient for CH_3Hg in phytoplankton was directly computed from field data by dividing the CH_3Hg concentration in phytoplankton by the dissolved CH_3Hg concentration in water. Other site-specific partition coefficients (CH_3Hg-fluvial solids, CH_3Hg-detritus, ionic Hg-fluvial solids, ionic Hg-detritus) were indirectly estimated from field data by dividing the particulate

concentration by the dissolved concentration of the two mercury species (CH_3Hg and ionic Hg). The particulate concentrations were determined as an average over all particulates measured in Onondaga Lake as suspended solids. The final partition coefficients were adjusted during model calibration to optimize the predicted dissolved and total concentrations of total Hg and CH_3Hg in comparison to field observations.

3.4.3. *Volatilization*

The O'Connor equations for a stagnant lake or pond were selected from options available in MERC4 (AScI, 1992) to estimate both the liquid and gas film transfer coefficients for volatilization of elemental Hg. This approach calculates a shear velocity based on observed wind speed and liquid and gas film transfer coefficients based on shear velocity, media densities, and Schmidt numbers. The liquid and gas film transfer coefficients are used to estimate the overall transfer rate as a function of the universal gas constant, Henry's law constant, and air temperature.

4. Model Calibration

The OLMM was calibrated to most effectively model water column concentrations of Hg species measured in Onondaga Lake during the April to November field sampling program in 1992 (Jacobs *et al.*, 1995). In general, parameters internal to the lake were manipulated within ranges of observed data. Other inputs and outputs (i.e., loading, atmospheric deposition, groundwater, and volatilization) were specified as described in Henry *et al.* (1995). Tables I and II present the calibrated and observed values for these internal parameters.

TABLE I
Net methylmercury production, dissolved flux, and remineralization rates

Parameter	Value in the OLMM		Observed value[a]
	Annual average	Range	
Net CH_3Hg production (ng/L-day)	0.034	0–0.13	0.003–0.11
Dissolved flux (ng/m^2-day)			
Total Hg	21	8.0–52	6.0–50
CH_3Hg	6.1	1.3–25	-0.3–38
Remineralization (ng/m^2-day)			
Total Hg	2,690	1,100–5,480	−275–500
CH_3Hg	300	25–1,100	380–495

[a] Henry *et. al.* (1995).

TABLE II
Total mercury and methylmercury flux from Onondaga Lake sediments

Site	Dissolved oxygen in overlying water[a] (mg/L)	Concentration in 0–4 cm sediment[b]		Flux[b] (ng/m^2-day)	
		Total mercury (mg/kg dry)	Methylmercury (μg/kg dry)	Total mercury	Methylmercury
S4A	2.9	49.5±6.4	10.6±2.2	6.0 (n=1)	-0.30±3.4 (n=2)
S73A	2.6	1.08±0.03	4.87±0.48	5.2±2.1	0.90±0.45
S90A	NA[c]	1.25±0.07	3.71±0.18	50±22	38±10

NA - not analyzed
[a] Average during course of experiment.
[b] Values are means ± standard error. N=3 unless noted.
[c] Samples contained an average of 0.68 μmol sulfide/L.

Final calibrations for total Hg and CH_3Hg in both total (i.e., unfiltered) and dissolved (i.e., filtered) forms are illustrated in Figures 3 and 4, respectively. Data ranges for the hypolimnion reflect the large total Hg and CH_3Hg concentration differences between the thermocline and the lake bottom. With two exceptions, the model simulates the average epilimnetic and hypolimnetic total Hg and CH_3Hg concentrations. First, the calculated hypolimnetic concentrations of total Hg (Figure 3) and ionic Hg (not shown) in early spring do not increase to the levels observed in the 1992 data set. The elevated total Hg and ionic Hg concentrations observed in April may be the result of spring runoff or unexamined mercury cycling processes (e.g., settling of particles) occurring during winter months. Neither calculated nor observed CH_3Hg concentrations are elevated in April, suggesting that little methylation occurs in winter when the water column is aerobic (Walker, 1991).

Second, the model slightly undercalculates the observed epilimnetic concentrations of total Hg (Figure 3) and ionic Hg (not shown) during stratification in late summer. Greater mixing between the epilimnion and hypolimnion at the end of summer would alleviate the discrepancy. However, it would also aggravate the overcalculation of CH_3Hg in the epilimnion during this same period (Figure 4). The reasons for these two exceptions may become clear with further data collection and/or model calibration.

5. Conclusions

The OLMM effectively simulates the concentrations of Hg species and provides a framework for understanding important processes involved in Hg cycling in Onondaga Lake. A real strength of the modeling effort was the ability to calibrate the model to an extensive data set from the 1992 field investigation. In addition, the ability to model the transport and fate of solids and the inclusion of remineralization to simulate release of Hg from settling particles were valuable aspects of the model. The model is general enough to be applicable to other systems, given appropriate data. The OLMM will be used to evaluate the relative impact of different source control and remedial alternatives.

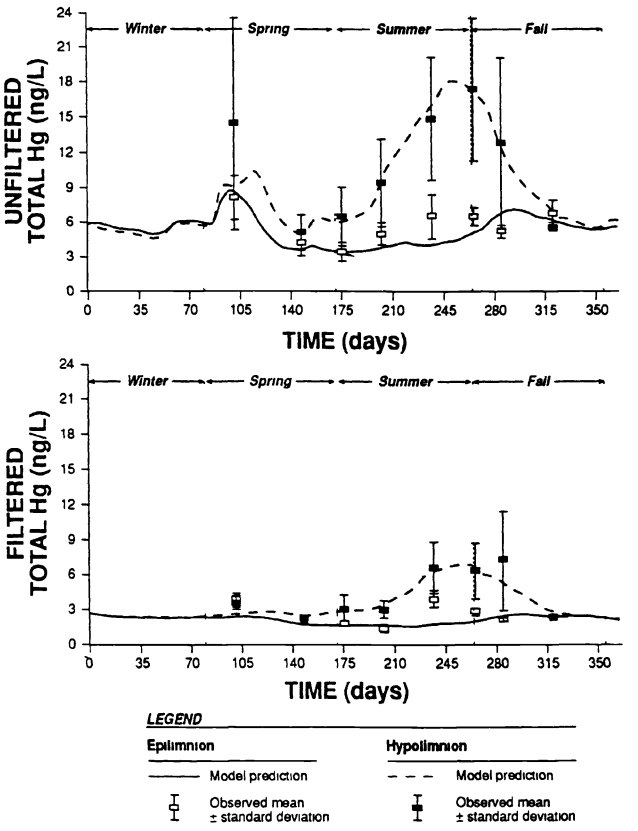

Fig 3 Observed water column data (Jacobs *et al* , 1995) and model-calibrated values for total Hg in Onondaga Lake in 1992

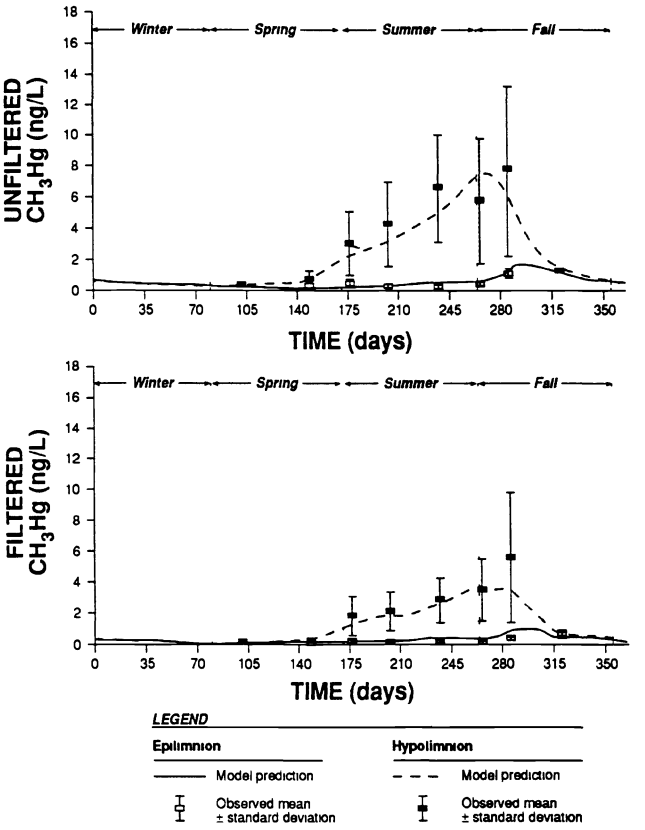

Fig 4 Observed water column data (Jacobs *et al* , 1995) and model-calibrated values for CH_3Hg in Onondaga Lake in 1992

Acknowledgements

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THE ROLE OF DISSOLVED ORGANIC CARBON IN THE CHEMISTRY AND BIOAVAILABILITY OF MERCURY IN REMOTE ADIRONDACK LAKES

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Abstract. A number of recent studies have documented elevated concentrations of mercury (Hg) in fish caught in remote lakes and a pattern of increased concentrations of Hg in fish tissue with decreasing water column pH. Because of the potential linkage between fish Hg and surface water acidification, factors regulating water column concentrations and bioavailability of Hg were investigated in Adirondack lakes through a field study and application of the Mercury Cycling Model (MCM). Concentrations of total Hg and total MeHg were highly variable, with concentrations of total MeHg about 10% of total Hg in lakes which did not show anoxic conditions. In lakes exhibiting anoxic conditions in the hypolimnion during summer stratification, concentrations of total MeHg were elevated. Concentrations of total Hg and total MeHg increased with decreasing pH in remote Adirondack lakes. However, more importantly, concentrations of total Hg and total MeHg increased with increasing concentrations of dissolved organic carbon (DOC) and percent near-shore wetlands in the drainage basin. Mercury concentrations in muscle tissue of yellow perch from Adirondack lakes were elevated above the U.S. FDA action level (1 μg/g Hg) in 7% of the fish sampled or in one or more individual fish from 9 of the 16 lakes sampled. Fish Hg concentrations generally increased with increasing fish length, weight and age. Patterns of increasing Hg concentration with age likely reflect shifts in prey of yellow perch and the bioconcentration of Hg along the food chain. For age 3 to 5 perch, concentrations of Hg increased with increasing concentrations of DOC and percent near-shore wetlands in the drainage basin. However, for a lake with very high DOC concentrations, fish concentrations of Hg declined. Calculations with the MCM also show that concentrations of Hg species increase with increasing DOC due to complexation reactions. Increases in DOC result in increasing concentrations of Hg in biota but decreases in the bioconcentration factor of Hg in fish tissue. This research suggests that DOC is important in the transport of Hg to lake systems. High concentrations of DOC may complex MeHg, diminishing its bioavailability. At high concentrations of monomeric Al, the complexation of MeHg with DOC apparently decreases, enhancing the bioavailability of MeHg.

1. Introduction

High concentrations of Hg in fish tissue have been reported in remote, low ionic strength lakes. Several studies have shown a correlation between fish Hg concentration and lake pH (Grieb *et al*,. 1990; Suns and Hitchin, 1990; Winfrey and Rudd, 1990; Simonin *et al.*, 1994), and a linkage between surface water acidification and fish Hg content has been inferred. An important issue in the U.S. Environmental Protection Agency (EPA) assessment for Section 112 in Title III (Hazardous Air Pollutants) of the Clean Air Act Amendments of 1990 is the establishment of causal relationships between fish Hg and environmental factors (e.g. pH, DOC, atmospheric deposition; Keating, 1994). Factors regulating fish Hg concentrations warrant critical evaluation because the EPA will make recommendations regarding the need for future Hg emission controls.

Many of the studies investigating Hg concentrations in fish have developed regression models based on water and sediment quality, and morphometric characteristics (Hakanson, 1980; Wren and MacCrimmon, 1983; Sorensen *et al.*, 1990). These models

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have been successful in predicting fish Hg concentrations for a particular study. However, because these empirical relationships are site/region specific, they are not easily applied to lakes in other regions (Verta, 1990). A general understanding of the basic mechanisms controlling aqueous Hg speciation and its uptake by the food chain has allowed for the development of conceptual and mechanistic models for Hg cycling (Harris and Snodgrass, 1993; Hudson *et al.*, 1994). One such model, the Mercury Cycling Model (MCM), was applied to Oregon Pond in this study to assess the role of naturally occurring organic acids in the concentration, speciation and bioavailability of Hg.

The objectives of this study were to determine aqueous concentrations of total and MeHg and concentrations of Hg in fish in lakes in the Adirondack region of New York, USA, and to evaluate mechanisms regulating the concentration of Hg in fish, particularly the role of DOC.

2. Methods

The Adirondack region is a large (2,400,000 ha) predominately forested area in northern New York. The bedrock material is primarily granitic gneisses and metasedimentary rocks. The mountains and uplands are mantled glacial till, thicker in the valleys and becoming progressively more shallow upslope. Soils of the region are generally acidic Spodosols, developed from glacial till. The Adirondack region receives large inputs of precipitation (approximately 100 cm/yr) and has high stream runoff (approximately 60 cm/yr). Within the Adirondack Ecological Zone, there are 2,796 lakes and ponds > 0.2 ha in surface area.

For the present study, 16 lakes were selected which represent many classes of Adirondack lakes (Driscoll and van Dreason, 1993). In addition a beaver impoundment, Pancake-Hall Creek, was sampled to investigate the role of wetlands in supplying Hg to downstream lakes. Two of the study sites are seepage lakes (Oregon Pond and North Pond), while the remainder are drainage lakes. Two of the lakes (Sunday Lake and Halfmoon Lake) exhibit depletion of O_2 in the hypolimnion to 0 or near 0 mg/L during summer stratification. The percentage of near-shore wetland area was estimated from topographic maps of individual watersheds.

The yellow perch (*Perca flavescens*) was selected as an index species because it is widely distributed throughout lakes in the Adirondacks, as well as the upper midwest and southeastern Canada. A total of 977 yellow perch were collected from the 16 study lakes, from 16 September to 29 October 1992. Collection methods and details of sample preparation and processing are provided in Driscoll *et al.* (1994).

Water samples were collected from the 16 lakes twice between 15 and 22 October 1992 and between 30 September and 3 October 1993. In addition, stream samples were collected above and below the beaver impoundment at Pancake-Hall Creek (Cirmo and Driscoll, 1993) on 2 October 1993. Clean techniques were followed during all phases of sample collection and handling (Bloom, 1989). Details of sampling and analytical techniques used are provided in Driscoll *et al.* (1994).

The MCM was developed to investigate the biogeochemistry of Hg in seepage lakes. In the model the lake is divided into epilimnetic, hypolimnetic and sediment compartments, and the food chain includes four trophic levels. A detailed description of the MCM is given in Hudson *et al.* (1994).

Oregon Pond, a small, oligotrophic, mounded seepage lake located in the northeast Adirondacks was selected for application of the MCM. The 8.7 ha lake has a mean depth of 4.5 m, with a maximum depth of 11.3 m. Although the lake thermally stratifies, the hypolimnion remains oxic during the summer.

The variability of Hg concentrations in water and fish from remote lakes (Driscoll *et al.*, 1994; Sorenson *et al.*, 1990; Grieb *et al.*, 1990) suggests that several factors affect the ultimate concentration of Hg in the water column and biota. One factor of potential importance is DOC (Driscoll *et al.*, 1994). Model scenarios were conducted varying DOC concentrations from 2.7 mg C/L (observed value) to 40 mg C/L, to observe the effect on simulated Hg concentrations in the water column and biota.

3. Results

3.1. Water Chemistry

The lakes evaluated in this study were generally low ionic strength waters. Values of acid neutralizing capacity (ANC) ranged from below 0 to above 200 μeq/L, with pH values from below 5 to near 7.0. The study lakes also had a range of DOC concentrations (from 2.0 to over 20 mg C/L). Lake DOC concentrations were influenced by the presence of near-shore wetlands within the drainage basin (DOC concentration (mg C/L) = 1.28* % wetland + 0.98, $r^2 = 0.85$; where % wetland is the % of the total watershed area that is near-shore wetlands).

The seepage lakes (North and Oregon Ponds) had among the lowest observed concentrations of total Hg, less than 2 ng/L. The concentrations of total Hg in drainage lakes ranged from below 1 ng/L to above 6 ng/L. Most of the total Hg was in the dissolved fraction (mean dissolved Hg/total Hg = 0.61), although there was considerable lake-to-lake variability in the fraction of particulate Hg. There was no relationship with the fraction of dissolved Hg and water chemistry parameters, such as pH or DOC concentration.

Considerable variability was also evident in concentrations of total MeHg (from 0.03 to 0.70 ng/L). The seepage lakes (North and Oregon Ponds) also showed low concentrations of total MeHg. Lakes with anoxic hypolimnia during summer stratification (Sunday Lake and Halfmoon Lake) had relatively high concentrations of total MeHg. This observation is consistent with the formation of MeHg under anaerobic conditions (Gilmour *et al.*, 1991). In the Adirondack lakes studied, there was generally a good relationship between concentrations of total MeHg and total Hg for oxic lakes (total MeHg (ng/L) = 0.1* total Hg (ng/L) - 0.06, $r^2 = 0.86$). Total MeHg was about 10% of total Hg in most Adirondack lakes. An exception to this pattern was evident for the lakes with anoxic hypolimnia, which had about 20% of total Hg as total MeHg.

In the Adirondack lakes, there was a weak pattern of increasing concentrations of both total Hg and total MeHg with decreases in pH below 6.0 (Figure 1). Moreover, for a given pH, lakes with concentrations of DOC greater than 6 mg C/L had higher concentrations of both total Hg and total MeHg than lakes with concentrations of DOC less than 6 mg C/L.

There were strong relationships between both concentrations of total Hg and DOC (total Hg (ng/L) = 0.25* DOC (mg C/L) + 0.87, $r^2 = 0.79$) and total MeHg and DOC (total

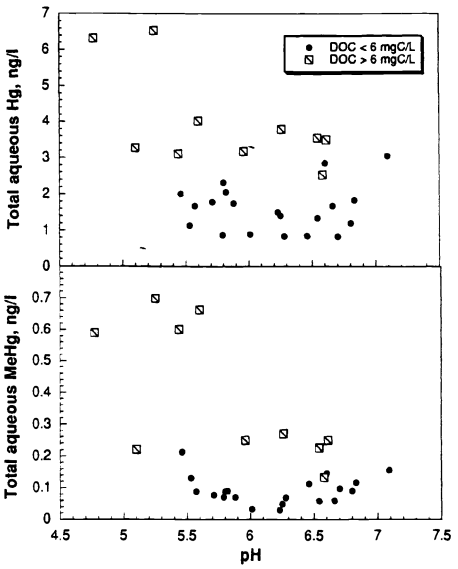

Fig. 1. Concentrations of total Hg (a) and total MeHg (b) as a function of pH for Adirondack study lakes. Lakes with high (> 6 mg C/L) and low (< 6 mg C/L) DOC concentrations are shown.

MeHg (ng/L) = 0.03* DOC (mg C/L) + 0.001, r^2 = 0.89; excluding Sunday Lake and Halfmoon Lake). In addition, concentrations of total Hg and total MeHg were correlated with the percent near-shore wetlands of the drainage basin (total Hg (ng/L) = 0.32* % wetland + 1.15, r^2 = 0.68; total MeHg (ng/L) = 0.03* % wetland + 0.04, r^2 = 0.82).

To investigate the role of wetlands in regulating the supply of Hg to downstream lakes, Pancake-Hall Creek was sampled above and below a beaver impoundment. Streamwater was enriched in total Hg (1.9 to 2.7 ng/L), total MeHg (0.09 to 0.16 ng/L) and DOC (4.0 to 7.6 mg C/L) after transport through the wetland system. Through a mass balance study, Cirmo and Driscoll (1993) showed that Pancake-Hall Creek was a source of DOC and a sink of SO_4^{2-}, particularly in the summer season. Given these conditions, it is not surprising that the wetland system enhanced the supply of total and total MeHg to the downstream lake.

3.2. Mercury in Fish

Concentrations of Hg generally increased with increasing length, weight and age for the yellow perch sampled in Adirondack lakes, except for one of the seepage lakes, Oregon Pond (Figure 2). This pattern of increasing Hg concentration in older fish likely reflects changes in prey selection and bioconcentration of Hg along the aquatic food chain. Marked increases in concentration of Hg in fish muscle tissue were evident from age 0+ to 2+. This trend is probably due to changes in feeding of young fish from zooplankton to larger invertebrates with higher Hg content. Concentrations of Hg remained relatively constant for age 3+ to 5+ yellow perch, with mean values near 0.5 µg/g. A two-way analysis of variance of age 3+ to 5+ yellow perch Hg concentrations, as a function of age

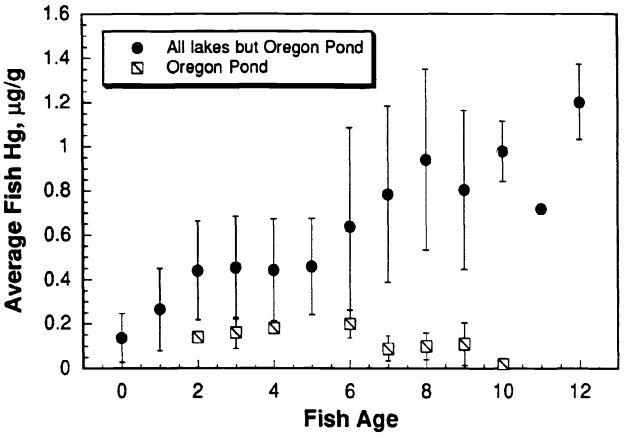

Fig. 2. Concentrations of Hg in the muscle tissue of different age classes of yellow perch in Adirondack study lakes. The error bars represent standard deviations.

and lake, indicated no significant ($p > 0.05$) age effects between lake comparisons of mean Hg concentrations. Further increases in fish Hg above age 5+ probably reflect a shift to piscivory. The latter increase in Hg concentration of older age fish occurred at a length of approximately 200 mm, above which piscivory or cannibalism is common to yellow perch populations (Tarby, 1974).

In Oregon Pond, concentrations of fish Hg increased up to age 6+ and declined thereafter. This unusual pattern may be due in part to a lack of fish prey species in this pond and high variability in growth rates of older fish. For example, Hg concentrations in age 9+ perch were inversely related to growth rates (fish Hg (µg/g) = 0.80 - 1.872*Growth Rate, $r^2 = 0.86$, $p = 0.0017$) and Hg concentrations in perch age 7+ to 10+ were inversely related to body weight (fish Hg (µg/g) = 0.45 - 0.001*Weight (g), $r^2 = 0.45$, $p = 0.0018$). These relationships suggest that growth dilution (i.e., rate of muscle tissue elaboration exceeds rate of Hg uptake in food) is responsible for the decline in Hg concentration of older, faster growing perch in the Oregon Pond population.

In the study lakes, 33% of the yellow perch caught exceeded the 0.5 µg/g Action Level, while 7% exceeded the U.S. FDA Action Level of 1.0 µg/g. Additionally, one or more perch with Hg concentrations exceeding the 0.5 µg/g level were found in 14 of the 16 study lakes and one or more perch exceeding the 1.0 µg/g level were found in 9 of the 16 study lakes.

Unlike other studies (Gill and Bruland, 1990), none of the simple regressions between concentrations of Hg in age 3+ to 5+ perch and aqueous measurements of pH, DOC and total MeHg were significant ($p > 0.05$) when the high DOC (24 mg C/L) Rock Pond was included in the analysis. Excluding Rock Pond, significant ($p < 0.05$) regressions were obtained between fish Hg and total MeHg concentrations in the water column (fish Hg (µg/g) = 0.35 + 0.58*total MeHg (ng/L), $r^2 = 0.32$), and pH (fish Hg (µg/g) = 1.46 - 0.17*pH, $r^2 = 0.30$) and DOC (fish Hg (µg/g) = 0.2 + 0.05*DOC (mg C/L), $r^2 = 0.28$). The only water chemistry parameter significantly correlated with fish Hg, with all 16 lakes included, was total monomeric Al (fish Hg (µg/g) = 0.20 + 0.003* Al

(μg/L), $r^2 = 0.46$. Total monomeric Al tends to be highest in low pH lakes with high DOC (Driscoll, 1989) and appears to be a better indicator of fish Hg concentrations than either pH or DOC alone. This observation suggests that fundamental hydrologic and geochemical processes controlling the transport and solubility of Al also influence the bioavailability of Hg in these lakes. Hypolimnetic anoxia is another factor that may influence Hg bioavailability in Adirondack lakes. For example, concentrations of Hg in age 3+ to 5+ yellow perch were high in Sunday Lake and Halfmoon Lake, lakes with anoxic hypolimnia and high aqueous concentrations of MeHg in the water column.

In Adirondack lakes, concentrations of Hg in age 3+ to 5+ yellow perch increased with increasing concentrations of DOC and percentage of near-shore wetlands in the drainage basin (fish Hg (μg/g) = 0.08*% wetland + 0.19, $r^2 = 0.65$), without considering the highly dystrophic Rock Pond. The Rock Pond data suggest that with increases in DOC concentration at some value above 8 mg C/L, concentrations of fish Hg decrease.

The bioconcentration factor (BF) of MeHg is defined as the ratio of MeHg concentration in fish tissue to the total MeHg concentration in water. For age 3+ to 5+ yellow perch, the log BF ranged from 5.73 to 7.03. The log BF decreased significantly with increasing concentrations of DOC, but showed no significant ($p > 0.05$) pH effect. For given concentrations of DOC, the presence or absence of potential fish prey species also significantly influenced the MeHg BF (log BF = 6.3 - 0.04*DOC (mg C/L) + 0.41*prey presence/absence, $r^2 = 0.59$). For the Adirondack lakes studied, the log BF was lowest in dystrophic Rock Pond and the lakes with anoxic hypolimnion, Sunday Lake and Halfmoon Lake.

In multiple regression analysis, mean Hg concentrations for age 3+ to 5+ yellow perch increased with increasing total dissolved Al and decreased with increasing DOC. Although aqueous total MeHg concentrations were higher in lakes with high DOC concentrations, bioavailable MeHg appears to be regulated primarily by the extent of Hg binding with organic ligands. Aluminum may compete with MeHg for organic binding sites, thus leading to greater bioavailability of MeHg in lakes with high Al/DOC ratios (fish Hg (μg/g) = 0.01*Al/DOC (μg Al/mg C) + 0.21, $r^2 = 0.73$).

As a further test of this idea, a MeHg speciation algorithm was used to calculate the concentrations of organically bound MeHg and inorganic complexes of MeHg (CH_3Hg^+, CH_3HgOH, and CH_3HgCl) for measured concentrations of total dissolved MeHg, pH, DOC, monomeric Al, total F and Cl. Methyl Hg complexation constants were obtained from Hudson et al. (1994), while Al complexation constants were obtained from Driscoll (1989). Free F and organic ligand ($RCOO^-$) were iteratively adjusted simultaneously until calculated and measured concentrations of total F and total organic ligand were equal (assumed 2μM total ligand/mg DOC gave best agreement between calculated and measured organic monomeric Al).

Comparison of the relationships between yellow perch Hg and the calculated concentrations of dissolved inorganic and organic MeHg reveal no significant relationship between fish Hg and organic MeHg, a marginally significant relationship between fish Hg and inorganic MeHg calculated without invoking competitive Al complexation ($r^2 = 0.31$), and a highly significant relationship between fish Hg and inorganic MeHg calculated with competitive Al complexation. An even stronger relationship ($r^2 = 0.78$) was obtained for the regression between fish Hg and the sum of only the neutral inorganic MeHg complexes ($CH_3HgOH + CH_3HgCl$). The model predicts that at $pH < 6$ and low DOC, increasing monomeric Al will increase the inorganic proportion of MeHg for a given concentration

of total dissolved MeHg. This analysis strongly suggests that only inorganic species of dissolved MeHg are available for bioaccumulation and that both Al and DOC are important determinants of MeHg bioavailability in acidic drainage lakes.

3.3. Modeling of Oregon Pond

For Oregon Pond, the MCM model was configured such that there were two fish populations representing different age groups of the same species; younger fish (ages 0+ to 6+) which have higher Hg concentrations, and the older population (7+ to 10+) which exhibit lower concentrations of Hg. To ensure stability in model calculations, comparisons of the various scenarios were made using average values from the final year of a 20 year simulation.

The calibrated version of the MCM produced results which compared favorably with the observed data (Table I). The simulated concentrations of all three Hg species (Hg^0, Hg(II), MeHg) in the epilimnion increased with increasing DOC concentrations (Figure 3a). Concentrations of Hg^0 and Hg(II) began to level off at high DOC (> 30 mg C/L), while MeHg concentrations increased steadily up to the maximum DOC concentration investigated, 40 mg C/L. This relationship reflects patterns observed in the field, although maximum simulated concentrations of Hg were much lower than the observed range from the study lakes.

Model simulations suggest that concentrations of Hg in the biota increase with increasing DOC to about 30 mg C/L, after which they level off (Figure 3b). An annually averaged maximum concentration of about 0.35 µg/g occurs in the younger fish (total

TABLE I

Observed and calibrated values for Oregon Pond

Parameter	Model	Observed
cumulative fish biomass (kg/ha)	16	--
young fish MeHg (µg/g)	0.189	0.184
old fish MeHg (µg/g)	0.074	0.07
log BF young fish	6.35	6.38
log BF old fish	6.02	6.01
epilimnion Hg^0 (ng/l)	0.016	<0.02
epilimnion total Hg(II) (ng/l)	0.83	0.84
epilimnion dissolved Hg(II) (n/l)	0.30	0.28
% dissolved Hg(II)	36	33
epilimnion total MeHg (ng/l)	0.071	0.069
epilimnion dissolved MeHg (ng/l)	0.015	0.015
% dissolved MeHg	21	22
sediment Hg(II) (µg/g)	0.203	0.006-0.205*

*from Little Rock Lake, WI (Rada *et al.*, 1993).

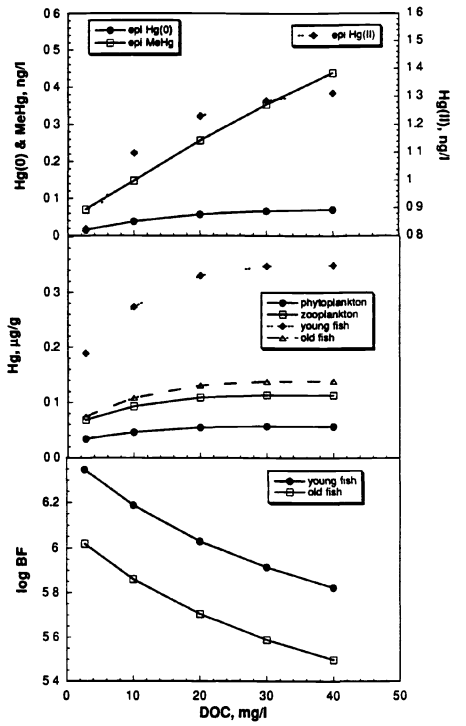

Fig 3 Simulations of the aqueous speciation of Hg (a), the concentrations of Hg in biota (b) and the bioconcentration factor of MeHg in fish (c) as a function of DOC concentration in Oregon Pond using the Mercury Cycling Model

range of 0.1 to 0.7 µg/g). Elevated concentrations of organic ligands facilitate the mobilization of Hg from particulate to aqueous phases. This process is illustrated in the simulations as the percent of dissolved Hg(II) and MeHg increased with increasing DOC to greater than 70% at a DOC concentration of 40 mg C/L, from basecase values of 20 and 36%, respectively. Because DOC-complexed Hg is not easily assimulated by phytoplankton, the BF decreases as DOC increases (Figure 3c).

4. Discussion

Concentrations of Hg in muscle tissue of yellow perch obtained from remote Adirondack lakes were higher than values reported for other lake districts in eastern North America (Table II). The most obvious factor regulating the concentration and availability of both total and MeHg in Adirondack lakes is DOC. A number of investigators have reported relationships between Hg and concentrations of DOC or color in surface waters (Mierle and Ingram, 1991; Lindqvist *et al.*, 1991). However, patterns between DOC concentrations and fish tissue Hg have been inconsistent. Concentrations of DOC explained a significant

TABLE II
Comparison of mercury concentrations in yellow perch in this study with yellow perch from other locations.

Location	Age Group	Fish Hg* (μg/g)	Reference
Ontario (16 lakes)	0+	0.12±0.05 0.03-0.23	Suns and Hitchin, 1990
Adirondacks (7 lakes)	0+	0.15±0.10 0.04-0.35	this study
Ontario (6 lakes)	1+	0.07±0.04 0.03-0.14	Bodaly *et al.*, 1993
Wisconsin-Little Rock Lake	1+	0.11-0.14	Weiner *et al.*, 1990
Adirondacks (13 lakes)	1+	0.28±0.16 0.09-0.75	this study
Wisconsin (10 lakes)	2+	0.12±0.04 0.06-0.19	Cope *et al.*, 1990
Adirondacks (16 lakes)	2+	0.41±0.19 0.11-0.78	this study
Michigan (35 lakes)	3+ to 5+	0.25±0.16 0.06-0.51	Grieb *et al.*, 1990
Adirondacks (12 lakes)	3+ to 5+	0.36±0.17 0.08-0.76	Simonin *et al.*, 1994
Adirondacks (16 lakes)	3+ to 5+	0.45±0.24 0.17-0.88	this study

*Means and ranges calculated using the average concentration of fish mercury for an age class in each lake for a specific study.

amount of the variation of Hg in lake trout in Ontario (McMurty *et al.*, 1989). Likewise, Haines *et al.* (1992) observed a positive correlation between lake color and concentrations of Hg in perch in the Soviet Union. In contrast, Grieb *et al.* (1990) reported that Hg content of yellow perch decreased with increasing DOC concentrations in Michigan seepage lakes.

The results of our study suggest that DOC plays a complicated role in the transport and bioavailability of Hg in lake ecosystems. The transport of total and MeHg to Adirondack lakes seems to be linked to DOC production from wetlands within the basin. Therefore, DOC seems to be important in regulating lake concentrations of both total and MeHg, and ultimately the supply to fish. On the other hand, DOC appears to bind with MeHg, limiting its bioavailability. This conflicting role of DOC is shown by the increase in fish Hg concentrations with increasing DOC up to about 8 mg C/L followed by lower Hg concentrations in yellow perch caught from highly dystrophic Rock Pond (DOC = 24 mg C/L), and the observed decreases in the BF of MeHg with increasing DOC. In addition, inputs of other metals, like Al, which complex with DOC appear to decrease the binding of MeHg with organic ligands, increasing its bioavailability. This process is particularly relevant for lake districts, like the Adirondacks, that have been impacted by acidic deposition and exhibit elevated Al concentrations.

In addition to DOC and Al concentration, other factors such as lake pH concentration, anoxic hypolimnia, fish age and food sources appear to be important in the regulation of fish Hg concentrations. This myriad of factors undoubtedly contributes to the weak relationship between MeHg and fish Hg concentrations.

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TOTAL MERCURY AND METHYLMERCURY MASS BALANCE IN AN ALKALINE, HYPEREUTROPHIC URBAN LAKE (ONONDAGA LAKE, NY)

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Abstract. A total mercury (total Hg) and methylmercury (CH_3Hg) mass balance was developed for Onondaga Lake, NY, based on sampling of tributaries, sediments, water column, and biota in 1992. The *in situ* flux of total Hg and CH_3Hg from sediments to the overlying water and the rate of net CH_3Hg production in the water column were determined experimentally. Fluxes from atmospheric deposition, groundwater, and volatilization were estimated from limited field data and the literature. Ultraclean sampling and analytical techniques developed specifically for Hg were used. Results indicate that tributaries contribute the majority of total Hg entering the lake (13.6 kg in 1992). Other sources of total Hg included groundwater flux (0.02 kg), atmospheric deposition (0.44 kg), and flux from sediments (0.056 kg). Net sedimentation (11.1 kg), outflow (2.8 kg), and volatilization (0.016 kg) were sinks for total Hg. The two major sources of CH_3Hg were tributaries (0.26 kg) and net CH_3Hg production in the water column (0.60 kg). Flux from sediments accounted for only 0.017 kg CH_3Hg. Net sedimentation (0.47 kg), outflow (0.24 kg), and net uptake by fish (0.20 kg) were sinks for CH_3Hg. Gross sedimentation of CH_3Hg exceeded net sedimentation by 90%, suggesting that release of CH_3Hg from settling particles is a significant process.

1. Introduction

The sources of mercury (Hg) and the dynamics of Hg cycling have been studied in pristine oligotrophic systems in recent years. For example, total Hg mass balances have been proposed for two seepage lakes in Wisconsin: Little Rock Lake (Fitzgerald and Watras, 1989) and Pallette Lake (Krabbenhoft and Babiarz, 1992). Researchers in Canada (St. Louis *et al.*, 1994) and Sweden (Johansson *et al.*, 1991; Meili, 1991) have reported total Hg and methylmercury (CH_3Hg) mass balances for drainage systems. Non-contaminating analytical speciation methods developed specifically for Hg, as well as experimental approaches only recently applied (i.e., flux and methylation measurements made at ambient Hg concentrations), have proven extremely useful in attempts to quantify the sources and sinks of various Hg species in these systems.

The methodology and concepts used in studies of Hg cycling in pristine systems have rarely been applied to Hg-contaminated systems. Clear Lake, California, a reservoir located adjacent to a former Hg mine, is an exception and is currently undergoing extensive investigation (Suchanek *et al.*, 1993). Onondaga Lake, New York, is another exception. PTI Environmental Services (PTI) has been conducting a large remedial investigation and feasibility study on the lake since 1991. The lake provides an interesting contrast to previously studied sites because it is slightly alkaline and hypereutrophic and received historical discharges of Hg from two Hg-cell chloralkali plants. The only previous work on the lake with respect to Hg cycling has been the work of Bloom and Effler (1990), who documented seasonal variability in water column concentrations of Hg species, and the work of Wang (1993), who determined patterns of total Hg concentration in the lake.

Extensive data were collected as part of the remedial investigation and feasibility study to document the temporal and spatial variability of Hg species as well as the dynamics of Hg cycling

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and bioaccumulation in the lake. A mass balance analysis was also developed to identify and quantify the major sources and sinks for total Hg and CH_3Hg in the lake.

2. Materials and Methods

2.1. Site Description

Onondaga Lake is an urban lake located in Onondaga County, New York, next to the city of Syracuse. The lake itself has a surface area of 12 km^2 and receives runoff from a drainage basin estimated to cover 600 to 620 km^2 (Onondaga County, 1971). Surface water flows into the lake from seven tributaries (Figure 1). The Metropolitan Syracuse Sewage Treatment Plant (Metro) contributes a significant amount of water (i.e., approximately 30% of the annual load) to the lake. Onondaga Lake is considered hypereutrophic as evidenced by low transparency, large phytoplankton blooms and depletion of dissolved oxygen during fall turnover (Bloom and Effler, 1990). Like other marl lakes in the region, the lake is slightly alkaline, with an average pH of 7.5. Onondaga Lake is dimictic. During summer stratification, the thermocline is located at approximately 9 to 10 m below the water surface, and the hypolimnion is anoxic and sulfidic.

Historically, Onondaga Lake has received loadings of industrial wastewater. Industrial effluent from two Hg-cell chloralkali plants contributed up to 42 lb total Hg/day before the imposition of discharge limits by the U.S. Environmental Protection Agency in 1970. Loading of Hg to the lake decreased dramatically at this time with the implementation of large-scale changes in operations at the chloralkali plants. The plants were later closed in 1977 and 1988, respectively.

2.2. Sampling Methods

Water samples were collected from the primary tributaries (Figure 1) twice a month from April to December of 1992, and analyzed for total Hg, CH_3Hg, and suspended solids. Grab samples were collected during low flow events, and grab samples followed by composites were collected during the high flow events. Samples were collected in Teflon® bottles using Hg-clean techniques (Fitzgerald and Watras, 1989).

Flow rates during sampling of Ninemile Creek, Onondaga Creek, Ley Creek, and Harbor Brook were obtained from U.S. Geological Survey (USGS) monitoring records. Flow rates during sampling of Metro effluent were obtained from Onondaga County Department of Drainage and Sanitation monthly monitoring reports. Elevation was continuously monitored in the remaining tributaries by PTI. These elevation records were converted to flow rates using ratings developed from concurrent intermittent flow rate measurements collected using a Marsh-McBirney Portable Meter (Marsh-McBirney, 1990).

For dating purposes and estimation of net sedimentation, sediment cores were taken in the north and south basins (Figure 1) to a depth of 2.5 m. Sediment samples were also taken with an acrylic Soutar-design box corer (15 cm×15 cm) at several sites in the lake (Figure 1) to provide intact sediment for flux studies.

Sediment traps approximately 20 cm in diameter were deployed from May through November of 1992, 2 m above the sediment in the north and south basins (Figure 1), to estimate gross sedimentation. Traps were sampled monthly for total Hg concentration, CH_3Hg concentration, and total solids. To avoid contamination, traps were made of acrylic plastic.

Sediment cores were taken in August 1992 to determine the diffusive flux of dissolved total Hg and CH_3Hg from sediment to overlying water. The cores were taken from box core samples using

acid-cleaned Teflon® chambers machined from 2-L Teflon® jars with Savillex® screw tops. Chambers were incubated in the laboratory under *in situ* conditions of temperature and dissolved

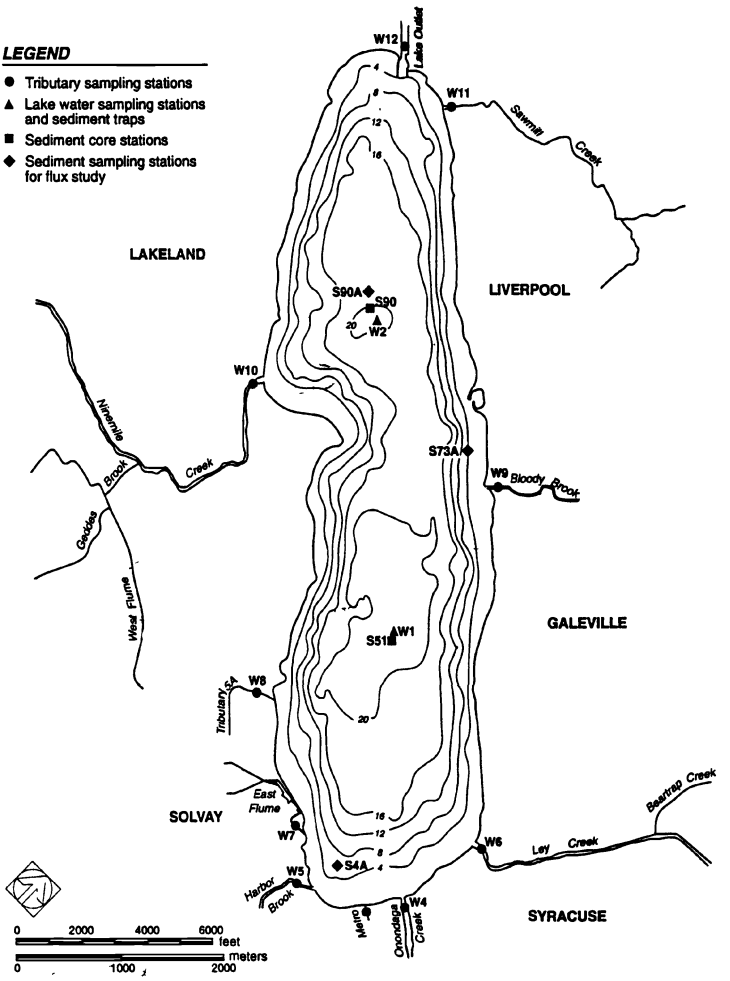

Fig. 1. Locations of sampling stations.

oxygen concentration. Hg flux was determined by measuring the change in the amount of dissolved total Hg and CH_3Hg in water overlying each sediment core over time.

Also in August 1992, water column samples to estimate Hg methylation rates were collected at depths of 3, 9, and 15 m from the north basin directly into acid-cleaned Teflon® chambers using a non-contaminating pumping method as described above. Chambers were incubated and sampled, as were the flux chambers. Net water column methylation was determined by measuring the change in the amount of dissolved CH_3Hg in the water samples over time. More detail on flux and methylation methodology is provided in Gilmour (1995).

2.3. Laboratory Analysis

All Hg analyses were performed by Brooks Rand, Ltd., using cold vapor atomic fluorescence spectroscopy (Bloom and Fitzgerald, 1988). Sediments were digested and analyzed for total Hg according to Bloom and Crecilius (1983, 1987). Total Hg in water samples was measured following bromium chloride oxidation (Bloom and Fitzgerald, 1988). Analysis of total Hg samples followed the gold amalgamation technique (Gill and Fitzgerald, 1987). CH_3Hg in sediments and water was measured by the ethylation technique following separation by ether extraction (Bloom, 1989) or distillation (Horvat *et al.*, 1993a,b).

In addition to Hg analysis, stratigraphic cores were sectioned at 2.5-cm intervals and analyzed for ^{210}Pb and ^{137}Cs for dating purposes. ^{210}Pb activity was determined by measuring the activity of its granddaughter isotope, ^{210}Po, using alpha spectrometry (Bennett and Carpenter, 1979; Carpenter *et al.*, 1981, 1982). ^{137}Cs activity was determined by ß-ray measurement after nitric and hydrofluoric acid extraction followed by cation exchange purification (Carpenter *et al.*, 1981; Beasley *et al.*, 1982).

2.4. Modeling Approach

Long-term flow records and flow records developed from elevation monitoring were combined with total Hg, CH_3Hg, and suspended solids concentrations by the FLUX Model (U.S. COE, 1987) to develop annual loading estimates of these constituents from the tributaries and Metro to Onondaga Lake. Contributions from atmospheric deposition, groundwater, volatilization, and flow through the outlet were estimated based on literature and observed data.

The mass balance of total Hg and CH_3Hg was constructed with a version of MERC4 (AScI, 1992) specifically modified by PTI for application to Onondaga Lake. The model was calibrated to most effectively match water column concentrations of total Hg, elemental Hg, ionic Hg, and CH_3Hg observed in Onondaga Lake in 1992 (Jacobs *et al.*, 1995). Details of model development and calibration are presented in Henry *et al.* (1995).

3. Results and Discussion

3.1. Total Mercury

3.1.1. *Sources*

Approximately 14.1 kg of total Hg entered Onondaga Lake in 1992. Of this amount, tributaries including Metro contributed 13.6 kg or 96% of total Hg loading. Specific yields of total Hg were calculated for four tributaries monitored by USGS, based on annual loading estimates and area of the respective drainage basins (Table I). Ninemile Creek had the highest yield of total Hg. This creek also carries the largest suspended solids load to the lake and receives runoff from a former

chloralkali plant site. Yields of the three remaining tributaries were comparable to, although on the high end of, those reported for catchment areas in Sweden affected by atmospheric deposition of mercury (i.e., 0.8–5.9 g/km^2-year or 8–59 mg/ha-year) (Johansson *et al.*, 1991). Yields were several times greater than those reported for pristine drainage areas in a Canadian boreal forest ecosystem (i.e., 3–23 mg/ha-year) (St. Louis *et al.*, 1994).

TABLE I
Specific yields of total Hg and CH_3Hg for four tributaries of Onondaga Lake

Tributary	Area of drainage basin (ha)	Loading to lake (g/year)		Specific yield (mg/ha-year)	
		Total Hg	CH_3Hg	Total Hg	CH_3Hg
Harbor Brook	2,930	220	8.7	75	3.0
Ley Creek	7,740	409	5.2	53	0.7
Onondaga Creek	28,500	1,811	49.2	64	1.7
Ninemile Creek[a]	24,640	2,737	25.3	111	1.0

[a] Not including the lower reaches of Ninemile Creek which are strongly affected by resuspension.

Three other sources (i.e., atmospheric deposition, groundwater, and flux from sediments) accounted for the remainder of total Hg entering the lake. Atmospheric deposition was estimated at 0.44 kg/year based on values of 30 ng total Hg/L in wet deposition (Glass *et al.*, 1991; Iverfeldt, 1991), 3.5 μg/m^2-year in dry deposition (Fitzgerald et al., 1991), total wet deposition to Onondaga Lake of 43.58 inches (NOAA, 1992), and surface area of the lake equal to 12×10^6 m^2.

Groundwater was estimated to contribute 0.02 kg total Hg to Onondaga Lake in 1992. A background concentration of 4 ng/L was assigned to the majority of groundwater entering the lake based on surface water concentrations in Sawmill Creek and Bloody Brook (i.e., 2–4 ng total Hg/L) and groundwater sampling in Pallette Lake, Wisconsin (Krabbenhoft and Babiarz, 1992). Groundwater data on dissolved total Hg (i.e., average of 620 ng/L) were available from an area adjacent to a former chloralkali plant and were applied to the appropriate volume of water expected to enter the lake from this site.

Diffusive (i.e., non-advective flux) of total Hg from sediments appeared to depend strongly on the dissolved oxygen concentration in the overlying water, with highest flux values observed at lowest dissolved oxygen concentrations (Table II). The concentration of total Hg in bulk sediment appeared to have little influence on flux. The flux value was adjusted in the course of model calibration (Henry *et al.*, 1995) and contribution from sediment flux was calculated to be 0.056 kg in 1992.

3.1.2. *Sinks*

The four sinks for total Hg in Onondaga Lake in 1992 were net sedimentation (11.1 kg), outflow (2.8 kg), net uptake by fish (0.20 kg), and volatilization (0.016 kg). Net sedimentation of total Hg was estimated to be 2,900 μg/m^2-year (Table III); this value was adjusted during model calibration (Henry *et al.*, 1995). Outflow through the outlet was calculated by the model based on a water balance for the lake and epilimnetic concentrations of total Hg; data collected from the outlet were considered unreliable because flow rates were often less than detection. Net uptake by fish was

calculated by the model as the difference between the amount of CH_3Hg consumed in prey and the amount of CH_3Hg released through egestion and excretion. Loss of Hg from the lake surface by volatilization of elemental Hg was calculated by the model based on calculation of liquid and gas film transfer coefficients as a function of observed wind speed (Henry *et al.*, 1995).

TABLE II
Total Hg and CH_3Hg flux from Onondaga Lake sediments

Site	Dissolved oxygen in overlying water[a] (mg/L)	Concentration in 0–4 cm sediment[b] (mg/kg dry)		Flux[b] (ng/m²-day)	
		Total Hg	CH_3Hg	Total Hg	CH_3Hg
S4A	2.9	49.5±6.4	10.6±2.2	6.0 (n=1)	-0.30±3.4 (n=2)
S73A	2.6	1.08±0.03	4.87±0.48	5.2±2.1	0.90±0.45
S90A	NA[c]	1.25±0.07	3.71±0.18	50±22	38±10

NA - not analyzed
[a] Average during course of experiment.
[b] Values are means ± standard error. N=3 unless noted.
[c] Samples contained an average of 0.68 μmol sulfide/L.

TABLE III
Annual estimates for net and gross sedimentation of solids, total Hg, and CH_3Hg for the south (W1) and north (W2) basins of Onondaga Lake in 1992

	Solids (g/m²-year)	Total Hg (μg/m²-year)	$CH_{30}Hg$ (μg/m²-year)
Net sedimentation			
W1	2,800	5,000	NA
W2	2,700	2,900	13
Gross sedimentation			
W1	3,300	4,900	190
W2	3,000	3,100	150

NA - not analyzed

3.2. METHYLMERCURY

3.2.1. *Sources*

The total input of CH_3Hg to Onondaga Lake was estimated to be 0.88 kg in 1992. Tributary loading, including Metro, accounted for 29% of the annual load. The specific yield of CH_3Hg was similar for the four USGS tributaries with Harbor Brook being slightly higher than the others (Table I). The elevated total Hg yield observed for Ninemile Creek was not reflected in the CH_3Hg yield, suggesting that Hg species other than CH_3Hg made up the majority of the total Hg loading from this creek. These specific yield estimates are higher than those reported for drainage in a pristine

Canadian boreal forest ecosystem (i.e., 0.06–0.96 mg/ha-year), (St. Louis *et. al.*, 1994). However, the yields are comparable to those from Sweden (0.8 to 1.7 mg/ha-year) in an area affected solely by atmospheric deposition (Lee *et.al.*, 1995).

Net CH_3Hg production in the water column supplied 0.60 kg CH_3Hg in 1992 and accounted for 68% of the annual load. Rates increased dramatically with depth, presumably due to decreased dissolved oxygen concentration in the hypolimnion (Table IV). Net methylation rates in the hypolimnion were adjusted during model calibration within the range of values determined experimentally (Henry *et al.*, 1995).

TABLE IV
Net CH_3Hg production rates at three depths in Onondaga Lake

Depth (m)	Dissolved oxygen[a] (mg/L)	Net CH_3Hg production[b] (ng/L-day)
3	4.4	0.003 ± 0.002
9	0.9	0.03 ± 0.01
15	NA[c]	0.11 ± 0.03

NA - not analyzed
[a] Average during course of experiment.
[b] Values are means (n=3) $\pm$ standard error.
[c] Samples contained an average of 1.2 μmol sulfide/L.

Dissolved oxygen concentration in overlying water also had a dramatic effect on CH_3Hg flux from sediments, with flux from sediments under anoxic/sulfidic water approximately 40 times greater than at 2.5 to 2.9 mg dissolved oxygen/L (Table II). This observation supports other studies that indicate enhanced CH_3Hg production and flux in anoxic sediments (Gilmour and Henry, 1991). CH_3Hg flux from sediments was adjusted during model calibration and contributed 0.017 kg to the lake in 1992.

Atmospheric deposition (0.006 kg) and groundwater (0.001 kg) were relatively minor contributors of CH_3Hg to Onondaga Lake. An annual average CH_3Hg concentration in wet deposition of 0.45 ng/L was assumed. This value is higher than that reported by Fitzgerald *et al.*, (1991) (i.e., 0.16 ng/L over Little Rock Lake) and was chosen to reflect the higher concentrations expected over Onondaga Lake because of its urban environment. Data on CH_3Hg concentrations in groundwater are few; therefore, an estimate of 0.13 ng/L based on background concentrations in Sawmill Creek and Bloody Brook was applied to the volume of groundwater estimated to enter Onondaga Lake.

3.2.2. *Sinks*

The three sinks for CH_3Hg in Onondaga Lake were net sedimentation (0.47 kg), outflow (0.24 kg), and net uptake by fish (0.20 kg). Net sedimentation rates were estimated (Table III) and then adjusted during model calibration (Henry *et al.*, 1995). Outflow and net uptake by fish were calculated by the model (Henry *et al.*, 1995).

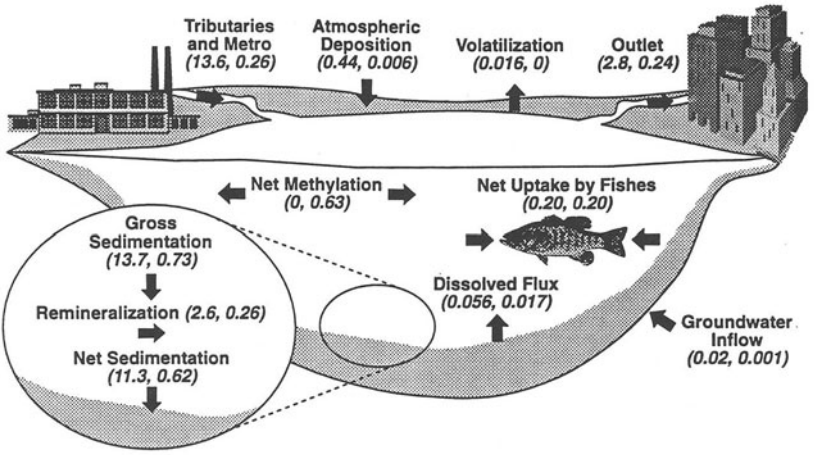

Fig 2 Total Hg and CH_3Hg mass balance in Onondaga Lake in 1992 (kg/year)

3.3. Mass Balance of Total Mercury and Methylmercury

The overall mass balance for total Hg and CH_3Hg in Onondaga Lake is shown in Figure 2. Tributary loading is a major source of both total Hg and CH_3Hg to the lake, as has been observed in other drainage systems (Johansson *et al.*, 1991). While the mass of Hg entering the lake is large relative to other studies, specific yields are comparable to, or only slightly higher than, other systems affected by atmospheric deposition (Johansson *et al.*, 1991) with the exception of total Hg from Ninemile Creek. The high suspended solids load and input from a Ninemile Creek tributary that runs through a former Hg-cell chloralkali plant account for the high total Hg load from Ninemile Creek. CH_3Hg production in the hypolimnion is the major *in situ* source of CH_3Hg to the lake. Low dissolved oxygen concentrations (i.e., <0.2 mg/L) and high sulfate concentrations (i.e., 150 mg/L; PTI, unpublished data) may provide conditions suitable for CH_3Hg production by sulfate-reducing bacteria (Gilmour, 1995; Gilmour and Henry, 1991). Flux from the sediments appears to be a relatively minor source of total Hg and CH_3Hg to Onondaga Lake. The lake experiences a high rate of net solids sedimentation (Table III) and this probably aids in the burial of more contaminated sediment from which Hg efflux is unlikely to occur (Johansson *et al.*, 1991). Sediments therefore serve as a net sink for both total Hg and CH_3Hg.

Gross sedimentation calculated from hypolimnetic sediment trap data exceeded net sedimentation by 90% for CH_3Hg and by 6% for total Hg in the north basin (Table III). Resuspension was considered negligible at this station. In Little Rock Lake (treatment basin), gross sedimentation of total Hg exceeded net sedimentation by a factor of three (Hurley *et al.*, 1994). The difference between gross and net sedimentation suggests that total Hg and CH_3Hg is released from settling particles prior to incorporation into surficial sediment. Release or "remineralization" was incorporated into the model and was an important "source" of dissolved CH_3Hg to the hypolimnion

of Onondaga Lake. The model-calculated estimates of remineralization for total Hg and CH_3Hg were 2.7 and 0.29 kg/year, respectively.

4. Conclusions

Tributaries supply the vast majority of total Hg and a substantial portion of CH_3Hg to Onondaga Lake, as expected of a drainage system. With the exception of total Hg discharge from Ninemile Creek, loadings, as depicted in specific yields, appear to be consistent with expected contributions from areas affected solely by atmospheric deposition of Hg. CH_3Hg production within the anoxic hypolimnion appears to be an important source of CH_3Hg. Although the sediments of Onondaga Lake contain an enormous mass of total Hg at depth, they are a net sink rather than a source for both total Hg and CH_3Hg to the lake. The large difference in gross and net sedimentation rates for CH_3Hg suggests considerable remineralization of CH_3Hg before incorporation into sediment.

Mass balance analysis is an effective tool for identifying the major sources and sinks for total Hg and CH_3Hg in Onondaga Lake. By quantifying the relative importance of these sources and sinks, this analysis will aid in management decisions regarding appropriate remedial alternatives.

Acknowledgements

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USE OF THE MERCURY CYCLING MODEL (MCM) TO PREDICT THE FATE OF MERCURY IN THE GREAT LAKES

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Abstract. In response to U.S. EPA's proposed Great Lakes water quality criteria for mercury (Hg), a field-validated Hg cycling model (MCM) was used to predict Hg levels in the abiotic and biotic components of Lake Superior and Lake Erie. The U.S. EPA criteria are based on water column Hg concentrations and simple trophic level transfer and, thus, do not consider sediment interactions and water chemistry factors. The model, using data from published reports, was run to simulate a 25 year steady state period. For these simulations, methylmercury (MeHg) represented 5% of total Hg in Lake Erie and 8% of total Hg in Lake Superior. These proportions are roughly 3-5 times lower than U.S. EPA's estimate that MeHg contributes about 25% of total Hg in the water column of the Great Lakes. The predicted median concentrations of total Hg in top-carnivore fish were 0.13 mg/kg in Lake Superior and 0.16 mg/kg in Lake Erie. Predicted median MeHg concentrations in Lake Superior and Lake Erie (water column) were 0.019 and 0.075 ng/L, respectively. For both lakes, most (>55%) of the Hg was partitioned to sediments. Although the MCM simulation does have practical limitations (e.g., lakes are treated as fully-mixed open systems), the results demonstrate that generic assumptions of Hg behavior in all Great Lakes waterbodies are too simplistic.

1. Introduction

Mercury (Hg) has long been recognized as a pollutant exhibiting toxic effects at levels slightly or only modestly higher than background levels. Because Hg and its compounds have no known biological function and less toxic forms can be transformed into more toxic forms through natural processes (Eisler, 1987), the presence of Hg in environmental components is often regarded as a potential risk for effects in higher trophic levels (fish and piscivorous birds and mammals). A crucial determinant of potential Hg effects in freshwater systems is the cycling of various inorganic and organic forms. It has become apparent that site-specific factors affect Hg speciation, bioconcentration, and bioaccumulation in each waterbody (Jackson, 1991; Lange et al., 1993). Recent studies of Hg cycling in freshwater rivers and lakes are given in Watras et el. (1994), Parks (1988) and Driscoll et al. (1994). Zillioux et al. (1993) provide a comprehensive review of Hg cycling in freshwater wetlands, some of which are common along the coastline of the Great Lakes (e.g., the south shore of Lake Erie).

In the Great Lakes region of North America Hg has been identified as a pollutant of concern since the early 1970s, when elevated levels in sport fish resulted

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in consumption advisories or bans. Though substantial reductions of Hg in wastewater has occurred throughout the Great Lakes region, various components of the Great Lakes fauna continue to exhibit elevated, but some cases declining, body burdens of Hg (Bèland, et al., 1993; Ropek and Neely, 1993). Long-term contaminant monitoring of Great Lakes fishes has shown that, presently, Hg does not pose a widespread fish consumption concern (Ontario Ministry of Environment and Energy, 1993). Mercury levels in Lake Erie walleye have actually decreased since the early 1970s (Armstrong and Sloan, 1980). Mercury concentrations in recently collected Lake Erie walleye, in fact, are similar to levels in pre-1900 museum specimens (personal communication, Ontario Ministry of Environment and Energy).

In 1993, U.S. EPA proposed new water quality criteria for the Great Lakes drainage basin (U.S. EPA, 1993). Three water quality criteria were proposed for Hg based on protection of aquatic life, human health, and wildlife. The most stringent of these was the wildlife criterion (0.18 ng/ L), which is between 1-2 orders of magnitude lower than measured Hg in rainfall (Kelly et al., 1991). For calculation of the Hg human health and wildlife water quality criteria, EPA established a set of generic assumptions to apply throughout the entire Great Lakes drainage basin. These assumptions dictate that Hg levels in fish are determined largely by water column concentrations and that a generic bioconcentration factor (52,000), a constant methylmercury (MeHg) to total Hg ratio (25%), and a fixed bioaccumulation factor (144,000) can be valid defaults for deriving protective criteria. The purpose of this research was to simulate the cycling of Hg in two differing lakes and address the generic assumptions established by EPA.

2. Materials and Methods

The MCM Lake Mercury Model (Hudson et al., 1994) dynamically simulates the biogeochemical cycling of Hg in lakes. It was developed as part of the Mercury in Temperate Lakes Program sponsored by the Electric Power Research Institute and the Wisconsin Department of Natural Resources. The model simulates Hg in elemental, methyl, and divalent (mercuric and inert) forms - each of which may comprise several species - in the epilimnion, hypolimnion, and sediments of lakes. Four trophic levels of biota are included: phytoplankton, zooplankton, planktivorous fish, and piscivorous fish. The major processes included in the model are given in Hudson et al. (1994) and Figure 4 of Zillioux et al. (1993). The primary input components are listed in Table I. The MCM model dynamically simulates the transport and transformation reactions in each of the main lake compartments based on principles of mass conservation, chemical equilibria and kinetics, and ecosystem bioenergetics. The model routes Hg up the food chain using four trophic levels. Required input parameters include lake physical characteristics, water quality parameters, atmospheric and other inputs, and biomass characteristics.

The MCM model was set up for a simplified two layer representation of Lake Superior and Lake Erie. The input data for deposition, climate, lake water quality, sediment chemistry, temperature profiles, and stage-flow data were obtained primarily from published articles. A recent accurate measurement of Hg in Lake Superior was also obtained from Wisconsin DNR, which showed a total Hg concentration (unfiltered) in the water of 0.9 ng/l and a MeHg concentration of 0.035 ng/l at a depth of 10 m (personal communication, Doug Knauer, Wisconsin DNR). Gill and Bruland (1990) reported a total dissolved Hg concentration of 1.8 ng/L in Lake Erie water samples.

First, the hydrologic budget and hydraulic calibration for the lakes were achieved. Then, the ecosystem was calibrated with phytoplankton biomass profiles and specific growth rates for the lakes so that a steady state biomass was achieved for the zooplankton and two fish types. The characteristics for the planktivorous fish were based on those for yellow perch (Perca flavescens), while the higher trophic level was based on walleye (Stizostedion vitreum). Adjustments to the various rate coefficients were made to obtain a good match between simulated and observed lake water Hg levels and fish tissue levels for the given input loadings. The model was run to achieve steady state Hg concentrations in the lake water and fish populations. A 25-year time interval was chosen as this time; mercury levels in the various ecosystem compartments did not vary appreciably after this time. The model results for Hg water column and fish concentrations were then used to calculate fish bioaccumulation factors. Lastly, a sensitivity analysis was conducted using the model to determine how variations in selected input parameters affected resulting bioaccumulation factors.

3. Results and Discussion

3.1 MERCURY PARTITIONING AMONG COMPONENTS

The MCM model simulated the partitioning of Hg among three forms (elemental, divalent, methyl) between all abiotic and biotic components. This analysis provided estimates of total Hg inputs and sinks at steady state. Results of the modeling for Lake Superior and Lake Erie are given in Tables II and III, respectively. For Lake Superior, almost all Hg inputs (93%) originate from deposition. Once Hg enters the lake, most of this (60%) is buried in the sediments. The difference between deposition input and sediment burial is mostly accounted for in porewater and outflow. The percent of total Hg partitioned in fish biomass is very small ($2x10^{-2}$); of the total Hg in fish, about 99% is in the methylated form (Table IV). The annual Hg accumulation in fish is estimated to be 0.47 mg/kg carbon of fish.

TABLE I

INPUT PARAMETERS FOR LAKE ERIE AND LAKE SUPERIOR

Parameters	Lake Erie	Lake Superior
River Input		
Flow (m^3/d)	4.95×10^8 [1]	1.33×10^8 [2]
Hg (mol/L)	7.1×10^{-11} [3]	1.5×10^{-12}
Mercury		
Rain (mM)	6.5×10^{-11} [3]	6.6×10^{-11}
Dry Dep.(mol/ha/yr)	5.6×10^{-4} [3]	2.5×10^{-4}
Epilimnion		
pH	6.8-8.0 *	7.8-8.2 [4]
Cl (μM)	563 *	33.8
DOC (mg/L)	3 *	0.3
Particles (mg/L)	19 *	4
SO_4 (μM)	437.0 *	66.6
Oxic Sediments		
pH	6.5	7.3
Cl (μM)	563	33.8
DOC (mg/L)	10	10
Particles (kg/L)	0.05	0.05
SO_4 (μM)	30	30
O_2 (μM)	300	300
Monthly Inputs [1],[5],[6],[7],[8],[9]**		
Phytoplankton Biomass (g/cm)	0.05-1.2	0.05-0.2
Epilimnion depth (m), Epilimnion	15-25.7	10-145
Temp. (°C) Hypolimnion Temp. (°C)	0.1-15	1-13
Rainfall (cm)	0.1-15	3-4
Evaporation (cm)	2.8-30	2.8-10.3
Hypolimnion D.O. (mg/L)	0.5-18	0-10.5
	0-9	13

Sources:

* Ohio Edison Co., Edgewater Plant, Lake Erie

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** Values given are the minimum and maximum monthly value in a year.

TABLE II

MERCURY MASS-BALANCE FOR LAKE SUPERIOR (25-YEAR SIMULATION) USING MCM MODEL

Category		Mercury Mass (Kg)				Percent of Input/Output
		Hg(O)	Hg(II)	MeHg	Total	
Input	Discharges	0	1,825	0	1,825	6.00
	River	0	375	0	375	1.23
	Wet deposition	0	17,833	146	17,979	59.08
	Dry deposition	0	10,252	0	10,252	33.69
	Total Input	–	–	–	30,432	100.00
Output	Gas exchange	783	12	155	641	2.10
	Sediment burial	0	15,792	2,683	18,474	60.71
	Porewater	1	597	473	1,071	3.52
	Outflow	20	7,854	529	8,403	27.61
	Total Output	–	–	–	28,589	93.94

In Lake Erie, atmospheric deposition accounts for about 20% of all Hg inputs (Table III). It is interesting to note that tributary inputs are relatively high for this lake (80%), reflecting the natural influence of large tributary flows and anthropogenic sources within an industrialized basin. Like Lake Superior, most of the Hg in Lake Erie is partitioned to the sediments (55%). Unlike Lake Superior, however, the mass of Hg accumulated within fish biomass per year is relatively small (0.026 mg/kg carbon in Lake Erie). Like Lake Superior, almost all of the Hg in Lake Erie fish is the methylated form. However, the percent of total Hg in Lake Erie partitioned to fish is almost negligible (8.8×10^{8} %).

TABLE III

MERCURY MASS-BALANCE FOR LAKE ERIE (25-YEAR SIMULATION) USING MCM MODEL

Category		Mercury Mass (Kg)				Percent of
		Hg(O)	Hg(II)	MeHg	Total	Input/Output
Input	Discharges	0	0	0	0	0.00
	River	0	64,599	0	64,599	80.30
	Wet deposition	0	8,503	74	8,577	10.66
	Dry deposition	0	7,275	0	7,275	9.04
	Total Input	–	–	–	80,451	100.00
Output	Gas exchange	17	0	-48	-31	0.04
	Sediment burial	0	42,547	1,725	44,272	55.03
	Porewater	0	1,579	314	1,893	2.35
	Outflow	34	31,256	3,027	34,317	42.66
	Total Output	–	–	–	80,451	100.00

The relatively high outflow from Lake Erie (the annual discharge is 50% of lake volume) causes a considerable amount of the total Hg loading to be partitioned to its outflow. Although the large inflow and outflow rates tend to mask the importance of sedimentation, a comparison of the mass of Hg in the water column and biota (<10%), versus that in sediments validates the importance of sedimentation in Lake Erie.

TABLE IV

PREDICTED TOTAL AND METHYLMERCURY CONCENTRATIONS IN EPILIMNION (WATER COLUMN) AND WALLEYE FOR LAKES SUPERIOR AND ERIE. PREDICTED BIOACCUMULATION FACTORS AND SENSITIVITY RESULTS ALSO GIVEN. (NOTE: Cl = CHLORIDE, DOC = DISSOLVED ORGANIC CARBON, SS = SUSPENDED SOLIDS)

	Lake Superior			Lake Erie		
Analysis	Epilimnion (ng/L)	Walleye (mg/kg)	BAF[1]	Epilimnion (ng/L)	Walleye (mg/kg)	BAF
Base[2]	0.63	0.13	204,000	1.03	0.16	158,000
MeHg	0.019	0.13	6.7×10^6	0.075	0.16	2.2×10^6
10 x Cl	0.78	0.13	171,000	–	–	–
10 x DOC	4.20	0.08	19,500	–	–	–
0.1 x DOC	–	–	–	0.11	0.17	1,550,000
0.1 x SS	–	–	–	9.48	0.67	70,400
0.1 x Deposition	0.08	0.02	260,000	0.17	0.03	188,000
10 x Deposition	6.37	0.20	30,600	9.40	1.53	163,000

[1] Bioaccumulation factor (walleye concentration ÷ epilimnion total Hg concentration).
[2] Base case represents model results of total mercury using input variables from Table I.

3.2 MERCURY IN WATER AND BIOCONCENTRATION FACTORS

The model-predicted total Hg concentrations in the water column and top-carnivore fish for both lakes are given in Table IV. For the base case (i.e., data from Table I), the predicted epilimnion (water column) concentrations were higher for Lake Erie. This reflects the much higher levels of Hg input (due mostly to river inflow contribution) to Lake Erie.

Predicted MeHg concentrations in the water column are also given in Table IV. For Lake Superior, the predicted MeHg concentration of 0.019 ng/L represents 3% of total Hg. In Lake Erie, the predicted MeHg concentration of 0.075 ng/L represents 7.3% of total Hg. These proportions are 3-5 times lower than U.S. EPA's default proportion for the Great Lakes drainage basin (25%). In walleye from both lakes, the MeHg concentration comprised the total Hg concentration. This pattern has been observed in several field studies (Grieb et al., 1990).

For the base case, the predicted bioaccumulation factor (BAF) for Lake Superior walleye was 204,000. This value is approximately 23% higher than the predicted bioaccumulation factor for Lake Erie walleye (BAF = 158,000). The relatively higher BAF for Lake Superior is not surprising as the standing crop biomass in this lake is expected to be substantially lower relative to Lake Erie. A lower biomass pool allows a greater concentration potential for each walleye.

While the MCM has the capability to simulate these processes, accurate input parameters should be available to define the system. For both Lake Superior and Lake Erie, the large areas and volumes result in heterogeneity of water quality, habitat, and hydrologic partitioning (e.g., epilimnion vs hypolimnion). This data limitation can only be corrected by using measured lake-specific input values. The model-predicted results can be compared to actual measurements of Hg in aqueous samples and fish. For Lake Superior, a BAF value of 422,000 is obtained from limited walleye tissue results (0.38 mg/kg; Ontario Ministry for the Environment) and an aqueous total Hg measurement of 0.9 ng/L (Wisconsin DNR). For Lake Erie, a BAF value of 95,000 is obtained from measured Hg concentrations in walleye (mean = 0.19 mg/kg; Ontario Ministry for the Environment) and an estimated total Hg aqueous concentration of 2 ng/L. Although the predicted BAF results agree with the calculated BAF values for actual samples from the lakes (at least on a relative scale), our modelling results must be considered preliminary and subject to in-situ validation. The relative importance of feeding ecology, trophic transfer, and water quality influences upon Hg bioaccumulation in Great Lakes biota probably varies both within and among lakes.

Sensitivity analysis results (Table IV) indicated that for Lake Superior, a ten-fold increase in dissolved organic carbon (DOC) had a much larger influence on predicted walleye levels and BAF values compared to a similar increase in chloride levels. DOC had an inverse relationship with predicted BAF values in both lakes; DOC complexes active Hg in the water column, apparently making Hg less bioavailable to higher trophic levels. This relationship was observed in Wisconsin seepage lakes (Grieb et al. 1990). Gilmour and Henry (1991) reported that increased DOC levels decreased the methylation rate of Hg. For Lake Erie, a ten-fold decrease in suspended solids resulted in higher aqueous concentrations and higher walleye concentrations, but a lowered BAF value. When Hg deposition rates are decreased, a similar proportional decrease of aqueous Hg and walleye Hg levels are observed for both lakes. When deposition rates increase, however, the resulting increase in walleye Hg concentrations is more marked for Lake Erie. The sensitivity analysis results highlight the deficiencies of using bioconcentration factors as a predictive measure of Hg levels in fish at high trophic levels.

3.3 APPLICATION OF MODEL FOR REGULATORY PURPOSES

The chief advantage of the MCM model is that it accounts for sediment interactions in the cycling of Hg. Moreover, the model incorporates measured, lake-specific input variables to simulate the partitioning, speciation, and bioaccumulation potential of Hg in lakes. We feel that these features provide a much more realistic estimate of allowable, protective Hg loadings compared to U.S. EPA's generic

bioconcentration assumption. As indicated previously, these assumptions fail to distinguish even large-scale limnological and morphometric differences among the Great Lakes. The MCM model, in contrast, can utilize measured sediment characteristics as input variables. Because Hg methylation is often driven by sediment processes (both abiotic and biotic), the predictive power of the model is greater than simple calculations that do not account for sediment characteristics.

U.S. EPA's proposed water quality criteria for human health and wildlife protection are expressed as a total Hg concentration. Because MeHg is the form of concern for human health effects and bioaccumulation, any regulatory criteria for Hg should have a reasonable ability to predict the concentration of MeHg at various trophic levels. Some research findings (e.g., Kelly et al., 1994) have demonstrated a lack of any predictable relationship between total Hg and MeHg concentrations in the water column. When using the MCM model, a calibration of the mercury cycle for Lakes Superior and Erie was accomplished by partitioning the incoming mercury (mostly in the Hg^{+2} form) among compartments based on observed water column and fish tissue (essentially all MeHg) concentrations. If the basic cycling processes known to occur in smaller lakes are valid for larger lakes such as those studied, then the MCM approach, wihich includes sediment processes, may be a more accurate paradigm compared to the water column-based, total Hg criteria advocated by U.S. EPA.

4. Conclusion

For two Laurentian Great Lakes differing in morphometric characteristics and biological productivity, the predicted water column Hg concentration and bioaccumulation factor (top carnivore fish) for Hg was different also. Most of the Hg entering the two lakes was predicted to be buried in sediments. These results have practical application for regulatory concerns of Hg in the Great Lakes. Because most of the mercury entering the Great Lakes is from atmospheric sources and the concentration of mercury in rainfall is about ten times greater than that in surface waters of the Great Lakes, mercury cycling and sediment burial are significant processes in these systems.

The application of the MCM to the Great Lakes does have limitations. Because the model treats the water column of a given lake as two layers (epilimnion and hypolimnion, each of which is completely mixed), site-specific habitats such as embayments, marshes, or other hydrologically-disjunct areas cannot be treated separately. Data limitations included the lack of fish biomass estimates and sparse data for aqueous Hg concentrations. Nonetheless, we feel that the MCM model can provide good predictions of Hg behavior, especially among lakes having marked physicochemical or biological differences. Further research on lake-specific processes will enhance the applicability of the model.

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Modeling the Elemental Mercury Cycle in Pallette Lake, Wisconsin, USA

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Abstract

The spatial and temporal distribution of elemental Hg (Hg^0) and reactive Hg (Hg_R) has been studied on Pallette Lake, Wisconsin during May - August, 1993 and May, 1994. In general, Hg^0 concentrations near the lake surface greatly exceeded saturation with respect to atmospheric Hg^0 indicating a flux out (-) of the lake. Evasional losses were estimated using a thin film model and averaged -101 pmol m^{-2} d^{-1} during July and August, 1993. A large portion of atmospherically deposited Hg is re-emitted. Thus, in-lake Hg^0 production and evasion to the atmosphere will significantly reduce the amount of Hg which is transported to the sediments, the principal site of methylation. Laboratory experiments were conducted to ascertain the rate of Hg^0 formation from Hg(II). Reduction was significantly lower in heat sterilized lakewater suggesting Hg^0 production was biologically mediated. The temporal distribution of epilimnetic Hg^0, as measured at the lake center, was influenced by Hg^0 evasion, Hg^0 production and advective transport of water parcels of differing Hg content. Spatial gradients in Hg^0 and Hg_R were identified and a transport model was employed to estimate the advective flux of Hg^0. The importance of atmospheric deposition and sediment-water interaction as sources of Hg_R to epilimnetic waters were examined. Porewater concentrations of Hg^0 and Hg_R were determined on several occasions. During May, 1994, the depletion of lakewater Hg_R following a input pulse due to rain was observed and the estimated removal rate (16-20% d^{-1}) agrees well with reduction rates obtained in the laboratory (23% d^{-1}).

1. Introduction

Elemental Hg exists as a dissolved gas in natural waters and often at supersaturated levels. Thus, Hg^0 exchange with the atmosphere can lower the lakewater Hg burden. In-lake production of Hg^0 may compete with methylation for the Hg substrate and lakes with conditions favoring the formation of Hg^0 may have lower fish methyl-Hg levels. Indeed, lower Hg^0 and higher fish methyl-Hg burdens were observed for the acidified basin of an experimental lake compared to the unacidified basin. (Vandal et al., 1991; Wiener et al., 1990). Furthermore, lower pH lakes were found to have higher areal Hg burdens in surficial sediments compared to circumneutral lakes in a study of Wisconsin seepage lakes (Rada et al., 1993). In-lake reduction of Hg(II) to Hg^0 and its transfer to the atmosphere can reduce the amount of Hg accumulating the sediment.

In Wisconsin seepage lakes, during the summer months, the rate of Hg removal from the lake by gaseous evasion of Hg^0 may be greater than 60 ng m^{-2} d^{-1} under windy conditions (Vandal et al., 1993). This flux greatly exceeds the average rate of atmospheric Hg deposition, 27 ng m^{-2} d^{-1} (Fitzgerald et al., 1991). Realization of the potential importance of Hg^0 in the aqueous Hg cycle has lead to interest in understanding mechanisms of Hg^0 production in natural waters. Previous studies of Hg^0 cycling in temperate seepage lakes have shown a seasonal cycle in Hg^0 production with highest levels occurring during the warmer summer months (Vandal et al., 1991; 1993). Elemental Hg concentrations are consistently highest in the epilimnion compared to meta and hypolimnetic waters. In addition, analytical speciation of dissolved volatile Hg determined Hg^0

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as the principal gaseous Hg component in northern Wisconsin lakes.

The goal of our work in northern Wisconsin Lakes, as part of the Mercury Pathways and Processes Project (MAPP), is to understand the mechanisms controlling the formation and distribution of Hg^0 in lakewater. Here we use a model which incorporates gas exchange and advective transport to interpret field observations of spatial and temporal variations in Hg^0 in epilimnetic waters of Pallette Lake during the summer of 1993. Additional measurements of Hg^0 and Hg_R from Pallette in May, 1994 are included. Laboratory experiments were designed to elucidate Hg(II) reduction pathways and rates. This information was integrated into the model to constrain the production of Hg^0 in this system. In addition to the modeling results, the effect of sediment- water interactions and atmospheric deposition on the distribution of Hg^0 and Hg_R in Pallette Lake is discussed.

2. Experimental

Pallette Lake is a small circumneutral seepage lake within the Northern Highlands State Forest in north-central Wisconsin, USA (46°00'N, 86°40'W'). The Northern Highlands Lake District is mostly wooded and half of the forest is state owned. This region is sparsely populated and lacks heavy industry. There is limited public access to Pallette Lake. Atmospheric deposition represents approximately 85% of the annual hydrologic input while ground water inflow constitutes the remainder (Krabbenhoft and Babiarz, 1992). Pallette Lake has a surface area of 0.7 km^2 and a maximum depth of 18.2 m. It is a clear water lake that becomes thermally stratified during the summer with a anoxic hypolimnion.

Lakewater Hg^0 concentrations were measured regularly between May 28 and August 10, 1993. Additional measurements of the spatial distribution of Hg^0 and Hg_R were obtained in May, 1994. Dissolved oxygen (DO) and water temperature were determined concurrently using a dissolved oxygen meter (Yellow Springs Instruments) which was periodically calibrated for DO by Winkler titration. Porewater profiles of Hg^0 and Hg_R were obtained on several occasions during May, 1994. Wind speed, water temperature and air temperature (Campbell Instruments) were monitored continuously from a meteorological raft located at the lake center. Atmospheric Hg^0 concentrations were measured at a nearby lake (Lamborg et al., 1993) and were used in the estimate of the air/water exchange of Hg^0.

Water samples were collected in acid-cleaned 2L Teflon® bottles and using trace metal clean protocols (Gill and Fitzgerald, 1985). Sampling was conducted from a fiberglass boat using a non-metallic pump. Samples were kept cool (ca. 10°C) and analysis was carried out within 3 to 24 hours of sample collection. Analysis of replicate collections over a 48 hour period indicated no change in the Hg^0 concentrations with storage. Porewater sampling was conducted with the assistance of Janita Benoit (U of Wisconsin) and David Krabbenhoft (USGS, Madison, WI) using a teflon device designed by Dr. Krabbenhoft. A teflon seepage meter was used for collecting inflowing porewater (Krabbenhoft and Babiarz, 1992).

Elemental Hg was determined using a purge and trap technique. This volatile species is sparged from the water sample in a 2L Pyrex® bubbler with Hg-free argon and trapped on gold. Analysis of Hg was by two-stage Au amalgamation with detection by atomic fluorescence (Bloom and Fitzgerald, 1988). The detection limit for Hg^0 (defined as 3x the standard deviation of the blank) was 25fM. Percision of the analysis was generallly 5% for replicate collections. Reactive Hg was determined by reduction - aeration technique outline elsewhere (Gill and Fitzgerald, 1987) after purging Hg^0. Laboratory prepared standards of $HgNO_3$ were run regularly. In 1993, Hg_R was

determined on 250 ml aliquots, while 1 L aliquots were analyzed in 1994 to improve the detection limit (0.3 and 0.1 pM, respectively). Porewater concentrations of Hg^0 and Hg_R were measured on sample volumes of 200 ml and 100 ml , respectively. The detection limit for Hg^0 in porewater was 50 fM and 0.2 pM for Hg_R.

Elemental Hg production rates were determined from laboratory experiments. Lakewater samples were spiked with $HgNO_3$ (50 ng/L), purged with air and the quantity of Hg^0 evolved during four to six consecutive 30 minute intervals determined. The Hg(II) standard used in these experiments was prepared in deionized water, as not to interfere with the ambient water chemistry of the samples, and checked daily. The amount of Hg^0 evolved decreased dramatically after an initial surge of Hg^0 production to a steady state value. The reported reduction rates are steady state values and are given as a fraction of the Hg(II) added. Sterilized samples were prepared by heating for 1 hour in an autoclave (15 psi and 120° C) and allowed to cool overnight before determining reduction rates.

3.Results

3.1 Lakewater and Porewater Hg^0 and Hg_R

An averaged profile of the distribution of Hg^0 in Pallette Lake during the 1993 sampling period is given in Figure 1. As previously observed for Pallette Lake, Hg^0 was highest in the epilimnion and decreased with depth (Vandal et al., 1993). The daily average epilimnetic concentration of Hg^0 ranged between 130 and 360 fM with a mean for the entire sampling period of 220 fM. Elemental Hg measurements from July 8, 1993 were excluded from the average because they were anomalous (averaging 1200fM). Below the epilimnion, Hg^0 decreased to mean values of 160 fM and 75fM for the thermocline and hypolimnion, respectively. Reactive Hg concentrations in Pallette Lake ranged from 1 to <0.3 pM, the detection limit for this set of experiments. In the early summer, highest concentrations of Hg_R were found in the epilimnion while concentrations at 11m, at the base of the thermocline were at the detection limit. However, in late July through mid August, epilimnetic Hg_R was at detection limit (0.3 pM) with a higher concentration (6 pM) found at the top of the thermocline (6 m) on one occasion.

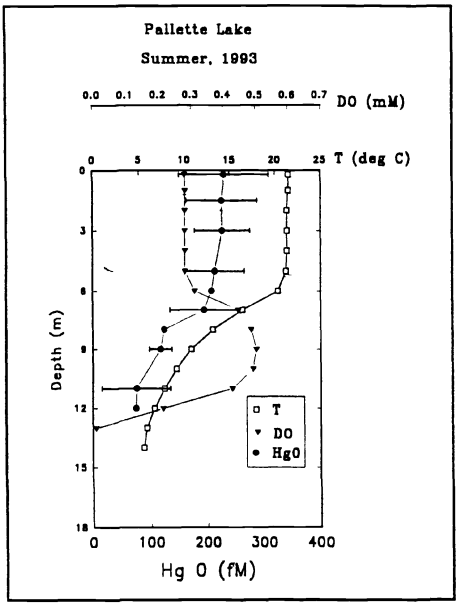

Fig. 1. Pallette Lake Hg^0, DO and temperature, Summer, 1993. Average Hg^0 for July and August are given with standard deviation.

The spatial distribution of Hg^0 was determined on 4 occasions (July 28, August

2, 4 and 10, 1993). Figure 2 illustrates the vertical distribution of Hg° at two near shore locations (noted as downwind and sheltered) and a mid-lake site (center) on July 28, 1993. The Hg° concentration is highest at the western nearshore site (240-413 fM) which was sheltered from the wind. The deepwater site had the lowest Hg° levels (118-153fM) while the eastern nearshore location had intermediate Hg° levels (92-201 fM) even in the presence of strong wind induced gas exchange. Spatial variations in Hg_R were not detected.

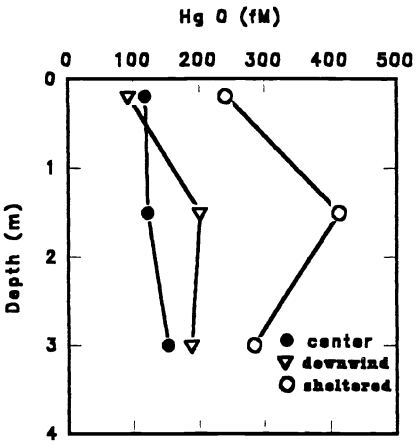

Fig. 2. Spatial distribution of epilimnetic Hg° on July 28, 1993.

The spatial distribution of Hg° and Hg_R was determined on two additional sampling dates, May 13 and 16, 1994. Five stations along a transect across Pallette Lake were sampled. Station 1 represeted a nearshore site above the outflow region where water leaves the lake through the sediment. Station 2 was midway between Station 1 and Station 3, at the lake center. Station 4 was located midway between Station 3 and Station 5, a nearshore site in the region of ground water inflow. The stations were separated by approximately 200m. On these dates, in agreement with our prior measurements, Hg° was highest at the surface and decreased with depth. On May 13, Hg° ranged from 70 fM at Station 4 (10m) to 726fM at Station 2 (0.5m). Reactive Hg on this day was, generally, highest at the surface (<0.1 to 1.9pM), decreased to a subsurface minima (>0.2-0.9pM) and increases near the sediment (0.5-1.1pM). There was a substantial increase in $Hg_R$and Hg° on May 16th compared to May 13. These changes coincided with a rain event on May 14. Reactive Hg was highest in the upper 2 m (0.2-5.9pM), while the lowest values were detected at 6m (1-1.2pM). Water above the sediment receiving ground water inflow (Station 5) contained the highest Hg_R(4.0pM).

Pore water Hg° and Hg_R concentrations were determined during the May, 1994 study. Inflow porewater profiles were obtained near the water sampling Station 5 while outflow porewater profiles were obtained near Station 1. In addition, seepage meter samples of inflowing porewater were collected near Station 5. Three depths (2,5 & 10 cm) were sampled at each site. Near surface (2 cm) porewater Hg° concentrations (182-430 fM) were lower than overlying waters. A higher Hg° concentration were dectected at 10cm in the inflow region. However, porewater Hg_R levels were generally higher than lakewater. The concentration of Hg° and Hg_R in seepage meter samples of inflowing porewater averaged 324 ± 135 fM and 3.1±1.2 pM, respectively.

3.2 Mercury Reduction Experiments

Rates of Hg(II) reduction based on laboratory experiments are presented in Table 1. Rates for unamended epilimnetic lakewater were between 1 and 29 x 10^{-7} s^{-1}. Reduction rates were found to be approximately 50% lower for metalimnetic waters (6.1 x 10^{-7} s^{-1}) compared to epilimnetic samples (11.4 x 10^{-7} s^{-1}). In May, 1994, epilimnetic reduction rates (4 - 43 (x10^{-7} s^{-1})

with a mean rate of 26 x 10^{-7} s^{-1}) were higher than the previous summer period. Reduction rates were lower for heat sterilized sample <2 x 10^{-7} s^{-1}, suggesting Hg(II) reduction is biologically mediated. Previous studies of Hg reduction in seawater have implicated cyanobacteria (Mason et al., 1993).

Table I. Laboratory derived reduction rates based on spiking lakewater

July-August, 1993	Reduction Rate x 10^{-7} s^{-1}	Average x 10^{-7} s^{-1}
Epilimnetion (1-3m)	1 - 29	11.4
Metalimnion (9m)	4.6 - 6.6	6.1 ± 0.8
Heat sterilized	1.2 - 2.0	1.6
May, 1994		
Epilimnion (1-6m)	4 - 43	26

4. A Model of Elemental Mercury Cycling

The Hg^0 distribution at a particular location in the lake is a function of several chemical, biological and physical factors. These are: (1) the production of Hg^0 from Hg(II) by biologically mediated processes or abiotic mechanisms, P; (2) evasion to the atmosphere by gas exchange, F_e; (3) advective and diffusive transport, T_a. Oxidation of Hg^0 is assumed to be unimportant. This is explained in the equation below:

$$d[Hg^0]/dt = P + T_a + F_e \quad (1)$$

Production of Hg^0 can be estimated using the equation

$$P = k * [Hg(II)] \quad (2)$$

where k is the reduction rate for Hg(II) to Hg^0 derived from Hg(II) spiked lakewater. This reduction rate is not specific for a particular mechanism (i.e., abiotic or biotic). [Hg(II)] is taken as the measured Hg_R concentration.

The magnitude of the horizontal advective flux is approximated as follows:

$$T_a = h * u * (0.01) * d[Hg^0]/dx \quad (3)$$

where h equals the depth of wind impacted layer taken as 0.25m; u * (0.01) is the horizontal transport of water due to wind where u equals wind speed and $d[Hg^0]/dx$ is the horizontal gradient in Hg^0 concentration (J. O'Donnell, pers. comm.).

The loss of Hg^0 to the atmosphere is approximated using the thin film gas exchange model given below:

$$F_e = K (C_a * H^{-1} - C_w) \quad (4)$$

here C_a & C_w are the concentrations of Hg° in the air and water, respectively; H is the Henry's law constant which is temperature dependent (Sanemasa, 1975); K, the transfer velocity (cm/hr), is estimated from the empirically derived relationship $K(600) = 0.45 * u^{1.64}$ (Wanninkhof, 1992) and is dependent on windspeed (u), and the Schmidt number (i.e. 600) which is a function of temperature and diffusivity.

Surface water Hg° was always supersaturated relative to the atmosphere. During July-August, 1993, the water concentration in equilibrium with the atmosphere containing 1.8 ± 0.4 ng m^{-3} and an average surface water temperature of 21 °C was 31±6 fM. This was a factor of 3 to 12 below the observed surface water Hg° levels resulting in a strong chemical gradient out of the lake. Using Equation 4, Hg° evasion rates for the period from July 25 - Aug 4 varied from 11 to 346 pmol m^{-2} d^{-1} with a mean value of 101 pmol m^{-2} d^{-1}. This represents a large portion of the Hg entering the lake by way of atmospheric deposition which averaged 135 pmol m^{-2} d^{-1} in 1989 (Fitzgerald et al., 1991). However, it is important to note that high levels of Hg° supersaturation in lakewater exist only during a 3 to 4 month period (mid-May to mid-September). Nonetheless, during the late spring and summer, the production of Hg° and its emissions at the lake surface may control the Hg_R cycle in the epilimnion and limit the amount of Hg transported to the sediment. This is of great importance since the sediments are the principal location for methyl-Hg production in these systems (Gilmour, this issue).

Table II. Temporal variations in epilimnetic Hg° concentrations, efflux and production based on the July-August observations. Fluxes are normalized to per day.

date	Hg° epi	d[Hg°]/dt	F_e	P	P+F
	(fM)	pmol m^{-2} d^{-1}	pmol m^{-2} d^{-1}	pmol m^{-2} d^{-1}	pmol m^{-2} d^{-1}
7/25	256				
$7/26_{am}$	268	+58	-346	<+180	<-166
$7/26_{pm}$	163	-521	-346	<+180	<-166
7/27	196	+162	-165	<+180	<+15
7/28	131	-323	-84	<+180	<+96
$7/30_{am}$	228	+243	-21	<+180	<+159
$7/30_{pm}$	274	+460	-21	<+180	<+159

The temporal variation in the average epilimnetic Hg° content of lakewater collected at the lake center are listed in Table II. Temporal changes in Hg° were between +97fM (7/28 to $7/30_{am}$) and -105fM ($7/26_{am}$ to $7/26_{pm}$). These fluctuations correspond to Hg° fluxes between +460 and -521 pmol m^{-2} day^{-1}, assuming a depth of 6 meters for the well mixed epilimnion. Temporal variations in the average epilimnetic Hg° are compared with predicted evasion and production in Table II. An upper limit for the production of Hg° from Hg_R in the epilimnion was

approximated at 180 pmol m^{-2} d^{-1} using a Hg_R concentration of 0.3pM and a reduction rate of 10% d^{-1}. In general, the observed changes in Hg° (d[Hg°]/dt) could not be entirely accounted for by gas evasion and/or Hg° production (P+F). An additional mechanism is indicated which significantly influences the Hg° distribution. Advective transport can result significant horizontal Hg° fluxes and this process can be a major factor in temporal fluctuations of Hg° measured at the lake center.

Unfortunately, the spatial Hg° distribution necessary for the advective flux calculation and temporal variation in Hg° for comparison with model results are available for only one date, July 28, 1993. Elemental Hg concentrations were determined at a nearshore site at approximately 300m from the lake center site (Fig.2). The advective flux was assessed using the spatial gradient in Hg° at the surface (0.25m). Furthermore, we assumed the depth of the wind impacted layer to be 25cm and the velocity of this surface layer to be 1% of the measured wind speed (Eq. 3). Model results are compared with observed variations in Figure 3 for July 28-30. The advective flux, +380 pmol m^{-2} d^{-1} is comparable to observed d[Hg°]/dt, of +243 pmol m^{-2} d^{-1} and P+F, <159 pmol m^{-2} d^{-1}. Estimates of the advective flux were made for three additional dates in August to assess relative importance of this physical process. Strong horizontal Hg° gradients were always apparent and translate into a wind driven transport of Hg° to the deephole from between -185 to +330 pmol m^{-2} d^{-1} depending on wind speed and the horizontal Hg° gradient. The range of advective Hg° fluxes are similar to observed temporal changes, d[Hg°]/dx, (-521 to +460 pmol m^{-2} d^{-1}) given in Table II.

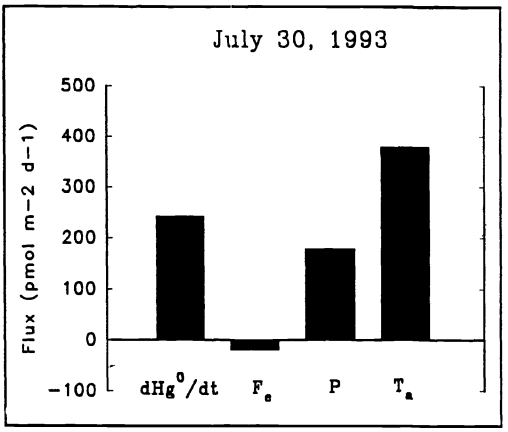

Fig 3. Measure change in Hg° (dHg°/dt) between July 28- 30, 1993, is compared with model predictions.

Table III. Spatial Variations in Hg° and Predicted Advective Transport Flux. Near surface (0.25m) Hg° concentrations at the center and upwind location are listed.

Date	Hg° (fM) upwind	Hg° (fM) center	Wind speed m s^{-1}	T_a pmol m^{-2} d^{-1}
7/28	240	118	4.3	+380
8/2	279	345	4.1	-185
8/4	356	212	3.2	+330
8/10	434	250	0.03	4

Advective transport fluxes were estimated from spatial gradients in Hg° determined on

May 13 and 16, 1994 and described in Sec. 3.1. Advective fluxes of Hg^0 ranged from +190 to +370 pmol m^{-2} d^{-1} on May 13. On May 16, the advective flux was estimated at between -97 to -405 pmol m^{-2} d^{-1}. These values are within the same range of those calculated for July-August, 1993. In conclusion, spatial inhomogeneities in Hg^0 in Pallette lake can translate into significant advective fluxes. Though the data are limited, horizontal transport appears to have a major impact on temporal variations at the lake center. Therefore, for small lakes in which the Hg cycle may be strongly impacted by sediment-water interactions, the spatial distribution of Hg^0, Hg_R (and presumably other Hg species) and their advective fluxes must be included to accurately interpret watercolumn distributions of these species.

5. Elemental and Reactive Mercury Cycling in Pallette Lake

The two main sources of Hg to Pallette Lake are atmospheric deposition and remobilization from sediment. We have conducted an experiment to elucidate the affect of these processes on the aquatic cycling of Hg^0 and Hg_R. The importance of rain was demonstrated over a one week period in May, 1994. Figure 4 describes the variation in the average Hg^0 and Hg_R concentration in the upper 6 meters of Pallette Lake between May 13 and May 20. The Hg_R concentration increased dramatically between May 13 and May 16 and coincides with a rain event on May 14. We estimate a Hg_R flux of 225 pmol m^{-2} into the lake due to wet deposition based on the measured Hg_R in this rain (3 pM) and a rain amount of 1.5 cm (Lamborg, unpublished data). We calculate an increase in Hg_R in the upper 6 m of the lake of 900 pmol m^{-2} between May 13 and May 16 indicating and additional source of Hg_R (i.e. porewater) during this time. From May 16 through May 20 epilimnetic Hg_R levels decrease. The reduction rate necessary to deplete Hg_R over this time period is estimated at 1.8 to 2.3 (x 10^{-6} s^{-1}). This agrees extraodinarily well with laboratory determined reduction rates during this period which averaged 2.6 x 10^{-6} s^{-1}.

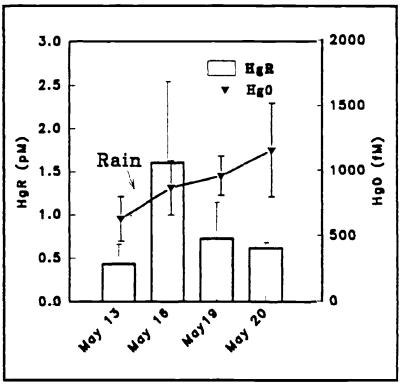

Fig 4. Change in average Hg_R and Hg^0 concentration in upper 6 meters, May, 1994

Exchange with the sediments can be an additional source of Hg to the watercolumn. While diffusion rates are rather slow, advective transport of porewater, enhanced by wind induced stirring of the overlying water, may be important. There is a nearly constant flux of ground water into Pallette Lake at the inflow region that comprises approximately 10% of the sediment surface. Elemental Hg concentrations were generally low in porewater. Porewater, however, could be an important source of Hg_R to the water column. For example, in May, 1994, elevated Hg_R concentrations in the surface porewaters at Station 1, an outflow region, were found and indicate a flux of Hg_R. The magnitude of this flux was calculated based on the Hg_R gradient between the pore water and the overlying water and a diffusion coefficient of 1 x 10^{-6} s^{-1} (Krabbenhoft and Babiarz, 1992). A flux of 0.8 pmol m^{-2} d^{-1} was determined for strictly diffusive processes. Advective wind induced mixing of the sediment water interface could elevate the rate of supply to the overlying water by a factor of 10 -100 providing an upper estimate of 80 pmol m^{-2} d^{-1}. Diluted over a 1 meter watercolumn, this Hg input will contribute 0.08 pM and is insufficient to

maintain the elevated nearshore Hg_R values. Krabbenhoft and coworkers calculated an maximum back diffusive flux for total Hg of 238 pmol m^{-2} d^{-1} which would also increase by an order of magnitude, or more under, advective conditions. Back diffusion into the epilimnion occurs only over ca. 10% of the sediment surface and is not a major Hg input when normalized over the entire lake. It may be very significant locally. For example, this Hg flux could increase the near sediment lakewater Hg concentration by 0.24 pM. It is possible that Hg bound pore water, say to humic material, becomes reactive when introduced to lake water due to oxidation of the organic ligand. However, little is known about the change in porewater Hg speciation when it enters lakewater.

The flux of Hg_R into lakewater from the inflow region, 13 pmol m^{-2} d^{-1}, was calculated using the average concentration measured in seepage meter samples, 3.1 pM, and a ground water inflow rate of 4.3 L m^{-2} d^{-1} (Krabbenhoft and Babiarz, 1992). Krabbenhoft and Babiarz (1992) reported an average total Hg concentration of 60 pM for inflowing porewater which would translate into a flux of 50 pmol m^{-2} d^{-1}. The inflow region incorporates about 5% of the surface area and is less significant when distributed across the whole lake. Near sediment water Hg would increase by 0.05 pM assuming mixing into a 1 meter water column. These estimates indicate that, under average conditions, porewater at the inflow region does not significantly impact the ambient lakewater Hg concentration. However, a large increase in Hg_R in the 1 meter sample from Station 5, taken 0.5m off the bottom above the sediments receiving ground water inflow, was evident on May 16, 1994 (see Sec. 3.1). This increase may be attributed to enhanced ground water transport following a rain event.

Spatial distributions of reduction capacity were determined on several occasions. On August 2, a distinctly higher reduction rate was found at the nearshore downwind location compared to the lake center (7 and 1 x 10^{-7} s^{-1}, respectively), while higher Hg^0 concentrations were measured at the center compared to the downwind site (345 and 280 fM, respectively). The higher Hg (II) reducing capacity may be due to a sedimentary source of reductant to the water above the epilimnetic sediments. The flux of material from the sediments to the overlying water would increase under the strong wind conditions that were encountered on Aug 2 (see Table III). The nearshore water Hg(II) content may also increase due to wind enhanced exchange at the sediment surface. To the contrary, on August 4, epilimnetic reduction rates were similar for surface water collections from the lake center and the nearshore upwind location (9.6 and 9.0 x 10^{-7} s^{-1}, respectively). This indicates that horizontal variations in the observed Hg^0 concentration at the two sites (See Table III) did not result from differences in reduction capacity. However, the higher concentrations of Hg^0 nearshore site compared to the center may have resulted from reduced gas exchange and removal of Hg^0 to the atmosphere at the sheltered (upwind) location (see Fig. 2).

6. Conclusion

Spatial and temporal variability in Hg^0 and Hg_R is evident in Pallette Lake, and presumably in many other lakes. We have presented a model defining the important processes influencing epilimnetic Hg^0 concentrations. Gas exchange at the lake surface is a significant removal mechanism and may have a profound effect on Hg^0, as well as the amount of Hg reaching the sediments, the site of Hg methylation. The average evasional losses during July and August, 1993, (-101 pmol $m^{-2}d^{-1}$) were comparable to the atmospheric input (+135 pmol m^{-2} d^{-1}). Moreover, a link between precipitation input of Hg_R and Hg^0 production was demonstrated for Pallette Lake during May, 1994. The spatial distribution of Hg^0 and Hg_R in Pallette Lake and horizontal advective transport will greatly impact short-time scale changes in Hg^0 and Hg_R

determined at a particular location. Modelling the aquatic Hg^0 cycle and, by implication, methylation will require a knowledge of lake circulation effects on the distribution and biogeochemical reactivity of these species. Porewater concentrations of Hg^0 were generally low indicating the sediments are not an contributor of Hg^0 to the water column. Reactive and total Hg concentrations were greatly elevated in porewater with respect to the overlying water. Porewater may contribute a significant flux of Hg_R to the water column under advective conditions or if strongly bound forms become labile when introduced into the watercolumn. However, little is know about possible changes in porewater Hg speciation in the watercolumn. Laboratory experiments indicate that Hg^0 production in Pallette Lake is biologically mediated and agrees with the studies of Mason et al., 1993. The elucidation of mechanisms leading to inter-lake variation on Hg^0 production may prove useful in explaining difference in methyl-Hg accumulation in fish among lakes.

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MERCURY SPECIATION IN LAKE BAIKAL.

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Abstract. Research on mercury (Hg) distribution and speciation was carried out in Lake Baikal, a large, strong-oligotrophic freshwater reservoir in Siberia, Russia, during June 1992 and march 1993. In summer, total Hg in the water column ranged from 0.14 to 0.77 ng Hg/L, with the highest concentrations observed in the central basin of the lake in surface water samples. Labile inorganic Hg was found to be 7 to 20 % of the total Hg content. Highest total Hg concentrations were found in river waters : up to 2 ng Hg/L. Labile methylmercury (MeHg) concentrations ranged from 2 to 38 pg Hg/L in the water column, with the higher concentrations in the central part of the lake, and showing a slight increase in near bottom waters. Labile MeHg makes up 1 to 15 % of the total Hg content in the water column, with larger fractions in deep waters. The slight increase of the MeHg gradient with depth corresponds with the O_2 minimum region. Highest MeHg concentrations were observed in river waters (up to 145 pg Hg/L) and in some bays of the lake (up to 160 pg Hg/L). In these high temperature- and phytoplankton-rich water masses, the MeHg-fraction increased up to 35 % of total Hg. Labile MeHg concentrations in water samples taken in winter in the southern basin (under the ice cover), showed slightly higher concentrations than in summer, possibly due to an early spring bloom. In rainwater, total Hg ranged from 3 to 20 ng Hg/L and MeHg from 0.1 to 0.25 ng Hg/L. In snow, a large fraction of total Hg is bound to particulate matter; concentrations of total Hg ranged from 8 to 60 ng Hg/L and labile MeHg from 0.1 to 0.25 ng Hg/L. Atmospheric Hg was found to be 0.73 to 2.31 ng/m^3 as gaseous Hg and 0.005 to 0.02 ng/m^3 in its particulate form. Spatial distribution patterns of atmospheric Hg show slightly higher concentrations over the central part of the lake and the Selenga river delta. In winter, atmospheric Hg values (measured in the southern region), ranged from 1.2 to 6.1 ng/m^3 as total gaseous Hg and 0.02 to 0.09 ng/m^3 as total particulate Hg, and are higher than in summer, probably influenced by coal burning and traffic by the local population. MeHg contents in fish ranged from 20 ng Hg/g dry weight in small Cottocomephorus to 300 ng Hg/g dry weight in pike and trout species, which were caught in organic-rich waters.

1. Introduction.

Lake Baikal is a large, unique freshwater rift lake situated in eastern Siberia (Russia) : it is the largest lake on earth by volume, containing 1/5 of the total reserve of freshwater; and 636 km long with an average width of 40 km; it is the deepest lake with a maximum depth of 1640 m; and the oldest with its 20 million years. The lake is divided in 3 basins : the northern with depths ranging from 800 to 900 m, the central (1200 to 1637 m) and the southern (1300 to 1400 m). The lake water is supplied by 300 rivers, with 50 % of the water inflow coming from the Selenga river; the Angara river, situated in the southern basin is the biggest exit of the lake. Lake Baikal is strongly oligotrophic, having new production rates that are similar to open-ocean values (Weiss *et al.*, 1991) and a 4 time nutrient recycling before removal to deep-waters.

Unlike most other deep lakes, the deep waters of Baikal are constantly supplied by oxygen at no less than 75 % of saturation (Kozhov, 1963). This is not only due to the variation of water density with temperature (decreasing below 4 °C), the mechanism responsible for the turn over twice a year in other large lakes, since Baikal's deep waters seem to be more than 1 year old. Moreover, free convection in spring due to the melting of the ice layer, only penetrates to 250 to 300 m (Shimaraev *et al.*, 1993). The deep water

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ventilation is accomplished by forced convection (due to an instability resulting from the decrease in temperature of maximum density of freshwater with increasing pressure) and subsequent movement of cold water along the underwater slope to maximum depths. The near bottom waters are younger (8 years) than those at intermediate depths (14 to 16 years old) (Weiss *et al.*, 1991). The vertical distribution of major and minor elements in Lake Baikal waters are quite homogeneous; given a residence time of 330 years (the same age as that of the lake water, predominantly controlled by riverine fluxes) and a mean mixing time of 10 years, major ions undergo ± 30 mixing cycles during their residence in the lake, resulting in uniform concentrations (Falkner *et al.*, 1991).

The remote Lake Baikal appears to be in its pristine state; the only big city nearby, Irkutsk, is situated 70 km downstream of the Angara river; and, besides a paper-pulp plant on the southern shore at Baikalsk, no other industrial or agricultural activities take place around the lake. Lake Baikal is a remote, unpolluted ecosystem, which could serve as a natural background reference system for comparison with other large freshwater reservoirs to better understand anthropogenic inputs and activities. Especially for Hg, a volatile toxic trace metal, it could be an indicator for anthropogenic atmospheric pollution over long distances since some possible sources of pollution to lake Baikal could originate from chemical industries in the Angara or the Selenga Valley by atmospheric transport. Recently, DDT and PCB analyses showed higher concentrations in the water column of the southern basin of Lake Baikal, probably due to atmospheric transport along the Selenga river or from Irkutsk (Kucklick *et al.*, 1994). Hydrothermal vents, found in the sediment floor in the north-eastern corner of the lake at 440 m depths (Crane *et al., 1991*), could also be potential sources of natural Hg emissions.

In this work, speciation of Hg was carried out in several environmental compartments of Lake Baikal in order to study atmospheric transport and deposition to the lake, transformations of Hg compounds in the water column and the bioaccumulation of MeHg.

2. Materials and Methods.

2.1. CLEANING AND SAMPLING PROCEDURES.

Sampling equipment was treated according to Hg contamination-free techniques described by Gill and Fitzgerald (1985).

The Teflon (F.E.P.) sampling bottles were boiled in concentrated nitric acid (new bottles for 48 hours and already used bottles for 6 hours), rinsed with Milli-Q water, filled with 1 % HCl and placed in an oven overnight at 70 °C, rinsed with Milli-Q and filled again with 1 % HCl. The bottles were then double bagged and stored until use. Borosilicate glass bottles were rigorously cleaned with diluted HNO_3, filled with 1 % HCl, and stored double bagged until use. The sampling bottles were emptied just before use, and rinsed 3 times with the sampled water masses. The NOEX-bottles were cleaned by filling them with diluted HCl during 2 days, and rinsing with Milli-Q. The funnel was soaked for several days in diluted HCl, rinsed with Milli-Q water, and dried in a laminar flow bench. The funnel and NOEX bottles were double bagged for storage until use.

Surface water samples were collected by hand from a row-boat by submerging the F.E.P.-bottles (for subsequent MeHg analysis) and the glass bottles (for inorganic and total Hg determinations) approximately 20 cm beneath the surface. The rowboat was at a

hundred meter distance from the main ship; sampling was carried out while moving the boat slowly against the water current and/or the wind. Deep-water samples were collected with (Go-Flo-like) 5 L NOEX-bottles (Technicap, France), and a new steel winch from the Balkhash research vessel. The water volumes were immediately transferred to F.E.P. and glass bottles, and stored double bagged at room temperature until analysis, which was performed usually the same day. During the winter expedition, water samples were taken through a 1 m^2 opening in the ice; the winch was then mounted in a truck.

Rain water was sampled using an all Teflon set-up : a Teflon (P.T.F.E.) funnel coupled to a F.E.P. bottle, which was protected by a wooden housing.

Air sampling was done on quartz wool plugs for total particulate Hg determinations (3 cm quartz wool packed in a 6 mm i.d. quartz tube). The quartz wool was protected from rain by a 10 cm long plexi-glass tube, mounted downwards at the head of the sampling chain. The air was sampled by a membrane pump (Verder NO35 AN18) at a flow rate of 8 to 20 L/min, controlled by a needle valve (Whitey) and a flow meter (Brooks, in combination with a vacuum meter (Gast AA 604)); the sampled volume was measured by a gas meter (Contigea Schlumberger model 4). On separate lines, total gaseous Hg was collected on gold-columns (34 mm Au-coated sand in 5 mm i.d. quartz tubes) in duplicate. The air, passed through quartz wool plugs to retain particulate Hg, was sampled first over the collecting Au-trap, secondly over a control Au-column (in case saturation or break-through of the Au-collection trap would occur), and then over a third gold column, which served to avoid back diffusion of Hg from the pump. Air was pumped at a flow rate of 200 to 300 ml/min. The gold- and quartz-columns were decontaminated before sampling by desorption under a Hg-free argon flow at 450 °C. After sampling, the collection and control columns were dried by passing Hg-free He gas trough the columns at room temperature during a few minutes, the traps were closed with Teflon plugs and stored in P.E.- tubes until analysis. During the summer 1992 expedition, the sampling train was mounted on the bridge of the Balkhash; in winter 1993, the apparatus was set up at the meteostation in Listvyanka, approximately 50 m from the shore of the lake and the Angara river.

Snow samples were taken in winter 1993 from various locations : from snow covers on land near Listvyanka, or from the ice on the southern part of the lake.

Biological samples were taken during the summer 1992 campaign. Muscle tissue of freshly caught fish was immediately removed and kept deep-frozen in precleaned P.E.-bottles. The small fish (cottocomephorus) were mixed together in pools of various length-intervals, because of their small size. The samples were taken deep-frozen to the home laboratory in Brussels, where they were lyophilised and homogenised with a glass rod. Samples were kept in the freezer until analysis.

2.2. ANALYTICAL PROCEDURES.

Total and labile inorganic Hg concentrations in water samples were determined by Au-amalgamation C.V.-A.F.S. (Cold Vapour-Atomic Fluorescence Spectrometry) : the labile inorganic Hg concentration was determined by a $SnCl_2$-reduction step; total Hg was liberated from the sample by BrCl-oxidation, followed by addition of NH_2OH to neutralise the excess amount of oxidising agent, prior to reduction (Bloom and Crecelius, 1983; Fitzgerald and Gill, 1979). The detection limit of these methods is 5 pg Hg/L as labile Hg and 50 pg Hg/L as total Hg, when a 200 ml sample is used. Labile MeHg species were determined by the sensitive method presented by Bloom (1989) : all labile Hg species are

transformed to volatile Hg-compounds by aqueous phase ethylation and purged out of the solution. The ethylated Hg compounds are collected on a Carbotrap, subsequently removed at 270 °C, and transferred to a cryogenic gas chromatographic trap, held in liquid nitrogen (-196 °C). The Hg species are separated while eluting through the gas chromatographic column by controlled heating from -196 ° C to 180 °C. The detection limit is 3.5 pg Hg/L as MeHg. All water samples were analyzed unfiltered.

Atmospheric samples were analyzed for total gaseous Hg and total particulate Hg. The Hg compounds were released from the trapping columns by controlled heating and determined by two-stage Au-amalgamation C.V.-A.F.S. (Baeyens and Leermakers, 1989). Organic Hg species, collected on Carbotrap columns, were released and analyzed by cryogenic gas chromatography A.F.S. (Bloom and Fitzgerald, 1988). DiMeHg or other organic Hg compounds were not found (or were lower than 2 pg/m^3; or less than 0.1 % of atmospheric Hg) in the air above Lake Baikal.

MeHg in biological samples was determined by H.S.-G.C.-A.F.S. (Headspace - gas Chromatography - Atomic Fluorescence Spectrometry, Lansens *et al.*, 1993). MeHg is cleaved from the biological material by H_2SO_4, transformed to the more volatile iodide form (MeHgI) by addition of ICH_2COOH, and then headspace injected on a G.C.-column. All handling take place at one time in one vial. A detection limit of 1 ng MeHg/g dry weight is reached using this technique.

All samples were calibrated for Hg or MeHg using a standard addition method.

3. Results and discussion.

Total Hg, labile inorganic Hg and labile MeHg were determined in water samples (including surface waters, depth profiles and river water samples). Total Hg and MeHg were determined in rain water and snow; atmospheric samples were analyzed for total gaseous Hg, MeHg and total particulate Hg. In addition, MeHg was determined in various fish species caught during the summer 1992 campaign.

Analyses were performed directly on board of the Balkhash research vessel during the summer 1992 expedition (except for the biological samples, which were analyzed in the home laboratory); the samples taken during the winter 1993 campaign were stored according to the procedures described by Leermakers *et al.* (1990) and Lansens *et al.* (1990), and analyzed a few weeks later in the clean laboratory in Brussels.

3.1. SAMPLING LOCATIONS.

The sampling stations of both summer and winter expeditions are shown in Figure 1.

In June 1992, water samples (surface and deep water) were taken all over the lake and in the rivers (stations 1 to 21). Air was only sampled on the lake. Fishes were caught in the central and southern basin of the lake. Rain sampling was performed during the expedition in the northern and southern part of the lake.

In march 1993, water samples were taken from the southern basin (station march), atmospheric samples were taken at the shore at Listvyanka, and snow samples were collected in Listvyanka and from the ice cover on the southern part of the lake.

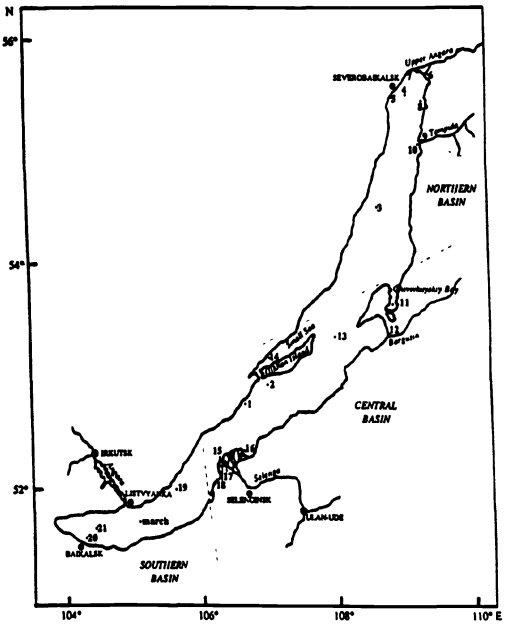

Fig. 1. Sampling stations in Lake Baikal (stations 1 - 21 : water samples taken in June 1992; station march : water samples taken in March 1993).

3.2. ATMOSPHERIC CONCENTRATIONS ABOVE LAKE BAIKAL.

During the summer expedition, concentrations of total gaseous Hg were found in the range of 0.73 and 2.31 ng Hg/m^3, and of total particulate Hg between 0.005 and 0.020 ng Hg/m^3. Atmospheric concentrations found over Lake Baikal in summer are of the same order of magnitude as in continental regions of Lake Wisconsin and above the Pacific Ocean (see Table I). Spatial distribution patterns show slightly higher concentrations over the central part of the lake and over the Selenga river delta (Figure 2a), probably due to atmospheric pollution by the cities Ulan-Ude and Selenginsk, located at the Selenga river.

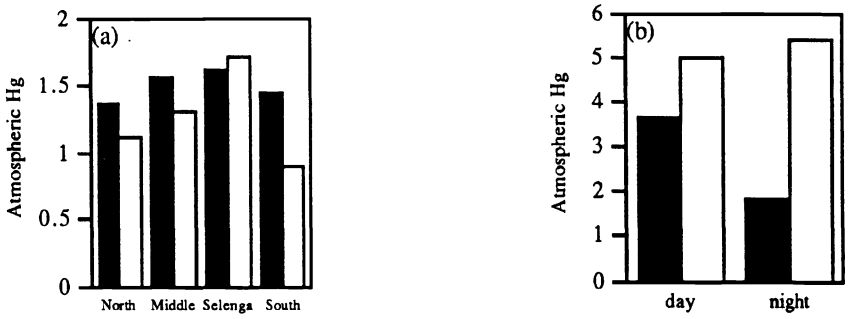

Fig. 2. Atmospheric Hg distribution above Lake Baikal in June 1992 (a) and March 1993 in the southern part (b) (■ : total gaseous Hg (ng Hg/m^3); □ : total particulate Hg (10^{-2} ng Hg/m^3)).

TABLE I

Comparison of Hg concentrations found in Lake Baikal and other natural water systems.

		Location	Hg concentrations	
ATMOSPHERE			total gaseous Hg (ng/m^3)	total particulate Hg (ng/m^3)
	land	Wisconsin[a]	1.57 ± 0.4	0.022 ± 0.019
		Sweden summer[b]	1.5 - 2	-
		Sweden winter[b]	3 - 4	-
		Lake Baikal summer[c]	1.45 ± 0.44	0.011 ± 0.005
		Lake Baikal winter[c]	2.9 ± 1.6	0.052± 0.025
		Baikal, previous results[d]	2 - 25000	48 - 8000
	open ocean	Pacific Ocean[a]	1 77 ± 0.15	0.0004 - 0.020
RAIN			total Hg (ng/L)	MeHg (ng/L)
	land	Wisconsin[a]	10.5 ± 4.8	0.156 ± 0.068
		Sweden[e]	7 - 90	< 0.05 - 0.6
		Great Lakes, Minnesota[f]	18.0	-
		Washington[g]	2 - 5	0.015 - 0.3
		Lake Baikal[c]	9.95 ± 7.38	0.192 ± 0.08
	coast	North Sea[h]	11 ± 3	-
		Mace Head, Ireland[i]	2.1 - 16.3	-
		Atlantic, USA[j]	up to 26	-
	open ocean	Pacific[k]	2 8 ± 1.6	-
		Pacific[l]	-	0
SNOW	land	Wisconsin[g]	4	0.05
		Lake Baikal[c]	26 9 ± 19.5	0.158 ± 0.110
WATER			total Hg (ng/L)	MeHg (ng/L)
	unpolluted lake	Crescent, Washington[m]	-	< 0.10
		Little Rock Lake, Wisconsin[n]	0.4 - 11	0.04 - 0.1
		Sweden[e]	1.3 - 15	0.04 - 0.8
		Lake Baikal[c]	0 14 - 0.77	0.002- 0.038
		Baikal, previous results[o, p]	100 - 200	-
		Baikal, previous results[q]	< 10	-
	polluted lake	Onondaga, New York[r]	2 - 25	0.03 - 0.7
	open ocean	Pacific[s]	0.2 - 0 7	-
		Pacific[l]	-	0.01 - 0.056
BIOTA			MeHg (ng Hg/g f.w.)	
Pike	lake	Canada, Ontario[t]	300 - 1100	
		Canada, Manitoba[u]	400 - 800	
		Lake Baikal[c]	30	
Whitefish	lake	Canada, Ontario[t]	60 - 150	
		Canada, Manitoba[u]	100 - 250	
(omul)		**Lake Baikal**[c]	5 - 13	

[a] Fitzgerald *et al*, 1991, [b] Lindqvist, 1991, [c] this work, [d] Novukov *et al*, 1990, [e] Lee and Iverfeldt, 1991; [f] Glas *et al*, 1991; [g] Bloom and Watras, 1989b, [h] Baeyens *et al*, 1991, [i] Leermakers (unpublished); [j] Gill and Fitzgerald, 1987b, [k] Gill and Fitzgerald, 1987a, [l] Mason and Fitzgerald, 1990, [m] Bloom, 1989; [n] Bloom and Watras, 1989a; [o] Belova and Vetrov, 1985, [p] Izrael *et al*, 1987; [q] Saprykin *et al*, 1993; [r] Bloom and Effler, 1990; [s] Kim and Fitzgerald, 1986, [t] Bodaly et al, 1993, [u] Jackson, 1991

Lake Baikal is situated in an intermountaneous depression, and when the surrounding high mountain ranges are interrupted by riverine valleys, a more intensive air circulation exists between the depression and adjacent territories (Khodzher and Obolkin, 1992). No influence of the rift zone in the northern part of the lake was noticed.

In winter, concentrations were slightly higher than in summer: from 1.2 to 6.15 ng total gaseous Hg/m^3 and 0.022 to 0.09 ng total particulate Hg/m^3, measured at the shore of the southern basin. Gaseous Hg concentrations during day-time are twice as high as during night-time (Figure 2b), with a mean of 3.65 ± 1.68 ng Hg/m^3 during the day-, and 1.85 ± 0.75 ng Hg/m^3 during night-time. Atmospheric Hg is not a result of volatilization from the lake surface (the ice cover in the southern basin, at he exit of the Angara river, had already partially melted), as observed in Ontario for Lake Eagle, where day-time volatilization rates are significantly higher than night-time rates (Schroeder *et al.*, 1992). Here, atmospheric Hg concentrations are predominantly influenced by coal burning, local traffic and winds from the Angara Valley.

3.3. MERCURY CONCENTRATIONS IN WET DEPOSITION.

Hg concentrations in rainwater and snow are listed in Table II.

TABLE II
Mercury concentrations in rain and snow.

	location	total Hg (ng Hg/L)	labile inorganic Hg (ng Hg/L)	MeHg (ng Hg/L)
Rain	NB, Severobaikalsk	20.10	-	-
(June 1992)	SB, Baikalsk	14.60	-	-
	SB, Kultuk	8.70	-	0.253
	SB, Listvyanka	2.92	-	0.101
	SB, Port Baikal	3.44	-	0.223
Snow	SB, hill Listvyanka	13.5	4.6	-
(March 1993)	SB, hill Listvyanka	60.0	-	0.099
	SB, ice on lake, centre	39.5	6.9	0.091
	SB, ice on lake, near shore	15.6	0.4	-
	SB, meteostation, fresh snow	23.9	-	-
	SB, ice on lake, fresh snow	8.6	4.6	0.285

(NB : northern basin, SB : southern basin)

Total Hg in precipitation ranged from 2.92 to 20.1 ng Hg/L in rainwater collected in summer, and from 8.6 to 60 ng Hg/L in snow samples taken near Listvyanka in winter. Total rain water concentrations at Lake Baikal are higher than above the open ocean, but are of the same order of magnitude as in other continental or coastal areas (see table 1). Hg speciation in rainwater showed MeHg concentrations from 0.1 to 0.25 ng Hg/L, comparable to those in other continental zones but higher than for the open ocean, where Mason and Fitzgerald (1990) did not observe any MeHg in precipitation. MeHg makes up 3 to 7 % of total Hg : percentages that are comparable to the results of Bloom and Watras (1989b), who found 2 to 10 % MeHg in continental rain. In snow samples, labile inorganic Hg makes up 3 to 53 % (0.4 to 6.9 ng Hg/L) and MeHg 0.2 to 3 % (0.09 to 0.29 ng Hg/L) of the total Hg amount. These low percentages of labile Hg-species in snow indicate that a large fraction of the total Hg should be bound to particulate matter.

3.4. MERCURY SPECIATION IN THE WATER COLUMN.

Depth profiles of total Hg, labile inorganic Hg and labile MeHg are shown in Figure 3.

During the summer campaign, lowest labile inorganic and total Hg concentrations were measured in the northern basin of Lake Baikal, ranging from detection limit (0.005) to

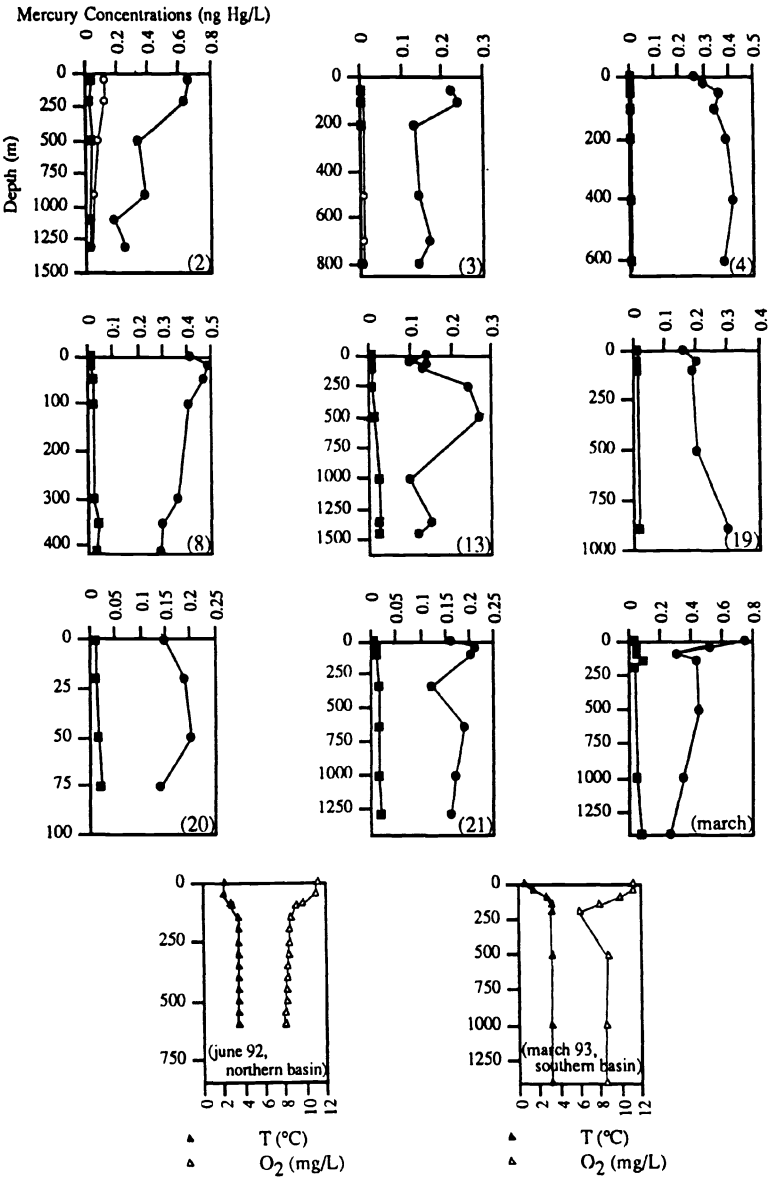

Fig. 3. Hg depth profiles in Lake Baikal. (●: total Hg; ■: labile MeHg; ○: labile inorganic Hg), and temperature and oxygen profiles.

0.02 ng Hg/L and from 0.14 to 0.48 ng Hg/L, respectively. Highest concentrations were found in the central part, near Olkhon Island (stations 1 and 2) with 0.04 to 0.13 ng Hg/L as labile inorganic Hg and 0.2 to 0.77 ng Hg/L as total Hg. In the southern basin, total Hg was typically 0.1 to 0.2 ng Hg/L. Labile inorganic Hg was only determined in the first water samples (stations 1 to 3) because of the extremely low concentrations. Total Hg concentrations in Lake Baikal are comparable to those in open ocean waters, but are remarkably lower than concentrations reported for other remote or unpolluted freshwater systems (Table I). The few results of labile inorganic Hg obtained in Baikal are even lower than in open ocean waters : 0.16 to 0.44 ng Hg/L in the Pacific (Fitzgerald *et al.*, 1984), or in the Atlantic (0.5 ± 0.1; Dalziel and Yeats, 1985). Percentages of labile inorganic to total Hg are 7 to 20 %. Gradients of labile inorganic and total Hg with depth do not show the same trend over the lake, but, in general, concentrations are a little higher in the upper water masses than in deep waters.

Labile MeHg in Lake Baikal ranged from 0.002 to 0.038 ng Hg /L. The higher MeHg concentrations were found in the central part of the lake, near Olkhon Island and the Small sea (stations 1, 2 and 14), with concentrations ranging from 0.026 to 0.038 ng Hg/L. Lowest labile MeHg was found in the northern basin (0.002 to 0.008 ng Hg/L), except for station 8 (Frolikha Bay), were concentrations ranged from 0.018 to 0.037 ng Hg/L. Frolikha Bay is characterised by hydrothermal vents on the bottom of the lake. Unfortunately, an accurate positioning of the sampling point was not performed, so that it is difficult to relate the water masses to the vents. Total Hg at this site did not differ from other northern stations, similar to the results of Falkner *et al.* (1991), who found that hydrothermal discharge did not seem to be significant enough to affect the budget of major ions on the 330 year-time scale of water renewal by rivers. The small increase of MeHg in Frolikha Bay might be related to higher temperatures of the sediment (16 °C , compared to an ambient temperature of 3.47 °C) beneath the bacterial mat, which covers the area around the vents (*Crane et al.*, 1991). In the southern basin, which is subjected to industrial activity (paper mill at Baikalsk, station 19 to 21), labile MeHg ranged from 0.009 (surface) to 0.022 pg Hg/L in deep waters. MeHg concentrations in Lake Baikal are of the same order of magnitude as in the Pacific Ocean and other unpolluted freshwater lakes (Table I).

In the northerly stations, MeHg depth profiles show a uniform distribution : the ice, which covers the whole lake during winter, had just melted and induced a very strong water circulation. In the central basin, the station at the deepest point of the lake showed slightly higher concentrations in deep waters compared to surface waters. The MeHg gradient is, however, most pronounced in the southern basin. A direct correlation between MeHg and temperature or oxygen profiles was not observed, but the small increase of MeHg towards near bottom waters, corresponds to lower oxygen levels (below 150 m, O_2 shows a uniform pattern and decreased concentrations). In other aquatic systems, highest MeHg concentrations were found in the thermocline (Mason and Fitzgerald, 1990; Bloom *et al.*, 1991; Bloom and Effler, 1990; Mason and Fitzgerald, 1991); the increasing MeHg gradient with depth coincided to low oxygen and labile inorganic Hg levels, indicating in situ production of MeHg in the O_2 minimum.

Labile MeHg makes up 1 to 5 % of the total Hg in the northern basin, 3 to 14 % in the central basin and 7 to 15 % in the southern basin. In all 3 basins, the MeHg portion reaches a maximum in deep waters. The percentages are comparable to literature data, reporting 1 to 12 % (Lee and Iverfeldt, 1991) and 7 to 25 % (Bloom *et al.*, 1991) for

freshwater systems.

Highest MeHg-concentrations (and percentages) were found in (shallow) bays : from 86 pg Hg/L (Chivyvkuyskiy Bay) to 161 pg Hg/L (Proval Bay). Although total Hg levels also show an increase in these samples (0.44 to 2.02 ng Hg/L), the MeHg-fraction is still higher than in lake water : 8 to 20 %. These water masses are characterized by higher temperatures and visible higher concentrations of organic matter.

During the late winter/early spring period, when an early spring bloom occured in the water column, MeHg concentrations found in the southern basin are slightly higher than in summer, with a maximum at 150 m depth, corresponding to a temperature increase and relatively lower oxygen concentrations. Total Hg was similar to summer concentrations.

3.5. MERCURY IN RIVER WATERS.

Results of Hg analyses in river waters are listed in Table III.

In river waters entering the lake, total Hg levels ranged from 0.4 to 1.7 ng/L, and MeHg from 0.014 to 0.146 ng Hg/L. Concentrations of both species are much higher than in lake waters. The MeHg fraction reaches up to 35 % of the total Hg content, having lower values (<1 to 10 %) in the rivers of the northern region and 6 to 35 % in rivers entering the central basin. As in the bay water masses of the lake, higher MeHg fractions in river waters seem to correspond to higher temperatures and the (visible) presence of suspended matter loads.

TABLE III

Mercury in Riverwater and some surface waters of Lake Baikal.

station	location (distance from lake)	temperature (°C)	total Hg (ng Hg/L)	labile MeHg (pg Hg/L)	MeHg/total Hg (%)
5	NB, Tygov (1 km)	5.0	1.67	< 14	< 1
6	NB, Upper Angara (1 km)	13.2	1.51	48.9	3
7	NB, Kichiere (1 km)	13.2	0.98	34.5	4
9	NB, Tomnyda (1 km)	-	0.79	82.3	10
10	NB, Tomnyda (0 km)	-	0.69	41.8	6
12	CB, Barguzin	-	0.61	33.6	6
16	CB, Proval Bay, Selenga	17	2.02	160.7	8
17	CB, Selenga (5km)	18	0.42	145.9	35
18	CB, Selenga (3km)	18	0.55	81.1	15
1	CB, C. Buryatskaya	-	0.77	38.3	5
11	NB, Chivyvkuyskiy Bay	-	0.44	86.1	20
14	CB, Small Sea	-	0.15	25.9	17
15	CB, Selenga delta	-	0.26	23.7	9

(CB : Central Basin; NB : Northern Basin)

3.6. MeHg IN FISH SAMPLES.

Several fishes, used for consumption by the local inhabitants, were analyzed : MeHg levels in muscle tissues ranged from 15 to 39 ng Hg/g d.w. in Cottocomephorus grewenki (length 10 to 13 cm); from 23 to 59 ng Hg/g d.w. in Cottocomephorus inermis (14 to 16 cm); from 40 to 105 ng Hg/g d.w. in Omul (23 to 32 cm); from70 to 300 ng Hg/g d.w. in

Baikal trout (25 to 37 cm) and about 250 ng Hg/g d.w. in pike species (42 cm in length). The latter were caught in nutrient-richer bays, where higher labile MeHg levels were found in the water column. MeHg is known to be bioaccumulated by fishes; also in Lake Baikal, a positive correlation exists between MeHg-content and the age (or length) of the organism. The bioconcentration factor (C_{biota}/C_{water}) for MeHg is 10^5 to 10^7, for labile MeHg concentrations in lake- and bay- waters of 5 to 160 pg Hg/L.

3.7. ESTIMATIONS OF Hg FLUXES IN LAKE BAIKAL.

Some estimations of annual Hg fluxes in Lake Baikal have been made in Figure 4, including wet deposition and riverine contribution to the yearly input of Hg (and MeHg) to the water column of Lake Baikal; MeHg uptake by biota, and the subsequent uptake by the human population by fish consumption; and the importance of Hg outflow by the Angara river. Unfortunately, the sediment compartment of Lake Baikal was not included, since these samples could not be taken during the campaigns.

Wet depositional fluxes were calculated from annual snow and rain fall all over Lake Baikal. Only the direct deposition to the lake surface has been taken into account; the Hg input by run-off waters was not included. Hg input by wet deposition is probably underestimated, since retention of Hg by soils, rivulets and rivers in the large (450 000 km^2, Kozhov, 1963) catchment area of Baikal is probably not complete. Dry depositional fluxes were adapted from Fitzgerald *et al.* (1991), since aerosol concentrations in Baikal are similar to those in remote regions (Khodzer and Obolkin, 1992; Koutsenogii *et al.*, 1993). Riverine input of Hg was extrapolated from discrete summer measurements to an annual water volume of 60 km^3 that flows into the lake. No data on the total fish stock of Lake Baikal exist in order to calculate the MeHg-uptake by biota. It was estimated at 250 000 t, assuming that the annual catch of 12 500 t (Kozhov, 1963) represents 5 % of the total fish

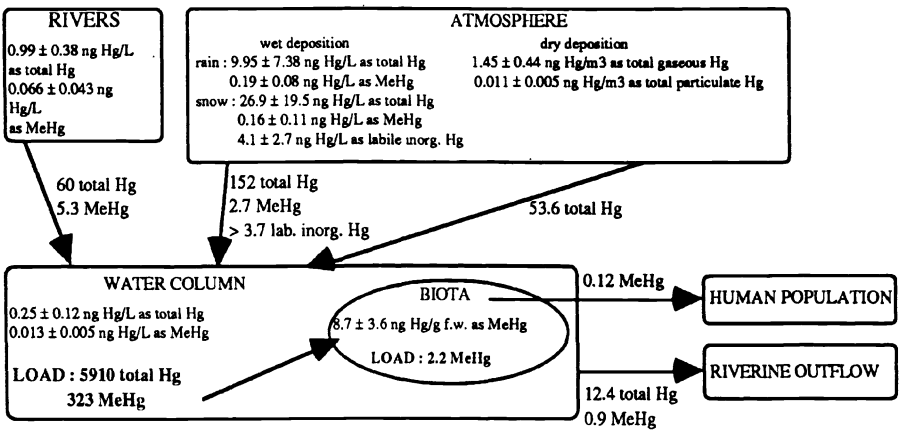

Fig. 4. Estimations of annual Hg fluxes in Lake Baikal (Fluxes are given in 10^3 g Hg)

biomass. The MeHg uptake by biomass is underestimated, since zooplankton, crustaceans and large mammals (Baikal seals) are not included. All water that is supplied to Baikal over the year is evacuated by the Angara river (with the exception of 12 % expended on evaporation).

Atmospheric deposition and riverine input are important Hg-sources to the lake. Annually, they account for 1 % and 3 5 %, respectively of the total Hg burden of lake Baikal water (which is only totally renewed every 300 years (Falkner *et al*, 1991)). Wet deposition and riverine input are the major MeHg sources to the lake : annually they are responsible for respectively 0 8 and 1.6 % of the lake water's MeHg burden. These levels could largely explain the MeHg burden in biota No Hg° was measured in the surface waters of Lake Baikal, so no estimations of losses due to evaporation could be made. In the remote Wisconsin lakes, the flux of Hg as Hg° due to gas evasion is estimated at approximately 10 % of the annual atmospheric input of Hg to the lakes. (Vandal *et al*, 1991).

4. Conclusions.

Hg concentrations in the remote Lake Baikal ecosystem are very low. Water column Hg and MeHg levels are comparable to open ocean systems, and MeHg concentrations in biological samples are lower than those reported for North American or Canadian remote lakes. The atmospheric concentrations in Baikal (wet deposition and gaseous Hg), however, are similar to continental levels, and in rivers or in shallow, semi-enclosed bays of the lake, concentrations are more elevated Estimations of Hg cycling in Baikal indicate that the atmospheric and riverine inputs to the lake are important sources of total Hg and MeHg

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MERCURY CYCLING IN THE WATER COLUMN OF A SEASONALLY ANOXIC URBAN LAKE (ONONDAGA LAKE, NY)

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Abstract. Onondaga Lake, New York, is a hypereutrophic, urban lake that was subjected to industrial discharges of mercury (Hg) between 1947 and 1988. Water samples were collected from April through November 1992 and analyzed for filtered and unfiltered total Hg, methylmercury (CH_3Hg), dimethylmercury, ionic Hg, and elemental Hg to characterize the biogeochemical cycling of Hg during water column stratification and hypolimnetic anoxia. In the spring and late fall when the water column was isothermal, total Hg and CH_3Hg concentrations were relatively constant throughout the water column, at approximately 3–7 ng/L and 0.3–1 ng/L, respectively. Through the summer and early fall, CH_3Hg concentrations systematically increased in the deeper waters, reaching peak concentration in August and September. In September 1992, CH_3Hg concentrations increased from 0.3 ng/L in the epilimnion to 10.6 ng/L in the hypolimnion, an increase of nearly 2 orders of magnitude. At the same time, total Hg increased from 6.6 ng/L in surface water to 21.7 ng/L at depth, a 3-fold increase. The spatial and temporal patterns observed for CH_3Hg agree well with manganese, suggesting that CH_3Hg and manganese are controlled by processes of the same or parallel cycles.

1. Introduction

The behavior of mercury (Hg) in aquatic environments has been shown to be highly sensitive to a number of water quality characteristics (e.g., dissolved oxygen concentration, pH, temperature). The factors controlling methylmercury (CH_3Hg) concentrations are of particular interest because CH_3Hg is toxic and tends to bioaccumulate. Several studies of pristine lakes have shown a seasonal buildup of total Hg and CH_3Hg under anoxic conditions in hypolimnia (e.g., Bloom *et al.*, 1991). In general, increased production of CH_3Hg is expected under conditions of elevated temperature and reduced dissolved oxygen concentration (Gilmour and Henry, 1991). A study of Pallette Lake, Wisconsin, suggests that increased total Hg concentrations in the hypolimnion may result from the release of Hg from settling particles before incorporation into sediment (Hurley *et al.*, 1994).

In contrast to pristine systems, Onondaga Lake, New York, is an alkaline, hypereutrophic, urban lake that was subjected to historical Hg releases. The lake is uniquely suited to the assessment of major processes controlling Hg behavior in a freshwater system under conditions of neutral pH (7.5–8.5), excess sulfate (110–200 mg/L), and seasonal anoxia. The results presented in this paper represent a portion of the data collected for a large remedial investigation of Onondaga Lake. A major objective of this study is to identify and quantify the major processes that control the speciation, transport, and fate of total Hg and CH_3Hg in the water column. The mass balance of total Hg and CH_3Hg in Onondaga Lake is described in Henry *et al.* (in press). In this paper, the seasonal buildup of CH_3Hg in the anoxic hypolimnion is examined in terms of its relationship to water quality characteristics (e.g., dissolved oxygen concentration) and concentrations of other redox-sensitive species (e.g., manganese [Mn]).

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2. Materials and Methods

2.1. Site Description

Onondaga Lake is located in Onondaga County, New York, next to the city of Syracuse (Figure 1). The lake has a surface area of 12 km^2 and mean and maximum depths of 12.0 and 19.9 m, respectively (PTI, unpublished data). Surface water enters the lake from seven tributaries and the Metropolitan Syracuse Sewage Treatment Plant. Commercial and industrial development in Syracuse is concentrated along the southern and southwestern shores of the lake. Onondaga Lake is hypereutrophic (Bloom and Effler, 1990) and dimictic. During summer stratification, the thermocline is located at approximately 9–10 m below the water surface and the hypolimnion is anoxic and sulfidic.

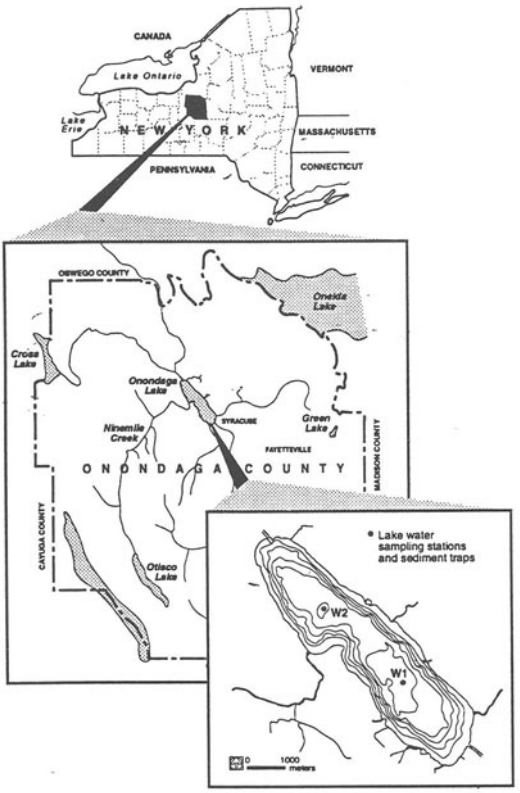

Fig. 1. Location of Onondaga Lake and lake water sampling stations.

Historically, Onondaga Lake received Hg loadings from the industrial effluent of two Hg-cell chloralkali plants. Loading of Hg to the lake decreased dramatically in 1970 with the implementation of wastewater treatment improvements at the chloralkali plants. The plants were later closed in 1977 and 1988. A fishing advisory is currently in effect for the lake because fish Hg concentrations exceed 1.0 mg/kg.

2.2. Sampling Methods

Lake water samples were collected monthly from April through November 1992 at two stations located approximately in the centers of the north and south basins of the lake (Figure 1). Unfiltered water samples were collected at each station from water depths of 0, 3, 6, 9, 12, 15, and 18 m during summer stratification (May–September) and from water depths of 3, 9, and 15 m during the remaining months (April, October–November). Filtered water samples from the same depths were collected at one of the two stations.

Lake water samples were collected from a fiberglass boat using a peristaltic pump (for analysis of total suspended solids [TSS], iron [Fe], Mn, and Hg species) or an acrylic Kemmerer sampler (for conventional analytes). Beginning with the 0-m depth, samples for analysis of TSS and metals were collected using weighted Teflon® tubing attached to the peristaltic pump. Sampling for Hg was conducted using the clean-hands technique (Fitzgerald and Watras, 1989; Gill and Fitzgerald, 1985). To further avoid potential contamination, samples for Hg analysis were collected first at each depth using the peristaltic pump; samples for other analytes were then collected using a Kemmerer sampler. Samples were collected into Teflon® bottles, packed on ice, and shipped overnight to the laboratory where they were filtered and preserved.

Temperature, pH, conductivity, and dissolved oxygen measurements were collected using a Hydrolab Surveyor 3 instrument, which was calibrated in accordance with the operations manual before measurements were taken.

2.3. Laboratory Analysis

Mn and Fe analyses were performed on unfiltered samples using inductively coupled plasma-atomic emission spectrometry. TSS was determined gravimetrically and total organic carbon (TOC) was determined by combustion. Hg analyses were performed on filtered (0.45-μm pore size) and unfiltered samples by Brooks Rand, Ltd., using cold vapor atomic fluorescence spectroscopy (Bloom and Fitzgerald, 1988). "Acid-labile" (i.e., reactive or ionic) Hg was measured before and total Hg was measured after bromine chloride oxidation (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988) with use of the gold amalgamation technique (Gill and Fitzgerald, 1987). CH_3Hg was measured by the ethylation technique following separation by methylene chloride extraction (Bloom, 1989). Elemental Hg and dimethylmercury were analyzed in unfiltered samples according to Bloom and Fitzgerald (1988). All results were validated and reviewed in accordance with U.S. Environmental Protection Agency guidelines (U.S. EPA, 1988a,b).

3. Results and Discussion

The thermal stratification and concurrent development of anoxia in Onondaga Lake is portrayed in Figure 2. During the first sampling event in April, the water column was isothermal and oxic. With the onset of thermal stratification in May, oxygen rapidly became depleted in the hypolimnion and anoxic conditions existed in water below 10 m from June through September. A well developed

"redoxcline" was present throughout the period of stratification, with oxygen levels present at 7–14 mg/L in the epilimnion (a p*e* of at least 12) and sulfide detected in the hypolimnion at levels of 1 mg/L or greater (indicating a p*e* of less than −3). Fall turnover occurred prior to the last sampling event in November, and the water column was again isothermal and well-oxygenated.

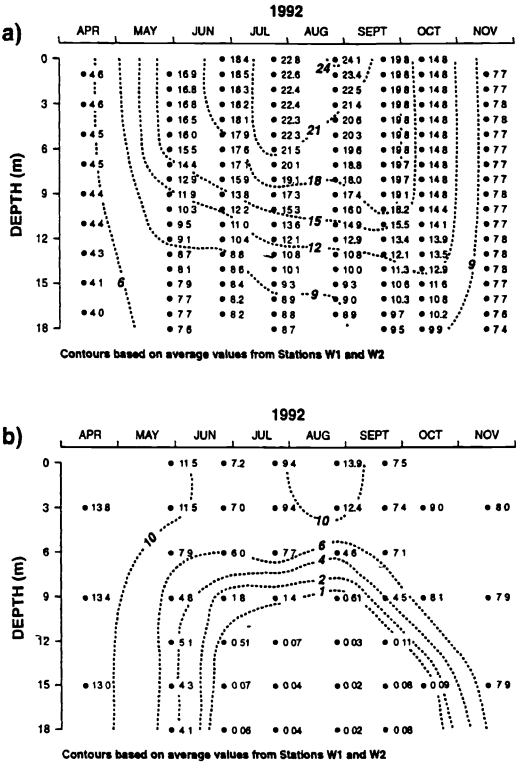

Fig. 2. Spatial and temporal variations in temperature (a) (°C) and dissolved oxygen (b) (mg/L) in Onondaga Lake.

Mn and Fe are sensitive to changes in redox potential (Stumm and Morgan, 1981), and the reductive dissolution of Mn and Fe oxides under anoxic conditions leads to elevated concentrations of dissolved Mn and Fe in the hypolimnion (Figure 3). Between April and May, Mn concentrations in the deepest waters increased by an order of magnitude. Concentrations continued to climb through the summer, reaching highest values just prior to turnover in late September/early October. The period in which elevated Fe concentrations were observed in the hypolimnia was much more limited, with noticeably elevated Fe concentrations (3–6 times surface water concentrations) occurring only from August through October.

The contrasting behavior of Mn and Fe in anoxic water columns is well known and can be attributed to differences in the redox potential of their respective half-reactions and differences in their

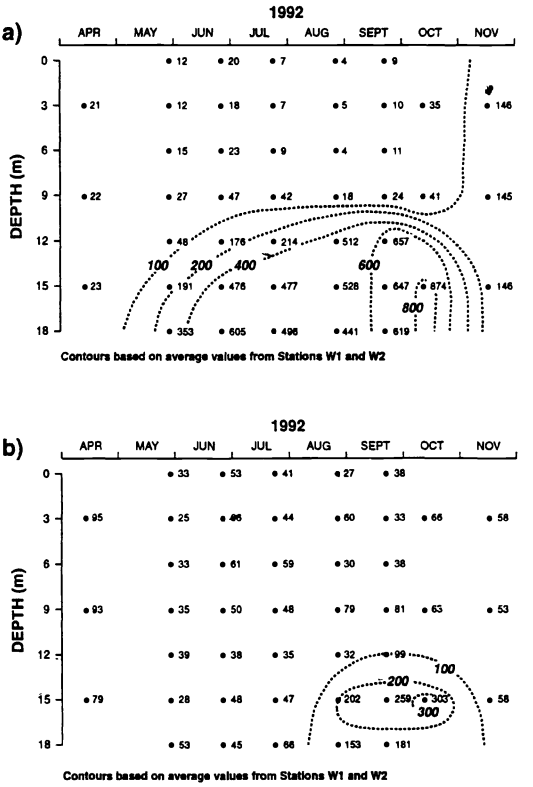

Fig. 3. Spatial and temporal distributions in manganese (a) (ng/L) and iron (b) (μg/L) in Onondaga Lake.

oxidation rates. The reduction of Fe (III) requires a lower redox potential (or p*e*) than Mn. In addition, the oxidation of Fe (II) in the presence of oxygen is typically very rapid; thus, Fe diffusing across the redoxcline is rapidly converted to the particulate form [Fe (III)]. Mn oxidation kinetics are slower, and Mn oxidation has been attributed to Mn-oxidizing bacteria that are present at the redoxcline.

Because Hg strongly sorbs and complexes, the spatial and temporal distributions of TSS and TOC also provide a framework for interpreting Hg distribution (Figure 4). Concentrations of TSS were generally below 4 mg/L throughout the water column, with the exception of April and September/October. Elevated concentrations of TSS in April may be attributable to the high solids loads introduced to the lake during the spring floods of 1992. Elevated particle concentrations were also observed in the bottom waters during September and October. With the exception of April, TOC concentrations were fairly uniform with depth. The reason for the high TOC value observed in April is unknown.

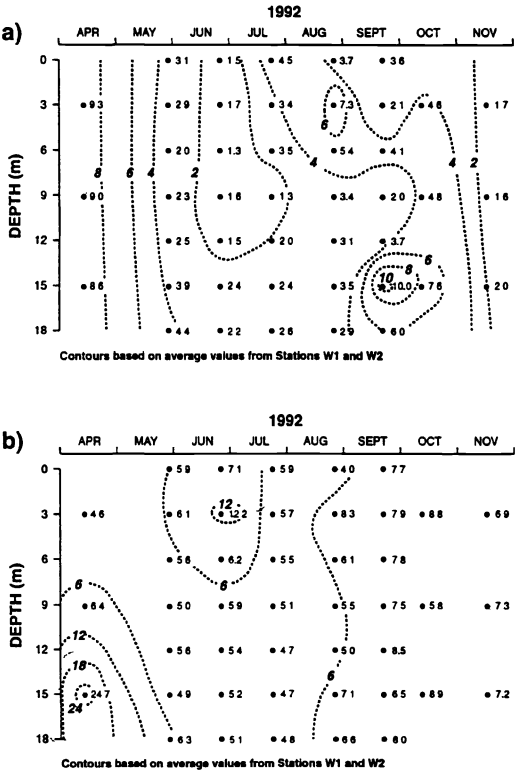

Fig. 4. Spatial and temporal distributions in suspended solids (a) (mg/L) and total organic carbon (b) (mg/L) in Onondaga Lake.

The spatial and temporal distributions observed for total Hg and CH_3Hg are shown in Figure 5. The elevated concentrations of total Hg in April (not observed for CH_3Hg) are consistent with the elevated TSS concentrations, and the very high total Hg concentration at 15 m corresponds to high TOC concentration. Concentration patterns for dissolved Hg (not shown) are similar to those of total Hg, except that elevated concentrations are not observed in April (consistent with the hypothesis that elevated total Hg concentrations are associated with high particle concentrations). Like Mn, total Hg and CH_3Hg concentrations in the hypolimnion increased throughout the summer and reached highest values in late September. Dissolved concentrations of total Hg and CH_3Hg were typically 40–50 percent of unfiltered concentrations.

Ionic Hg concentrations (not shown) were elevated in April at 3 ng/L (explained by the elevated levels of particles) and nearly uniform the remainder of the year (typically 0.3–1 ng/L), suggesting that the processes controlling CH_3Hg concentrations are, in large part, responsible for patterns observed for total Hg. Concentration of elemental Hg (not shown) varied somewhat through the

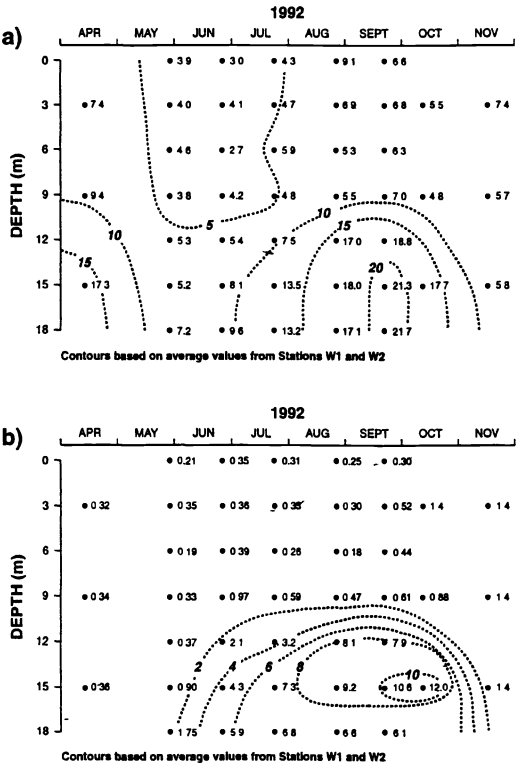

Fig. 5. Spatial and temporal distributions in total mercury (a) (ng/L) and methylmercury (b) (ng/L) in Onondaga Lake.

year, displaying the lowest concentration (less than 0.05 ng/L) in the hypolimnion during periods of anoxia and reaching highest concentrations (from 0.1 to 0.3 ng/L) in near surface waters in April and August. Dimethylmercury concentrations were undetected (at detection limits ranging from 0.01 to 0.001 ng/L) through the study period.

The concentrations and temporal pattern of total Hg and CH_3Hg in Onondaga Lake differ from a 1989 study of the lake by Bloom and Effler (1990). In general, total Hg concentrations in the epilimnion were lower in April and June of 1992 (7.4 and 3.0 ng/L, respectively) than in corresponding months of 1989 (18.8 and 7.3 ng/L, respectively). CH_3Hg concentrations were also lower for April and June in 1992 (0.32 and 0.35 ng/L, respectively) than in 1989 (2.02 and 0.56 ng/L, respectively). In contrast to the current study, Bloom and Effler (1990) observed maximum Hg concentrations early in the year that did not increase as stratification progressed.

Similar spatial and temporal patterns in total Hg and CH_3Hg were observed in Little Rock Lake, Wisconsin (Bloom *et al.*, 1991; Hurley *et al.*, 1994), a soft-water seepage lake remote from any

point source of Hg that experiences seasonal anoxia in the hypolimnion. In this lake, epilimnetic total Hg concentrations varied from 1–2 ng/L throughout the year and hypolimnetic levels increased to 15 ng/L by late August. The buildup of total Hg in the hypolimnion of Little Rock Lake was attributed to releases from settling particles based on differences in the gross sedimentation and net accumulation rates of Hg. Similar to total Hg, CH_3Hg concentrations increased in the hypolimnion of Little Rock Lake during summer stratification and reached maximum levels similar to those observed in Onondaga Lake. In late summer, surface concentrations of CH_3Hg were less than 0.5 ng/L, while concentrations near the bottom were 3–10 ng/L (Bloom *et al.*, 1991).

Temporal variations in Mn and CH_3Hg in the hypolimnion are contrasted to the temporal variations in Fe in Figure 6. As noted earlier, Mn and CH_3Hg start increasing earlier in the season than Fe. The close correspondence between Mn and CH_3Hg further illustrates the degree to which their cycles are linked in the hypolimnion. The relationship between Mn and CH_3Hg is evaluated in more detail in Figure 7. The relationship between Mn and CH_3Hg in spring (April and May) is strongly correlated, suggesting that the reductive dissolution of Mn oxide is accompanied by mobilization of CH_3Hg at a constant stoichiometry. The CH_3Hg/Mn ratio increased from June through October, indicating that CH_3Hg builds up more rapidly than Mn. This could be due to methylation in the hypolimnion or settling of particles into the hypolimnion that contain CH_3Hg. Following turnover in November, a concentration decrease is observed for both Mn and CH_3Hg, and concentrations are uniform throughout the water column. Concentrations of both constituents are 5–7 times greater in November than in April.

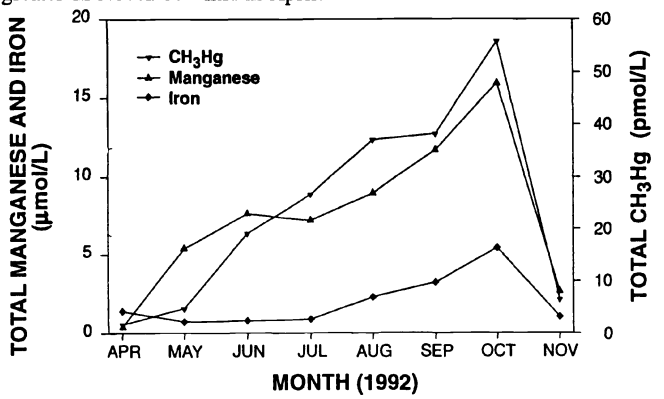

Fig. 6. Methylmercury, iron, and manganese in the Onondaga Lake hypolimnion.

4. Conclusions

As observed in other systems, CH_3Hg is particularly sensitive to dissolved oxygen concentration and temperature and increases dramatically in the hypolimnion during summer stratification. The spatial and temporal patterns observed for Hg and CH_3Hg in Onondaga Lake are similar to those observed in Little Rock Lake (Bloom *et al.*, 1991; Hurley *et al.*, 1994), a pristine system whose only source of Hg appears to be atmospheric deposition. Maximum concentrations of CH_3Hg in the hypolimnion of Onondaga Lake are comparable to those observed in Little Rock Lake; however, total Hg

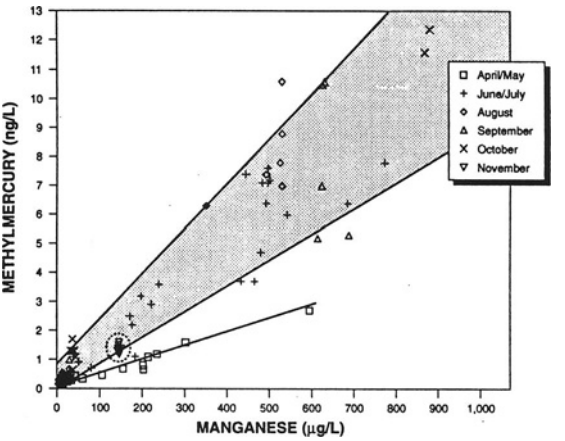

Fig. 7. Methylmercury vs. manganese.

is much higher in Onondaga Lake, suggesting that total Hg is not the sole determinant of CH_3Hg. Total Hg and CH_3Hg concentrations observed in this 1992 study are lower than those observed in a 1989 study of the lake by Bloom and Effler (1990).

The spatial and temporal patterns observed for CH_3Hg correlate well with Mn. The observed relationship between CH_3Hg and Mn suggests that either 1) mercury methylation is part of the Mn biological redox cycle, 2) CH_3Hg cycling is controlled by a cycle parallel to Mn, or 3) Mn and CH_3Hg share processes of different cycles. For example, redox transformations for both may be caused by different communities, but CH_3Hg may sorb to Mn oxides because both are dispersed into oxygenated water and both settle to the hypolimnion. Both Mn and CH_3Hg are rapidly removed from the water column following lake turnover, during which time Mn oxides precipitate and settle out of the water column.

Acknowledgements

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DISTRIBUTION OF MERCURY IN THE AQUATIC FOOD WEB OF ONONDAGA LAKE, NEW YORK

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Abstract. Historical discharges of mercury (Hg) to Onondaga Lake, New York, have resulted in elevated Hg concentrations in lake fishes In 1990, a remedial investigation and feasibility study (RI/FS) was initiated to evaluate problems related to Hg and other hazardous substances in the lake As part of the RI/FS, the distribution of Hg in the aquatic food web was determined to provide input to a site-specific model of Hg cycling and to evaluate potential ecological risks of Hg in the lake Mercury concentrations were measured in surficial sediments, sediment interstitial water, lake water, phytoplankton, zooplankton, benthic macroinvertebrates, and fishes (including planktivores, benthivores, and piscivores) The percentage of total Hg accounted for by methyl-Hg (CH_3Hg) generally increased with higher trophic levels, confirming that CH_3Hg is more efficiently transferred to higher trophic levels than is inorganic Hg Concentrations of total Hg in amphipods and chironomids were closely related to concentrations of total Hg in sediments, suggesting that sediments are a likely source of Hg for benthic macroinvertebrates Mercury concentrations in edible muscle tissue (fillets) of lake fishes have declined substantially from values found in the early 1970s, reflecting the large reductions in Hg discharges to the lake that have occurred since that time The CH_3Hg concentrations in fillets and whole bodies of fishes generally were similar, indicating that concentrations in fillets often can provide estimates of concentrations in whole bodies Methyl-Hg concentrations and bioaccumulation factors increased with higher trophic levels in both the pelagic and benthic components of the lake food web

1. Introduction

The distribution of mercury (Hg) in aquatic food webs has received considerable attention because of the tendency for methyl-Hg (CH_3Hg) to bioaccumulate in organisms. The recent development of ultraclean sampling techniques and ultrasensitive analytical methods has facilitated evaluations of Hg in aquatic food webs, especially in lower trophic levels where Hg is often present at trace concentrations (Bloom, 1989; Watras and Bloom, 1992).

Onondaga Lake is a shallow hypereutrophic lake in central New York that has received industrial and municipal discharges for more than 100 years (Murphy, 1978). In 1970, an advisory was issued against fishing in the lake. The advisory was based on results of a survey conducted by New York State Department of Environmental Conservation (Sloan *et al.*, 1987). The survey documented that Hg concentrations in edible muscle tissue (fillets) of many fishes in the lake exceeded the U.S. Food and Drug Administration (FDA) action level of 0.5 mg/kg (which was in effect at that time). The current FDA action level is 1.0 mg/kg. In 1986, the advisory was modified to discourage only consumption of fish captured from the lake. The 1986 advisory is in effect today.

In 1990, a remedial investigation and feasibility study (RI/FS) was initiated to evaluate problems related to hazardous substances in Onondaga Lake. A key component of the RI/FS is an evaluation of Hg in various components of the lake ecosystem. A model is being devel-

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oped to describe cycling of Hg in the lake and predict the likely results of various remedial alternatives. To support development of the Hg model, the distribution of Hg in water, sediments, and biota was determined during an intensive field investigation conducted in 1992. The objective of this paper is to describe the distribution of Hg (primarily CH_3Hg) in the Onondaga Lake aquatic food web, based on information collected during the summer (July and August) of 1992.

2. Materials and Methods

Mercury concentrations were measured in the major elements of the Onondaga Lake aquatic food web, including surficial sediments, sediment interstitial water, lake water, and a variety of biological groups. The biological groups included phytoplankton, zooplankton (cladocerans), benthic macroinvertebrates (amphipods and chironomids), and adult fishes. The fishes included seven species from different trophic groups, including planktivores (gizzard shad [*Dorosoma cepedianum*] and white perch [*Morone americana*]), benthivores (carp [*Cyprinus carpio*], channel catfish [*Ictalurus punctatus*], and bluegill [*Lepomis macrochirus*]), and piscivores (smallmouth bass [*Micropterus dolomieui*] and walleye [*Stizostedion vitreum*]).

Both total Hg and CH_3Hg were measured in all media except surficial sediments, for which only total Hg was measured. Concentrations of Hg in water, phytoplankton, zooplankton, and benthic macroinvertebrates were determined using recently developed ultraclean sampling techniques and ultrasensitive analytical methods (Bloom, 1989; Watras and Bloom, 1992). Mercury was measured in fillets of all seven fish species. Mercury was also measured in whole bodies of four species (gizzard shad, white perch, bluegill and smallmouth bass) to determine whether Hg concentrations in fillets can be used to estimate whole-body concentrations. Estimation of whole-body concentrations from the extensive database of concentrations in fillets is essential for modeling the mass balance of Hg in the lake and for evaluating potential ecological risks posed by fish consumption.

Surficial sediment samples were collected for Hg analysis at eight locations throughout Onondaga Lake using a 0.06-m^2 stainless-steel van Veen bottom grab. Those locations corresponded to stations at which benthic macroinvertebrates were collected for bioaccumulation analysis (Figure 1). The top 2 cm of each sample was removed and homogenized using stainless-steel equipment. A subsample of each homogenized surficial sediment sample was transferred to a polyethylene jar and frozen. Surficial sediments (0–4 cm) were also collected at three stations for analysis of Hg concentrations in interstitial water (Gilmour, 1994). Those stations were close to locations at which benthic macroinvertebrates were collected for bioaccumulation analysis (Figure 1). Samples were collected using a 0.05-m^2 acrylic Soutar-design box corer. Cores were held at 4 °C after collection and later sectioned in the laboratory. Interstitial water was then removed by centrifugation and filtration (pore size = 0.2 μm). Three replicate Hg analyses were conducted for each station.

Lake water and phytoplankton were sampled at two stations in the centers of the north and south basins of the lake (Figure 1). Samples were collected in Teflon® bottles from depths of 0, 3, and 6 m using a peristaltic-pumping system with Teflon® tubing. Three replicate

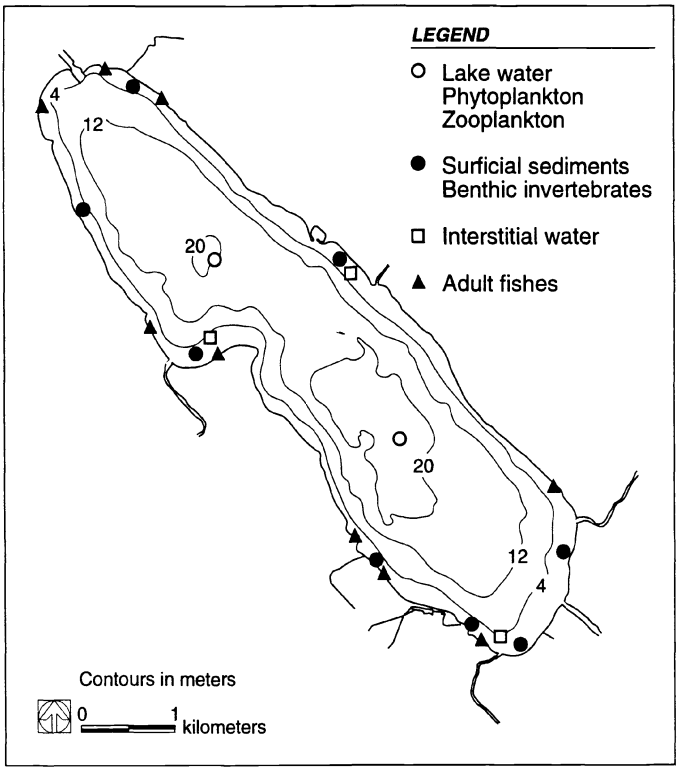

Fig. 1. Station locations in Onondaga Lake.

samples were collected from each depth at each station. Samples were held at 4 °C and analyzed within 24 hours of collection. Phytoplankton were collected from samples of lake water using 0.8-μm quartz-fiber filters.

Zooplankton were sampled at the same two stations as lake water and phytoplankton using a nonmetallic net (mesh size = 80 μm). Each sample was collected by a vertical net haul from a depth of 12 m and rinsed into Teflon® bottles. Within 8 hours of collection, cladocerans were transferred to Teflon® vials using glass pipets and frozen. Three replicate composite samples, each containing 20 cladocerans, were collected for each station.

Benthic macroinvertebrates were collected at eight stations distributed throughout the littoral zone of the lake (Figure 1). These organisms were collected using a 0.06-m^2 stainless-steel van Veen grab sampler, sieved with a polyethylene sieve (mesh size = 0.6 mm), transferred to Teflon® vials using stainless-steel tweezers, and frozen. Single composite samples of 10 amphipods and 10 chironomids were collected at each station.

Fishes were captured at various locations in the northern, western, and southern parts of the lake using trap nets and gill nets (Figure 1). Captured individuals were either maintained

whole or filleted immediately after collection using a stainless-steel knife. All whole bodies and fillets were frozen immediately after collection. Ten replicate whole bodies and 20–30 replicate fillets were collected for each target species.

3. Results and Discussion

3.1. Methylmercury Fraction

The percentage of total Hg occurring as CH_3Hg varied throughout the lake food web and generally increased in higher trophic levels (Figure 2). In the pelagic component of the food

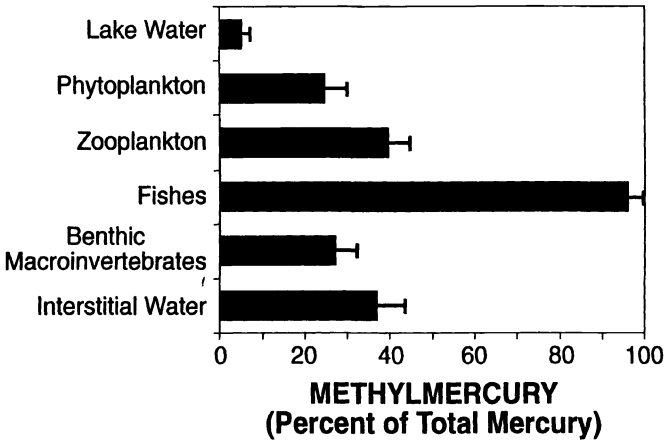

Fig. 2. Percent methylmercury (mean ± SE) in various elements of the Onondaga Lake aquatic food web.

web, the mean percentage of CH_3Hg increased from lake water (5%) to phytoplankton (24%) to zooplankton (40%). In the benthic component, the mean percentage of CH_3Hg in interstitial water (37%) was higher than the value found for benthic macroinvertebrates (26%). Almost all Hg in fish fillets (mean=96%) was in the form of CH_3Hg. Watras and Bloom (1992) found similar relative patterns of CH_3Hg fractions in the food web of Little Rock Lake, Wisconsin. The authors found CH_3Hg fractions of 5, 13, 29, and >90% for lake water, phytoplankton, zooplankton, and fishes, respectively. In addition, Bloom (1992) found that the CH_3Hg fractions in a wide variety of freshwater and saltwater fishes typically were >95%. The results of the present study confirm the conclusions of previous studies that CH_3Hg is more efficiently transferred to higher trophic levels of aquatic food chains than is inorganic Hg (Boudou and Ribeyre, 1981, 1985; Watras and Bloom, 1992).

3.2. Benthic Macroinvertebrates and Sediments

Concentrations of total Hg in amphipods and chironomids were correlated significantly ($P \leq 0.05$, Spearman's coefficient of rank correlation) for the seven stations at which both groups of organisms were collected (Figure 3). Amphipods were not present at one of the eight stations evaluated. Concentrations of total Hg in both groups were also closely related to concentrations of total Hg in nearby surficial sediments (Figure 4). The correlation

between tissue and sediment concentrations was significant ($P \leq 0.05$) for amphipods and close to being significant ($P \leq 0.06$) for chironomids. These results indicate that sediments are a likely source of Hg for benthic macroinvertebrates.

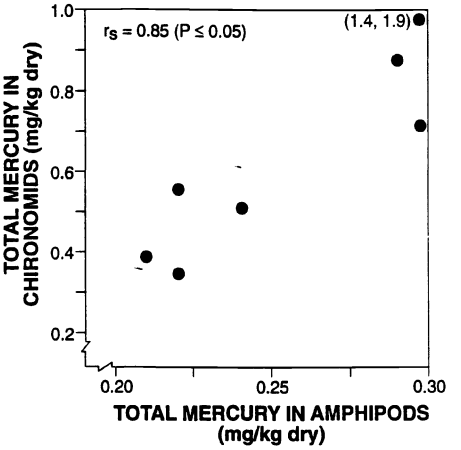

Fig. 3. Comparison of total mercury concentrations in chironomids and amphipods from Onondaga Lake.

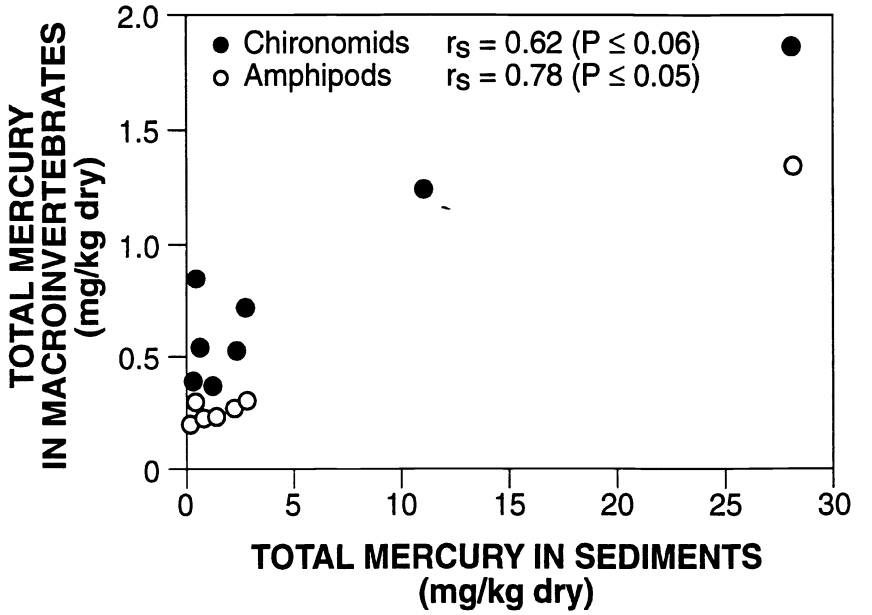

Fig. 4. Comparison of total mercury concentrations in benthic macroinvertebrates and surficial sediments from Onondaga Lake.

3.3. Temporal Trends in Fishes

In general, Hg concentrations in fillets of Onondaga Lake fishes have declined substantially from the values found in the early 1970s (Figure 5). During the early 1970s, mean Hg concentrations in five of the seven species evaluated exceeded the current FDA action level of 1.0 mg/kg (Sloan *et al.*, 1987), and mean concentrations in channel catfish and walleye were very high (i.e., between 4.0 and 6.0 mg/kg). In 1992, only mean Hg concentrations in walleye and white perch (1.5 and 1.1 mg/kg, respectively) exceeded the current FDA action level, and the magnitude of those exceedances was relatively small. Because mean total length for 1992 was not significantly less ($P>0.05$, t-test) than the value observed for the early 1970s for any of the seven target species, it is unlikely that the observed declines in Hg concentrations were affected by differences in fish size (and age) between the two sampling periods. Fishes could not be compared with respect to age because that variable was not determined for the fishes collected in the early 1970s. The general decline of Hg concentrations in fish tissue since the early 1970s parallels the substantial reductions in Hg discharges to Onondaga Lake that have resulted from various regulatory actions initiated in 1970.

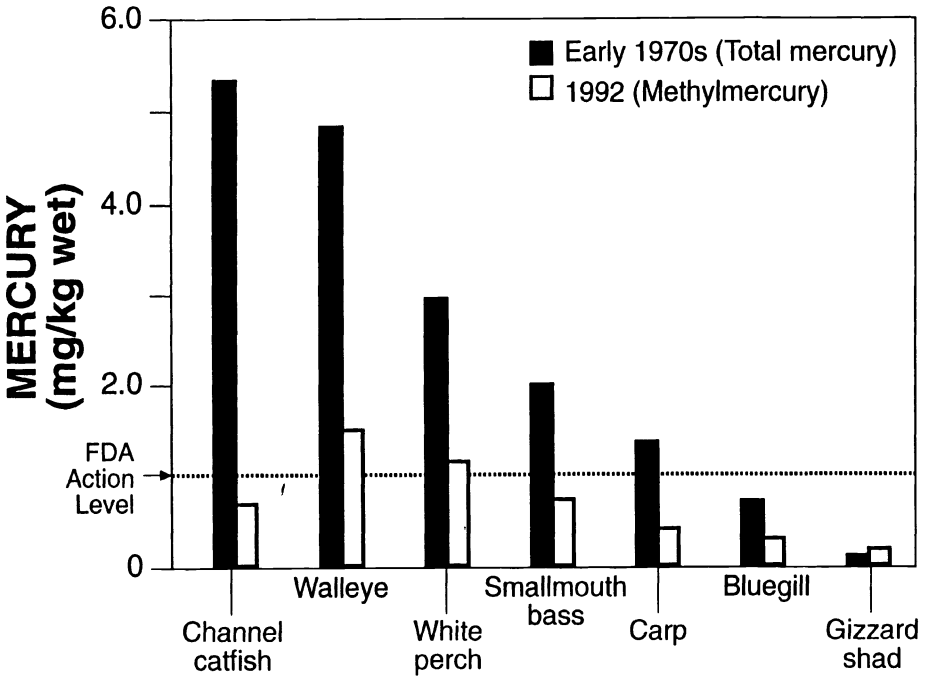

Fig. 5. Temporal patterns of mean mercury concentrations in fillets of fishes from Onondaga Lake.

3.4. Fish Fillets and Whole Bodies

Mean CH_3Hg concentrations in whole bodies of fishes were slightly lower than concentrations in fillets for the four species evaluated (Figure 6). However, the differences were significant ($P \leq 0.05$, t-test) only for bluegill. Results for gizzard shad, white perch, and bluegill were based on two consecutive age classes (3–4, 4–5, and 4–5 years, respectively) whereas results for smallmouth bass were based on four consecutive age classes (6–9 years). Because mean age for each species did not differ significantly ($P \leq 0.05$, t-test) between fishes sampled for fillets and those sampled for whole bodies, it is unlikely that comparisons of CH_3Hg concentrations were affected by that variable. Results of these comparisons indicate that CH_3Hg concentrations in fillets often can provide acceptable estimates of CH_3Hg concentrations in whole bodies of fishes.

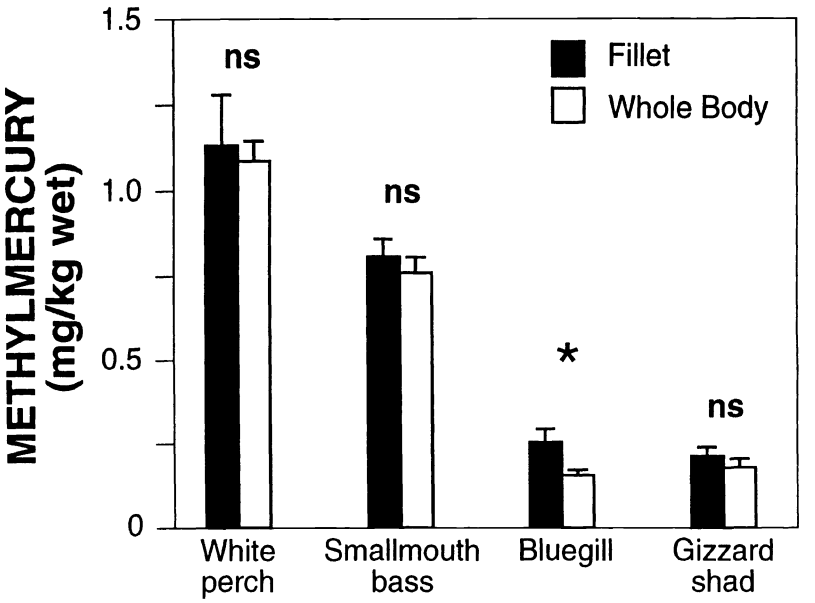

Fig. 6. Comparison of methylmercury concentrations (mean ± SE) in fillets and whole bodies of fishes from Onondaga Lake (ns = $P > 0.05$; * = $P \leq 0.05$).

3.5. Methylmercury in the Lake Food Web

The distribution of CH_3Hg in various elements of the Onondaga Lake food web is presented in Figure 7. Concentrations increased with higher trophic levels in both the pelagic and

benthic components of the food web. Bioaccumulation factors (BAFs) also increased with higher trophic levels in both the pelagic and benthic components of the food web and ranged from $8.3x10^4$ for benthic macroinvertebrates to 3.7×10^6 for piscivores (Figure 8). BAFs were calculated as the ratio of the CH_3Hg concentration in each trophic level to the CH_3Hg concentration in lake water.

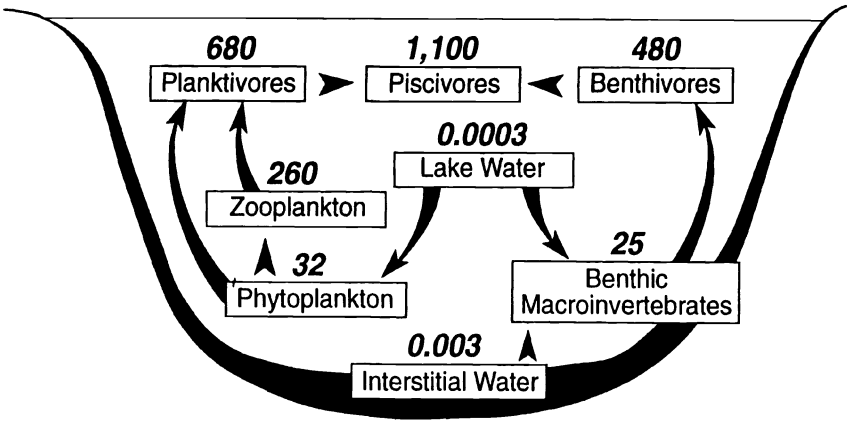

Fig. 7. Schematic of methylmercury concentrations (μg/kg wet) in the Onondaga Lake aquatic food web.

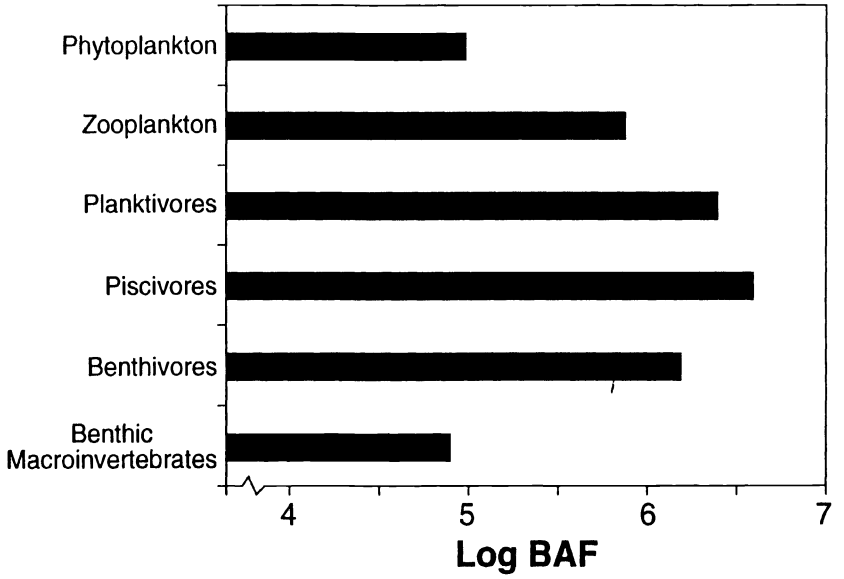

Fig. 8. Observed bioaccumulation factors (BAFs) for methylmercury in various elements of the Onondaga Lake aquatic food web.

4. Conclusions

Based on the observed distribution of Hg in the Onondaga Lake aquatic food web, several conclusions can be made. The percentage of total Hg occurring as CH_3Hg generally increased in higher trophic levels, confirming that CH_3Hg is more efficiently transferred to higher trophic levels of aquatic food chains than is inorganic Hg. Concentrations of total Hg in amphipods and chironomids were closely related to concentrations of total Hg in sediments, suggesting that sediments are a likely source of Hg for benthic macroinvertebrates. Mercury concentrations in the fillets of Onondaga Lake fishes have declined substantially from the values found in the early 1970s, reflecting the large reductions in Hg discharges to the lake that have occurred since that time. The CH_3Hg concentrations in fillets often can provide estimates of CH_3Hg concentrations in the whole bodies of fishes. Finally, CH_3Hg concentrations and BAFs increased with higher trophic levels in both the pelagic and benthic components of the lake food web.

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FLUXES OF MERCURY THROUGH BIOTA IN THE LG-2 RESERVOIR AFTER FLOODING

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Abstract. The purpose of this study was to estimate the temporal fluxes of mercury (Hg) among the diverse biotic components of the aquatic ecosystem of the LG-2 reservoir before and shortly after flooding, and to compare the relative magnitudes of these fluxes. Flooding took place from autumn 1978 to autumn 1979. The basic food chain considered was: Phytoplankton ==> Zooplankton ==> Prey Fish ==> Predatory Fish.

1. Methods and Results

Complete details can be found in Thérien and Morrison (1993). Data on fish coming from 6 sampling stations in the reservoir were compiled to permit estimation of standing stocks and total Hg burdens in these 2 compartments. Biomass fluxes through these compartments were calculated based on simple bioenergetics, and Hg fluxes were then calculated using the appropriate concentrations. A previously-validated model of plankton dynamics was used to estimate biomass fluxes through phyto- and zooplankton, and again Hg fluxes were estimated by using appropriate concentrations. For each compartment the necessary fluxes were calculated to explain observed biomass and Hg quantities, and the fluxes available from the observed compartments lower in the hierarchy were also calculated (Tables I and II respectively). Fluxes of both biomass and Hg increased greatly through the 2 fish compartments after flooding, consistent with greater productivity and increased Hg concentrations. Increases for biomass fluxes were less than an order of magnitude, while for Hg increases were 1 to 2 orders of magnitude. For predatory fish, the amounts both of biomass and Hg available from measured prey species were markedly insufficient to explain the quantities found, representing on average only 12 and 6% of necessary quantities respectively. For the measured prey species, plankton could only account for 45 and 7% on average of the necessary biomass and Hg respectively. Calculations were taken a step further, for fluxes necessary from plankton to support a prey fish compartment sufficient to support observed predator biomass and Hg (Table III). Fluxes from the plankton could only account for 5 and 0.5% of the quantities of biomass and Hg respectively found in predatory fish.

2. Conclusions

These observations lead to the following conclusions:

- there was a quantitatively large but unmeasured fish stock being exploited by predators, and this stock had higher Hg levels than measured prey
- both measured and unmeasured prey stocks were exploiting a food source other than plankton, most likely benthos, which was quantitatively greater in both biomass and Hg fluxes than plankton.

Because of the magnitude of the discrepancies involved, these conclusions are valid in spite of uncertainties in the calculations. The first conclusion is not surprising since sampling was done more from a fisheries-management perspective than a limnological one, and thus smaller species were poorly represented. Both conclusions are also consistent with recent observations on fish stomach contents and on Hg levels in benthos. Unfortunately, there are no quantitative data on benthic biomass after reservoir flooding as this proved impossible to measure.

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Water, Air, and Soil Pollution **80**: 573–576, 1995.

TABLE I

Food fluxes required by the observed biomass as compared to that available from lower trophic levels [kg/ha/yr]

PREY FISH		Station					
	FOOD	G2400	G2402	G2403	G2404	G2405	G2406
1978	Available	0 26	0 07	5 69	4 04	11 20	0 06
	Required	2 90	2 97	8 28	16 38	13 89	1 11
1979	Available	1 45	2 93	4 84	5 19	10 70	0 30
	Required	0 00	2 12	0 00	4 65	17 15	4 09
1980	Available	2 43	6 01	6 80	3 98	5 90	0 36
	Required	3 10	5 31	9 60	123 15	0 00	7 47
1981	Available	2 98	10 39	8 70	7 40	13 10	1 75
	Required	1 37	10 91	8 71	0 00	17 21	55 63
1982	Available	3 39	12 20	5 40	4 40	13 90	4 48
	Required	6 14	10 82	18 89	37 78	42 39	0 00
1983	Available	4 30	12 50	5 80	4 80	13 30	2 67
	Required	6 87	15 54	15 35	13 23	16 69	0 00
1984	Available	5 30	12 60	5 30	4 80	11 80	3 62
	Required	9 31	6 73	3 75	34 27	32 09	5 87
Average	Available	3 99	11 92	6 30	5 35	13 03	3 13
1981-1984	Required	5 92	11 00	11 68	21 32	27 09	15 38

PREDATORY FISH		Station					
	FOOD	G2400	G2402	G2403	G2404	G2405	G2406
1978	Available	0 70	0 72	2 00	3 95	3 35	0 27
	Required	0 02	1 24	4 55	19 51	10 32	4 31
1979	Available	0 34	0 64	0 63	2 91	3 64	0 53
	Required	0 75	0 00	0 00	0 00	11 44	0 00
1980	Available	0 49	0 88	1 25	12 76	0 91	1 00
	Required	0 50	7 83	1 85	43 55	0 00	3 88
1981	Available	0 43	1 52	1 56	7 11	2 10	5 56
	Required	0 51	20 37	16 73	78 54	24 32	34 14
1982	Available	0 82	1 92	2 66	7 85	5 08	3 47
	Required	5 19	21 25	34 40	71 20	37 20	39 93
1983	Available	1 13	2 59	3 05	6 14	4 70	1 82
	Required	2 90	28 64	38 00	70 45	6 74	0 00
1984	Available	1 54	2 24	2 26	6 92	5 82	1 67
	Required	8 44	28 68	24 83	38 26	26 83	44 36
Average	Available	0 98	2 07	2 38	7 01	4 42	3 13
1981-1984	Required	4 26	24 73	28 49	64 61	23 77	29 61

TABLE II

Hg fluxes required for observed quantities as compared to that available from lower trophic levels [mg/ha/yr]

PREY FISH		Station					
	Hg	G2400	G2402	G2403	G2404	G2405	G2406
1978	Available	0 01	0 00	0 28	0 20	0 56	0 00
	Required	0 11	0 11	0 31	0 62	0 52	0 04
1979	Available	0 07	0 15	0 24	0 26	0 54	0 02
	Required	0 24	0 61	0 25	2 59	3 66	0 59
1980	Available	0 12	0 30	0 34	0 20	0 30	0 02
	Required	0 65	1 14	1 85	21 68	0 00	1 46
1981	Available	0 15	0 52	0 44	0 37	0 66	0 09
	Required	0 57	3 01	2 68	3 76	4 51	13 63
1982	Available	0 17	0 61	0 27	0 22	0 70	0 22
	Required	1 83	3 45	5 70	12 56	12 37	1 47
1983	Available	0 22	0 63	0 29	0 24	0 67	0 13
	Required	2 03	4 60	4 60	4 36	5 16	0 00
1984	Available	0 27	0 63	0 27	0 24	0 59	0 18
	Required	2 85	2 18	1 33	10 62	9 87	1 87
Average	Available	0 20	0 60	0 32	0 27	0 65	0,16
1981-1984	Required	1 82	3 31	3 58	7 83	7 98	4 24

PREDATORY FISH		Station					
	Hg	G2400	G2402	G2403	G2404	G2405	G2406
1978	Available	0 05	0 05	0 14	0 27	0 23	0 02
	Required	0 00	0 14	0 53	2 28	1 20	0 50
1979	Available	0 07	0 13	0 13	0 58	0 73	0 11
	Required	0 29	0 51	0 00	0 00	8 47	0 24
1980	Available	0 15	0 26	0 38	3 83	0 27	0 30
	Required	0 38	4 89	1 48	27 33	0 00	2 79
1981	Available	0 18	0 65	0 66	3 02	0 89	2 36
	Required	0 52	17 50	14 00	69 22	20 59	28 41
1982	Available	0 41	0 96	1 33	3 92	2 54	1 73
	Required	5 39	23 66	36 53	81 12	40 17	43 60
1983	Available	0 58	1 34	1 57	3 17	2 43	0 94
	Required	2 81	28 65	38 22	67 92	4 37	0 00
1984	Available	0 82	1 20	1 21	3 70	3 11	0 89
	Required	9 04	29 07	23 98	33 69	27 54	48 26
Average	Available	0 50	1 04	1 19	3 45	2 24	1 48
1981-1984	Required	4 44	24 72	28 19	62 99	23 17	30 07

TABLE III

Food and Hg fluxes required from zooplankton to support the food chain for observed quantities in predatory fish as compared to that available [kg/ha/yr and mg/ha/yr respectively]

		Station					
	FOOD	G2400	G2402	G2403	G2404	G2405	G2406
1978	Available	0 26	0 07	5 69	4 04	11 20	0 06
	Required	2 90	5 14	18 86	80 82	42 76	17 83
1979	Available	1 45	2 93	4 84	5 19	10 70	0 30
	Required	1 69	2 12	0 00	4 65	49 44	4 09
1980	Available	2 43	6 01	6 80	3 98	5 90	0 36
	Required	3 14	34 12	12 07	250 73	0 00	19 40
1981	Available	2 98	10 39	8 70	7 40	13 10	1 75
	Required	1 68	88 99	71 45	295 94	109 27	174 04
1982	Available	3 39	12 20	5 40	4 40	13 90	4 48
	Required	24 27	90 88	150 35	300 24	175 44	151 04
1983	Available	4 30	12 50	5 80	4 80	13 30	2 67
	Required	14 24	123 45	160 16	279 64	25 16	0 00
1984	Available	5 30	12 60	5 30	4 80	11 80	3 62
	Required	37 89	116 28	97 25	164 11	119 16	182 70
Average	Available	3 99	11 92	6 30	5 35	13 03	3 13
1981-1984	Required	19 52	104 90	119 83	259 98	107 26	126 95

		Station					
	Hg	G2400	G2402	G2403	G2404	G2405	G2406
1978	Available	0 01	0 00	0 28	0 20	0 56	0 00
	Required	0 11	0 33	1 22	5 24	2 77	1 16
1979	Available	0 07	0 15	0 24	0 26	0 54	0 02
	Required	0 75	1 48	0 25	2 59	21 49	0 89
1980	Available	0 12	0 30	0 34	0 20	0 30	0 02
	Required	1 20	11 78	4 40	75 77	0 00	7 2
1981	Available	0 15	0 52	0 44	0 37	0 66	0 09
	Required	1 33	41 79	33 38	156 11	49 85	73 58
1982	Available	0 17	0 61	0 27	0 22	0 70	0 22
	Required	13 29	55 68	86 72	190 25	98 97	97 85
1983	Available	0 22	0 63	0 29	0 24	0 67	0 13
	Required	7 15	67 44	88 95	153 37	9 63	0 00
1984	Available	0 27	0 63	0 27	0 24	0 59	0 18
	Required	21 76	66 35	53 75	79 65	66 09	110 9
Moyenne	Available	0 20	0 60	0 32	0 27	0 65	0 16
1981-1984	Required	10 88	57 82	65 70	144 85	56 14	70 58

CONCENTRATIONS AND AMOUNTS OF METHYLMERCURY IN WATER AND FISH IN THE LIMED AND ACID BASINS OF A SMALL LAKE

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Abstract. Three months after neutralization concentrations of methylmercury (MeHg) were higher in the water of the limed than in the control basin of a small lake. After two years, the concentrations in the limed basin were somewhat lower than in the control (0.056-2.19 ng L^{-1} and 0.129-2.65 ng L^{-1}, respectively). The highest concentrations were found in the anoxic hypolimnia. The total amount of MeHg in the water mass of the lake varied from 19 to 68 mg, showing a drop after spring and autumn overturns and a maximum during stratification periods. The total Hg concentrations of fish in L. Iso Valkjärvi varied from 0.06 to 0.14 μg g^{-1} (ww) in whitefish to 0.1 to 0.7 μg g^{-1} in perch and to 0.2 to 1.4 μg g^{-1} in pike. The total amount of MeHg bound in the fish of the lake was quite similar to that in the water column, 43 to 59 mg in 1990-1993, 33 to 47 mg of which was in the perch population.

1. Introduction

The Lake Iso Valkjärvi (L. IVA) liming experiment is a multidisciplinary study on the effects of liming on different trophic levels of an aquatic ecosystem and the processes involved (Rask, 1991; Järvinen, 1993; Kuoppamäki, 1993) including the dynamics of mercury (Verta *et al.*, 1994). Estimates of the amounts of total mercury (TotHg) and methyl mercury (MeHg) in lakes have shown that only a minor part of the TotHg pool or flux is enriched in the aquatic organisms and stored in fish (Verta, 1990; Wiener *et al.*, 1990; Lindqvist *et al.*, 1991), but a large proportion of MeHg pool can be found in fish populations (Fitzgerald and Watras, 1989; Verta, 1990; Hultberg *et al.*, 1994). Therefore, attention was paid to the dynamics of MeHg in the Hg studies of L. IVA (Verta *et al.*, 1994; Matilainen, 1994). In this paper we calculated the amounts of MeHg in the water column of the lake and compared them with the amounts bound in fish. The effects of liming were also considered, and the changes in fish Hg that had occurred compared to levels ten years before (Metsälä and Rask, 1989; Rask and Metsälä, 1991).

2. Material and methods

The Lake Iso Valkjärvi (L. IVA) liming experiment was started in 1990. In spring 1991 the lake (3.9 ha, pH 5-5.5) was divided into two parts with a plastic curtain and one of the halves was neutralized (Rask, 1991). Lake water samples for Hg studies were collected in 1991-1992, from the deepest part of both subbasins, using an acid-washed, Teflon-coated water sampler. In 1993 samples were taken using a thin-layer sampler with a peristaltic pump and an acid-washed Teflon tube. During all sampling, ultraclean techniques were employed. The samples were analyzed in Seattle, WA (Brooks Rand Ltd., Frontier Geosciences). MeHg was analyzed following extraction from a KCl/HCl

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matrix with CH_2Cl_2, as well as back-extraction into deionized water (Bloom, 1989; Bloom *et al.*, 1991). The deionized water extract was analyzed by aqueous phase ethylation, Carbotrap™ (Supl Eco Inc., Bellefonte, PA, USA) precollection, and cryogenic GC separation of formed MeHg. The Hg was quantified by CVAFS, as Hg°, following on-line pyrolytic breakdown of the organo-Hg species.

Samples from fish (European perch, *Perca fluviatilis* L., northern pike, *Esox lucius* L., and whitefish, *Coregonus* sp.) were taken from the dorsal axial muscle and frozen until analyzed. Concentration of TotHg was determined from HNO_3-H_2SO_4 (1:4) digestion using CVAAS (Armstrong and Uthe, 1971). It was assumed that 95 % of the TotHg in fish was of MeHg (Bloom, 1992). The amount of MeHg bound in the perch population was calculated on the basis of mean concentrations in different sizes of fish and population data obtained from annual mark and recapture studies (Rask, unpublished). For whitefish and pike, the calculations were based on annual catches.

3. Results and discussion

Concentrations of MeHg in the water column of the limed basin were more than two times higher at the start of the experiment compared to the control (0.11-0.34 ng L^{-1} and 0.06-0.07 ng L^{-1}, respectively, after spring turnover). This was due to the higher proportion of the anoxic hypolimnion of the treatment basin during the lake division. Until the autumn turnover in 1992 the concentrations were equal in both basins (0.23-0.30 ng L^{-1} and 0.20-0.29 ng L^{-1}), and at the end of summer stratification in 1993, the overall concentrations were somewhat lower in the limed basin than in the control (0.056-2.19 ng L^{-1} and 0.129-2.65 ng L^{-1}, respectively). The highest concentrations were found in the anoxic hypolimnia of both basins during stratification periods. This was especially true during summer (Figure 1), but to some extent during winter stagnations, as well. Immediately after spring turnover and the decrease of algal biomass of phytoplankton spring bloom (Järvinen, 1993), the MeHg level in water dropped, indicating algal absorption and sedimentation of MeHg (Verta *et al.*, 1994).

An estimate of the total amount of MeHg in the water of both subbasins during sampling in winter and summer stagnations indicates some decrease in the limed basin from 1991 to 1993 (Table I). The amount was at its minimum during 1992. MeHg amounts in the control basin showed little variation in 1991-1993 (Table I).

The Hg concentrations of whitefish in L. IVA were 0.06-0.14 μg g^{-1} (ww) showing no difference between the two basins. Hg concentrations of perch varied between 0.1 to 0.7 μg g^{-1}. No response to the liming could be detected (Figure. 2). The lower Hg concentration of perch from the control basin in 1993 is a consequence of a fish kill in autumn 1992 (> 95 % of perch population died) and the subsequent increase in the growth rate of the remaining perch in 1993 (Rask, unpublished).

The Hg concentrations of pike varied according to size between 0.2 to 1.4 μg g^{-1}, and showed no difference between the basins of the lake. As in the case of perch (Figure 2), the mean concentrations were lower from 1990-1993 compared to 1983. The reason for this is uncertain. According to the few data available, the deposition of TotHg in the area has decreased (the mean annual bulk deposition of TotHg from 1987-1989 was 11 g km^{-2} in central Finland (Iverfeldt, 1991) whereas the annual mean of totHg in wet deposition in the study area was 4 g km^{-2} from 1991-1992 (Verta, unpublished)).

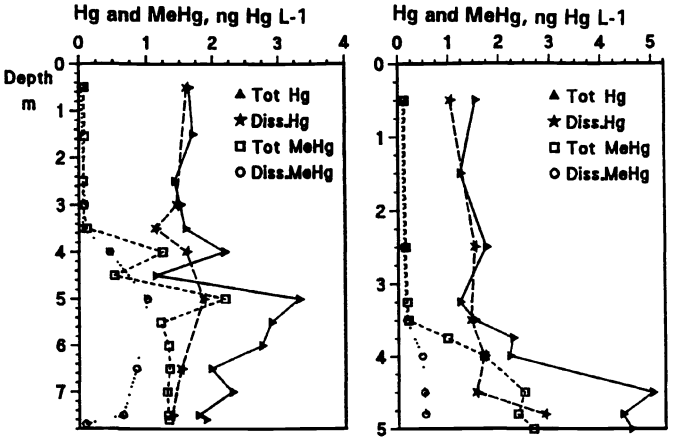

Fig. 1. Vertical distribution of concentrations of different forms of Hg in the limed basin (left) and in the control basin (right) of L. Iso Valkjarvi on August 24th 1993.

TABLE I

Amounts of MeHg in the water during stratification periods and in the fish biomass of Iso Valkjarvi in 1991-1993. Amounts in parentheses indicate limed basin + control basin.

Year	MeHg in water (mg) March	August	MeHg in fish (mg)
1990	n.d.	n.d.	59
1991	58 (40+18)	56-68[1)] ((37-49)+19)	56 (31+25)
1992	19 (12+7)	32 (15+17)	47 (31+16)
1993	n.d.	49 (32+17)	43 (41+2)

1) Large range because of insufficient sampling; n.d.= not determined

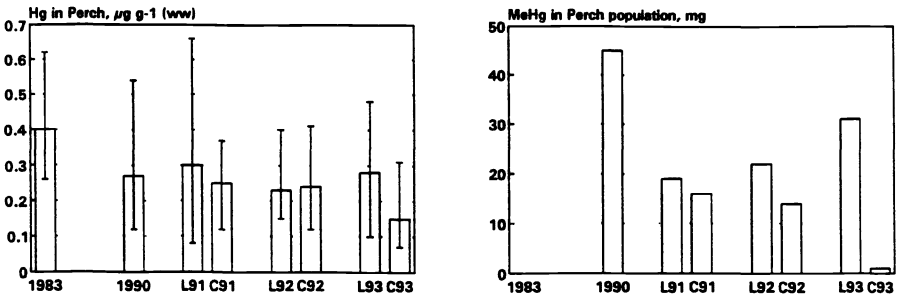

Fig. 2. Mean mercury concentrations (range indicated with bars) of perch in Iso Valkjarvi (left) and the amounts of MeHg bound in the perch population during 1990-1993 (right). Values for the limed basin are indicated with L and for the control basin with C.

The amount of MeHg bound in fish from L. IVA varied between 43 to 59 mg from 1990-1993 (Table I). A major part of this, 65 to 78 %, was in the perch population (Figure 2). The increase of perch bound MeHg in the limed basin from 1991-1993 was due to an increase of the mean size and biomass of perch (Rask, unpublished) whereas the sudden drop in the control basin in 1993 was due to the fish kill of 1992.

Our calculations suggest that the amount of MeHg in the water column of L. IVA is quite similar to that bound in fish. The decrease in the amounts and concentrations of MeHg in the water of the limed basin could not yet be recorded in fish.

The mean annual wet deposition of MeHg in the research area has been estimated to 0.11 g km^{-2} for 1991-1993 (Verta, unpublished) resulting in about a 4 mg deposition on the lake surface. The MeHg flux from the catchment is probably considerably greater, from 30 to 40 mg per year, based on an estimate of 0.21 to 0.24 mg km^{-2} a^{-1} from a neighboring catchment (Verta *et al.*, 1994). Thus, the amount of MeHg in the water and fish biomass of L. IVA would exceed the annual flux to the lake by a factor of 2 to 3. The yearly variations in MeHg flux from the catchment probably affect the entire MeHg pool in the lake, and consequently, the amounts of MeHg in the water and fish.

Acknowledgments

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MERCURY CONCENTRATIONS IN TWO "GREAT WATERS"

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Abstract. Although many sources of Hg to surface waters have been identified including atmospheric deposition, re-suspension of contaminated sediments, and direct discharges, there are very few recent data on ambient concentrations in the large lakes. Thus, an investigation of Hg concentrations in Lake Champlain and Lake Michigan was completed in the summer of 1993. Three depths of water including the microlayer, 30 cm below the surface, and 1 m below the thermocline were collected for each sampling event using ultra-clean techniques. All samples were processed in the field for dissolved and particulate fractions in a portable plastic enclosure equipped with a HEPA filter, and then analyzed by dual amalgamation and cold vapor atomic fluorescence spectroscopy in a Class 100 clean room at the University of Michigan. In addition, samples were analyzed for other trace metals by ICP-MS. Results from the two field investigations include the following: (1) On average, Lake Michigan water samples had higher concentrations of Hg than Lake Champlain; (2) There was no consistent pattern of Hg concentrations in the water column; (3) There was variability in the concentrations of Hg from the same depths over consecutive sampling periods. This paper discusses these results, and examines the relationship between the patterns in mercury concentrations and other physical and chemical data collected during the investigation.

1. Introduction

Concentrations of mercury (Hg) in surface waters are of great concern and interest because of fish consumption advisories triggered by elevated Hg levels. In the Great Lakes, the ingestion of fish with high concentrations of Hg has been associated with reproductive problems in eagles, otters, mink, and other animals (Douglas, 1991). Because of its ability to bioaccumulate, even the lowest surface water concentrations of Hg are important.

There is a surprising paucity of Hg data for many freshwater systems. This is especially true for the "Great Waters", that includes among others, the Great Lakes, Lake Champlain and Chesapeake Bay. Since many of these bodies of waters have restrictions or warnings on fish consumption due to high Hg levels, more information is needed about the levels and forms of Hg found in the surface waters. Thus, the purpose of this investigation was to measure the concentrations of Hg and other trace metals at three different depths in Lake Champlain and Lake Michigan, and describe the temporal variability of these pollutants over a 4 to 6 day period at each site. A secondary objective was to determine if there were any relationships between levels of Hg and other trace metals at the different sampling depths and between the lakes.

Lake Champlain, bordered by New York, Vermont and Quebec, is the sixth largest natural freshwater lake in the United States. It is about 193 km long, 19 km across at its widest point and has a surface area of 1,124 km^2 (Watzin, 1992). The ratio of the drainage basin to the surface area of the lake is about 19. In contrast, Lake Michigan has a surface area of 57,800 km^2 with a ratio of drainage basin to surface area of only about 2 (Watzin, 1992). Thus, the two lakes have very different physical characteristics, which in turn, are likely to affect the input and cycling of Hg and other trace metals in the respective ecosystems.

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2. Materials and Methods

2.1. SAMPLE COLLECTION AND PROCESSING

All collection, processing and analysis of Hg and metals samples were performed using ultra-clean techniques. This included putting all supplies through an 11-day acid cleaning procedure (Hoyer and Keeler, 1994) and transporting all materials to the field triple-bagged. Once in the field, all sample handling was performed with particle-free gloves and upwind of the handlers so as to minimize possible sample contamination.

The Lake Champlain samples were collected 20 - 25 July 1993 at a location approximately 1.6 km west of Burlington, VT (44°29'N, 73°14'W) in the main lake where the depth of the water is approximately 33 m. This part of the lake has the deepest, coldest water and is most similar to the Great Lakes. Ten sets of water samples were collected including 0.3 and 15 m depths. Due to choppy waves and high winds, only 6 concurrent microlayer samples were collected. The Lake Michigan samples were collected from 2 - 5 September 1993 at a location about 6.4 km east of Chicago, IL (41° 50'N, 87°50'W) where the water depth was approximately 12 m. Eight sets of water samples were obtained at depths of 0.3 and 10 m, as well as 7 microlayer samples.

The microlayer samples were collected with a Teflon coated rotating drum sampler (Hardy, 1988). Prior to each sampling period, the drum was cleaned with ultra-pure water and particle-free clean wipes and then rinsed with ultra-pure water in the field to remove any possible contamination on the drum. The bulk water samples were obtained using a plastic bilge pump and silicone-based tubing. The pump was lowered to the designated depth from a non-metallic boat, and the tubing was flushed for five minutes with the lake water to be sampled. During this time, approximately 40 L of water passed through the pumping system. Lake water samples were collected in acid-cleaned 10 L low density polyethylene (LDPE) carboys which were rinsed with the respective sample water three times, filled, capped and placed into plastic bags for transport back to the University of Vermont School of Natural Resources (Lake Champlain) or the R/V *Lake Guardian* (Lake Michigan) for processing.

At the laboratory, unfiltered water for Hg and trace metals analysis was dispensed directly into borosilicate glass (BSG) and LDPE bottles, respectively, inside a HEPA-filtered clean space. A filtered sample was processed by passing lake water through a 0.45 μm nitrocellulose filter pre-rinsed with 1 L of ultra-pure water using a desiccator set-up (Rossman and Barres, 1988). Due to a water system problem on the R/V *Lake Guardian*, the water used to rinse the Lake Michigan filters was contaminated with Hg. Thus, only unfiltered Hg values are reported in the results for Lake Michigan. Samples for Hg were preserved with bromine monochloride (1% final concentration) and metals samples were preserved with Seastar nitric acid (0.2% final concentration).

2.2. SAMPLE ANALYSIS

Mercury analysis was performed by dual amalgamation and cold vapor atomic fluorescence spectroscopy inside a Class 100 clean room at the University of Michigan as described in Hoyer and Keeler (1994). Replicate analyses were completed on all samples with an average precision of 9%. Metals samples were analyzed by a Perkin Elmer Elan 5000A Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) equipped with a pneumatic nebulizer.

3. Results and Discussion

Total Hg concentrations of filtered water from Lake Champlain are presented in Figure 1. The average Hg concentrations for the different depths were 3.4 ng/L for the microlayer, 3.2 ng/L for 0.3 m, and 2.2 ng/L for 15 m, while the median concentrations were 3.1 ng/L, 2.6 ng/L, and 1.5 ng/l, respectively.

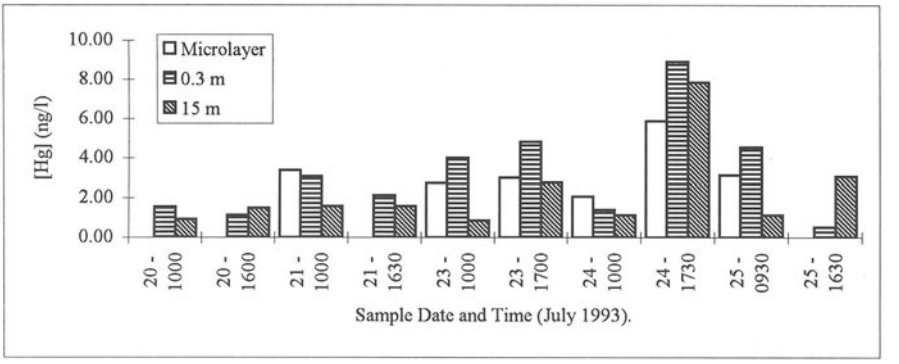

Figure 1. Total Hg Concentrations (ng/l) of Filtered Water from Lake Champlain.

There is a considerable amount of variation in the Hg levels within the respective depths between sampling periods. A similar magnitude of variability was not seen for other dissolved trace metals such as zinc (Zn) (0.76 to 1.58 μg/L for the microlayer, 0.53 to 0.80 μg/L for 0.3 m, 0.51 to 0.81 μg/L for 15 m) and copper (Cu) (0.83 to 0.91 μg/L for the microlayer, 0.50 to 0.84 μg/L for 0.3 m, 0.62 to 0.92 μg/L for 15 m).

Mercury levels at the 0.3 m depth were significantly correlated ($p<0.10$) with vanadium (V) and manganese (Mn) while at the 15 m depth Hg concentrations were significantly correlated with V and chloride ions (Cl^-). (All correlations are positive unless noted). In the microlayer, Hg levels were significantly correlated with strontium (Sr). Thus, Hg in Lake Champlain is related to primarily crustal elements, perhaps indicating a drainage basin or sediment source.

The results of the total Hg analysis of unfiltered water from Lake Michigan are presented in Figure 2. The average Hg concentrations for the respective depths were 7.2 ng/l for the microlayer, 8.0 ng/L for 0.3 m, and 6.3 ng/L for 10 m while the median values were 5.7, 6.3, and 3.3 ng/L, respectively. Once again, a strong impact of the extreme values on the average Hg concentrations is seen. The values are higher than those from Lake Champlain, but Hg in filtered and unfiltered water are being compared. A similar magnitude of variability was not seen for other dissolved trace metals such as Zn (0.83 to 2.59 μg/L for microlayer, 0.61 to 0.89 μg/L for 0.3 m, 0.50 to 1.21 μg/L for 10m) and Cu (0.51 to 0.75 μg/L for microlayer, 0.49 to 0.53 μg/L for 0.3 m, 0.50 to 0.81μ g/L for 10 m).

For Lake Michigan, microlayer Hg levels were significantly negatively correlated with Mn and Zn. At the 0.3 m depth, Hg was significantly negatively correlated with magnesium (Mg) while at the 10 m depth no element correlated with Hg. Thus, in contrast to Lake Champlain, it appears that Hg levels are not associated with elements of

crustal origin. Rather, it is probable that Hg comes from a multitude of sources in the heavily industrialized region surrounding the Southern Lake Michigan Basin.

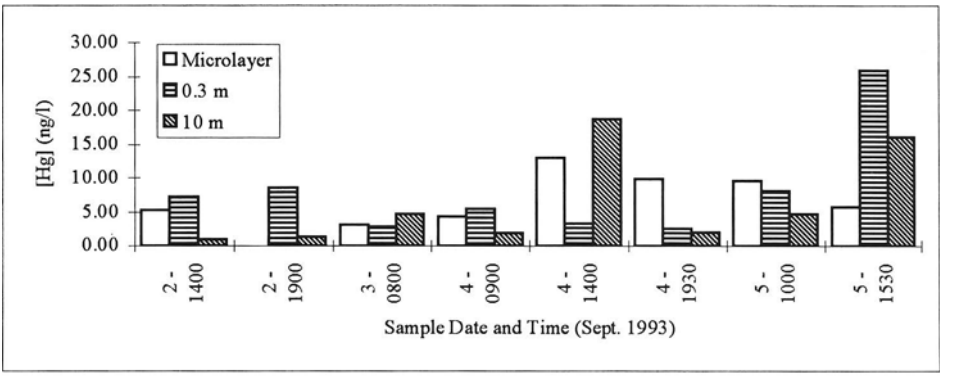

Figure 2. Total Hg Concentrations (ng/l) of Unfiltered Water from Lake Michigan.

The levels of Hg found in water from Lakes Champlain and Michigan are higher than previously reported studies for other lakes (Driscoll *et al.*, 1994; Meili *et al.*, 1991). However, higher values have been found in lakes with known point sources (Bloom and Effler, 1990; Gill and Bruland, 1990). This study shows that more surface waters should be studied in order to determine the range of Hg concentrations present in a variety of water bodies.

4. Conclusions

This intensive field investigation of Hg levels in water from Lakes Champlain and Michigan revealed large fluctuations in concentrations from the same sampling locations and depths over a 4 to 6 day period. Similar variations in levels of other trace metals were not observed. Thus, in order to better describe Hg dynamics in surface waters, spatial surveys should be complemented with intensive sampling at single sites.

Acknowledgments

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METHYLMERCURY DISTRIBUTION AND PARTITIONING IN STRATIFIED FINNISH FOREST LAKES

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Abstract. TotHg and MeHg were determined in water profiles, sedimenting seston and surface sediments of four stratified forest lake systems in Finland. The radiochemical method was applied to the methylation assays performed *in situ*. In the anoxic layers the MeHg concentrations were generally higher than in the epilimnia. The *in situ* MeHg production also increased in the hypolimnia, but MeHg increase in water was more closely associated to particles than *in situ* MeHg production. Methylmercury partitioning between particles and dissolved (0.2 μm) phase was similar in sediment traps and hypolimnetic water, the trap concentrations being one order of magnitude higher. Dissolved MeHg in the hypolimnia exceeded that in sediment surface. Particulate MeHg concentrations in the traps were higher than at the sediment surface. Methylmercury transport through sedimentation and MeHg production in hypolimnetic water are suggested as primary sources of increased MeHg in hypolimnia of the lakes studied.

1. Introduction

Increased methylmercury (MeHg) concentrations are frequently observed in the anoxic hypolimnia of stratified lakes (Bloom *et al.,* 1991; Cossa *et al.,* 1994; Watras and Bloom, 1994; Verta *et al.*, 1994). This may be caused by different mechanisms: 1) hypolimnetic sediments may serve as a source of MeHg to the water, 2) MeHg may be produced in hypolimnetic water, or 3) MeHg may be transported by deposition through the epilimnion. The objective of this study was to examine the role of these processes in typical Finnish stratified forest lakes.

2. Materials and Methods

Total mercury (TotHg) and MeHg were determined (Bloom and Crecelius, 1983; Bloom, 1989) during summer stratification in 1993 in water profiles, sedimenting seston and surface sediments of three stratified forest lakes. One of the lakes is an oligo-mesohumic seepage/closed lake (L. IVA, limed and control basins, mean epilimnetic TOC 6.0 mg l^{-1}) and two are polyhumic drainage lakes (L. HAKO, TOC 12 mg l^{-1}; and L. KEHA, TOC 22 mg l^{-1}) (Verta *et al.*, 1994).

The radiochemical method was applied to the methylation assays performed *in situ*. The samples were collected by a peristaltic pump, thin layer sampler, with ultraclean teflon tubing. The samples were quickly spiked with $^{203}HgCl_2$, capped and incubated in their original depths for 24 h. The incubation was terminated with HCl, the formed $Me^{203}Hg$ was extracted with toluene, and the radioactivity was measured with a liquid scintillation counter. A full description of the method is given by Matilainen (1995). Sedimenting seston traps were immersed 1 m above the bottom during spring turnover, and samples for TotHg and MeHg were collected at the end of the summer stagnation.

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3. Results and Discussion

Methylmercury concentrations were generally higher by more than one order of magnitude in anoxic layers than in the epilimnion (Figures 1a,b,c). The exception was the meromictic L. KEHA, dammed by beavers, in which no differences in the MeHg concentrations were found (Figure 1d). This was probably caused by MeHg production in inundated soils around the lake. As calculated from inflow/outflow data by Verta *et al.* (1994), L. KEHA acts as a net source of MeHg (about 100 ng $m^{-2}d^{-1}$).

The *in situ* MeHg production reached its maximum in the anoxic hypolimnia and was at the same level or lower in the sediment surface, exept for L. HAKO with a maximum at that layer (Matilainen, 1995). Methylmercury concentrations in water were more closely related to particles than *in situ* MeHg production (Figure 1a,b,c). In L. IVA the increase in particulate and dissolved MeHg started at the oxic/anoxic boundaries, above the methylation maxima, but with increasing contents of chlorophyll (Figures 1a,b). Diffusion from below seems unlikely, because most of the MeHg was in particles. In L. HAKO MeHg carrying particles were nonpigmented (Figure 1c), and MeHg followed closely the vertical distribution of Fe and Mn (Matilainen, 1995). Lake KEHA was exceptional again with virtually all MeHg in dissolved phase except at lowest concentrations in extremely anoxic bottom layers (Figure 1d).

The inflow/outflow data show that L. HAKO is a sink of MeHg (about 10 ng $m^{-2}d^{-1}$,

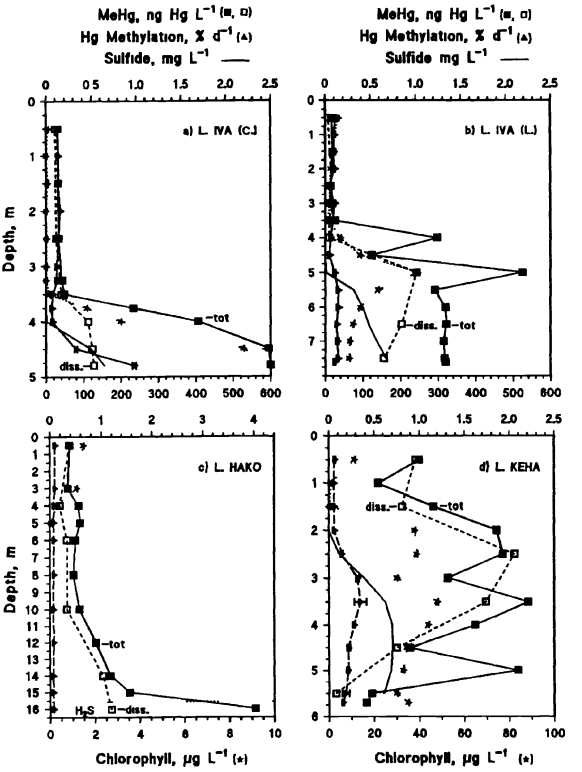

Fig. 1. Vertical distribution of total and dissolved MeHg, *in situ* mercury methylation, chlorophyll and sulfide in the study lakes in August-September 1993, (error bars represent ± standard deviation).

TABLE I

Mean particulate MeHg, dissolved MeHg (0.2 μm), and percentage of particulate MeHg in stratified lake water, in sedimentation traps, and at the surface sediment (0-1cm).

	$MeHg_P$ (ng l^{-1})	$MeHg_D$ (ng l^{-1})	$\frac{MeHg_P}{MeHg_{Tot}}$ (%)
Lake IVA (Control):			
Epilimnion	0.028	0.11	21
Hypolimnion	1.67	0.50	77
Above sediment surface (10 cm)	0.82	0.53	77
Trap	12.9	4.00	76
Sediment (0-1 cm)	28.5	<0.06	>99.8
Lake IVA (Limed):			
Epilimnion	0.007	0.058	11
Hypolimnion	0.59	0.75	44
Above sediment surface (10 cm)	0.67	0.65	51
Trap	5.77	5.67	51
Sediment (0-1 cm)	19.9	0.096	99.5
Lake HAKO:			
Epilimnion	0.19	0.29	40
Hypolimnion	0.20	0.68	22
Above sediment surface (50 cm)	2.83	1.20	70
Trap	23.1	4.00	85
Sediment (0.1 cm)	<2.3 (total)	lost	
Lake KEHA:			
Epilimnion	0.20	0.88	18
Hypolimnion	0.22	1.16	16
Above sediment surface (20 cm)	0.40	0.079	83
Trap	3.03	0.76	80
Sediment (0-1 cm)	0.72	0.25	74

Verta *et al.*, 1994), suggesting a net MeHg sedimentation or demethylation. Lake IVA also recieves MeHg from the catchment (2-3 ng $m^{-2}d^{-1}$ on lake surface, Rask and Verta, 1995), but has no permanent outlet, and possibly acts as a sink for MeHg too. Methylmercury sedimenting in these lakes is presumably partly derived from their catchments.

Particulate MeHg represented a minor fraction of total MeHg in epilimnia, but a major fraction (51-83 %) above the sediment surface in all lakes (Table I) also indicating scavenging in settling particles. Methylmercury partitioning to particulates and dissolved (0.2 μm) phase was similar in the traps and in the water overlying the sediment in each lake (Table I). The trap concentrations were one order of magnitude higher than the concentrations in hypolimnetic water, probably because of particulate accumulation and degradation. Earlier studies (Verta *et al.*, 1994) showed extremely low or no methylation in settling particles both in oxic and anoxic environments and do not support that significant methylation occured in traps during the deployment period.

At L. IVA (both basins, probably also L. HAKO) dissolved MeHg concentrations were higher in the water overlying sediment than at the sediment surface (Table I), indicating a diffusive flux of MeHg from the water to profundal sediments during late summer.

The low MeHg concentrations (as ng g^{-1}, dry weight) in the sediment surface compared

TABLE II

Concentrations of TotHg and MeHg (ng g^{-1}, dry weight) and MeHg (%) in sedimenting seston and in the sediment surface (0-1cm).

		TotHg (ng g^{-1})	MeHg (ng g^{-1})	MeHg (%)
Lake IVA (C):	Seston	72.3	16.1	22
	Sediment	134	8.0	6.0
Lake IVA (L):	Seston	57.4	10.3	18
	Sediment	172	7.60	4.4
Lake HAKO:	Seston	196	19.3	9.8
	Sediment	277	<0.3	<0.1
Lake KEHA:	Seston	118	14.5	12
	Sediment	254	0.07	0.03

to that in sedimenting seston, in the polyhumic lakes up to two orders of magnitude (Table II), suggest low MeHg production in profundal sediments.

4. Conclusions

The findings suggest that MeHg transport through sedimentation from the epilimnion and MeHg formation in hypolimnetic water were the primary sources of MeHg in the hypolimnion of the lakes. Pigmented particles seemed to control most of the MeHg in the oligohumic lake. The increase in hypolimnetic MeHg could not be explained by MeHg production in anoxic sediments.

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PART VII

MERCURY IN ARCTIC LAKES, ESTUARIES AND OCEANS

MERCURY IN VEGETATION AND LAKE SEDIMENTS FROM THE U. S. ARCTIC

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Abstract. Global atmospheric concentrations of mercury (Hg) appear to be increasing and with it the potential for ecosystem exposure and ecological effects. From 1990 to 1993 we examined U. S. arctic ecosystems over a broad spatial scale to develop baseline information on current concentrations of trace elements, heavy metals (including Hg), persistent organic compounds, and radionuclides in various components of the terrestrial and freshwater biosphere. Matrices reported here include, vegetation (lichens and mosses) and lake sediments. Total Hg in two lichen and two moss species from Alaska were generally low (0.02 - 0.112 μg/g dw), compared to reported values from other arctic locations and showed a statistically significant negative relationship between total Hg content and distance from the marine coastline. ^{210}Pb dated sediment cores indicated that average preindustrial total Hg accumulation rates were over four times greater in arctic Schrader lake than in subarctic Wonder Lake. Both lakes indicated a small increase (5 - 8%) in total Hg flux to the sediments during the last 145 years, much smaller than similar increases in total mercury for lakes in the north central U. S. The likely source of recent increases in Hg in these Alaskan ecosystems is long range atmospheric transport. While we can detect increases in mercury in lake sediments likely due to anthropogenic activities, values are low and there appears to be no immediate threat to terrestrial environments and inland freshwaters of arctic Alaska from long range atmospheric transport and deposition of Hg.

1. Introduction

The Arctic is not a remote, pristine ecological setting, but a remote region that is exposed to long range transport of airborne contaminants (Shaw and Khalil, 1989; Rahn and McCaffrey, 1980). Atmospheric contaminants pose a threat of uncertain magnitude to the function and structure of arctic ecosystems, as well as to arctic people that subsist on animals and plants (Barrie, 1986; Rahn *et al.*, 1989). In recent years the eight circumarctic nations have banded together under the Arctic Environmental Protection Strategy (1991) and implemented the international Arctic Monitoring and Assessment Program (AMAP Report, 1993). Along with chlorinated hydrocarbons, trace metals, in particular Hg, are of high interest due to their persistence in the environment and their known ability to adversely affect ecosystems, including humans (Schroeder, *et al.*, 1987; Clarkson, 1990). Environmental Hg may either be from natural sources (i.e. cinnabar deposits) or atmospheric emissions produced as a by-product of many forms of human industrial activities that include coal combustion, metal smelting, natural gas production and oil exploration (Mitra 1986, Nriagu and Pacyna 1988). Contaminants accumulating in the Arctic are generated within the Arctic as well as from more distant locations (Pacyna 1991). For some groups of contaminants, perhaps including mercury (Steinnes, this volume), the Arctic may function as an ultimate global sink due to the phenomenon of "global fractionation" (Ottar, 1981; Wania and Mackay, 1993).

Our understanding of the factors influencing the transport and mobility of various forms of Hg within temperate watersheds has improved in recent years (Bloom, 1989; Ramlal *et al.*, 1993; Engstrom *et al.*, 1994). This knowledge, however, may not translate directly to Hg dynamics in arctic environments, which differ in many significant ways from lower latitude ecosystems. Knowledge concerning concentrations and forms of Hg in arctic

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ecosystems is rudimentary; many investigators addressing metals in the Arctic have just begun to measure Hg. The objectives of this study are to report our finding with respect to (1) the status and extent of Hg in lichens and mosses in the U. S. arctic and (2) the recent chronology of Hg flux to Arctic and subarctic lakes.

2. Materials and Methods

Environmental samples were collected as part of the U. S. Environmental Protection Agency's Arctic Contaminant Research Program (ACRP). The ACRP was designed to evaluate the current status, chronology and potential ecological effects of a broad suite of contaminants including semivolatile organic compounds, trace elements, heavy metals, and radionuclides (Landers *et al.*, 1992) in the U. S. arctic. The data reported here are from samples collected in Alaska from 1990 to 1993. Sample matrices include vegetation (lichens and mosses) and lake sediments. The ACRP was designed to be an integrated research program. Therefore, at several sites multiple sample matrices, with the addition of fish, ground squirrels, and soils, were collected to investigate relationships between various potential sinks or pools of contaminants within individual watersheds. The specific sampling and analytical approaches for the matrices reported here are described below.

2.1 VEGETATION

We used lichens (*Cetraria cucullata* and *Masonhalea richardsonii*) and mosses (*Hylocomium splendens* and *Racomitrium lanuginosum)* to study the status and extent of our target contaminants (Ford et al., 1992) in 23 arctic locations (Figure 1). Sites were selected across arctic Alaska and were located in habitats that were common to the surrounding landscape. Lichens and mosses are non-vascular plants and generally lack the capacity for active uptake from soil solutions. Mineral nutrition is primarily derived from atmospheric sources; thus, lichens and mosses are considered to be good choices for defining exposure of terrestrial habitats to atmospherically derived substances, especially in remote regions with logistic constraints (Hale, 1981). Not all species were present at all sampling locations; at each site we collected as many species as were available. To minimize exposure to the samples from other than atmospheric sources of Hg, vegetation sampling sites were selected to be geomorphologically "independent" whenever possible, meaning that sampling sites were located on knolls, saddles, and hilltops with little or no drainage into the sampling sites.

Vegetation samples for Hg analysis were collected over areas of ca. 50 to 200 m^2. Collections were made using plastic or stainless steel forceps and powderless latex surgical gloves into washed (distilled, deionized water) plastic containers or Kapak™ metalized polyester bags. Samples were picked clean of visually obvious debris and transferred to pre-cleaned polyester mesh bags and dried to ambient moisture conditions in the field. Drying sites were remote from roads, generators and other potential point sources of Hg. Dried vegetation samples were placed into individual Ziploc™ or Kapak™bags and kept cool in insulated containers and in the dark until they could be shipped refrigerated via overnight courier to the analytical laboratory. Field storage of samples sometimes lasted for up to three weeks due to the remote field locations.

In the laboratory, samples were either oven dried at 35°C or transferred to sealed Spex™ jars in a Class 100 laminar flow hood and then freeze dried and homogenized with a Spexmixer™ mill or Spex™ ball mill. 1992 samples were digested with nitric/perchloric acid (Baker™ Instra-analyzed $\leq$ 0.01 ug/g total Hg) in an acid-cleaned Teflon™ bomb gently

warmed for 6-8 h followed by oven heating at 130° C for 4 h. 1990 samples were digested by nitric/perchloric acid digestion followed by hydrofluoric acid digestion (all acids were Fisher™ <0.004 ug/g total Hg). Samples were analyzed with an atomic absorption spectrophotometer using cold vapor atomic absorption (CVAA). Method detection limits (MDL) for Hg were 0.04 µg/g dw (1990) and 0.001 µg/g dw (1992).

Accuracy, precision, contamination, and recovery were assessed using standard reference materials (SRMs), field and laboratory duplicates, reagent blanks and spiked blanks and matrices. SRMs were either NIST 1572 (orchard leaves), NIST 1547 (peach leaves) or NIES 9 (Sargasso). Blanks were always negligible relative to sample values. Performance on quality control samples regularly fell within ± 20%, a reasonable envelope when operating close to the method detection limit. Duplicate analyses usually varied by no more than ±7%.

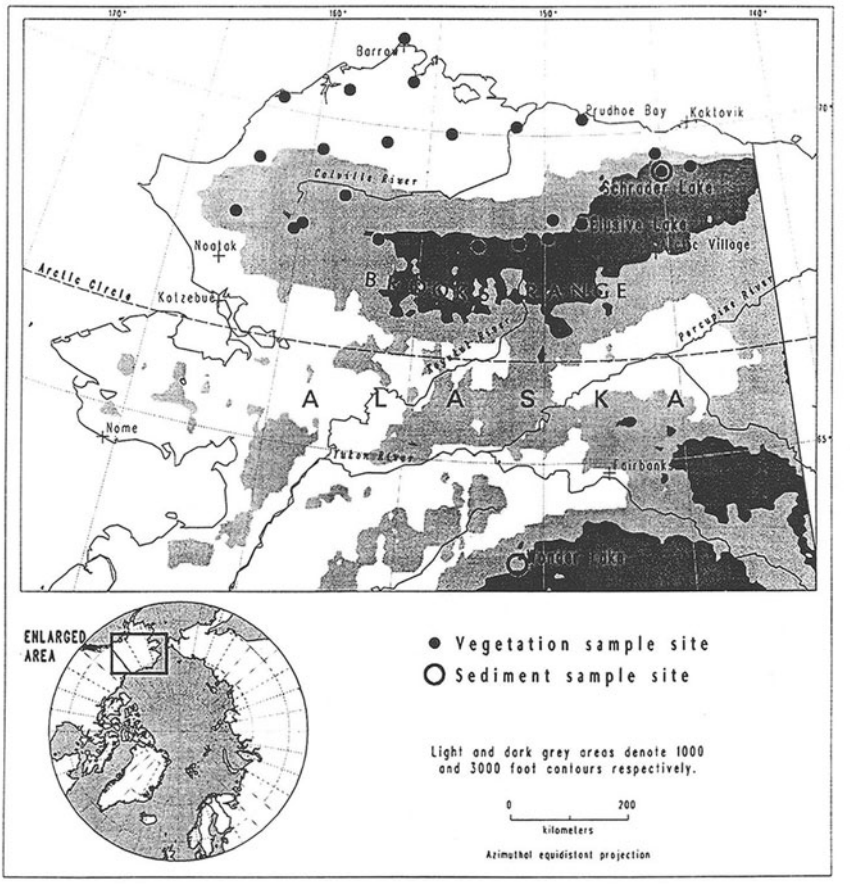

Fig 1 Map of Northern Alaska showing the locations of vegetation and lake sites sampled by the U S EPA Arctic Contaminants Research Program during 1990 to 1993

2.2 SEDIMENT

Lake sediment was obtained from the deepest basin of subarctic Wonder Lake (63° 28' N, 150° 52' W, Denali National Park and Preserve) and arctic Schrader Lake (69° 22' N; 144° 60' W, Arctic National Wildlife Refuge) (Figure 1) through the ice in the spring (April/May) of 1991. Both lakes are large glacial systems with gradual bathymetric characteristics suggesting stable sediments and regular sediment accumulations through the past 150 years (Wilding, 1940; Hobbie, 1961, 1962; Werner *et al.*, 1990). There are minimal current influences of man in the watersheds of the two lakes and access is limited.

We used a stainless steel gravity coring device with Plexiglas™ core liner tubes (internal diameter of 12.7 cm). Although physical disturbance associated with gravity coring may result in erroneous data and misinterpretations (Crusius and Anderson, 1991; Cumming *et al.*, 1993), the condition of our retrieved cores showed no apparent physical disturbance resulting from the coring operation as evidenced by an intact sediment water interface, undisturbed surficial worm and insect tubes, and horizontal uniformity of sediment texture and color. Cores were extruded and sectioned at either1 cm or 0.5 cm intervals from 0 to 10 cm (yielding approximately 125 cm^3 sediment per 1 cm interval), and at 2-cm intervals from 20 to 40 cm or the maximum depth of the core (yielding approximately 250 cm^3 per interval). Sediment samples were placed into commercially certified pre-cleaned glass jars with Teflon™ lid liners and kept near 4° C, but not frozen, in the field (< 4 weeks) until they could be refrigerated.

Sediment intervals were analyzed for total water and carbon content, radionuclides, and total Hg. Radiometric analysis of ^{210}Pb, ^{137}Cs, and ^{7}Be were first used in a constant rate of supply (CRS) model (Robbins, 1978) to assign approximate dates of deposition to the individual sediment intervals (Gubala *et al.* 1994). Based upon this information an analytical strategy was prepared regarding the selection of sediment slices for analysis.

For total Hg analysis, 1 to 5 g of wet sediment was totally dissolved in a sealed Teflon™ pressure vessel using a sequential, two-step digestion process with high purity nitric, perchloric, and hydrofluoric acids. Hg concentrations in the extract were then quantified using CVAA. Analysis of internal standard solutions, matrix recovery spikes, and standard reference materials were used to provide calibration and quality assurance for each analytical batch. Replicate analyses were conducted on 10% of the samples to assess precision of the analytical technique. Duplicate analyses varied by no more than 5%.

3. Results and Discussion

3.1 TOTAL Hg IN LICHENS AND MOSSES

Hg was present in all vegetation samples, but generally in low concentrations. Among the four species sampled, median concentrations of total Hg were similar, ranging from a low of 0.043 μg/g dw in *C. cucullata* to 0.056 μg/g dw in *M. richardsonii*. These median values were very close to the analytical method detection limit (MDL) of 0.04 μg/g dry wt. The "feather moss," *H. splendens,* that is used as a biomonitoring tool in Nordic countries (Rühling *et al.*, 1987, 1992; Steinnes *et al.* (in press)), had a median value of 0.055 μg/g dw; not significantly different from the median total Hg concentration in *M. richardsonii.* The highest concentration found among our four target sampling species, was 0.112 μg/g dw, in *R. lanuginosum* and *H. splendens*, with slightly higher concentrations

(0.146 to 0.156 μg/g dw) observed in the non-target taxon *Umbilicaria hyperborea*. Site specific studies show that even these low levels of Hg in our target monitoring species were higher than Hg concentrations in blueberries (*Vaccinium uliginosum*) and in a ground squirrel forage food (*Dryas octapetala)* (Ford *et al.*, in press).

While lichens and mosses are widely used in biomonitoring efforts worldwide, particularly in the Arctic (Thomas, 1986; Rühling, 1987, 1992), analyses of total Hg are rare. Steinnes *et al.* (1993) report total Hg concentrations of 0.15 to 0.32 μg/g dw for 11 samples *H. splendens* collected from throughout Norway as part of a laboratory methods intercomparison. The highest concentration of total Hg in our *H. splendens* from the Alaskan arctic (0.112 μg/g dw) is lower than the lowest Norwegian value (Steinnes *et al.* 1993). A bulk sample of *R. lanuginosum* from Svalbard had a total Hg content of 0.167 ug/g dw; *Cetraria nivalis* from the same arctic location had a concentration of 0.113 ug/g dw (Drbal *et al.*, 1992). Both of these samples had higher total Hg than any of our lichen and moss samples. Total Hg concentration in the epiphytic lichen, *Parmelia sulcata*, is reported for two surveys, 1982-83 and 1986-87, conducted in the Netherlands (Sloof and Wolterbeek, 1992); concentrations ranged from 0.1 to 3.7 μg/g dw in 1982-83, and 0.1 to 3.6 μg/g dw in 1986-87. Means were 0.4 and 0.5 μg/g dw in 1982-83 and 1986-87, respectively. Our minima concentrations were as low as the minima reported for the Netherlands but our mean concentrations were an order of magnitude less.

Even though total Hg in lichen and moss samples from this study were generally low, sampling sites closer to the ocean appeared to have higher concentrations of total Hg (Table I). Distance from the coast was determined by measuring the shortest distance from each sample site to the marine coastline. For 3 of the 4 species the relationship between total Hg and distance to the coast was significant at the 0.05 level. The strongest relationship was for the lichen *M. richardsonii* which demonstrated a very significant regression ($P < .001$) explaining over 40% of the variation in the data. The poorest relationship was that for *R. lanuginosum*, for which only 14% of the variation in the data was explained.

Table I
Regressions Statistics: Total Hg *vs* Distance from the Coast

Species	intercept	slope	Std. Error of the slope	R Square	Signifi-cance	No. of Observations.
C. cucullata	0.059	-0.0001	0.00005	0.29	.002	30
H. splendens	0.077	-0.0002	0.00005	0.35	<.001	36
M. richardsonii	0.068	-0.0002	0.00005	0.43	.001	20
R. lanuginosum	0.062	-0.0001	0.00007	0.14	.066	25

We offer four hypotheses regarding the potential source or cause of coastal Hg in arctic Alaska: ocean water containing ionic forms of Hg (e.g. $HgCl_4^{-2}$, $HgCl_3Br^{-2}$, and $HgCl_3^-$) distributed inland via windborne marine aerosols; lithologic sources associated with the coastal plain; industrial emissions resulting from the petroleum and natural gas industries located near Prudhoe Bay and Barrow, respectively; and temperature-mediated accumulation due to colder temperatures near the coast (Steinnes and Andersson, 1991).

Bering Sea water has been reported to contain 7.0 ± 3.3 ng/L of total Hg (Fowler, 1990). It is well documented for coastal regions that, in general, there is a strong marine chemical "signal" that can be detected inland from the coastlines some 10 - 100 km (Mairs, 1967; Sullivan, *et al.*,1988; Eilers, *et al.*, 1993). Thus, marine systems may provide a

consistent total Hg signal within the study area that is negatively associated with distance from the coast. The geology of the coastal plain of the Alaskan arctic differs significantly from the interior Brooks Mountain Range and foothills, possibly resulting in elevated Hg in vegetation. The causal factors responsible for the slightly elevated, but highly significant, total Hg concentrations in coastal vegetation may be a combination of these explanations. The temperature-mediated Hg accumulation hypothesis that seems tenable for the Norwegian situation (Steinnes and Andersson, 1991) appears not to apply to Alaska. Mean winter air temperature for arctic Alaska is warmer toward the west coast, decreasing to the east (National Foreign Assessment Center (U. S.) 1981). A similar, but less pronounced pattern is observed for mean summer temperatures. Large scale industrial activities in arctic Alaska are limited to oil and gas exploration and pumping, and localized mining. These activities have some atmospheric emissions and are mostly located around Prudhoe Bay and Barrow. If Hg was associated with these activities the relationship would not likely affect the westernmost coastal sites (Figure 1) which show the negative relationship with distance from the coast. Therefore, we suspect that the most likely hypotheses explaining these relationships are marine aerosol sources and/or geologic differences between coastal and interior sampling locations.

3.2 TOTAL Hg IN SEDIMENT

A primary objective of the stratigraphic studies in the two Alaskan lakes was to compare the concentrations of total Hg in recent *vs* preindustrial sediments. We also wanted to compare results for these lakes to those reported from other Arctic and lower latitude lakes in order to evaluate the relative status of Hg flux to the watersheds. Cores from the two lakes were similar with regard to the distribution of radionuclides used for dating. The entire inventories of ^{137}Cs and unsupported ^{210}Pb were found in the top 5 to 7 cm of the cores' and ^{210}Pb decreased at a uniform rate with sediment depth (Gubala *et al.*, in press). This suggests that the rate of sediment accumulation in the last 150 years has been constant and that the beginning of the 6 cm sediment interval in both cores is roughly equivalent to 145 years before present, or about 1845. Sediment deposited below the 5 cm interval is considered to represent pre-industrial conditions with regard to Hg loading. After correcting for focusing factors of 1.4 and 1.5, the average rates of sediment accumulation over the past 145 years are approximately 11 and 55 $g/m^2/yr$ for the Wonder Lake and Schrader Lake cores, respectively (Gubala *et al.*, in press). Figure 2 shows the accumulation rate of total Hg for both Wonder and Schrader Lakes.

Accumulation rates of total Hg were lower in Wonder Lake, ranging from a high of 1.64 $\mu g/m^2/yr$ at the 2 cm interval to a low of 1.07 $\mu g/m^2/yr$ at the 5 cm interval. These flux estimates are less than one half the background or pre-industrial estimates reported for lakes in the north central USA (3.7 $\mu g/m^2/yr$, Swain *et al.*, 1992) and arctic and subarctic Canadian lakes (mean 4.15 $\mu g/m^2/yr$, range 0.7 to 7.4 $\mu g/m^2/yr$, Lockhart *et al.*, this volume). Schrader Lake total Hg accumulation rates were higher (7.48 $\mu g/m^2/yr$) in the 1 centimeter interval. The lowest flux rate for Schrader Lake, 5.17 $\mu g/m^2/yr$, occurred at the 17 cm depth. The lowest Hg flux for Schrader Lake occurred at a sediment depth dated to be prior to 1845 while for Wonder Lake the lowest flux was for the period from about 1845 to 1885.

We compared mean total Hg flux rates between pre-industrialization (prior to c. 1845, depth intervals 6 to 22 cm) and post-industrialization (depth intervals 1 to 5) to create a flux ratio or enrichment factor. The Wonder Lake flux ratio was 1.08 and Schrader lake was

1.05. Both ratios suggest a slight (5 to 8%) increase in total Hg flux to the lake sediments during the last 145 years. Based upon the variance of the pre-1845 total Hg accumulation rates, recent flux ratios become statistically significant at the 95% confidence level (one-tailed Student's t test) at 1.15 (Wonder) and 1.08 (Schrader). Flux ratios for increments 1, 2 and 3 cm in Wonder Lake were 1.21 , 1.21 and 1.19 relative to the downcore average mercury flux of 1.36 $\mu g/m^2/yr$. Flux ratios for increments 1 and 2 cm in Schrader Lake were 1.24 and 1.10 relative to the downcore average flux of 6.05 $\mu g/m^2/yr$. Each of these five increments is statistically different ($P \leq .05$) from the downcore background (pre-industrial) flux. The average increase in total Hg accumulation over pre-industrial background during the last 40 years (increment 1) is remarkably similar between the two lakes, 21 and 24% in Wonder and Schrader Lakes, respectively. This is true even though the average preindustrial Hg flux in the two lakes differed by over a factor of 4. These small but similar increases in Hg flux to the two lakes in the surficial sediments indicates that there is a consistent, regional scale increase in the rate of total Hg atmospheric deposition. Since the formidable elevational barrier of the Brooks Range lies prominently between these two lakes (Figure 1) which are located over 600 km apart in a North - South direction, the consistent rate of total Hg flux in the surficial sediments is even more interesting.

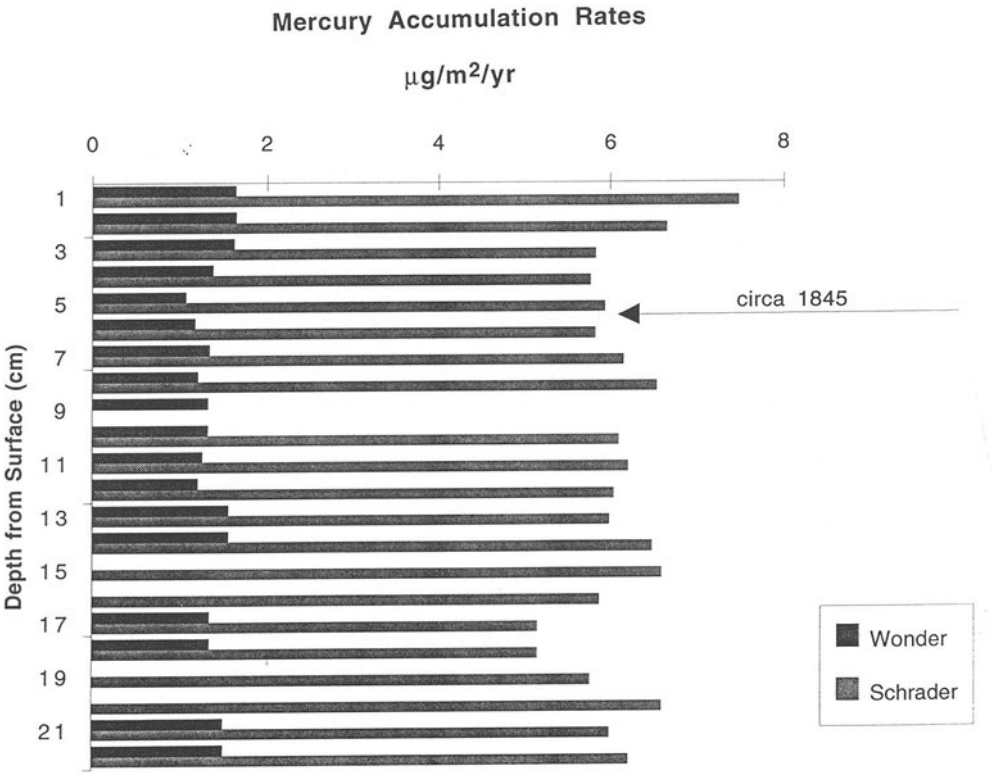

Fig. 2. Depth profiles of total Hg accumulation rates in lake sediment cores from Schrader and Wonder lakes in Alaska.

The flux ratios of total Hg to 7 lakes reported by Swain *et al.* (1992) ranged from 3.22 to 4.88, representing a three to five fold increase in total flux of Hg for these North American, mid-latitude (45^{o}- 49^{o} N) lakes. Lockhart *et al.* (this volume) reports flux ratios for Canadian arctic and subarctic lakes ranging from a low of 1.1 in Lac Belot to a high of 7.0 in Hawk Lake (mean of 8 lakes = 2.98). Our reported increase in total Hg flux in recent decades to the Alaskan lakes is consistent with, although of considerably lower magnitude than, increases in total Hg flux reported for arctic and temporal lakes in other countries (Fig 3). Swedish forest lakes demonstrate a flux ratio from about 2 in the most northerly, arctic lakes, to about 5 in the lakes located in southern Sweden (Johansson, 1983). Finnish lakes show a similar latitudinal gradient (Verta et al. 1990) with ratios ranging from 6.3 (range 0.7 to 15.7) in southern Finland to 2.9 (range 1.0 - 5.6) in northern Finland.

Increased Hg flux to lakes is very often associated with acidic deposition (Verta *et al.,* 1990; Grieb *et al.,* 1990; Winfrey and Rudd, 1990; Haines *et al.,* 1992). The two Alaskan lakes have circumneutral pH and acid neutralizing capacity greater than 100 μeq/L (Landers and Gubala unpublished) and are located in a geographic setting remote from any large regional sources of acidic precursors. These factors suggest that acidic deposition is not currently a significant environmental risk to these systems. We hypothesize that the slight increase in Hg loadings to the two Alaskan lakes is more closely associated with an increase in the global or at least northern hemisphere background concentrations of Hg due to increases in global air contamination by trace metals (Nriagu and Pacyna, 1988). There is ample evidence for transpolar transport of metals associated with industrial activities in Europe and Asia (Landsberger *et al.,* 1992). Although Hg concentrations were not reported by Landsberger *et al.* (1992), Hg is a known by-product of coal combustion and smelting activities that are common in Eurasia and is probably associated with and transported to the Arctic in the gas phase by the northern hemisphere air masses described. Hg, due to its potential for revolatilization after deposition may be affected by a "global fractionation" process (Wania and Mackay, 1993) resulting in the colder arctic regions acting as a sink for Hg that reaches these most northern destinations (Steinnes, this volume).

The transfer of Hg from terrestrial to aquatic systems depends on several factors. Large watershed to lake area ratio, low pH, low ionic strength, and high dissolved organic carbon all favor the flux of Hg into lake basins (Bodaly *et al.*, 1993; Engstrom *et al.,* 1994). Within-lake re-mobilization and bioaccumulation of Hg is also be affected by sediment redox conditions, primary and secondary production, basin morphometry, water temperature, and the concentrations of Zn and Se (Björnberg *et al.,* 1988; Winfrey and Rudd, 1990; Bodaly *et al.,* 1993). Hence, it is difficult to judge, *a priori,* the degree to which a relatively small amount of Hg deposited within the watershed of a freshwater system will appear in the associated food web.

An important consideration in the Arctic with respect to ecosystem Hg is the vast expanses of landscape containing shallow, freshwater thermokarst lakes and wetland systems moderately high in organic compounds. The aggregate Hg in these systems may be considerable and a portion could be mobilized if future climate change results in permafrost melting and a general increase in arctic temperatures. It is currently unclear if these systems function in the same way as more temperate freshwater systems with regard to Hg cycling. Therefore, the effect of warming on Hg in arctic ecosystems under a global warming scenario remains undetermined.

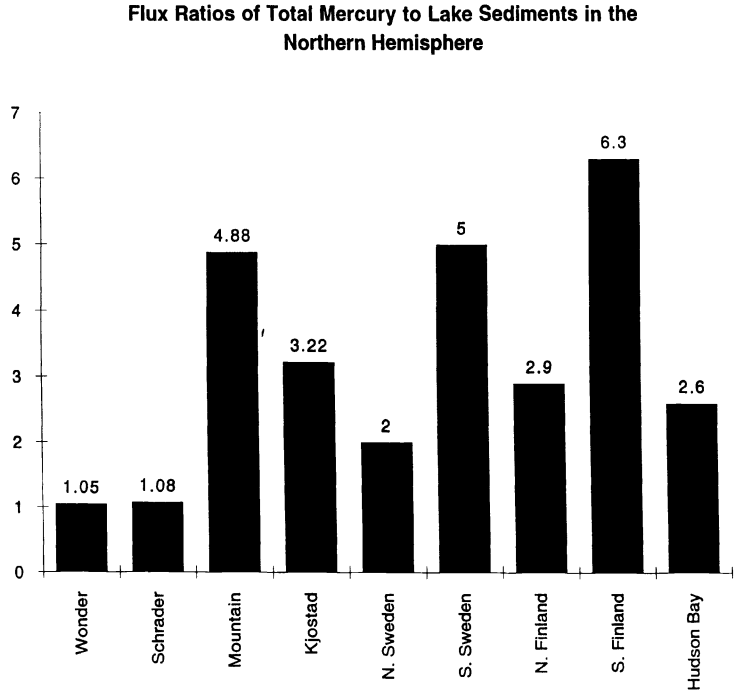

Fig. 3. Total Hg is compared for industrial vs. pre-industrial eras using flux ratios (enrichment factors). Total Hg flux ratios in lakes from throughout the northern hemisphere show a consistent decrease in flux ratios with increasing latitude. Flux ratios are printed at the top of each bar. Wonder and Schrader (this study); Mountain and Kjostad (Swain *et al.* , 1992); Sweden (Johansson, 1983); Finland (Verta *et al.* 1990); Hudson Bay (Hermanson 1993).

4. Conclusions

Total Hg concentrations in lichen and moss sampled in arctic Alaska are relative low when compared to results from similar samples collected in Norway. We found a significant, negative relationship between total Hg in vegetation and distance from the coast in Alaska. Marine aerosols and or the effect of coastal geology seem the most likely explanations of this spatial trend. There is evidence of a relatively small increase (21 to 24%) in anthropogenic contamination of Hg in arctic and subarctic Alaskan lakes in the last 40 years based on sediment analysis. The source of this increased flux to aquatic systems is probably from long range atmospheric transport of emissions from industrialized sources in Eurasia and N. America. Since global background Hg concentrations do appear to be increasing, select ecosystems in arctic Alaska should be monitored to detect changes in the rate of Hg loading.

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CURRENT AND HISTORICAL INPUTS OF MERCURY TO HIGH-LATITUDE LAKES IN CANADA AND TO HUDSON BAY

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Abstract. Sediment cores collected from several lakes in northern Canada have been analyzed for mercury and several other chemical contaminants. Sites ranged from the Experimental Lakes Area of northwestern Ontario, north to Cornwallis Island, and west to the southern Yukon. Cores were sliced at sites of collection and individual slices were freeze dried and analyzed for Pb-210 and Cs-137 to estimate average time intervals of deposition. The earliest date estimated by Pb-210 was about 1850, and mercury concentrations in some lakes were clearly increasing before then, assuming no vertical movements of mercury within the sediments. Extrapolation of dates downward to deeper slices, assuming a constant sedimentation rate, indicated that in some lakes mercury inputs increased slowly even in the 1500's, more rapidly after 1750, and more rapidly yet over the current century. These increases are interpreted as increased fluxes of mercury to the lakes as a result of long-range transport of atmospheric mercury, since there are no local industrial sources of mercury. Slices taken near the bottom of a core are taken to estimate the geological component while elevations in excess of that in surface slices are taken to represent contamination from fallout. This partitioning suggests that sediments in the eastern Northwest Territories are dominated by pollution, while those from the western Northwest Territories are influenced more by their geological settings. Two cores from Hudson Bay suggest that mercury is increasing there too, but has not yet exceeded geological sources. Mercury shows little or no tendency to decline in the most recent slices; indicating that inputs of mercury remain at or near their historical maxima. Given relatively high and continuing inputs of mercury to northern lakes it seems likely that some portion of that mercury may find its way into the food chain, hence the long-term prospect is for increasing levels of mercury in northern fish.

1 Introduction

Mercury has accumulated in arctic people (Health & Welfare Canada, 1978; 1984) as a result of consumption of relatively large quantities of marine mammals and fish, especially freshwater fish (Wheatley and Wheatley, 1981). Measurements of air over the North Atlantic by Slemr and Langer (1992) have inferred that atmospheirc mercury is increasing at about 1.47 per cent per year. The most important anthropogenic sources of atmospheric mercury are combustion of coal and municipal garbage (Nriagu and Pacyna, 1988). Previously we reported fresh snow containing several trace contaminants, apparently from Eurasia, reaching a small lake near the west coast of Hudson Bay in the Northwest Territories, Canada (Welch *et al.*, 1991). A sediment core from that lake (Hawk Lake, 63° 38' N, 90° 40' W) contained Cs-134 in the top slice, an unambiguous indication of fallout from Chernobyl (Lockhart *et al.*, 1993). Given natural and anthropogenic sources of mercury to air, the increases in atmospheric concentrations, and the existence of pathways to disperse trace contaminants from temperate source regions to the Arctic, one may ask to what degree the mercury found in the Arctic represents natural geological sources and to what degree it represents pollution.

Sediment core studies from more southerly locations in North America have been used to infer increasing inputs of mercury over the current century (Ouellet and Jones, 1983; Evans, 1986; Johnson, 1987; Swain et al., 1992). The most northerly core profiles reported to date from Canada are those from Far Lake (Lockhart, 1992) and Hawk Lake (Lockhart *et al.*, 1993), both on the west coast of Hudson Bay at latitude 63° north, and Initavik Lake in the Belcher Islands in southern Hudson Bay (Hermanson, 1993).

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2. Materials and Methods

Sediment cores from freshwater lakes were collected as described by Lockhart *et al.*, (1993) from several areas (Figure 1). During winter either a box corer or a KB corer was lowered through the ice to penetrate the sediment. Cores from Hudson Bay were obtained with a bulk box corer in August, 1992, from *C.S.S. Hudson* and September,

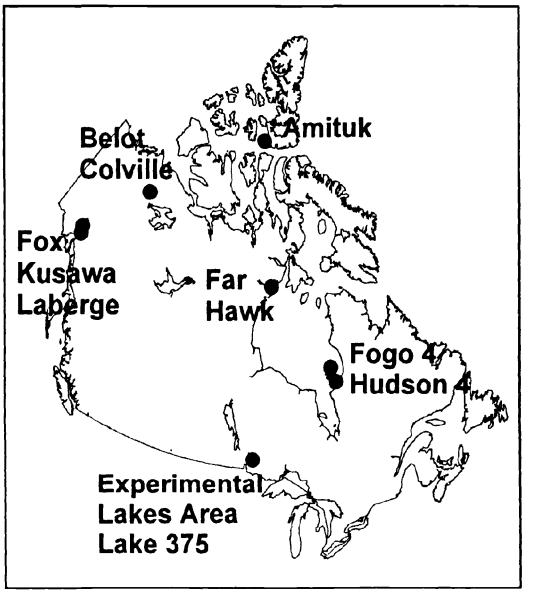

Figure 1. Approximate locations of core sites

1993, from M.V. Fogo Isle; 10-cm cores were taken on deck by easing plastic tubes into the box cores. Sediments were sliced in the field, usually at 1-cm intervals but sometimes at 0.5-cm intervals, and each slice was sealed in a Whirlpac bag. After shipment to the Freshwater Institute slices were freeze dried, homogenized and partitioned for various different analyses. Be-7, Cs-137 and Cs-134 were counted on a gamma spectrometer using a hyper-pure germanium crystal. Detector efficiencies were calculated using National Institute of Standards and Technology standard reference material ("Gamma-ray emission rate standard: spiked clay"). Aliquots of each slice were analyzed for Pb-210 and Ra-226 by leaching at 80°C with nitric and hydrochloric acids containing a known amount of Po-209 present as a tracer. Polonium was then autoplated onto a silver disc from 1.5 N HCl (Flynn, 1968) and the discs were counted on an alpha spectrometer using a silicon surface barrier detector and Pb-210 was determined as the activity of its daughter, Po-210. The remaining solution was placed in a sealed radon bubbling bottle and analyzed for Ra-226 by the radon de-emanation method (Mathieu, 1977). The error in counting replicate samples for Pb-210 in this way was under 8 per cent. Mean ages of slices were estimated from the slope of the regression equation of unsupported Pb-210 against accumulated dry weight.

A sub-sample (0.1 - 0.5 g) of freeze dried sediment from each slice was heated to a gentle boil with 8 mL aqua regia and adjusted to 50 mL with distilled water (Dow Chemical of Canada, Ltd., Method CAS-AM-70.13). The supernatant was analyzed for mercury by cold vapour atomic absorption spectrophotometry (Hendzel and Jamieson, 1976) using standards prepared in aqua regia. National Research Council of Canada marine analytical reference sediments were analyzed concurrently for quality assurance.

3. Results and Discussion

Sample plots of unsupported Pb-210 and Cs-137 activities in two of the cores are shown in Figure 2. The unsupported Pb-210 showed the expected exponential decline when plotted against accumulated dry weight. Cs-137 profiles were more variable, but generally gave peak values in the 1960s. The cesium profile for the Hudson Bay core (Hud-4) implies extensive mixing and presumably represents a blurred remnant of a sharper peak that has been mixed upward and downward. The current atmospheric supply of Cs-137 is much lower than that implied by the top of this core, and the high surface activities must come from sediment mixing, resuspension and redeposition. The total integrated Cs-137 throughout the core was about the same for the two cores shown in Figure 2 (0.113 Bq/cm^2 for Hudson Bay core 4 and 0.109 Bq/cm^2 for Fox Lake).

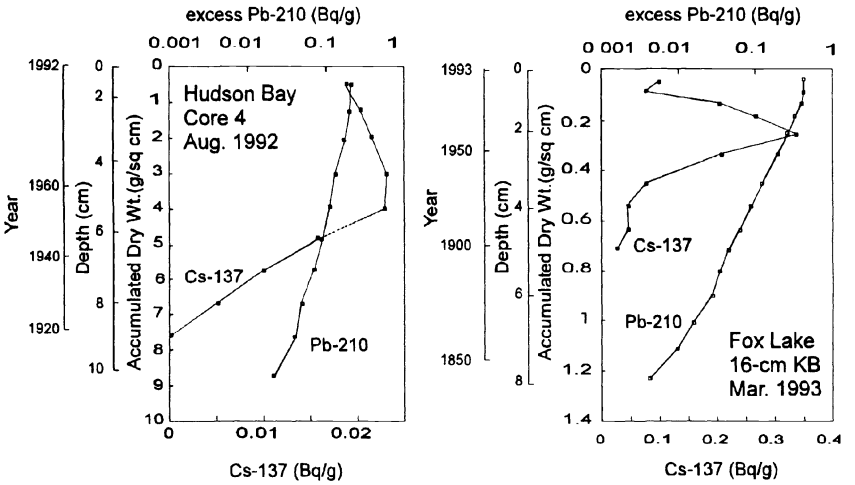

Figure 2. Pb-210 and Cs-137 profiles for cores from Hudson Bay (Grande Baleine Delta) and Fox Lake (Yukon)

Profiles of mercury concentrations in slices of several cores are given in Figure 3. In all these freshwater cores mercury concentrations increased in the upper, more recent slices relative to the deeper ones, although the difference was sometimes quite small. (Cores from two additional lakes further north have been collected, but the Pb-210 and Cs-137 profiles suggest extensive mixing, and these cores have not been interpreted fully yet; neither shows the tendency for mercury to increase near the top.) The concentrations of mercury in the top and bottom slices of each core are listed in Table I. Sedimentation rates calculated for each core are included in Table I. Mercury in surficial

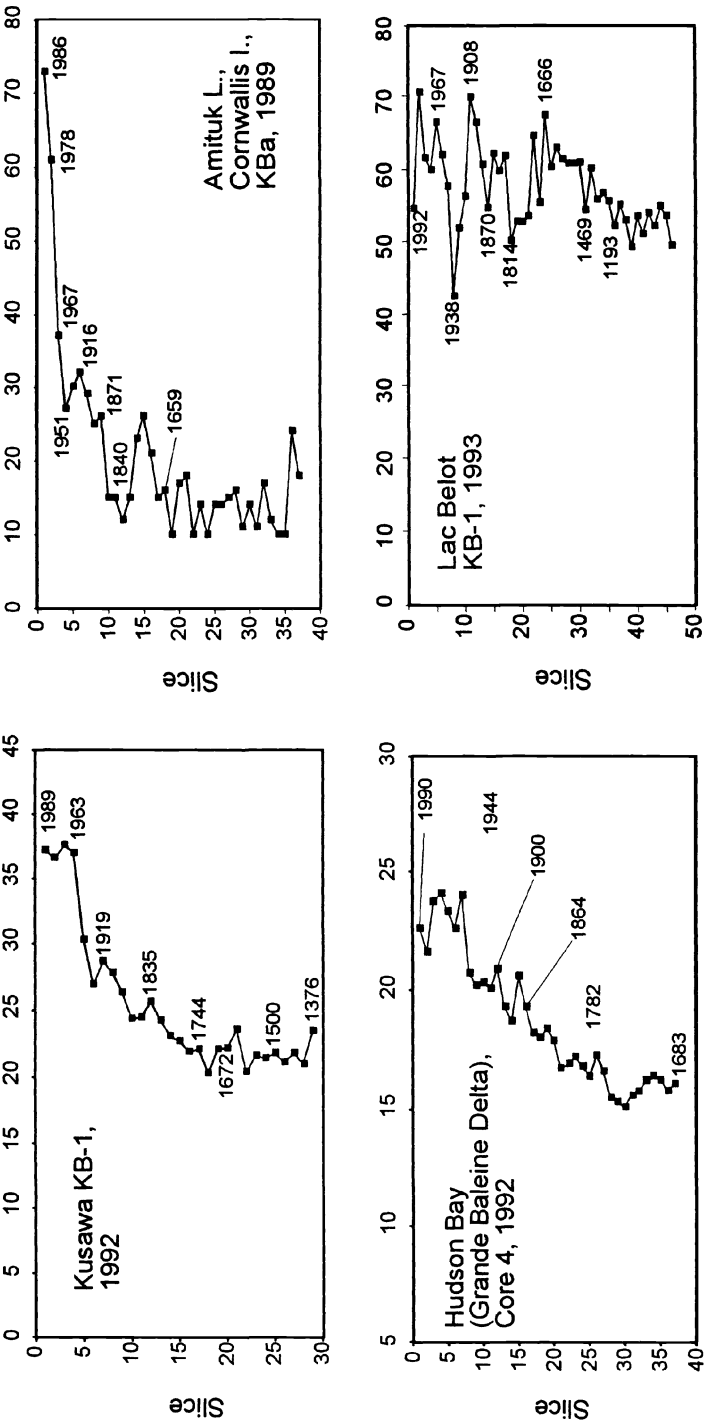

Figure 3. Profiles of mercury (ng/g dry wt.) in several cores. Dates earlier than 1850 are extrapolations based on sedimentation rates established from recent slices. (Scales vary among locations.)

freshwater lake sediments ranged from 27 to 185 ng/g, with no clear geographic pattern suggested except that the most southerly lake had the highest surface concentration. Surface sediment concentrations from about 110 to about 480 ng/g are typical of lakes in south-central Ontario (Evans, 1986). The flux of mercury to a given slice can be calculated as the product of its concentration in that slice and the sedimentation rate for the core and these have been tabulated in Table II. The flux to the top slice is taken as an estimate of the current rate of supply, while that to the bottom slice is taken as the historical rate of supply. Since none of the lakes has known local industrial sources of mercury, the historical rate is assumed to represent natural geological inputs. The ratio of current to historical inputs has been calculated as the "cultural enrichment" (Robbins and Edgington, 1976).

TABLE I.

Mercury concentrations and sedimentation rates in several Canadian lakes and at two sites in Hudson Bay

Source	core	Sedimentation rate ($g/m^2/yr$)	Hg, top slice (ng/g)	Hg, bottom slice (ng/g)
Lake 375	BCa	115	185	64
Hawk Lake	a	50.8	98	14
Far Lake	a	76.6	100	30
Amituk	KBa	389	73	18
Belot	Bel-1	69.6	54.9	49.7
Belot	Bel-2	56.9	75.8	42.5
Belot	Bel-3	49.7	79.4	66.6
Colville	Col-1	139	58.3	30
Fox	Fox-1	76.6	105.1	60.2
Kusawa	Kus-1	227	37.2	23.5
Laberge	Lab-3	650	27.2	22.3
Hudson Bay	Hud-4	1180	22.6	16.1
Hudson Bay	Fogo-4	1390	34	22.5

At the most southerly location in the Experimental Lakes Area (ELA) of northwestern Ontario, the mercury profile for Lake 375 showed a long period of very slow increase followed by a more rapid increase in the present century (Lockhart et al., 1993). On the west coast of Hudson Bay, Hawk Lake (Lockhart et al., 1993) and Far Lake (Lockhart, 1992), both in the the Saqvaqjuac research area (Welch, 1985), also showed consistent increases in uppermost slices. Amituk Lake on Cornwallis Island had a long basal period with very little net change followed by a striking increase in the top few slices representing the past century (Figure 3). Lakes Belot (Figure 3) and Colville are close together northeast of Great Bear Lake, and they both showed somewhat lower enrichments than lakes further east. To date, three cores have been analyzed from Lac Belot, and all indicated relatively low enrichment factors, the average being only 1.4.

The three lakes in the southern Yukon (Fox, Kusawa (Figure 3) and Laberge) also had low enrichment factors, averaging 1.4.

TABLE II

Surface and deep fluxes of mercury to core sites and enrichment factors caclulated as the ratio of the current flux to the historic flux.

Source	Core	Surface flux ($\mu g/m^2/yr$)	Historic flux ($\mu g/m^2/yr$)	Enrichment factor
Lake 375	BC a	21.3	7.4	2.9
Hawk Lake	a	5.0	0.7	7.0
Far Lake	a	7.7	2.3	3.3
Amituk Lake	KBa	28.4	7.0	4.1
Belot	Bel-1	3.8	3.5	1.1
Belot	Bel-2	4.3	2.5	1.8
Belot	Bel-3	3.9	3.3	1.2
Colville	Col-1	8.1	4.2	1.9
Fox	Fox-1	8.1	5.3	1.7
Kusawa	Kus-1	8.5	5.3	1.6
Laberge	Lab-3	17.7	14.5	1.2
Hudson Bay	Hud-4	26.7	19	1.4
Hudson Bay	Fogo-4	47.3	31.3	1.5

Current fluxes for lakes all range from 3.8 to 28.4 $\mu g/m^2/yr$ and historic fluxes range from 0.7 to 14.5 $\mu g/m^2/yr$. Johnson (1987) included two lakes from the Experimental Lakes Area in his survey of Ontario lakes and found current fluxes of 28 and 20 $\mu g/m^2/yr$; we obtained a current flux of 21 $\mu g/m^2/yr$ at Lake 375. Johnson's other sites in Ontario gave current fluxes in the range of 7 to 52 $\mu g/m^2/yr$. The two marine cores from Hudson Bay had high fluxes of 27 and 47 $\mu g/m^2/yr$ because of their high sedimentation rates. The lake core taken closest to these Hudson Bay cores is that of Hermanson (1993) who found a current flux of 16 $\mu g/m^2/yr$ in a shallow lake in the Belcher Islands. Core Hud-4 was taken from the Grande Baleine Delta and presumably reflects sediments delivered from the river. Core Fogo-4 was taken in the north Belcher Islands away from any large riverine inputs.

Considering only the lakes from the more easterly locations (Lake 375, Hawk, Far, Amituk), the average enrichment was 4.3, largely due to the high value of 7 from Hawk Lake. Omitting Hawk Lake, the average enrichment for the other three lakes was 3.4. Swain et al. (1992) found an average enrichment of 3.7 for lakes in eastern Minnesota and Wisconsin. Rada et al. (1989) reported enrichments ranging from 0.8 to 2.8 for lakes in north-central Wisconsin. Evans (1986) found lakes in southern Ontario often had surficial sediment mercury concentrations two to four times those in deeper layers. Hermanson (1993) obtained an enrichment of 3.2 at Imitavik Lake in the Belcher Islands. Ouellet and Jones (1983) reported enrichments of 1.2-4.3 for lakes with no anthropogenic activities within the watersheds in Quebec. The results for these lakes are generally consistent with enrichment factors reported for other lakes from eastern and central North America. There have been fewer studies of mercury deposition in western

North American Lakes. Landers et al. (1994) reported very low enrichments in two lakes from Alaska using calculations averaging several slices. Schrader lake had a maximum recent flux of 7.5 $\mu g/m^2/yr$ in the uppermost layer while the lowest flux was 5.17 $\mu g/m^2/yr$ suggesting an enrichment of about 1.45 when calculated as the simple ratio used for the Canadian lakes. Similarly Wonder Lake had a maximum flux of 1.6 $\mu g/m^2/yr$ as compared with a deep flux of 1.2 $\mu g/m^2/yr$, producing an enrichment of 1.3.

These observations suggest that there is relatively little difference in in enrichments of mercury in eastern North America throughout a geographic range extending from northern U.S.A. to Cornwallis Island. The implication is that sites with enrichment factors lower than two derive mercury inputs primarily from geological (or at least not from anthropogenic sources) sources within the watersheds, and those with enrichments greater than two derive mercury primarily from other sources, presumably atmospheric fallout. By this criterion, the western N.W.T. sites and Yukon sites are dominated by their geological settings, while the central freshwater sites are dominated by fallout. Regional differences are suggested, with segregation by longitude rather than latitude. The two marine cores from Hudson Bay were both dominated by geological sources. From studies of the distribution of mercury in marine mammals, Wagemann et al. (1994) concluded that geological settings of the principal habitats occupied by these animals were the most likely source of differences observed among populations.

The importance of supply rates to the bioaccumulation of mercury through aquatic food chains is not understood well. Johnson (1987) reported statistical associations between loading rates and concentrations in several species of fish in 14 lakes in Ontario. Analyses of fish from the lakes reported here are underway in order to test for similar relationships in northern lakes.

Several other independent lines of evidence indicate increases in mercury over time. Air samples over the Atlantic Ocean (1977-1990) indicate increasing air concentrations (Slemr and Langer, 1992). Hair samples recovered from human mummies in Canada (Wheatley and Wheatley, 1988) and Greenland (Hart-Hansen et al., 1991) also suggest long-term slow increases. The core profiles suggest slow but real increases in loadings of mercury to northern Canadian lakes and also to Hudson Bay. The source of the increases over basal geological loadings is assumed to be atmospheric fallout. Several published sediment core studies at lower latitudes also show similar increases in inputs of mercury (Ouellet and Jones, 1983; Evans, 1986; Johnson, 1987; Swain et al., 1992). Mason et al. (1994) have concluded that anthropogenic emissions have tripled the concentrations of mercury in the air and in the surface ocean. The atmospheric source appears to be more important for lakes in north-central North America than for north-western North America.

Acknowledgements

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INTERNATIONAL FIELD INTERCOMPARISON OF ATMOSPHERIC MERCURY MEASUREMENT METHODS

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Abstract. To determine the extent of comparability of sampling and analytical procedures for atmospheric mercury (Hg) being used by different scientific groups around the world and hence the compatibility of measurement results, the Atmospheric Environment Service (AES) co-ordinated a field intercomparison study in Windsor, Ontario, over a period of 5 days during Sept./Oct.,1993. This study brought together 2 groups (University of Michigan Air Quality Laboratory; Chemistry Institute of GKSS) which performed conventional (manual) sample collection procedures for total gaseous mercury (TGM) and for particulate-phase mercury (PPM), followed by cold-vapor atomic fluorescence spectrophotometric (CVAFS) analysis in the respective laboratories. Two other groups (Ontario Hydro, and the Ontario Ministry of Environment & Energy) each operated a novel mercury vapor analyzer produced by Tekran Inc. of Toronto. As is the case for the manual methods, this analyzer also uses gold amalgamation and CVAFS. During the intercomparison, meteorological parameters (air temperature, barometric pressure, wind speed/direction and relative humidity) were obtained at the study site.

1. Introduction

Significant advances in the determination of Hg in various environmental media (at trace or ultra-trace levels) have occurred during the last 10 to 15 years (Fitzgerald and Gill, 1979; Schroeder,1982; Bloom and Fitzgerald,1988; Bloom,1989; Lindqvist,1991; Baeyens,1992). Atmospheric Hg measurements (this term includes both sampling and analytical operations) are being made with increasing frequency worldwide due to a growing awareness of the importance of the atmosphere in globally dispersing this heavy metal. In outdoor air--especially at rural or remote locations--Hg exists primarily in the vapor phase, with at most a few % of the total airborne Hg being associated with atmospheric aerosols. Moreover, almost all (generally > 95%) of the vapor-phase Hg consists of the elemental form (Hg^{o} atoms). In urban or industrial centers, the physical forms and/or chemical speciation of Hg in the atmosphere may, however, be significantly different.

Because of the extremely low concentrations at which Hg species normally exist in the atmosphere, current sampling techniques involve a pre-concentration step (filtration in the case of PPM; amalgamation with gold for vapor-phase Hg species). The latter air sampling technique (Schroeder et al.,1985) gives rise to the operational definition of "total gaseous Hg". Considerably less standardization of methods has occurred for the collection of PPM than for the collection of TGM. For PPM, air filtration is used almost exclusively, but the types of filter media employed vary considerably (e.g., quartz-wool plugs, glass fibre, Teflon or polycarbonate filter disks or organic/inorganic membranes). In most instances, after thermal release of the analyte in the form of Hg^{o}, either from the gold collector via "de-amalgamation" or from the filtered particulate matter via pyrolysis, detection and quantitation is achieved by CVAFS. Conventional (manual) methods for atmospheric Hg measurements employ a sampling train consisting of a filter medium to retain PPM folllowed by an adsorbent bed (e.g.,activated charcoal or proprietary products such as Carbosieve^{R}, Carbotrap^{R},or Tenax^{R}) or a noble metal "trap" (usually Au or Ag) which amalgamates gaseous Hg species (Dumarey et al., 1985; Schroeder and Jackson,1985; Schroeder et al.,1985).

Water, Air, and Soil Pollution **80**: 611–620, 1995.

Given the remarkable resurgence of interest and the impressive level of effort expended in recent years on atmospheric Hg measurements in North America and Europe, it is very important to intercompare the sampling and analytical methods used by different groups of investigators. Collaborative methodology intercomparisons are an effective way of testing the "maturity" and "ruggedness" of sampling and analytical protocols (ACS,1980; ASTM,1977; Youden and Steiner,1975). So far, standardization of methods and procedures for atmospheric Hg measurements has occurred only to a rather limited extent. Yet, our understanding of the atmospheric chemistry and the complex environmental behavior of Hg species released into the troposphere from a diverse array of anthropogenic and natural sources is critically dependent upon accurate and/or precise measurement methods. The recent development (by Tekran Inc. of Toronto) of an instrument which automates the sampling and analytical steps in atmospheric Hg measurements also provided an impetus for a field intercomparison between traditional methods of sampling and analysis and the Hg vapor analyzer described in this paper. In an effort to determine the intercomparability of sampling and analytical procedures currently in use and the degree of compatibility of measurement results obtained with environmental samples, AES co-ordinated a field intercomparison study in Windsor, Ont., over a period of 5 days during September/October,1993. To our knowledge,this is the first multi-national field intercomparison of atmospheric Hg measurement methodologies undertaken in North America (or perhaps anywhere).

2. Experimental Description

This intercomparison took place from Monday, Sept. 27 to Friday, Oct.1, 1993, on the premises of the West Windsor Water Pollution Control Plant in the City of Windsor which is located in south-western Ontario, Canada. It involved 2 laboratories practicing conventional, manual sampling and analytical procedures for atmospheric Hg (both total gaseous Hg and particulate-phase Hg) and 2 laboratories, each operating a Tekran Hg vapor analyzer. Project personnel and equipment were accommodated in an AES mobile laboratory parked on the study site. Manual sample collection methods followed an identical protocol: concurrent 6-hour and two 3-hour (or three 2-hour) runs during the day-time, followed by an over-night run lasting about 15 to 18 hours. Results from the Tekran analyzers (obtained at 5-minute intervals) were averaged over the same time periods as for the manual methods. A total of 13 runs were completed. Duplicate samples for TGM and for PPM were taken during most runs.

2.1 SAMPLING PROCEDURES

A generic schematic of the Hg sampling trains used in the manual methods is given in Figure 1. Sampling flow rates were in the range of 300 to 500 mL/min.

Mercury associated with airborne particulate matter was retained on carefully pre-cleaned filter media. Lab A used glass-fiber filters (Gelman type A/E) in Teflon filter cassettes, whereas Lab B used traps consisting of quartz-wool plugs contained in quartz tubes (6 mm o.d.; 4 mm i.d.). Filter media were changed on a daily basis. For determining PPM, Lab A collected separate samples on glass-fiber filters at a nominal flow rate of 30 L/min, whereas Lab B used the quartz-wool traps located ahead of the TGM sampling train.

For the collection of TGM, traps similar in design to that shown in Figure 2 were used. Lab A utilized traps (~ 12 cm long) containing either Au-coated glass beads or Au-coated quartz sand, whereas Lab B used only Au-coated glass bead traps (7.5 cm long). Each lab employed 2 traps in series to check on collection efficiency. The collection efficiency of both types of traps has been found to be $\geq$ 95% (Dumarey et al.,1985).

A flow diagram for the Tekran Model 2537A Hg vapor analyzer is provided in Figure 3. TGM is collected onto gold. PPM is removed by a 47 mm diam. Teflon filter located immediately upstream of the Au cartridges. The analyzer was programmed to sample ambient air at a flow rate of 2 L/min for 5-minute sampling intervals.

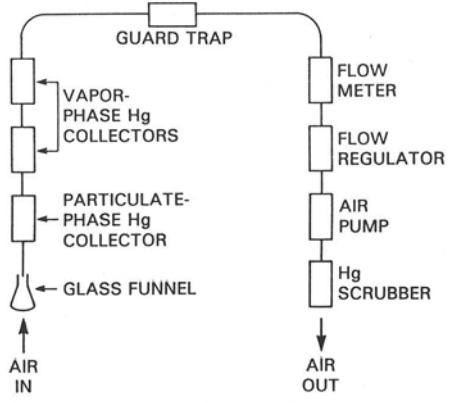


Figure 1. Schematic of generic atmospheric mercury sampling train

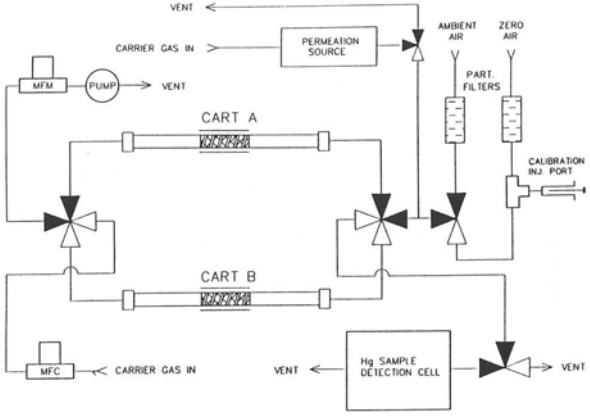
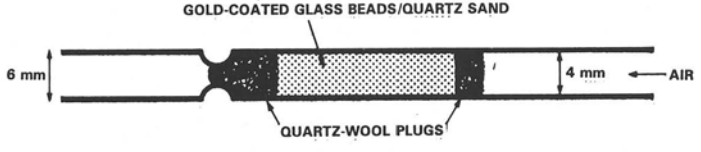


Figure 3. Flow diagram for Tekran (Model 2537A) mercury vapor analyzer for ambient air
MFC = mass flow controller
MFM = mass flow meter



Meteorological parameters (air temperature, barometric pressure, wind speed/direction & relative humidity) were measured at the study site with an instrumented 10 m tower located in an open field ~150 m from the mobile lab containing the sampling and analytical apparatus. The met. data (5 min averages) were obtained with the following instrumentation: pressure = SETRA (SBP 270); temp.& r.h. = ROTRONIC Model MP-100F; temp. gradient = 2 thermocouples with radiation shields at 1 & 9 m above ground; wind speed & direction = YOUNG Model 05103 anemometer. All parameters were collected with a 100% data capture rate over the entire study period.

2.2 ANALYTICAL METHODOLOGY

Figure 4 is a flow diagram describing the main components of the analytical systems employed for Hg analysis by the 2 labs using manual methods. The dual Au amalgamation/de-amalgamation technique (Fitzgerald and Gill,1979) was used in analyzing all samples generated by the manual methods. In each instance, after thermal release of the analyte as Hg^0, either from the TGM trap or from the PPM samples, detection and quantitation was achieved by CVAFS. Chemical analyses were performed in each lab by experienced personnel.

Each of the participating labs calibrated their CVAFS detector using a saturated Hg^0 vapor calibration method essentially the same as that described in a 1987 Canadian Standards Assoc. report (CSA,1987). The Tekran analyzers contain a Hg^0 permeation tube source (secondary standard) which was calibrated against manual injections from a saturated Hg^0 vapor calibration unit. Both instruments were calibrated daily, using the perm. source calibration procedure: each cartridge in the instrument goes through a "clean", "zero", "span", and "clean" sequence of operations.

As is customary in environmental measurements of trace contaminants, each study participant used "field blanks" or "procedural blanks" which were processed through the entire series of sampling and analytical steps as if they were actual samples, except that they did not have ambient air pulled through them. The resulting "blank" values were subtracted from the analytical results ("raw data") obtained for the field samples. For the instrumental method, the procedural blank values were obtained by sampling (UHP grade) zero air (10 L) through each of the two cartridges for the duration of one sampling period (5 minutes) before desorbing the cartridge. It should be noted, however, that this procedure is not directly comparable to a manual method field blank, since even UHP grade compressed gases can contain residual amounts of impurities, including Hg^0 vapor. The procedural blank obtained this way would include the full contribution from any Hg contained in the zero gas and a true "field blank" for the instrumental method would be expected to be smaller than the values reported here. A summary of field and procedural blank values from the Windsor intercomparison study follows (Table I).

3. Results and Discussion

3.1 TGM IN AIR

The results obtained in the study for [TGM] in ambient air are shown in Figure 5. Of the 13 runs comprising this study, 8 produced meaningful results. For these 8 runs, all measurement results were in reasonably good agreement. The maximum deviation of individual results from the arithmetic mean of all 8 sets of results was about 35%. Considering the difficulties inherent in making ultra-trace Hg measurements, this degree of agreement is quite satisfactory. For 4 runs (# 8,10,12,13) the agreement was especially good. Often, the mean value of the results produced by the Au-coated beads and the Au-coated sand traps used by Lab A was in satisfactory agreement with those from the Au-coated bead traps used by Lab B. Most of the time, the 2 Tekran instruments gave values that were somewhat lower than those produced by the manual methods. However, whereas there was considerable variability among the individual results reported by Labs A and B, the 2 automated analyzers produced results which were consistently in very good agreement (see Figure 6).

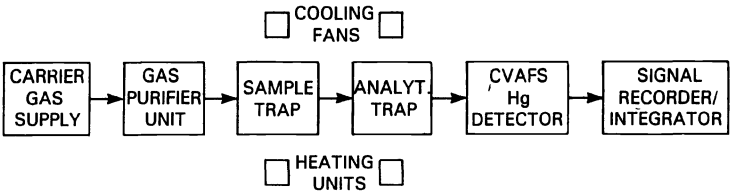


Figure 4. Schematic of generic atmospheric mercury analysis system

TABLE I

Summary of field blanks (manual methods) and zero air procedural blanks (automated instruments)

	n[a]	ARITH. MEAN pg Hg	STD. DEV. ±pg Hg	RANGE OF VALUES pg Hg
LAB A				
Au-B (A)	3	48	16	33-64
(B)	3	18	12	5-27
Au-S (A)	3	84	22	59-98
(B)	5	9	2	1-11
Partic	3	38	5	34-44
LAB B				
Au-B	6	28	23	<4-59
Partic	5	29	24	<4-53
INS A[b]	10	1.9	0.5	1.1-2.8
INS B[b]	8	1.6	0.9	0.7-3.8

a: number of determinations
b: based on runs with UHP "zero air"
Au-B: traps containing gold-coated glass beads
Au-S: traps containing gold-coated quartz sand
(A): for runs #1-6
(B): for runs #7-13
Partic: particulate-phase mercury filter media
INS: TEKRAN Model 2537A automated Hg vapor analyzer

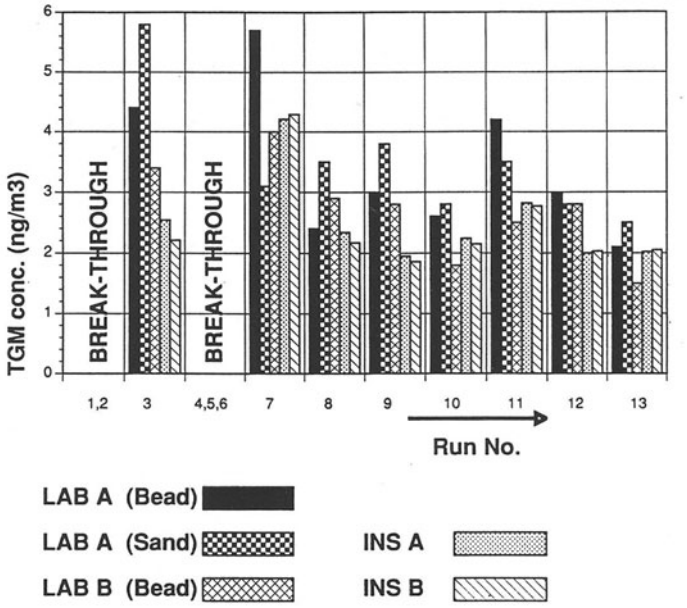


Figure 5. Total gaseous mercury (TGM) concentrations in ng/m^3 of air as reported by the 4 laboratories participating in the 1993 Windsor, Ontario, field intercomparison

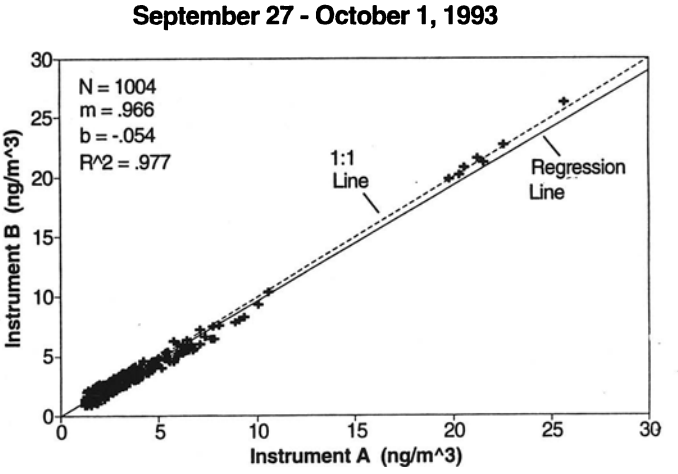


Figure 6. Correlation plot of TGM concentrations (ng/m^3) obtained with the 2 Tekran mercury vapor analyzers

As identified in Figure 5, five of the first 6 runs of the manual methods displayed break-through of Hg from the 1st trap onto the 2nd. Break-through is deemed to have occurred when more than the usual quantity of Hg is found on the 2nd (back-up) Au trap. Normally the amount of mercury detected on the 2nd trap is only a few % of that found on the first trap. Without implementing special diagnostic tests, the automated analyzers would not detect the occurrence of break-through since they do not use Au cartridges in series. Such tests were carried out on 2 occasions later in the week, after preliminary results of chemical analyses of traps from some manual runs indicated the occurrence of break-through. In these tests, a known amount of Hg^o vapor was added to the ambient air stream near the end of a 5-min sampling period to verify that the collection efficiency of the Tekran Au cartridge had not been compromised during the sampling cycle. The contribution of Hg from ambient air was known from the other instrument. In both instances complete recovery of the spike was found, confirming that at least for those runs (# 12 and 13) there was sufficient capacity for amalgamation of the Hg contained in the sample and in the spike.

For the 5 runs in which break-through occurred, the results obtained by Labs A and B were much higher than those obtained by the automated analyzers. Break-through of Hg on Au traps is a sampling artifact caused by "passivation" (i.e., de-activation) of the gold surface which collects the Hg contained in the air sample. Because both of the Au-coated sampling media utilized in the manual methods experienced considerable passivation (evidenced by break-through) the Hg vapor analyzers, since they too rely on the gold-amalgamation principle, may also have been affected. This could explain why the instruments gave lower values than the manual methods for runs 1,2,4,5,and 6. It cannot be ruled out, however, that for these runs the manual methods were subject to a positive bias (analytical interference) caused by one or more,as yet unknown,interfering substance(s). Sewage treatment plants may represent an especially challenging environment for atmospheric mercury measurements (Soldano et al.,1975).

During the runs which gave inconsistent results, the smell of hydrogen sulfide ("sewer gas") was quite strong. We know that H_2S and other 'reduced sulfur gases' (e.g., carbon disulfide, dimethyl sulfide, other alkyl sulfides & di-sulfides, as well as mercaptans) are sorbed onto gold surfaces. Also, for most of the time during the "anomolous runs", it was raining at the study site. The following trend in meteorological conditions prevailed: lower barometric pressure (~980 to ~990 mB); higher relative humidity (between 70 and 100%); weaker inversion conditions; milder air temperatures (~8 to ~14°C), as compared to the rest of the week; wind direction between ~200 deg (southerly air flow) and ~ 280 deg (westerly air flow). One or more of these parameters may have contributed to the observed anomolies.

Determination of atmospheric Hg based on the Au-amalgamation sampling technique coupled with CVAFS detection is subject to (at least) 2 possible sources of interference: (a) chemical species (other than Hg) present in air might interact with, be sorbed to, or be deposited on the gold surface (or the quartz-wool plugs in the traps used in the manual methods, but not the automated analyzers) so as to affect normal collection of Hg species. Indeed, one of the laboratories reported a distinct "sewer gas" odor during analyses of some traps used during the first 2 days of the study, clearly demonstrating that a significant quantity of sulfur compounds were collected along with (instead of ?) mercury. Potential chemical interferents include: hydrogen sulfide and other reduced sulfur compounds, gaseous ammonia, acidic gases such as HCl, HNO_3, H_2SO_4, NO_2, SO_2, Cl_2 and Br_2 (Cotton and Wilkinson,1962; McNerney et al.,1972; Ohkawa et al.,1976); (b) absorption of UV radiation (within the range of frequencies emitted by the instrument's light source) and fluorescence (or phosphorescence/light scattering/quenching) at the analytical wavelength by a substance in ambient air which is also retained on Au surfaces (initially in the sample trap and subsequently in the analytical trap) and then released into the detector cell along with the Hg^o vapor. Because of the multiple criteria which must be satisfied in case b), the occurrence of such an analytical interference is unlikely in the dual-stage amalgamation procedure for atmospheric Hg measurements. In practice, interferences of either type are not very common, at least in locations where the air is relatively clean/unpolluted.

Nevertheless, this is not the first time that measurement artifacts (methodological interferences) have been reported in connection with the use of gold (or other noble metals) as a collection medium for atmospheric Hg species (Schroeder et al.,1985). Thus, Slemr et al. (1979) reported that Au-coated quartz

wool collectors are "de-activated" by flushing them with 500 L of urban or "maritime air" (air passed through sea-water). While this de-activation appeared to have no effect on the subsequent collection of Hg^0, it did decrease the collection efficiency for dimethyl Hg from 94 to 73%. In an extensive study performed in a rural setting on the west coast of Sweden, Brosset and Iverfeldt (1989) sometimes observed a reduction in the Hg-amalgamating capacity of gold, increasing with the volume of air sampled through Au traps. This "blocking effect" resulted in lowered air concentration values for TGM at total sample volumes in excess of about 400 L. They observed that the extent of this "blocking effect" seemed to depend on climatological parameters (but did not elaborate on this statement). Brosset and Iverfeldt also observed that the Hg which broke through the first trap was "in no case" collected by the second Au trap in their sampling train. They report that "It looks as if Au, successively and in all the traps almost simultaneously, gets its surface blocked towards amalgamation during the exposure." In our study at the Windsor WPCP, the second traps (in those cases for which break-through occurred) did contain much higher amounts of mercury than was found for the "normal" runs. This suggests that the de-activation phenomenon in these 2 cases may have involved different substances and/or different mechanisms of action. Brosset and Iverfeldt showed that the blocking layer contained volatile, water-soluble constituents, "which may indicate that it consists of NH_4-salts, NH_3 complexes, or other substances." They note that the extent of de-activation/deposition seemed to vary from case to case.

The presence of a measurement artifact during the early part (only) of our study is also indicated by a comparison of the results from sequential 2- or 3-hour sampling periods vs concurrent 6-hour runs (Table II). The runs in which the Au-traps were changed after 6 hours (volume-weighted average concentration) generally resulted in values that were significantly lower than the time-weighted average concentration derived from successive concurrent 2- or 3-h sampling periods. In the absence of any measurement artifacts, the results from the short-term and longer-term sampling periods should, of course, agree (within the total measurement error).

3.2 PPM IN AIR

We cannot say at this time, whether the conditions which led to break-through of gas-phase Hg from the first Au traps onto the back-up traps of the manual sampling trains, on the first two days of our methods intercomparison, also affected the results determined for particulate-phase Hg by Labs A and B. The PPM concentrations reported by the two labs practicing the manual method are given in Table III. Lab A (which used glass fiber filters at a sampling flow rate of 30 L/min) consistently obtained results that were much lower than those obtained by Lab B (which used quartz-wool plugs at a flow rate of 300 to 500 mL/min). Only for the second sample were the results of the 2 labs even close; for the first sample they differ by as much as a factor of 10.

On the basis of some previous indications that small amounts (relative to Hg^0 concentrations normally encountered in the atmosphere, but of a similar order of magnitude as PPM atmospheric loadings) of elemental Hg vapor could be retained on quartz-wool plugs, Lab B used the following analytical procedure. Prior to the particulate-phase Hg determinations, the quartz-wool traps (while being maintained at a temperature of 100°C) were thoroughly flushed with argon gas for 4 minutes. However, for the PPM samples from Windsor, no significant release of Hg (taken here as >10 pg) was observed with this pre-treatment.

4. Summary and Conclusions

During the autumn of 1993, scientists from Canada, the U.S.A. and Germany met in Windsor, Ontario to take part in a field intercomparison of vapor- and particulate-phase atmospheric Hg measurement methods. This sampling and analytical methods intercomparison involved manual ("traditional") procedures as well as a new automated Hg vapor analyzer. It provided a valuable opportunity for

TABLE II

Comparison of time-weighted average (successive 2- or 3-h runs) and volume-weighted average TGM concentrations for concurrent 6-hour samples (as determined by the two laboratories using manual methods)

LAB A			LAB B	
Time-wt'ed average TGM conc. ng/m^3	Vol.-wt'ed average TGM conc. ng/m^3	Runs for Time-wt'ed average	Time-wt'ed average TGM conc. ng/m^3	Vol.-wt'ed average TGM conc. ng/m^3
22.8b (23.6;22.0)b	25.8b (21.5;30.2)b	1;2	14.0b (14.8;13.1)b	5.6b
11.0b (5.6;12.2;15.2)	4.3b (5.1;3.5)b	4;5;6	14.6b (10.7;12.8;20.4)b	5.7b
3.2 (3.0;3.4)	2.1 (N.D.;2.1)	8;9	2.8 (2.9;2.8)	N.D.
3.4 (3.8;2.9)	3.6 (4.5;2.8)	11;12	2.6 (2.4;2.8)	2.7

b: designates value(s) derived from trap(s) for which breakthrough occurred (i.e. higher than normal amount of Hg was found on the second (back-up) trap).
N.D.: no data. LAB A values in brackets, for "vol.-wt'ed average", are based on bead and sand traps, respectively.

TABLE III

Comparison of particulate-phase mercury concentrations (24-h average values) determined by Lab A and Lab B

Sample #	Lab A pg/m^3		Lab B pg/m^3	
1	82	81	810	600
2	190	184	250	270
3	107	102	2 peaks	2 peaks
4	43	45	240	230

collaborative testing of protocols for atmospheric Hg measurements under a range of field/meteorological conditions and methodological parameters. 13 runs were completed over a period of 5 days at the study site (a wastewater treatment plant). For 8 of the 13 runs, reasonable agreement on existing atmospheric TGM levels was obtained among all participants. However, in 5 of the 6 runs completed during the first 2 days of the study, measurement artifacts and inconsistent results were observed at this site (break-through of Hg from the 1st to the 2nd Au traps and unsatisfactory agreement between the manual and automated methods, and even among the two manual methods themselves). Agreement of results between the two labs which performed measurements of particulate-phase Hg is deemed to be unsatisfactory.

Even though great strides in atmospheric Hg measurements have been made in recent years, making reliable determinations of gaseous and/or particulate-phase Hg species in ambient air is not a trivial task. The scientific community should not become too complacent and assume that all challenges in this area have already been met. Measurement methods which are known to perform reliably and behave consistently in relatively clean air masses, as are generally encountered in rural locations or at remote sites, may not display the same levels of reliability and consistency in urban environments or industrial settings. Mercury is a multi-faceted chemical element which continues to display new or unexpected behavior and resists attempts to easily/readily determine the presence and abundance in the atmosphere of its ecologically/toxicologically significant species. Any given methodology for sampling and analysis of Hg present in the atmosphere (or other environmental media) must always be validated carefully in any new or unusual surroundings/circumstances.

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SOURCES OF MERCURY IN THE ARCTIC

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Abstract. *Global and regional emission inventories of mercury are reviewed with special emphasis on the source regions with potential impact on the Arctic environment. These sources are located mostly in Eurasia and North America and emit almost 1300 t of Hg to the air annually. Combustion of fossil fuels to produce electricity and heat is the major source of Hg. Major portion of the element emissions from this source is in a gaseous phase. A small portion of Hg emissions in Eurasia and North America is deposited in the Arctic region, perhaps 60 to 80 t annually. Additional amounts of Hg in the Arctic air originate from natural sources, although it is very difficult to quantify them. A small decrease of anthropogenic Hg emissions is observed in Europe at present. These emissions are expected to increase again in the near future.*

1. Introduction

Mercury has been measured in environmental samples collected in the Arctic and sub-Arctic region (e.g. SFT, 1994). Although the most of these measurements were carried out in the aquatic and terrestrial environments, atmospheric Hg deposition was also studied, particularly in northern Scandinavia (e.g. Iverfeld, 1991). A summary of recently reported concentrations, including those in the northern regions and deposition rates has been prepared by Munthe (1993). The atmospheric pathway is clearly contributing to the contamination of other compartments of the environment by Hg, also in the Arctic region. Both, direct and indirect estimates of total deposition of the element proved this hypothesis. Direct estimates of the total deposition can be carried out on the basis of information on emissions which are then used in various dispersion models. The indirect estimates are based on the element concentrations in peat bogs, lake sediments, and mosses.

During the last few years long- range transport of Hg within air masses has been studied in Europe and North America (e.g. Petersen, 1993). It was concluded that Hg deposition predicted by a Lagrangian trajectory model applied in Europe agrees with observations from the Scandinavian deposition network (Iverfeld, 1991) within a factor of two (Petersen *et al.*,

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1994). Even better agreement can be obtained through the improvement of mercury emission data, particularly with respect to the chemical speciation of the element.

Recent Hg measurements in peat bogs in Norway show a decrease of the element concentrations with depths corresponding to a time period of about 100 to 200 years (Steinnes and Andersson, 1991), thus, clearly indicating the effect of anthropogenic activities. The effect of long-range transport of Hg was also investigated using the element concentrations in moss as indicator of the atmospheric deposition over Scandinavia (Steinnes and Andersson, 1991). A south to north decreasing concentration gradient was observed except for the regions far north. The authors speculated that the enhanced dry deposition of Hg in the north can be related to a cold climate.

It can be concluded from the above mentioned and other studies that Hg can be transported within air masses to the Arctic and sub-Arctic regions and at least partially deposited there. How much of Hg can be brought to and deposited within these regions depends on many parameters. One of the most important parameters is the amount of emissions of the element, particularly in the regions with a potential impact on the Arctic environment. The purpose of this work is to assess emission fluxes of Hg with focus on emission regions having possible impact on the contamination of the Arctic and sub-Arctic air. Location of these sources is also described.

2. Global Fluxes of Mercury

Although quite extensive information exists on environmental and health effects of mercury and its behavior in the environment, much less information is available on the fluxes of the element to the air, water, and soils. The first quantitative worldwide estimate of the annual industrial inputs of 16 elements to the environment, including Hg has been prepared by Nriagu and Pacyna (1988). Summary of these estimates for the mid 1980's is presented in Table I. It can be concluded that the Hg emission to the air is comparable with direct inputs of the element to the aquatic environment and are almost a half of the direct releases to the terrestrial environment. No re-emission of Hg from the aquatic and terrestrial surfaces to the air was considered in these estimates.

Combustion of fossil fuels to produce electricity and heat is the major source of atmospheric emissions of Hg on a global scale. Major portion of Hg emissions from combustion of fuels is in a gaseous phase. In the combustion zone Hg present in coal or other fossil fuels evaporates in elemental form and then most likely a portion of it is oxidized while in the flue gases. The oxidized forms of Hg can be retained in modern flue gas cleaning systems. Mercury retained in fly ash (as well as in bottom ash) is then disposed on land or finds its way in a form of direct releases to the aquatic environment. It is very difficult to quantify these processes.

TABLE I

Global inputs of anthropogenic Hg to the environment (in 10^3 t/y) based on estimates by Nriagu and Pacyna (1988)

Environmental compartment	Source category	Emission
AIR	Combustion of fuels	0.7- 3.8
	Industrial manufacturing	0.1- 0.2
	Refuse incineration	0.2- 2.1
	Sub total	1.0- 6.1
WATER	Direct releases	0.1- 6.7
	Dumping of sewage sludge	0.1- 0.3
	Atmospheric deposition	0.4- 1.8
	Sub total	0.6- 8.8
SOIL	Direct releases	1.0-10.7
	Atmospheric deposition	0.6- 4.3
	Sub-total	1.6-15.0

Nriagu and Pacyna (1988) estimated that Hg in coal fly ash and bottom ash contribute up to 40% of the direct releases of the element to the terrestrial environment. As much as 40% of Hg entering the utility boilers in the United Kingdom is retained in flue gas control equipment and appears as liquid and solid wastes (in Pacyna, 1994). However, one should observe that

the flue gas control equipment, particularly the one for removal of gaseous pollutants is available mostly in the developed countries.

Refuse incineration seems to be the second largest source of Hg emissions to the atmosphere. Emission generation process for Hg during the incineration of wastes is similar to that during combustion of fossil fuels. However, more Hg in the oxidized form is expected from incinerators due to the higher content of chlorine in the wastes compared to fossil fuels.

While in the atmosphere, Hg undergoes various physical and chemical transformations (e.g. a review by Munthe, 1993) and finally is removed from the air by wet and dry deposition. Nriagu and Pacyna (1988) estimated that deposition on terrestrial surfaces is more than twice the deposition on aquatic surfaces (Table I).

Natural Hg emissions result from various processes including the off-gassing of Hg ladden rock, and volatilization of Hg from soils and vegetation, as well as from various water bodies. Mercury enters the atmosphere as a result of forest fires, volcanic activity, and other biomass burning. Elevated ambient temperatures tend to increase the rate of Hg loss from soils. Very few direct measurements of the flux of Hg, by species, have been made to date under a wide enough set of meteorological conditions to allow for extrapolation of the old data to the present day. On the basis of recent information on re-emission rate from water and soil it can be suggested that the natural emissions of Hg are of the same order as the emissions from anthropogenic sources.

It should be noted that emissions from natural sources are difficult to distinguish from secondary emissions and diffusive re-emissions from anthropogenic sources. These include re-emissions of previously deposited Hg, emissions resulting from discharge into water bodies and from contaminated soils. Hence, it is more appropriate to differentiate between pre-industrial and post-industrial diffuse sources (e.g. Lindqvist, 1991).

3. Sources of Atmospheric Mercury in the Arctic and sub-Arctic

Obviously, only a part of worldwide emission sources is responsible for the contamination of the Arctic environment. However, no quantitative assessment is available to conclude in details on the origin of Hg in the Arctic air. Therefore, information on the origin of other trace

elements and sulfur has been utilized in this paper to suggest the possible sources and source regions for mercury in the Arctic air. Of particular interest in this case are trace elements emitted from the combustion of fossil fuels and the incineration of wastes. They include antimony, arsenic, cadmium, zinc, selenium, nickel, and vanadium. The differences in the fate and the environmental behavior of Hg and the above mentioned trace elements were taken into account.

A quantitative assessment of the contribution of carbonaceous fuel combustion emissions to the Norwegian Arctic haze layers has been made using the receptor modeling approach (Maenhaut *et al.*, 1989), and two different dispersion modeling approaches (Pacyna *et al.*,1985; Akeredolu *et al.*, 1994). The assessment showed that up to 50% of various air pollutants, measured in the Arctic during winter and summer, were from fuel burning. Sulfur could not be quantitatively assessed owing to uncertainties in the magnitude of natural marine biogenic emissions and their fluxes to the Arctic. There is an indication, however, that over 50% of the non-sea salt sulfate present in the Norwegian Arctic is from fuel burning (Maenhaut *et al.*, 1989), and a similarly high percentage has been estimated for Barrow, Alaska, as well (Li and Winchester, 1989). Taking into account the above discussion on the presence of combustion-related air pollutants in the Arctic one can conclude that also Hg can be transported to this region.

An important question is where are the source regions which may contribute to the contamination of the Arctic and sub-Arctic air by Hg. No such source-receptor relationship studies have been carried out for the element. However, these relationships were studied for other trace elements emitted during the combustion of fossil fuels, as well as for sulfur (e.g. Maenhaut *et al.*, 1989). The results of these studies can be summarized as follows. Emissions from sources in Eurasia contribute more than half of the air pollution measured in the Arctic. The major source regions include the Urals, the Kola Peninsula, the Norilsk area, and the industrial regions in central Europe. Emissions from the Urals and the Norilsk area may be more important for the contamination of air over Alaska and the Canadian Arctic, whereas sources in the Kola Peninsula contribute more to the Norwegian Arctic. The contributions of the European and North American emissions to Arctic air pollution seem to be lower than the contribution from the Russian sources. The European and North American emission are,

however, major contributors to the contamination of the sub-Arctic regions, such as northern Scandinavia (the European emissions) and northern part of Canada (the North American emissions).

Obviously, there are also local sources within the Arctic and sub-Arctic region. Combustion of fossil fuels to produce electricity and heat is one of the major source categories present in the region, particularly for atmospheric Hg. However, the impact of these sources on the contamination of the Arctic air is on local scale only (e.g. Ottar et al., 1986).

4. Emissions of Mercury in Europe, North America, and Northern Asia

A summary of atmospheric emissions of Hg from anthropogenic sources in Europe, including the European part of Russia, the United States, and Canada is presented in Table II. The most recent European emission inventory for the element uses the 1987 statistical data (Axenfeld *et al.*, 1991). The inventory was prepared on the basis of emission factors and the results of these estimates are shown in Table II. These regional estimates were then compared with national emission data available from some countries. Both national and regional emission inventories indicate that the combustion of fuels, particularly coal, emits more than half of the atmospheric Hg in Europe (Pacyna, 1994). In some countries where combustion of coal is the predominant method to produce heat and electricity, the contribution of Hg emission from fuel combustion to the total national emission of the element is even bigger. A recent emission report from Poland concludes that fuel combustion generates more than 75% of the atmospheric Hg in the country (Hlawiczka, 1994).

Emissions from waste incineration in Table II are clearly underestimated. They represent emission data collected from 8 European countries only.

A national emission inventory of Hg and Hg compounds in 1990 has recently been prepared in the United States (US EPA, 1993). Emissions from combustion of fossil fuels contribute almost half of the US total emissions of Hg, followed by emissions from incineration of wastes. The estimates made in Canada are quite old and new data for 1993 levels are expected by the end of 1994 (UN ECE, 1994).

TABLE II

Atmospheric emissions of Hg from anthropogenic sources in Europe, the United States and Canada (in t/y)

Source category	Europe, 1987 (Axenfeld *et al.*, 1991)	The United States, 1990 (US EPA, 1993)	Canada, 1982 (Jacques, 1987)
1. Fossil fuel combustion	405	141	8
2. Industrial processes	275	32	16
3. Waste incineration	35	118	2
4. Other sources	11	19	5
TOTAL	726	310	31

Information on spatial distribution of Hg emissions is available for Europe and North America. European emissions are distributed within the UN ECE European Monitoring and Evaluation Programme (EMEP) grid system of 150 km by 150 km. This distribution is presented in Figure 1. Major emission sources are located in central and eastern Europe. Episodes of pollution transport from these regions to the Norwegian Arctic have been documented (e.g. Ottar *et al.*, 1986). In comparison, emissions in Scandinavia are low and the Hg concentrations measured in the Scandinavian environment are to a great extent due to the long-range transport from other parts of Europe. High emissions of Hg in the United Kingdom should also be noted.

Information on the location of major point sources of Hg emissions is available for the United States. In addition, the state-by state data are also estimated (US EPA, 1993). The largest emissions are estimated for the states around the Great Lakes, mostly due to coal combustion in the region. Atmospheric transport of pollution from this region northwards, with additional inputs from sources in Ontario has been a subject of preliminary studies (Clark, 1992). Combustion of fossil fuels in Alaska contributes about 1% of the Hg emissions from this source category in the country. A dozen of municipal waste incinerators and three sewage sludge incinerators in Alaska do not generate any significant emissions of atmospheric Hg.

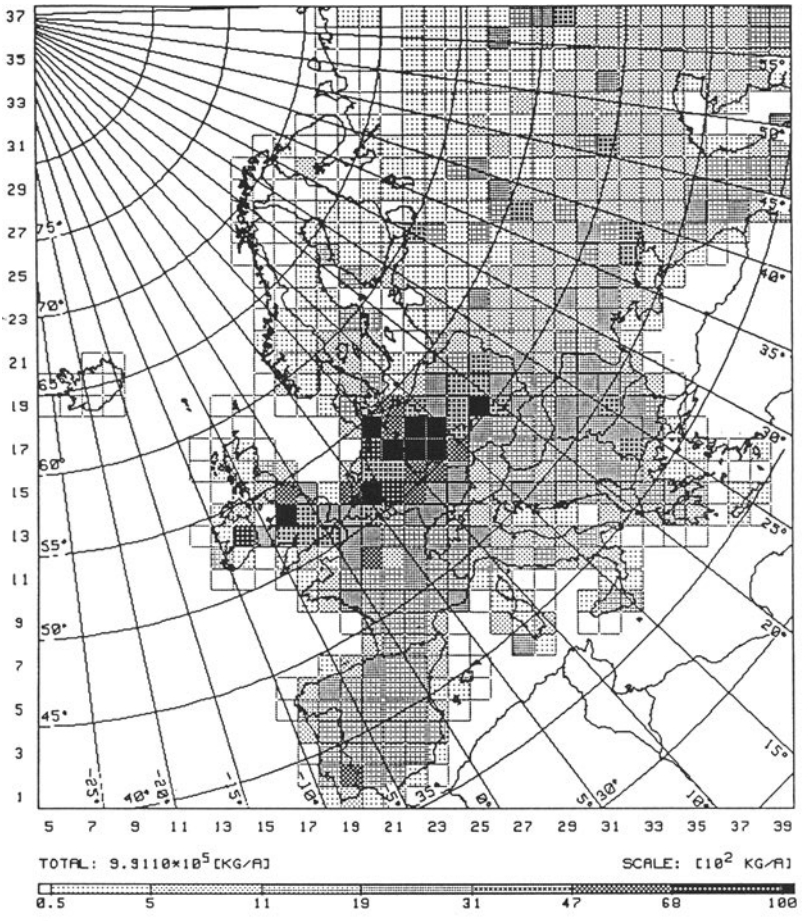

Fig. 1. Spatial distribution of total (anthropogenic and natural) emissions of mercury in Europe in 1987 within the EMEP grid system of 150 km by 150 km.

The Canadian emission data are available for all provinces, separately (Jacques, 1987). The largest emissions, about 10 t in 1982, were estimated for Manitoba, followed by North West Territories, Quebec, and Ontario. Huge emissions of about 3500 t/yr were calculated for natural sources in the country (in Voldner and Smith, 1989). These natural emissions are by far overestimated due to the overestimation of emission factors used in these calculations.

Less information is available on emissions of Hg in Asia, particularly in the northern part of the continent. Major emission source regions in the former Soviet Union and the emission quantities for several heavy metals were reviewed by Pacyna (1984). These data were used to assess the Hg emissions in this region. The results are presented in Table III. Again, the combustion of fossil fuels is the major source of atmospheric Hg emissions. The emissions from sources in the Ural dominate the emissions from other sources mentioned in Table III. The sources in the Ural include the production of non-ferrous and ferrous metals, chemical industry, and building material industry in addition to the combustion of fossil fuels (e.g. Pacyna, 1984). There are also other large source regions in the Asian part of the former Soviet Union, generating Hg and other trace element emissions to the air. They include the Kuznetsk area, the Fergana area, Caucasus, and the Baikal area. The location of these source regions in the southern part of the former Soviet Union raises a question whether sources a few thousand kilometers away can contribute to the Hg levels in the Arctic. Such very long range transport was suggested for some pesticides, e.g. lindane, used extensively in Asia and measured in the Arctic air (e.g. Pacyna and Oehme, 1988), and some crustal elements originating during dust storms in the Asian deserts and measured at elevated altitudes in the Arctic air (e.g. Pacyna and Ottar, 1989).

TABLE III

Mercury emissions from anthropogenic sources in the former Soviet Union at the beginning of the 1980's (in t/y)

Region	Combustion of fossil fuels	Industrial sources	Total
1. The Kola Peninsula	14	6	20
2. The Pechora Basin	6	2	8
3. The Norilsk Area	14	6	20
4. The Urals	110	44	154
5. The Yakutsk Area	22	2	24

The total emissions of Hg in Eurasia and North America are about 1300 t/y. No estimates were performed to assess what portion of these emissions enter the Arctic region and is

deposited there. Such calculations were made for other trace elements. An estimated 11 to 14% of antimony, arsenic, cadmium, lead, zinc, and vanadium, predicted to be entering the Arctic by the model used by Akeredolu *et al.* (1994) are deposited there. As much as 12% of the anthropogenic sulfur reaching this region from mid-latitudes is deposited in the Arctic (Jickells *et al.*, 1988). It was also estimated that up to 6% of the total emissions of arsenic, cadmium, lead, zinc, vanadium, and antimony in all of Eurasia is deposited in the Arctic (in UN ECE, 1994). About 6% of sulfur emissions in Eurasia is also deposited in the Arctic (Barrie *et al.*, 1989). If the same proportion is true for Hg, up to 60 t of the element emitted in Eurasia can be deposited from the air in the Arctic region annually. Additional quantities of the element would originate from anthropogenic and natural sources of Hg in North America.

5. Trends of Mercury Emissions

The decreasing trend of Hg levels in the atmospheric deposition in Scandinavia has been observed during the last few years (Munthe *et al.*, 1994). This trend was related to possible decline of Hg emissions, particularly in Central and Eastern Europe. As much as 30% decrease of these emissions can be expected. The decline of the economical growth in this part of Europe at the beginning of the 1990's, related to the transition of the centrally planned economies in these countries to the market oriented ones was suggested as the major reason for the possible changes of Hg emissions. No doubt, the lower consumption of fuels in Eastern Europe during the recent years has caused the decrease of Hg emissions.

Reasons for likely decrease of Hg emissions to the air in Western Europe and North America are different and relate mostly to the installation of control equipment removing sulfur and nitrogen compounds from exhaust gases in various industries. This equipment removes also other gaseous pollutants, including Hg.

An interesting question is whether the above mentioned-decline of Hg emissions into the air is a permanent process or whether an emission increase can be expected in the near future. Munthe *et al.* (1994) conclude that the industrial decline in Eastern Europe and consequently lower electricity and heat demands is only a temporary process. Therefore, emissions of Hg are expected to raise again in the near future.

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MERCURY CONCENTRATIONS IN FISH IN A REMOTE CANADIAN ARCTIC LAKE

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Abstract. Lac Ste. Thérèse, a remote Canadian Arctic lake in the Northwest Territories, Canada, has high natural (non-point source) mercury concentrations in fish. The high mercury levels have persisted for over 18 years. Lac Ste. Thérèse has had consistently higher mercury concentration in fish than the other three lakes sampled within the basin, regardless of species tested.

1. Introduction

The Canadian Arctic is perceived by the general public to be a pristine environment which is completely free of contamination. This is not the case, as global atmospheric deposition of anthropogenic contaminants and local physiographic factors can impact on the quality of northern ecosystems (Barrie *et al.*, 1992). The presence of mercury within the ecosystem is generally well documented. Lower levels are normally associated with either natural or long range transport from anthropogenic sources while higher levels are usually the result of some direct anthropogenic source, such as mining or dams (Lindqvist, 1985; Zillioux *et al.*, 1993). The elevated mercury levels in Lac Ste. Thérèse, a remote lake in the Johnny Hoe River basin, Northwest Territories, Canada, are of interest because there is no development within the basin.

This study examines the relationship of mercury concentration in fish from Lac Ste. Thérèse over time and compares the results to other lakes within the basin.

2. Methods and Materials

2.1. SAMPLE LOCATION

Lac Ste. Thérèse was the primary sampling site to determine if the historically high mercury values were still relevant to any future discussions about the lake in light of land claims. The other three lakes (Keller Lake, Lac Taché and Tseepantee Lake) in the Johnny Hoe River Basin (Figure 1.) were sampled to determine if high mercury concentrations in fish are consistent throughout the basin. The water quality is similar for all of the lakes with only minor differences (G.R. Stephens, unpublished data).

2.2. SAMPLE COLLECTION

The collection of fish species was prioritized by their importance for both human health consumption and the ecosystem. Top level piscivores such as walleye (*Stizostedion vitreum*) and lake trout (*Salvelinus namaycush*) were the primary focus. Northern pike (*Esox lucius*), another piscivore, was sampled because it is not generally restricted by lake chemistry like walleye and lake trout. Lake whitefish (*Coregonus clupeaformis*) was also collected since it represents a lower trophic feeder found in most northern Canadian lakes.

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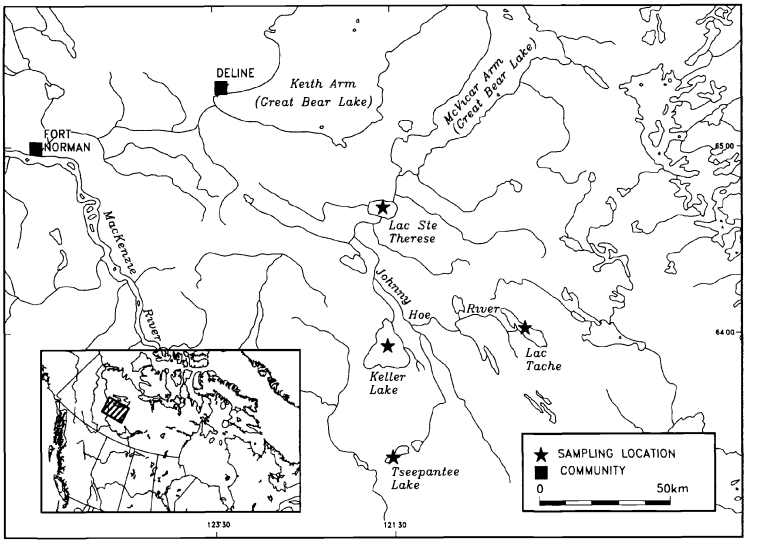

Fish were collected from Lac Ste. Thésèse in August 1992 and 1993 using 89 mm and 115 mm mesh gill nets with multiple sets of 4 to 12 hours in duration. The other three lakes were sampled in August 1993 using the same equipment and timing. In all instances, basic biological data were recorded including fork length, weight and sex. The appropriate ageing structures were recovered. A boneless, skinless fillet ($\sim$100 g) was collected from the area lateral and ventral to the dorsal fin. Each sample was placed in a whirl pack bag and frozen before being shipped to the Environmental Chemistry Lab at the Freshwater Institute in Winnipeg, MB. Total mercury concentrations were determined using the method described by Hendzel and Jamieson (1976).

3. Results

The reported mean mercury concentrations are unadjusted for length, weight or age of fish since both simple and exponential regression analysis showed no significant correlation.

3.1. TEMPORAL TRENDS IN LAC STE. THÉRÈSE

When the data collected in 1992 and 1993 for Lac Ste. Thérèse are compared with the 1975 (walleye) and 1980 (walleye, lake trout and northern pike) data from the Department of Fisheries and Oceans (DFO) Inspection Services Branch (Hendzel, pers. comm.), they create an 18 year record of mercury concentrations in walleye and a 13 year record for lake trout and northern pike. There is no historic information available for lake whitefish in Lac Ste. Thérèse.

Table I illustrates the unadjusted mean mercury concentrations in walleye, lake trout, northern pike and lake whitefish from Lac Ste. Thérèse over time. Both walleye and lake trout continued to have high unadjusted mean mercury concentrations. The concentrations in pike appear to have decreased along with mean length and weight. For

all species the 1980 samples had higher mean lengths and weights than the 1992 or 1993 samples. The lake whitefish had higher unadjusted mean mercury concentrations in 1993 than 1992, while the mean length and weight have decreased.

Table I
Historic unadjusted mercury concentrations and biological information for fish from Lac Ste. Thérèse.

YEAR	SPECIES	N	MERCURY (ppm)		LENGTH (mm)		WEIGHT (g)		AGE (years)	
			Mean	Range	Mean	Range	Mean	Range	Mean	Range
1975	Walleye	8	1.00	0.59-1.43	484	438-565	1126	907-1643	-	-
1980	Walleye	12	1.39	1.09-1.82	505	472-553	1457	824-1884	-	-
1992	Walleye	30	1.34	0.71-2.31	463	410-520	1016	700-1400	15.0	9-20
1993	Walleye	30	1.49	0.29-1.99	453	387-507	893	655-1191	14.0	9-17
1980	Lake Trout	12	1.25	0.80-2.52	849	700-1012	6962	4068-11291	-	-
1992	Lake Trout	4	0.949	0.68-1.40	658	620-688	2638	2250-3100	21.5	16-27
1993	Lake Trout	2	1.34	1.34	667	599-734	2593	2148-3018	35.5	32-39
1980	Northern Pike	9	1.45	0.62-2.51	841	729-985	4380	2674-6587	-	-
1992	Northern Pike	12	0.914	0.37-1.78	736	600-994	3079	1550-6300	11.7	6-21
1993	Northern Pike	4	0.735	0.25-1.09	684	535-750	2347	1160-2873	8.0	6-11
1992	Lake Whitefish	23	0.132	0.044-0.50	463	410-503	1324	850-1750	13.0	9-17
1993	Lake Whitefish	15	0.273	0.079-1.37	438	333-535	1109	445-2090	14.6	3-30

3.2. AREAL EXTENT WITHIN THE JOHNNY HOE RIVER BASIN

Table II summarizes the results of the comparison of mercury concentrations in walleye, lake trout, northern pike and lake whitefish from the four lakes within the basin for 1993. Not all of the species (walleye and lake trout) found in Lac Ste. Thérèse were present in all lakes. For all species the unadjusted means for mercury concentrations in Lac Ste. Thérèse fish were higher than those in the other lakes. While there might have been differences in length or weight between lakes, the ages of the fish were always similar.

4. Discussion

The results indicate that mercury concentrations in fish from Lac Ste. Thérèse have remained high over time implying that the input of mercury has been relatively constant. Since the data are not standardized, it is difficult to make definitive conclusions regarding the trend of mercury concentrations.

The comparison of lakes within the basin reveals that Lac Ste. Thérèse has the highest mercury concentrations in fish regardless of the species. While more work is required to accurately determine the reasons for these differences, the higher mercury concentrations can generally be attributed to water quality and basin morphology (Håkanson *et al.*, 1988; Wiener *et al.*, 1990; Bodaly *et al.*, 1993). Lac Ste. Thérèse is a brown-water lake located at the mouth of the drainage basin. Tseepantee Lake has the second highest unadjusted mercury levels and is also a brown-water lake but located at the headwaters of the basin. It is also a smaller, shallower lake than Lac Ste. Thérèse. Both

Keller Lake and Lac Taché are clear-water lakes that are part of independent subcatchments.

Table II
1993 unadjusted mercury concentrations and biological information for fish from the lakes within the Johnny Hoe River system.

LOCATION	SPECIES	N	MERCURY (ppm)		LENGTH (mm)		WEIGHT (g)		AGE (years)	
			Mean	Range	Mean	Range	Mean	Range	Mean	Range
Lac Ste. Thérèse	Walleye	30	1.49	0.29-1.99	453	387-507	893	655-1191	14.0	9-17
Tseepantee Lake	Walleye	15	0.926	0.25-1.42	439	364-479	820	531-973	16.9	11-23
Lac Ste. Thérèse	Lake Trout	2	1.34	1.34	667	599-734	2593	2148-3018	35.5	32-39
Keller Lake	Lake Trout	15	0.412	0.22-1.05	560	495-766	1811	1350-4325	19.6	8-32
Lac Taché	Lake Trout	5	0.345	0.13-0.59	662	556-774	2738	2029-4025	24.8	8-37
Lac Ste. Thérèse	Northern Pike	4	0.735	0.25-1.09	684	535-750	2347	1160-2873	8.0	6-11
Keller Lake	Northern Pike	1	0.445	0.445	769	769	2917	2917	-	-
Lac Taché	Northern Pike	10	0.347	0.13-0.68	689	520-987	2528	1000-6750	9.2	4-15
Tseepantee Lake	Northern Pike	6	0.475	0.39-0.71	512	453-557	770	565-870	7.5	6-8
Lac Ste. Thérèse	Lake Whitefish	15	0.273	0.079	446	336-535	1175	478-2090	14.1	6-24
Keller Lake	Lake Whitefish	15	0.064	0.036	471	377-553	1370	650-2313	11.6	7-19
Lac Taché	Lake Whitefish	15	0.068	0.025	402	312-500	797	420-1625	12.7	7-22
Tseepantee Lake	Lake Whitefish	15	0.102	0.037	425	345-460	1161	642-1440	11.7	6-21

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PRE-INDUSTRIAL ATMOSPHERIC DEPOSITION OF MERCURY: UNCERTAIN RATES FROM LAKE SEDIMENT AND PEAT CORES

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Abstract. Lacustrine sediment cores from depositional areas have frequently been used to estimate pre-industrial rates of atmospheric Hg deposition. However, this approach tends to result in overestimates, partly because of Hg inputs from the catchment, partly because of a horizontal redistribution of sediments within lakes. Peat core studies may suffer from a vertical migration of Hg due to water table fluctuations. A natural Hg deposition rate around 2 $\mu g\ m^{-2}\ y^{-1}$ is suggested to be more realistic than values of 3 to 12 $\mu g\ m^{-2}\ y^{-1}$ reported from recent studies. The anthropogenic impact on the present Hg deposition may have been underestimated accordingly.

1. Introduction

In temperate and boreal environments, atmospheric deposition rather than geology is usually the dominant source of Hg found in the organic compartments of lake sediments, soils, and biota (Lindqvist *et al.*, 1991; Nater and Grigal, 1992; Swain *et al.*, 1992). Pre-industrial deposition rates are of high interest for assessing both natural conditions and the anthropogenic contribution to the widespread contamination of aquatic and terrestrial environments even in remote areas.

The atmospheric residence time of Hg of up to around a year (Lindqvist *et al.*, 1991; Slemr and Langer, 1992) is long enough to allow atmospheric dispersal over large distances, but still short enough to lead to a rapid response to anthropogenic emissions in the form of increased deposition. Accordingly, the present distribution of atmospheric Hg is rather even (Slemr and Langer, 1992), and concentrations of Hg in precipitation are fairly constant or predictable over a wide climatic range (cf. Meili, 1994), whereas wet deposition rates of Hg may vary regionally with precipitation patterns.

Vertical profiles of Hg in lake sediments and peat soils have long been interpreted to reflect atmospheric deposition history (e.g., Johansson, 1980, 1985; Jensen and Jensen, 1991; Swain *et al.*, 1992). Careful comparisons suggest, however, that lacustrine sediment profiles rarely reflect the full extent of anthropogenic emissions (relative to a pre-industrial reference within the profile), and that the same may apply to peat profiles. In addition, Hg deposition rates in lake sediments usually exceed simultaneous atmospheric deposition. This paper is an attempt to reassess previous estimates of pre-industrial Hg deposition, which vary by an order of magnitude (1 to >10 $\mu g\ m^{-2}\ y^{-1}$).

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2. Methods

Primary data for demonstrating watershed effects on lacustrine sediment archives were obtained from sediment cores collected in the deep central part of small Swedish lakes without Hg emissions in the watershed (Johansson, 1980; El-Daoushy and Johansson, 1983; Björklund *et al.*, 1984; Johansson, 1985). Sediment characteristics at depths of 2 and 20 cm (Hg and organic content, interpolated from layers of 1-2 cm) were selected to represent present conditions (mixed surface layer, initial diagenesis completed) and pre-industrial conditions (around 1800), respectively (El-Daoushy and Johansson, 1983).

3. Results and Discussion

Pre-industrial Hg deposition in boreal and temperate areas has previously been estimated around 2 $\mu g\ m^{-2}\ y^{-1}$, of which about one third as dry deposition (Meili, 1991a and references therein). This value is supported by a recent study of a deep ombrotrophic peat bog record covering more than 10 centuries (Lucotte *et al.*, pers. comm.). In the following, this value is compared to recent studies of sediment and shallow peat cores.

Pre-industrial layers of sediments collected in the central part of remote Swedish lakes typically show a Hg concentration of 0.1 $\mu g\ (g\ dw)^{-1}$, a particle density of 0.1 $(g\ dw)\ cm^{-3}$, and an annual sediment deposition rate of 1 mm (Johansson, 1980). This corresponds to a pre-industrial Hg deposition on lake sediments of roughly 10 $\mu g\ m^{-2}\ y^{-1}$, which exceeds most recent estimates of pre-industrial atmospheric Hg deposition (1 to 5 $\mu g\ m^{-2}\ y^{-1}$; Meili, 1991a; Lindqvist *et al.*, 1991; Nater and Grigal, 1992; Swain *et al.*, 1992). A much higher deposition in lake sediments as compared to atmospheric deposition has also been suspected in Quebec (Lucotte *et al.*, 1995), with a pre-industrial Hg accumulation of 10 to 40 $\mu g\ m^{-2}\ y^{-1}$ in the sediment of remote shield lakes. Possible reasons are (1) a focusing of Hg from a catchment in steady-state (deposition = outflow) into a lake basin that has a much smaller area (e.g. Meili, 1991b), and (2) a focusing of fine sediments (e.g., Hilton, 1985) and associated contaminants (e.g., Edgington and Robbins, 1990) from shallow zones to deep zones within lakes. The geogenic contribution is usually negligible (Lindqvist *et al.*, 1991; Nater and Grigal, 1992; Swain *et al.*, 1992).

A pre-industrial Hg deposition of 3.7 $\mu g\ m^{-2}\ y^{-1}$ has been reported for midcontinental North America (Swain *et al.*, 1992). This value was elegantly derived by a linear extrapolation of a relationship between the pre-industrial Hg accumulation in lake sediments and the drainage ratio (catchment area / lake area), thus correcting for the Hg input from the catchments. However, estimates of pre-industrial Hg deposition as low as 1 $\mu g\ m^{-2}\ y^{-1}$ can be derived from the same data by non-linear extrapolation. Non-linearity is in fact more likely than linearity, as the retention in lake sediments of Hg from both direct deposition and catchment inputs declines with increasing drainage ratio due to an increasing export of Hg with the outflow (cf. Meili, 1991b). The assumption made of negligible Hg export in lakes with a drainage ratio of up to 6 (Swain *et al.*, 1992) may thus not be valid, and the pre-industrial Hg deposition derived by linear extrapolation of a

non-linear relationship is most probably overestimated. Further overestimation of Hg deposition in these lakes may have been caused by selectively studying depositional areas (Swain *et al.*, 1992), thus not fully accounting for the effect of sediment focusing.

Another effect of the watershed on estimates of pre-industrial or present rates of Hg deposition can be illustrated by comparing lakes with a wide range in drainage ratios within a small region (Figure 1). It is evident that the sedimentary Hg accumulation has increased substantially in all lakes, but also that the relative increase is strongly dependent on the drainage ratio. This dependence suggests a non-equilibrium of Hg in the catchment soils (input ≠ output), which is expected because of the slow turnover of soil Hg, and which results in a delayed response of sediment Hg to changes in Hg deposition (Meili, 1991a). As a result, the relative increase in sedimentary Hg accumulation does not reflect the full extent of change in atmospheric deposition, especially in lakes with a high drainage ratio. The same appears to be valid for the lake sediment data of Swain *et al.* (1992), who based on linear interpolations suggested a constant (ca. 3.5-fold) relative increase in Hg accumulation irrespective of drainage ratio. Non-linear extrapolations suggest instead that the increase over time changes with drainage ratio from 5-fold to 2- or 3-fold. This approach results in an estimate of present Hg deposition around 10 $\mu g\ m^{-2}\ y^{-1}$, thus improving the agreement with recent observations in the same area (cf. Swain *et al.*, 1992), and provides a pre-industrial Hg deposition of around 2 $\mu g\ m^{-2}\ y^{-1}$.

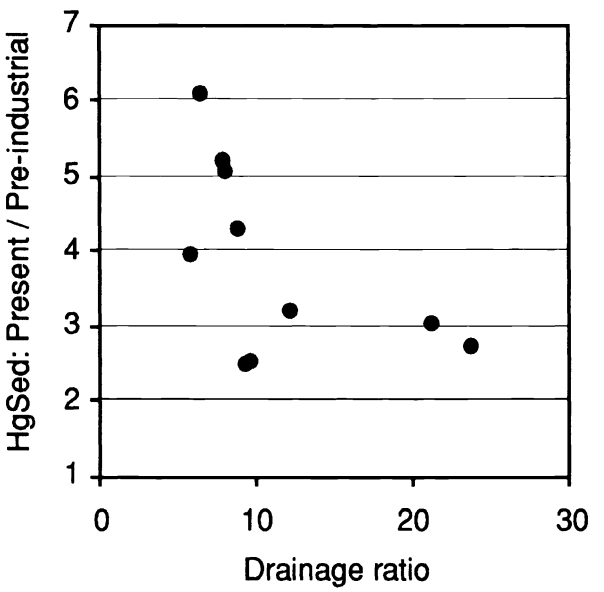

Fig. 1: Mercury in lacustrine sediment cores from small forest lakes in a minor region (80 x 120 km) of south-west Sweden: ratio of present and pre-industrial concentrations as a function of the drainage ratio (catchment area / lake area). Hg values were normalized for small differences in organic matter concentrations within cores by using ratios of Hg / org.

Mercury inventories in ombrotrophic peat bogs may be more closely related to atmospheric deposition of Hg, as catchment effects are absent. However, peat profiles may not always reflect atmospheric deposition properly in the surface zone, where water level fluctuations can lead to a vertical Hg transport over distances corresponding to decades or centuries of growth (cf. Grondin *et al.*, 1995). Accordingly, reconstruction of apparently historical patterns of recent Hg deposition over the past 200 years from shallow peat profiles (Jensen and Jensen, 1992) can show surprising patterns, such as an increase over time in remote areas but a decrease in industrialized areas. From these profiles, pre-industrial deposition was estimated at 4 to 12 $\mu g\ m^{-2}\ y^{-1}$, which exceeds most other estimates. This may be the result of a surficial downward migration of Hg in peat soils, which is supported by underestimates of present deposition from several cores.

4. Conclusions

Pre-industrial values of atmospheric Hg deposition in many temperate and boreal zones appear to be in the range of 1 to 5 $\mu g\ m^{-2}\ y^{-1}$ and may vary regionally with precipitation patterns. At precipitation rates of 0.5 to 1 $m\ y^{-1}$, a pre-industrial Hg deposition rate around 2 $\mu g\ m^{-2}\ y^{-1}$ (wet+dry) is suggested to be more realistic than values of 3 to 12 $\mu g\ m^{-2}\ y^{-1}$ reported from recent studies. The ratio of anthropogenic / natural Hg deposition may have been underestimated accordingly. Actual values and eventual regional patterns, however, remain to be assessed with greater accuracy.

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MERCURY SPECIATION IN THE SCHELDT ESTUARY

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Abstract. Surface waters of the Scheldt Estuary were sampled on various occasions between 1991 and 1994. Longitudinal particulate Hg (PM) concentrations ranged from 0.4 - 1.7 μgHg/g and are essentially controlled by physical mixing of polluted fluvial particulates with relatively unpolluted marine particulates. Total dissolved mercury (TDM)concentrations ranged from 0.5 to 5.2 ng/L and are strongly influenced by removal and mobilization processes in the upper estuary, while in the lower estuary mixing processes cause a progressive decrease in TDM towards the mouth. Speciation studies showed that dissolved Hg is predominantly bound to strong complexing ligands (organic substances) in the upper estuary , but this fraction decreases with increasing salinity. In June 1993, however, the reactive mercury fraction was also high in the upper estuary. Model calculations showed that a conditional stability constant for Hg- humic acid interactions of 10^{19} was a good estimate for the Scheldt estuary. Dissolved methylmercury was analyzed on three occasions. Significant seasonal variations were observed with concentrations ranging from 11 to 120 pg/L in the winter and 80 to 400 pg/L in summer. Supersaturation of Hg° is observed throughout the whole estuary resulting in an estimated evasion flux of 140-1400 ng/m^2.day .

1. Introduction

The river Scheldt crosses France, Belgium and The Netherlands on its way to the North Sea. It has a length of 355 km and a drainage area of 22000 km^2, mainly on Belgian territory. The average water flow is about 100 m^3/s and varies from 20 m^3/s during summer to 400 m^3/s during winter. The Scheldt estuary is a macrotidal coastal plain estuary, with an average tidal range of 4 to 5 m and an average depth of 11m. Under normal water discharges the estuary is well mixed. The residence time of the water is one to three months depending on the river discharge.

Morphologically, the estuary can be divided into three zones (Fig. 1). The lower estuary, called Western Scheldt, extends from the North Sea to the Belgian- Dutch border (km 0-60), the upper estuary is situated between the border and the river Rupel (km 60-100) and the fluvial river (fresh water zone) is situated between the Rupel mouth and Ghent (km 100-160) where a tidal range of two meter still exists. The upper estuary consists of one channel with a width between 0.4 and 2 km. The lower estuary is wider, up to 8 km, and consists of deep and shallow parts, with different ebb and flow channels. The zone under investigation (estuarine mixing zone) is situated between Rupelmonde and Vlissingen, covering an area of about 100km.

Physicochemically the estuarine mixing zone can further be divided in three zones (Baeyens et al., 1988). Zone 1 corresponds to the Western Scheldt, is characterized by coarse bottom sediments, aerobic conditions in the water column and salinities varying from 10 to 30 °/$_{oo}$. Zone 2 is situated between the Belgian Dutch border and the city of Antwerp and is characterized by a turbidity maximum, high sedimentation rates, fine grain bottom sediments (Wartel, 1977), oxygen undersaturation particularly in the summer (Somville and DePauw, 1982) and salinities varying from 2 to 10 °/$_{oo}$. Zone 3, situated from Antwerp to the confluence of the rivers Scheldt and Rupel, has salinities ranging from

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0 to 2 $^{o}/_{oo}$, clay bottom sediments, low sedimentation rates and oxygen depletion throughout a large part of the year.

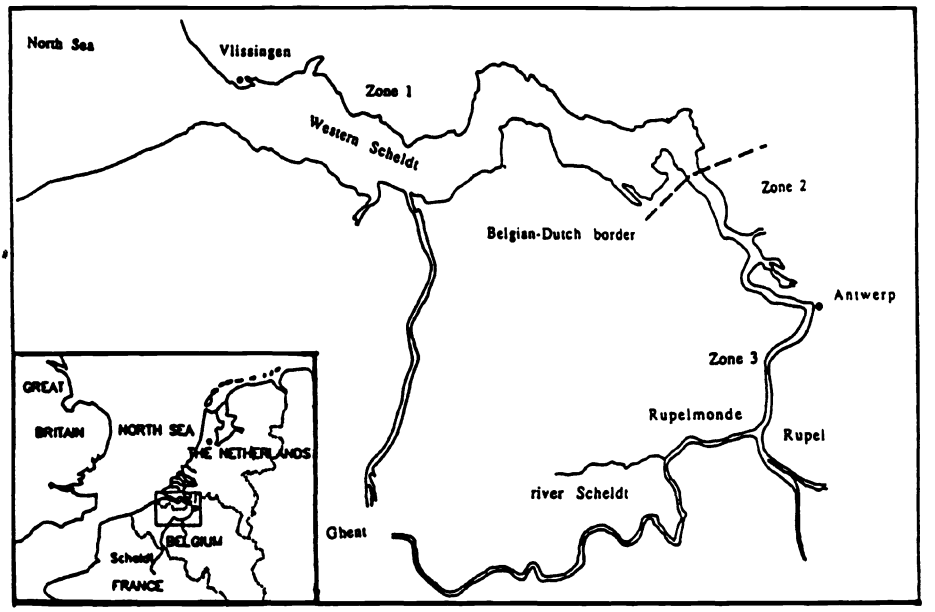

Fig 1. The Scheldt estuary

Both the fluvial and the upstream river are heavily polluted as a result of large domestic, industrial and agricultural waste waters discharges. A large fraction of the waste water is discharged without prior treatment, causing an intensive degradation of organic matter in the fluvial and upstream estuary. In this zone a permanent oxygen undersaturation and often complete depletion of dissolved oxygen in the water column is common. During summer, an anoxic zone from the mouth of the Rupel till the Belgian - Dutch border. In winter, the totally anoxic zone is much smaller or missing, though a pronounced undersaturation of oxygen is still present.

Due to the marked chemical and physical gradients in the estuary, the Scheldt estuary forms an interesting environment to investigate factors which control the speciation of mercury in aquatic systems. Seasonal profiles of particulate Hg and dissolved Hg species (labile Hg, Hg°, MeHg, Hg-tot) are presented and their relationship with various physicochemical parameters are discussed. Complexation of Hg with inorganic and organic ligands have also been simulated by model calculations and compared to the operationally defined speciation.

2. Methods and Materials

Samples of surface water were collected by hand from a rubber boat positioned approximately 100m up current of the research vessel R. V. Belgica. Sampling was

performed using teflon (FEP) or borosilicate glass bottles wearing arm-length gloves. The rubber boat moved gently against the current during sampling. FEP and borosilicate glass bottles had been rigorously cleaned by consecutive washes with Deacon-90, boiling HNO_3 and HCl 1% at 60°C in a laboratory oven. After the final rinse with Milli-Q water, the bottles were filled with Milli-Q water acidified to 1% with HCl (Merck, suprapur) and stored double bagged until use. The sampling bottles were rinsed twice with the estuarine water before being filled. The bottles were capped while immersed in the water to prevent oxidation of reduced waters in the time between sampling and handling. Once on board of the ship the samples were filtered on 0.45µm cellulose acetate (Millipore) filters by pressure filtration using a FEP filtration apparatus placed in a laminar flow hood and Ar as inert gas. Filtered samples were collected in FEP or borosilicate glass bottles. Samples for reactive mercury and total mercury were acidified with 1% HCl (Merck, suprapur). Samples for methylmercury analysis were stored deep frozen (unacidified). Measurements of Hg°, reactive and total Hg were carried out on board of the R.V. Belgica directly after sampling.

Total dissolved mercury, labile dissolved mercury and dissolved gaseous mercury were determined by cold vapour atomic fluorescence spectrometry using a Au-amalgamation preconcentration step. Dissolved gaseous mercury was measured by purging a 1L sample with Ar for 1 hour at a flow rate of 400mL/min and collection on a gold column. The water sample had been collected directly in the 1L purging bottle and the bubbler had never been in contact with a $SnCl_2$ solution. The bottle was covered with Al foil during purging to prevent photochemical reduction. Dissolved reactive mercury was measured using $SnCl_2$ as reducing agent; total dissolved mercury was analyzed by BrCl oxidation and reduction with $NH_2OH.HCl$ prior to reduction with $SnCl_2$. Detection limits are respectively 5pg/L for Hg°,15 pg/L for reactive Hg and 50pg/L for total mercury. Particulate mercury was measured by digestion of the filters in 5ml HNO3/HCl (4:1) at 60°C for 12 hours. Dissolved methylmercury was analyzed by aqueous phase ethylation, followed by cryogenic gas chromatography after seperating methylmercury from the interfering chloride matrix by an extraction with methylene chloride.

Temperature and salinity were recorded continuously (Seabird CTD). pH and oxygen were measured by the University of Brussels (ULB) and by the University of Liege (ULg). Turbidity measurements were made by weighing filters loaded with suspended matter after drying in a laminar flow hood.

3.Results and Discussion

RESULTS

1. Mercury in the Scheldt estuary: pollution record

The Scheldt river has been one of the most contaminated rivers regarding heavy metals such as mercury for many years. Industrial applications of mercury are essentially the alcali-chlor industry, the non-ferrous industry, PVC production and fosfate industry, located around the industrial harbor of Antwerp or along the tributaries of the Scheldt river. Industrial consumption of mercury has however decreased significantly in the last ten years (Devolder et al., 1991). If we compare total dissolved mercury concentrations as well as particulate mercury concentrations in the Scheldt estuary between the the survey performed from 1981 to 1983 and the present survey from 1991 to 1994 (Fig. 2a and b) we see a drastic decrease in the mercury levels during the last decade. Although total mercury

concentrations have significantly decreased the overall pattern (concentrations as a function of the salinity) remains very similar as well as the ratio of particulate to dissolved mercury. This can be explained by the fact that the water quality parameters affecting the distribution of mercury are still comparable.

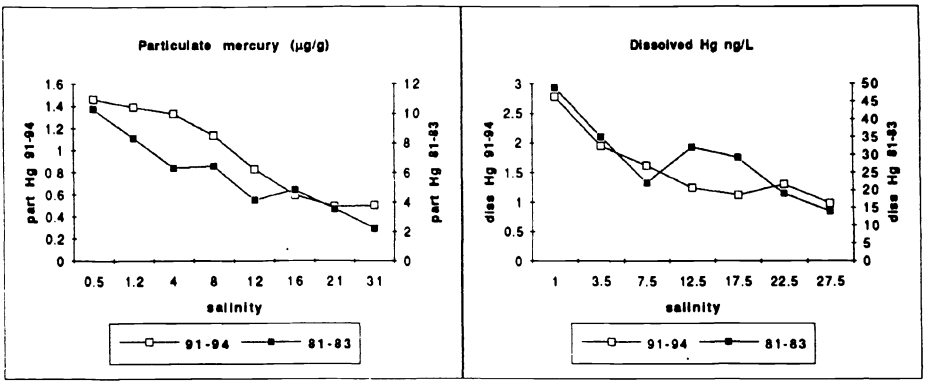

Fig 2. Comparison of Hg concentrations in the Scheldt estuary between the survey of 1981 to 1983 and the present 1991 to 1994 survey.

2. Speciation of dissolved inorganic mercury

Two cruises shall be used to explain the seasonal behavior of dissolved mercury forms in the estuary respectively the June 1993 and February 1994 cruise (Fig. 3). On both occasions inorganic speciation (Hg°, labile dissolved Hg, total dissolved Hg) was performed on board of the ship directly after sampling.

In Feb 1994 total dissolved mercury decreases exponentially from an upper estuary maximum to an almost constant level in the lower estuary. This type of profile was found in the majority of the cruises. Reactive mercury concentrations are low in the upper estuary (20% of the total dissolved mercury) and increase gradually to over 90% at the river mouth. The high amounts of dissolved organic matter entering the upper estuary by the tributaries of the Scheldt are responsible for the organic complexation of mercury in the upper estuary. A slight increase in total dissolved mercury is also found at a salinity of 10 $^{o}/_{oo}$. Highest turbidities were found at salinities of 0.5-1 and 7 $^{o}/_{oo}$ as well as a very high peak at 20$^{o}/_{oo}$. This peak is probably due to the influence of the canal Ghent-Terneuzen. The increased suspended matter did not contain very high amounts of mercury, diluting the particulate mercury concentrations, nor could a significant mobilization in the water phase be found at that site. The increased dissolved mercury at 10 $^{o}/_{oo}$ may be due to mobilization from suspended matter leaving the turbidity maximum zone. The cruise was also characterized by high residual flow rates (salinity < 4 $^{o}/_{oo}$ at the Belgian-Dutch border) excluding local inputs of the Antwerp harbor at 10 $^{o}/_{oo}$. Hg° concentrations were generally lower than observed in the summer (average 0.05 ng/L compared to 0.1 ng/L in the summer). A maximum concentration is found at 10 $^{o}/_{oo}$ salinity, corresponding to the zone where methylmercury concentrations are the highest. Bacterial demethylation may be an important process regulating dissolved metallic mercury concentrations in the estuary.

In June 1993 a totally different picture is obtained. Two production areas of dissolved mercury can be found; one with a maximum at a salinity of 6 $^{o}/_{oo}$ and a second at at salinity of 20 $^{o}/_{oo}$. Labile dissolved mercury concentrations follow the same pattern as total dissolved mercury. The fraction of labile bound mercury in the upper is higher than in the winter cruise. The large differences between labile and total dissolved mercury at the estuary mouth (more than 50%) can be explained by the methylmercury concentrations found there (39% of total dissolved Hg). The production zone at a salinity of 6 $^{o}/_{oo}$ may be caused by different factors. The observed maximum corresponds to the area where oxygen concentrations start to increase. Solubilization of precipitated HgS may occur. The area is also located in the industrial zone of the Antwerp harbor. Possible point sources of mercury cannot be excluded. The second maximum may also be influenced by inputs from the canal Ghent-Terneuzen followed by a gradual dilution towards the sea. Hg° concentrations remain fairly constant over the salinity range except in the phytoplancton rich water at the mouth of the estuary where Hg° concentrations are twice as high and reach up to 0.13 ng/L.

2. Dissolved methylmercury

Dissolved methylmercury concentrations vary significantly seasonally (Fig. 3). During the winter (Feb 1994; average temperature 3.8°C) the percentage of dissolved methylmercury ranged from 0.7 to 8% of the total dissolved mercury concentrations. During the summer (June 1993; average temperature 20 °C) dissolved methylmercury ranged from 7 to 39% of the total dissolved mercury.

In June 1993 two production areas of dissolved methylmercury were found in the estuary: one located at a salinity of 8 $^{o}/_{oo}$ and a second at the estuary mouth (salinity 32 $^{o}/_{oo}$); both around 0.4 ng/L. The maximum found at the mouth of the estuary is most likely due to the influence of the phytoplankton bloom which was observed at that time on the coastal stations of the North Sea and in the lower estuary (up to 25 $^{o}/_{oo}$ salinity). The upper estuary maximum may be due to an in situ production of methylmercury in the water column (biotic or abiotic) or a mobilization from particulate suspended matter. No relationship between dissolved methylmercury and oxygen concentrations was found. The methylmercury peak does also not coincide with the inorganic mercury peak, but is shifted 2 $^{o}/_{oo}$ higher towards the sea. An inverse correlation is found between methylmercury and dissolved reactive mercury.

In Feb 1994 dissolved methylmercury concentrations were much lower than in June 1993 (0.011-0.127 ng/L compared to 0.068-0.427 ng/L in summer). Maximum concentrations are found in the upper estuary (salinities 1-5 $^{o}/_{oo}$) where the oxygen concentrations are the lowest and two additional much smaller production zones are found: one with a maximum at 15 $^{o}/_{oo}$ salinity and a second at a salinity of 22 $^{o}/_{oo}$.

3. Particulate mercury

The particulate mercury concentration profile (Fig. 4) (µg/g) obtained on three sampling cruises slowly decreases from 0 to 5$^{o}/_{oo}$ salinity, then drops almost linearly between 5 and 20 $^{o}/_{oo}$ from 1.5 to 0.6 µg/g and reaches a constant value in the lower estuary.

Particulate mercury accounts for more than 90% of the total mercury. KD values (part Hg µg/kg)/(diss Hg µg/kg) vary from 200.000 in the lower estuary to 1.000.000 in the upper estuary.

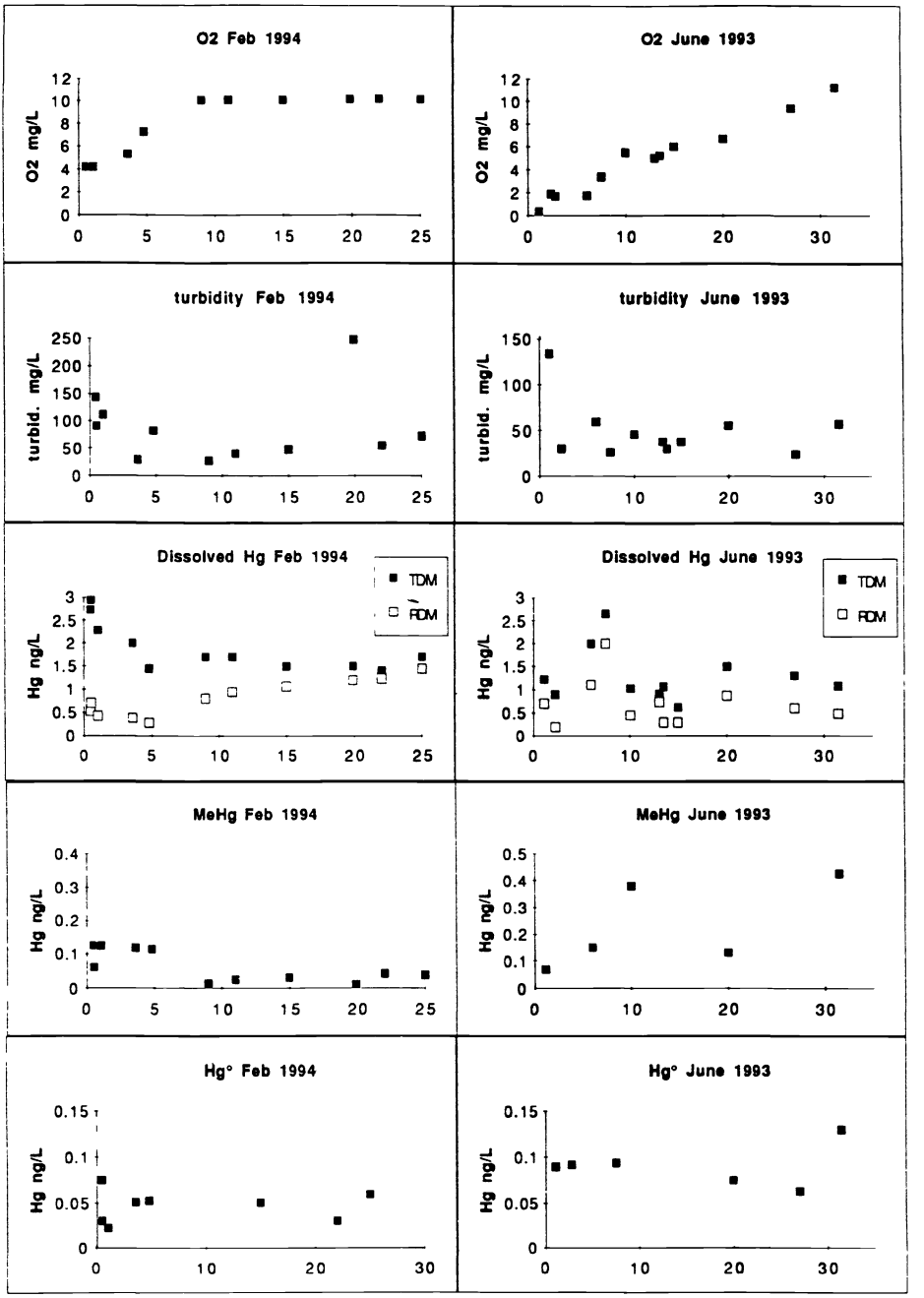

Fig 3. Dissolved Hg species, oxygen and turbidity profiles in the Scheldt estuary measured in June 1993 and February 1994

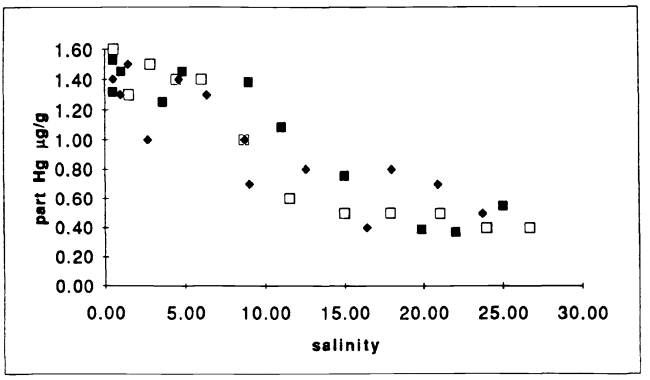

Fig 4. Average particulate mercury profile (µg Hg/g) in the Scheldt estuary

DISCUSSION

1. Distribution of mercury between particulate and dissolved phase

Association of mercury on particulate matter can be attributed to three main factors: 1) precipitation of insoluble forms (HgS), 2) adsorption or coprecipitation onto organic or inorganic solid phases and 3) uptake by living organisms.

The redox condition of the estuary is a crucial factor determining the speciation of dissolved and particulate mercury . Especially in summer months anoxic conditions prevail in the upper estuary, leading to the formation of sulfides in suspended matter and sediments (Zwolsman et al., 1993). Highly anoxic and contaminated sediments have been found on intertidal flats of the upper estuary (Panutrakul and Baeyens, 1991). HgS accounts for a large fraction of the total Hg in the estuarine sediments (Leermakers et al., 1991). HgS is highly insoluble (Ks 10^{-52}) and its oxidation very slow (Fagerström and Jernelöv, 1971).

The ratio of particulate to dissolved Hg is very high (KD ranging from 200.000 to 1.000.000). These values are in good agreement with the reported values by Balls (1989) as well as for results obtained by Nelson (1981) for the Thames estuary (KD 20.000 -200.000) and Imrer (1985) for the Elbe (KD 250.000 to 300.000). KD values in the lower estuary reflect physical adsorption desorption processes whereas in the upper estuary precipitation/oxidation of sulfides also have to be taken in account (KD values up to 1.000.000. The obtained KD values match previously reported KD values (Decadt,1986) although concentrations in dissolved and particulate phase were much higher at that time (Fig 2a and b).

Particulate mercury concentrations decrease gradually from the upper estuary towards the mouth due to conservative mixing of fluvial and marine suspended matter. However, a slight negative deviation from the average curve (Fig)is observed at the downstream end of the area of maximum turbidity which suggests mobilization from suspended matter during estuarine mixing. A small increase in dissolved mercury concentrations is observed in the water mass leaving that zone of maximum turbidity. As only a small fraction of mercury is present in the dissolved form, any factor affecting the distribution between dissolved and particulate phase may have an important affect on dissolved Hg concentrations. Enhanced dissolved mercury concentrations in the area of maximum turbidity have been reported for the St. Lawrence estuary (Cossa et al., 1988), the Gironde estuary (Cossa and Noel, 1987) and the Thames estuary (Nelson, 1981). This

increase may be attributed to a number of factors. In the upper estuary, high organic matter contents and high heterotrophic activity is found (Somville and Depauw, 1982). Mercury is preferably bound to organic matter in suspension and the degradation of this organic matter may release Hg into solution. The long residence time of suspended matter trapped in the zone of maximum turbidity may promote the more complete degradation of organic suspended matter. Dissolved mercury is predominantly complexed to organic ligands, probably deriving from the degradation of POM. Complexation may enhance the solubility of mercury. Another important factor is the oxidation of anoxic suspended matter and resuspended bottom sediments as oxygen is slowly restored in the estuary.

2. Speciation and complexation of mercury

Information on inorganic and organic speciation of mercury can be obtained using the operationally defined labile and total dissolved Hg forms in combination with specific MeHg analysis. If we look at the February 1994 cruise we see that the percentage of labile bound mercury is lowest (10-20%) in the upstream area where total dissolved mercury concentrations are highest and reach 80 to 90 % in the downstream area where total dissolved mercury concentrations are substantially lower. During the June 1993 cruise the labile mercury fraction in the upper estuary was substantially higher than normally expected which could reflect the influence on local pollution source for the first maximum obtained. The labile Hg fraction again attains 90% in the lower estuary as the organically bound mercury was shown to be predominantly methylmercury (Fig 3).

The extend of complexation of dissolved mercury in estuarine waters will vary markedly with the nature and concentration of the inorganic and organic ligands as well as their respective stability constants. Using the general equation:

$Hg_{(total)} = Hg_{(labile)} + Hg_{(non\text{-}labile)}$

$Hg(labile) = HgL_{inorg} + Hg_{(free)}^{2+} + Hg^{\circ}$ and $HgL_{inorg} = \Sigma\, Hg_{(free)}^{2+}(L_{inorg(free)})$

$Hg\ (non\text{-}labile) = HgL_{org} + MeHg$

The major species can be identified by calculations using known values of equilibrium constants and the concentrations of the ligands: $\beta HgL_n = [HgL_n]/[Hg_{(free)}^{2+}][L_n]$, where βHgLn is the conditional stability constant of the complex HgLn, while [HgLn], [Hg2+] and [L] are the concentrations of the complex, the free mercuric ion and the free ligand. A correct speciation involves a multitude of chemical equilibria as any metal can form a complex with any ligand.

Model simulations were made using the program TK-Solver for Macintosh. Concentrations of major ions (carbonate, bicarbonate, hydroxide, chloride and sulfate, calcium, magnesium) and DOC at 7 salinities (S= 1. 3.5, 7.5, 12.5, 22.5 and 30$^{o}/_{oo}$) were introduced into the model and stability constants for were obtained from Iverfeldt (1991) and Mantoura (1978). To describe the non-labile fraction it was assumed that besides methylmercury only mercury-humic compounds are to be considered and humic matter concentrations were estimated to be 10% of the total DOC (Valenta et al., 1986). Conditional stability constants (β)were calculated at the seven salinities based on the thermodynamic stability constant at infinite dilution and activity coefficients of the species that were calculated from ionic strength corrections using the Davies equation (Mantoura, 1978). Methylmercury species were not included in the model as no data are available on the formation constants between MeHg and DOC.

Simulations were made on basis of the results obtained in the February 1994 cruise, which is representative for an average profile. In a first simulation total mercury

concentrations (of which the methylmercury fraction was subtracted) were introduced into the model. The results are shown in Fig. 5a. Humic matter complexes account for more than 95% of the total dissolved mercury in the freshwater end and decrease to 2% at the river mouth were $HgCl_4^{-2}$ is the dominant complex. To check the validity of the model labile mercury was introduced into the model and labile mercury speciation was calculated. The results are presented in Fig. 5b. $HgCl_2$ is the principal labile Hg species in the freshwater end decreases towards the mouth proportionally to the increase in $HgCl_4^{-2}$. $HgCl_3^-$ accounts for 5 to 10% of the labile mercury . HgClOH accounts for 4.5% in the freshwater end but decreases rapidly towards the mouth. Concentrations of $Hg_{(free)}^{2+}$ were calculated to be 10^{-22} to 10^{-23} mM. Using this concentration the stability constant for the metal-humic complexes can be calculated as $Hg_{HA} = Hg_{(free)}^{2+} K_{HA}{}^{*}HA_{(free)}$ and free humic acid concentrations can be estimated as $HA_T = HA_{(free)} (1 + K_{Mg} Mg_{(free)} + K_{Ca}{}^{*}Ca_{(free)})$. The conditional stability constant obtained in this way was 10^{19} which was in good agreement with the constants reported by Mantoura et al.(1978) which have been used in the first model.

Both thermodynamic calculations and experimentally derived speciation are subject to several limitations.In thermodynamic calculations 1) equilibrium and homogeneity of the system are assumed 2) kinetic aspects are neglected 3) semi-empirical corrections are made for ionic strength and pH 4) the choice of thermodynamic constants is critical and there is a shortage of data for many Hg-ligand interactions especially MeHg-ligands 5) only major ions are considered as concentrations of ligands such as -SH, -CN which form strong complexes with Hg are unknown and 6) the interactions with multifunctional polyelectrolytes (humic and fulvic acids) is difficult to simulate due to the complex nature of these substances. Concentrations of humic matter are also based on estimations as only DOC data are available. On the other hand operationally defined species also have their limitations: sampling, pretreatment and analytical steps can change the original distribution in the sample. The reactive Hg fraction may increase depending on the time between sampling and analysis, the amount of acid added prior to analysis and the bubbling time due to a release of mercury from humic complexes ($HuHg + H^+ = Hu^- + Hg^{2+}$) in the acidic reduction solution (Millward and LeBihan, 1978). A large drawback is that the speciation MeHg complexes in estuarine waters cannot be simulated as no thermodynamic data exist for MeHg-DOC complexes and experimentally derived labile MeHg and total MeHg is subject to large uncertainties due to the interference of chloride in the direct ethylation of the sample.

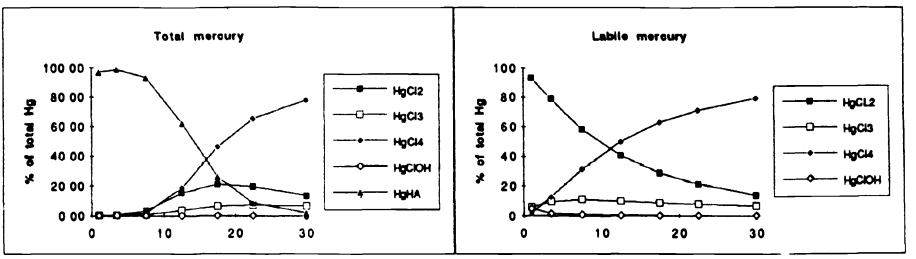

Fig 5. Thermodynamical derived speciation of dissolved Hg species: a. total dissolved Hg, b. labile dissolved Hg

3.Methylation and demethylation of mercury

The upper estuary provides a suitable site for the methylation of mercury (low O_2 concentrations, high organic matter contents, high heterotrophic activity and high Hg concentrations in sediments and suspended matter. Methylation reactions occuring in the sediments may also be an important source of methylmercury in the water column due to the high dynamic conditions (resuspension of bottom sediments). During the winter months we find an increased dissolved methylmercury in the upper estuary as oxygen concentrations drastically decrease though anoxia in not achieved. In summer the lack of high dissolved methylmercury concentrations in the upper estuary can be explained by the presence of dissolved sulfide (0.2-0.9μM) in the anoxic zone (Zwolsman, 1993) resulting in a scavenging of dissolved Hg^{2+} species from the water phase. Sulfide ion (S^{2-}) affects the methylation of mercury in sediments and water. At high sulfide concentrations, insoluble HgS will be formed and Hg^{2+} concentrations will be too low for a biotic or abiotic methylation reaction. In addition MeHg reacts abiotically in water and sediments to form HgS and volatile Me2Hg which may be volatilized (Craig and Bartlett, 1978,)

$2\ MeHg^{+} + S^{2-} \text{----} > Me_2Hg + HgS.$

Incubation experiments performed on sediments of an intertidal flat of the Scheldt estuary (Groot Buitenschoor) showed that sulfate reducing bacteria (or products formed by these bacteria) are involved in the of mercury in the anoxic sediments studied (Leermakers et al., 1993). Methylmercury concentrations in sediments of the Scheldt estuary range between 0.8 and 6 ng/g (0.5-1% of the total Hg, Muhaya et al., in preparation). Although no methylmercury was analyzed on suspended matter of the Scheldt estuary, we may consider that in the upper estuary, methylmercury concentrations on suspended matter will be comparable to methylmercury concentrations found in fine grain sediments accumulation on the intertidal flats. Estimations of particulate MeHg in the water column range, using an average turbidity of 60mg/L, from 48 to 360 pg/L MeHg. This is the same order of magnitude as dissolved MeHg concentrations. Thus only 50% of total MeHg is bound to particles in contrast to inorganic mercury of which 90% is bound to suspended matter. The difference in speciation may be attributed to 1) the stability of CH_3HgS^- and $(CH_3Hg)_2S$ complexes (Iverfeldt, 1991) and 2) the association of MeHg with DOC for which stability constant are unknown. The thiol group, -RSH, has a superior capacity to bind MeHg, in comparison to ligands containing O and N donor atoms and the inorganic ligands CN^-, Cl^- and OH^-.

During the summer dissolved methylmercury concentrations are much higher than during the winter, suggesting that heterotrophic bacterial activity plays an important role in the methylation of mercury in the estuarine waters. Two areas of maximum methylmercury concentrations were found. One in the mid-estuary, in the vicinity of the turbidity maximum and one at the mouth of the estuary. The mid estuarine maximum can probably be related to the intense degradation of organic matter occuring in this area. Exoenzymes produced by microorganisms may be involved in methylmercury production. (Parkman et al., 1992). Due to the high amounts of DOC in this zone methylmercury may also be formed by humic matter (fulvic acids) interactions (Nagase, 1982; Craig and Moreton, 1985). Methylmercury concentrations are inversely related to dissolved reactive mercury. This can be expected as reactive mercury is an important substrate for biotic and abiotic methylation of mercury.

The high methylmercury concentrations found at the oxygenated waters at the mouth of the estuary may be influenced by the phytoplancton blooms of the coastal waters. Significantly higher amounts of dissolved gaseous mercury was also found in this zone.

The physicochemical conditions prevailing in the estuary do not only promote methylation, but also the competitive demethylation and volatilization reactions. The formation of Hg° can be the result of either a) bacteriological reduction of inorganic mercury and methylmercury by narrow- and broad spectrum bacteria respectively (Nakamura et al.,1990), b) reduction of dissolved Hg by phytoplankton (Mason, 1993) c) an electron transfer reaction in Hg humic complexes; a mechanism which is also enhanced by solar radiation (Iverfeldt, 1984). Hg° concentrations are not significantly higher in the anoxic upper estuarine waters were they are thermodynamically more stable. Hg° concentrations range from 20 to 130pg/L. The latter high value was observed at the mouth of the estuary, in the summer, when high plancton concentrations were found at at the same time. Metallic mercury is supersaturated throughout the whole estuary, hence a daily efflux to the atmosphere of 140 ng/m^2day in calm weather conditions and an order of magnitude higher in the case of wave breaking conditions (stormy winds) can be estimated (Baeyens et. al., 1991).

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THE DISTRIBUTION OF DISSOLVED AND PARTICULATE MERCURY IN THREE SIBERIAN ESTUARIES AND ADJACENT ARCTIC COASTAL WATERS

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Abstract. Dissolved and particulate mercury distributions were determined in the three largest Siberian rivers and in adjacent Arctic coastal waters during two cruises. Water samples were collected in the Lena River and its mixing zone in the Laptev Sea in September 1991, and in the Ob and Yenisei Rivers and the adjacent Kara Sea in September 1993. Average total dissolved Hg concentration was 5.0 pM in the Lena River, 2.8 pM in the Ob River and 1.5 pM in the Yenisei River. Mercury content of suspended particulate matter was low, averaging 0.17 mg kg^{-1} in the Lena and 0.05 mg kg^{-1} in the Ob and Yenisei Rivers. These concentrations are lower than those observed in other world rivers affected by local input of man-made origin. In the estuarine mixing zones, higher concentrations of dissolved and particulate Hg which may originate from the spring flood were found. The carbon cycle is apparently a driving mechanism for Hg distribution in Arctic coastal waters. Particulate Hg content was positively correlated with the content of organic matter of the particles. In the Kara Sea, uptake by phytoplankton is suspected to be responsible for the increase in particulate Hg levels. Mercury fluxes from the three rivers to the Arctic Shelf are estimated and compared to direct atmospheric inputs.

1. Introduction

Arctic regions have long been considered to be pristine. However, volatile elements and substances, especially those from anthropogenic origin, have been shown to be subject to long range atmospheric transport. As a result of their volatilization and subsequent condensation, such chemical compounds may accumulate in polar regions (Barrie *et al.*, 1992). Mercury, which cycle is highly affected by anthropogenic emissions, is one of these compounds. Therefore, we suggest that the drainage basins of Siberian rivers flowing into the Arctic Ocean are collectors of atmospheric Hg deposition. Even though most of the deposited mercury may be trapped in the tundra, we hypothesize that part of it is transferred to the adjacent marine environment.

Owing to climatological conditions and logistics difficulties, Hg distribution in these major estuarine systems remains unknown. We report the concentrations of Hg in three Siberian estuaries during the summer season and discuss the fate of Hg during the fresh water - sea water mixing and the subsequent flux of Hg to the Arctic Ocean.

2. Study area

Three main rivers drain the Eurasian continent: Ob, Yenisei and Lena (Fig. 1). These rivers are the largest rivers draining to the Arctic Ocean in terms of water discharge.

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Together, they provide more than 50% of the annual water discharge and about 36% of the annual suspended particulate matter (SPM) export from the Eurasian Arctic basin into the Arctic Ocean (Gordeev *et al.*, 1993). The climate in the Siberian area is characterized by long cold winters and short cool summers. These rivers and the surface waters of the mixing zone have a thick ice cover during eight months. The temperature of the bottom waters of the Laptev Sea and the Kara Sea remains always below 0°C (Martin *et al.*, 1993). The rivers discharge about 60% of the annual water discharge and more than 70% of the annual SPM discharge during the flood period (May-July) (Gordeev *et al.*, 1993).

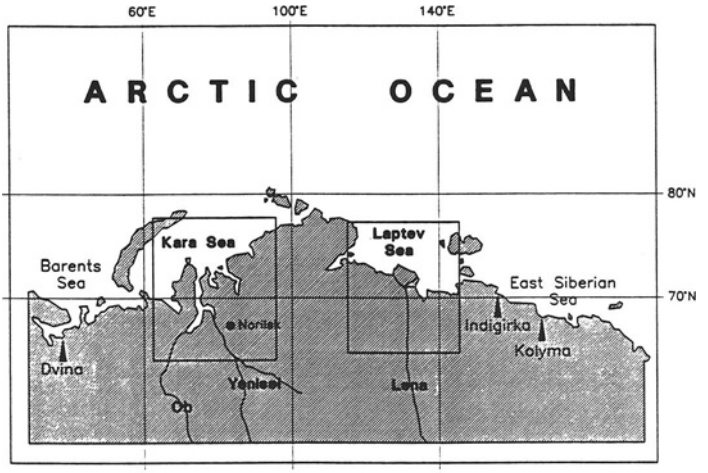

Fig. 1. The Arctic coast of northern Siberia.

The Lena River delta is located on the coast of the Laptev Sea which belongs to the East Siberian Basin (Fig. 1). The Lena represents the second largest river (after Yenisei) discharging to the Arctic Ocean and ranks first with regard to the total suspended matter export (Gordeev *et al.*, 1993) (Table I). It drains the Siberian forest (taiga) and tundra, and is characterized by a low particulate content as compared with other major world rivers, and by 'black' waters enriched in organic matter (Martin *et al.*, 1993).

TABLE I

Mean annual water and suspended matter discharge into the Arctic Ocean (Telang *et al.*, 1991; Gordeev *et al.*, 1993)

River	Drainage area ($\times 10^6$ km^2)	Length (km)	Mean annual water discharge (km^3 a^{-1})	Suspended solids discharge ($\times 10^6$ t a^{-1})
Lena	2.49	4,337	525	17.6
Ob	2.55	3,650	429	16.5
Yenisei	2.59	3,844	620	5.9

The Ob River is formed by the confluence of mountain streams Biya and Katun, both of them originating in the Altai Mountains. Ob represents the third largest river discharging into the Arctic Ocean (Gordeev *et al.*, 1993) (Table I). It flows through taiga forest then through the forest tundra zone and tundra (Telang *et al.*, 1991).

The Yenisei is the largest river of the Eurasian Arctic basin (Gordeev *et al.*, 1993) (Table I). The main hydrochemical characteristics of the Yenisei River are a low turbidity and a weak mineralization (Telang *et al.*, 1991). This is because the river flows across the mountains and the permafrost zones. The amount of SPM transported from Yenisei into the Arctic Ocean is the lowest of the three rivers (Table I).

In general, the low average turbidity observed in Laptev and Kara Sea basin rivers can be related to the wide-spread permafrost and the small thickness of the active layer on the drainage basins of these rivers and to the very short time with above freezing temperature (Telang *et al.*, 1991).

3. Sampling and analytical methods

3.1. Sample collection

Sampling was undertaken as part of a Russian-French cooperative program. Water samples were collected in the Lena River and the adjacent Laptev Sea from September 4 to 21 1991, and in the Ob and Yenisei Rivers and in the Kara Sea from September 15 to 29 1993. The location of the sampling stations is shown in Fig. 2.

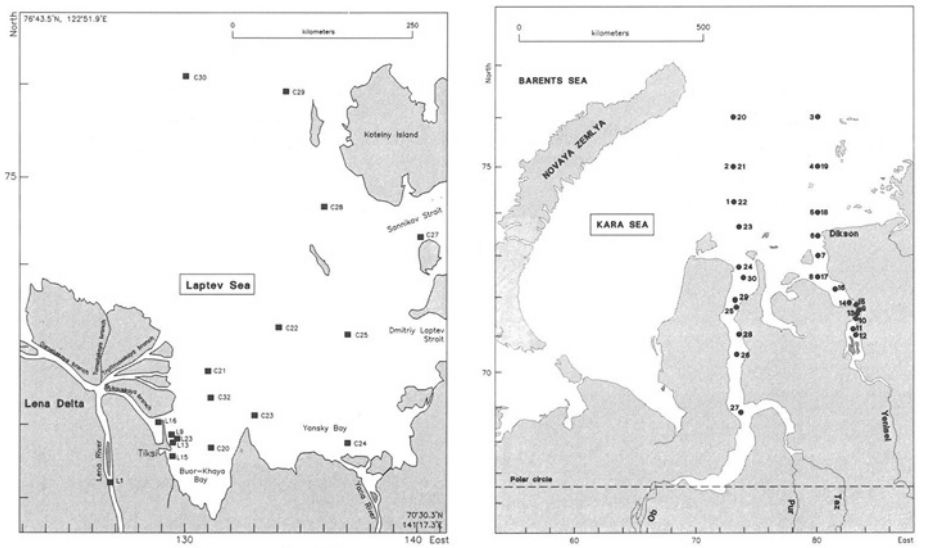

Fig. 2. Location of the sampling sites in the Laptev Sea and the Kara Sea.

For the Lena River, station L1 was located upstream of the divergence of the delta branches. River station L16 was established near the mouth of the Bykovskaya branch

which, on average, accounts for 27% of the river discharge to the sea (Létolle *et al.*, 1993). The Laptev Sea is shallow (generally less than 25 m) and subsurface samples were collected in the open brackish surface plume. Maximum salinity of the samples collected reached 19.6 and 32.6 in surface and deep waters, respectively, at the northernmost station (C30).

Two sampling transects were carried out in the Kara Sea, the first one at the Yenisei Estuary, from 76°N southward until we reached freshwater (stations 10 to 12), and the second one along the Ob Estuary, reaching river water at stations 26 and 27. Subsurface water samples were collected in the two estuaries. In the Kara Sea, subsurface samples were collected as well as samples from the halocline layer. The highest salinity obtained in subsurface samples was only 25.1, and deep water samples (salinity up to 34.1) were collected at four stations to provide sea water references.

Sub-surface samples were collected in 5 l Teflon bottles using a Teflon pumping system including an all-Teflon diaphragm pump (Asti, model PCS-2) and Teflon tubing. The tubing was maintained distant from the ship with the help of a 5m long pole. At two sites in the Kara Sea, surface samples were also collected from a small boat directly by hand in the 5 l Teflon bottles wearing arm-length polyethylene gloves, and the similarity of the Hg concentration measurements with pumped water samples was verified. Samples at depth greater than 10 m were collected with Teflon coated 5 l Go-Flo bottles (General Oceanics, FL, U.S.A.) fixed on a Kevlar hydrowire. Sample collection was performed under a laminar air flow hood and polyethylene gloves were used for handling operations to avoid sample contamination. All Teflon and plastic-ware was washed and stored according to Cossa *et al.* (1994).

3.2. ANALYTICAL METHODS

Samples were analyzed for total dissolved Hg ($[Hg_T]_D$) and total particulate Hg ($[Hg_T]_P$). For the separation of dissolved and particulate mercury species, water samples were filtered on board ship under a laminar flow hood through combusted (500°C) and acid-cleaned quartz fiber filters (Whatman QM-A, 0.8 μm) held in polypropylene filter holders. Filters were stored at -18°C in tightly closed polystyrene Petri dishes before analysis. Filtered water was transferred into acid-cleaned Teflon bottles and acidified with concentrated HCl (0.5% v/v, Suprapur Merck). The bottles were tightly sealed using pliers. Analysis were performed at the IFREMER laboratory. All Hg species were detected by cold vapour atomic fluorescence spectrometry after transformation to Hg^0 (Bloom and Fitzgerald, 1988) using a Merlin instrument (PSAnalytical). Concentrations of $(Hg_T)_D$ were determined after reduction by $NaBH_4$ and double gold amalgamation (Gill and Bruland, 1990). Concentrations of $(Hg_T)_P$ were measured after HNO_3/HCl (9:1) digestion of the particles in Teflon reactors, using Suprapur (Merck) acids, and reduction with $SnCl_2$ (Cossa and Fileman, 1991).

Detection limits, defined as three times the standard deviation of the blank expressed per unit sample analyzed, were: 0.7 pM for $(Hg_T)_D$ and 0.02 mg kg^{-1} for $(Hg_T)_P$. Method accuracy was routinely checked using available reference material (mercury in water 1641b from the U.S. National Bureau of Standards; marine sediments BEST-1 from the National Research Council of Canada). Precision, defined as a coefficient of variation of

duplicate or triplicate sample analyses, was lower than 20% (average 8%) for $(Hg_T)_D$, and lower than 10% (average 5%) for $(Hg_T)_P$ determinations.

Measurements of salinity, SPM concentrations, particulate organic carbon (POC) and chlorophyll pigments were performed using standard procedures.

4. Results and Discussion

4.1. Hydrology

Progressive mixing of the river waters in the Laptev Sea and Kara Sea results in the formation of large brackish surface plumes extending several hundred km northward, over more dense and saline waters. Examination of CTD (conductivity, temperature, depth) profiles in the Laptev Sea and the Kara Sea shows that a three-layer stratification could often be defined, with a thick brackish surface plume overlying an intermediate layer and a bottom water mass. According to these observations, tentative identification of the water masses from which samples were taken is presented in Table II.

In the Lena area, SPM content varies in subsurface waters from 29.6 mg l^{-1} in the river to 0.6 mg l^{-1} at the northern station in the Laptev Sea (Table II). For the Ob and Yenisei area, highest SPM content are also found in the river end members: 135.6 mg l^{-1} in the Ob and 20.4 mg l^{-1} in the Yenisei. In the surface water plumes, SPM content decreases as salinity increases to about 0.4 mg l^{-1} at the seaward extremity in the Kara Sea. The organic carbon content of SPM increases with the decrease of suspended load. Thus, higher POC content is found in particulate matter of the mixing zones than in the rivers. Such a relation between SPM and POC content of particles was previously described in several rivers by Meybeck (1982) and in the Lena (Gordeev and Sidorov, 1993).

4.2. Mercury in rivers

River water concentrations are represented by the freshwater data obtained for subsurface samples: stations L1 and L16 in the Lena, stations 26 and 27 in the Ob, and stations 10, 11 and 12 in the Yenisei. In these cases, a straight vertical profile of salinity was found showing the absence of stratification. Results of dissolved and particulate Hg analysis are given in Table II.

Total dissolved Hg concentrations in the rivers are comparable for the three rivers. Average $(Hg_T)_D$ concentrations range between 1.5 and 5.0 pM. These average values are low compared to the concentration range measured in other world rivers (Table III). Only the Krka (Croatia) and the Loire (France), which have no local sources of Hg contamination in their upper course, have comparably low levels. We restricted the comparison to a small number of recent credible data obtained in rivers draining climatologically and geologically diverse catchments.

Average Hg content of particulate material was 0.05 mg kg^{-1} in the Ob and Yenisei and 0.12 mg kg^{-1} in the Lena. The levels measured in the Ob and Yenisei are comparable to the lowest levels measured in non contaminated sites, for instance in deep marine sediments (Cox and McMurtry, 1981). Our values are lower than those of other world rivers (Table III).

TABLE II

Particulate and dissolved concentrations in the Lena, Ob and Yenisei Rivers and adjacent seas

Location	Station number	Water mass	Sample depth (m)	Salinity	SPM ($mg\ l^{-1}$)	POC (%)	$(Hg_T)_D$ (pM)	$(Hg_T)_P$ ($mg\ kg^{-1}$)
Lena	L1	river	2.5	0.1	28.8	3.5	5.4	0.03
	L16	river	-	0.3	18.5	3.1	4.5	0.21
	L9	surf.	-	0.4	10.4	5.9	3.2	0.11
	L13	surf.	-	1.9	4.2	-	3.0	0.32
	L15	surf.	-	3.7	2.9	13.2	3.5	0.35
	L23	surf.	2	0.8	29.6	3.7	2.5	0.08
Laptev Sea	C20	interm.	10	18.6	0.9	12.5	6.8	0.41
	C21	surf.	2.5	7.1	2.1	17.2	13.3	-
	C22	surf.	6	16.1	0.4	20.8	10.8	1.67
	C23	surf.	2.5	10.0	3.0	11.2	12.0	0.73
	C24	surf.	2.5	13.8	1.1	20.2	8.9	-
	C25	surf.	6	16.7	0.4	19.8	9.1	-
	C27	surf.	7	18.2	3.4	4.3	13.2	0.29
	C28	surf.	2.5	13.2	0.6	20.6	6.3	1.88
	C29	surf.	4	11.3	0.3	19.7	12.3	1.80
	C30	surf.	4	19.6	0.6	17.7	8.5	-
	C30	deep	35	32.6	-	0.9	4.0	-
	C32	surf.	3.5	8.2	1.5	20.0	9.4	0.11
Ob	26	river	9	<0.02	18.0	4.3	2.4	0.05
	27	river	9	<0.02	135.6	3.1	3.2	0.05
	23	surf.	5	17.79	2.8	3.6	2.1	0.04
	24	surf.	3	8.46	5.5	5.3	2.0	0.04
	25	surf.	0.2	1.37	16.2	4.1	3.1	0.03
	25	surf.	9	3.24	8.6	4.5	2.9	0.04
	28	surf.	9	1.11	14.5	3.7	2.9	0.06
	29	surf.	7	5.68	8.6	4.2	3.1	0.05
	30	surf.	4	16.09	4.1	3.8	3.8	0.05
Yenisei	12	river	9	0.02	5.5	6.8	2.1	0.04
	11	river	9	0.11	4.7	7.1	0.8	0.05
	10	river	9	0.24	20.4	4.3	1.5	0.06
	8	surf.	9	14.07	2.0	10.9	3.4	0.07
	9	surf.	9	0.99	3.9	5.4	2.8	0.10
	13	surf.	9	2.80	5.1	6.4	1.0	0.06
	13	surf.	13	11.23	10.7	4.3	1.4	0.05
	13	interm.	17	16.60	46.0	2.9	4.4	0.04
	14	surf.	7	2.09	4.2	8.4	0.8	0.07
	15	surf.	7	1.89	3.0	7.4	2.2	0.09
	16a	surf.	6	7.98	3.5	5.7	0.7	0.06
	16b	surf.	6	9.89	-	-	0.8	0.07

TABLE II (continued)

Location	Station number	Water mass	Sample depth (m)	Salinity	SPM (mg l^{-1})	POC (%)	$(Hg_T)_D$ (pM)	$(Hg_T)_P$ (mg kg^{-1})
	16a	surf.	8	9.18	3.4	4.6	1.7	0.07
	16b	surf.	8	8.30	-	-	1.1	0.06
	17	surf.	5	18.38	6.5	3.4	1.2	0.11
Kara Sea	2	surf.	8	21.32	0.42	10.2	6.7	0.11
	3	surf.	8	25.07	0.48	18.8	1.3	0.12
	4	surf.	9	23.64	0.40	11.3	0.7	0.03
	6	surf.	9	21.60	1.1	9.5	9.5	0.06
	18	surf.	0.2	16.14	1.3	7.3	2.0	0.09
	18	surf.	4	16.00	1.1	13.0	1.5	0.07
	19	surf.	5	23.66	0.36	7.6	1.2	0.11
	20	surf.	9	17.24	0.45	14.1	2.2	0.12
	21	surf.	9	22.07	0.31	11.2	6.5	0.25
	1	interm.	9	27.64	0.29	4.1	-	0.11
	4	interm.	15	29.18	-	2.3	12.1	-
	5	interm.	8	27.34	0.55	8.0	1.1	0.09
	7	interm.	9	31.40	1.4	7.4	4.6	0.06
	21	interm.	15	24.01	9.6	5.6	3.9	0.42
	22	interm.	9	27.11	0.20	8.8	5.1	0.24
	24	interm.	9	31.27	3.6	7.3	2.9	0.05
	3	deep	45	34.02	0.57	2.3	2.2	0.08
	4	deep	30	33.92	1.3	2.6	17.0	0.07
	20	deep	100	34.10	0.07	10.5	1.5	0.67
	21	deep	30	33.63	9.6	3.1	11.1	0.03

TABLE III

Comparison of average concentrations of dissolved and particulate Hg in the suspended matter of the Lena, Ob and Yenisei Rivers and other world rivers

	$(Hg_T)_D$ (pM)	$(Hg_T)_P$ (mg kg^{-1})
Lena (this study)	5.0 ± 0.6	0.12 ± 0.12
Ob (this study)	2.8 ± 0.6	0.05 ± 0.003
Yenisei (this study)	1.5 ± 0.7	0.05 ± 0.007
Seine (France) [1]	14.0 ± 14.0	1.22 ± 0.54
Loire (France) [2]	4.1 ± 2.1	0.19 ± 0.13
Rhône (France) [3]	7.0 ± 3.0	1.19 ± 0.99
Krka (Croatia) [4]	2.0 ± 1.0	

(1) Cossa *et al.*, 1994; (2) Coquery (1994); (3) Cossa and Martin, 1991; (4) Mikac *et al.*, 1989.

Concentrations measured in the Ob and Yenisei Rivers are more than one order of magnitude lower than heavily industrialized rivers like the Seine or the Rhône (France). Thus, in both the dissolved and the particulate phase, mercury concentrations are low in these Arctic rivers at the time of sampling. These low levels may result from a restricted human activity over the drainage basins and from the low temperature for most of the year, which limits the processes of erosion and weathering in the river drainage basins.

Particulate Hg represents the main fraction of mercury transported by the rivers: 64% in the Lena, 79% in the Ob and 59% in the Yenisei.

4.3. MERCURY IN THE MIXING ZONE

LENA

Examination of concentration variations in the mixing zone is restricted to the surface plume for the Lena, as mainly subsurface water samples were collected (Table II). Concentrations of $(Hg_T)_D$ are presented along the salinity gradient (Fig. 3a, b). Mercury concentrations are low in the river and for low salinity samples which correspond to recently formed brackish waters. Then, we observe a steep increase of Hg concentrations, from 5 pM to more than 13 pM, with higher salinity (above 5) that shows the $(Hg_T)_D$ enrichment in the mixing zone, away from the delta mouth.

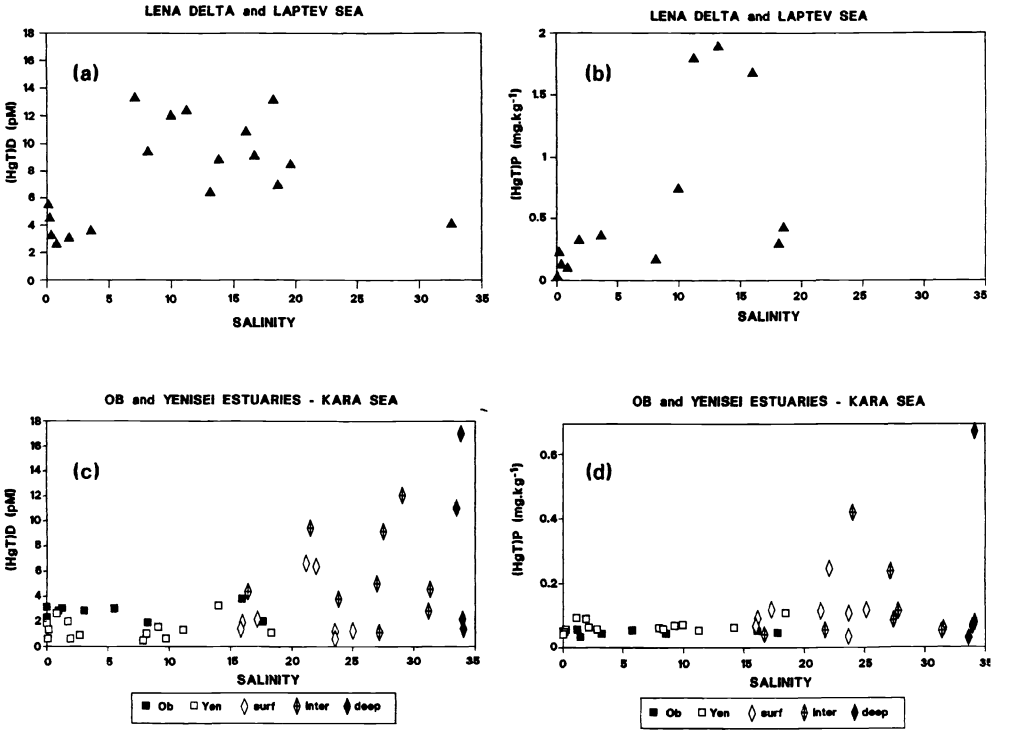

Fig. 3. Distribution of Hg concentrations (a) $(Hg_T)_D$ in the Laptev Sea; (b) $(Hg_T)_P$ in the Laptev Sea; (c) $(Hg_T)_D$ in the Kara Sea; (d) $(Hg_T)_P$ in the Kara Sea.

Concentration of $(Hg_T)_D$ in the deep marine water sample is lower (4.0 pM) and comparable to the two river values (5.4 and 4.5 pM, Table II).

Although scattered, particulate Hg content in the mixing zone is generally higher than in the river samples and increases up to 1.88 mg kg^{-1} in the mixing zone (Fig. 3b).

The dissolved Hg represents the main part of Hg in the Laptev Sea (average 69% for salinities above 5) and this partitioning is easily explained by the lower SPM content in the mixing zone than in the river samples.

OB AND YENISEI

Concentrations of Hg along the salinity gradient are showed in Fig. 3c, d. The distribution patterns for dissolved and particulate Hg are similar to those observed in the Lena Delta and Laptev Sea. Concentrations of $(Hg_T)_D$ are lower than 5 pM at low salinity and increase for higher salinities. In the Kara Sea, $(Hg_T)_D$ reaches up to 12 pM for salinities greater than about 20; whereas in the Laptev Sea, maximum concentrations were observed for intermediate salinities. This difference in the position of the maximum $(Hg_T)_D$ concentrations relatively to salinity suggests that the observed distribution is not a result of the formation of highly soluble chlorocomplexes as predicted by thermodynamic models (Morel, 1983)

Mercury concentrations in particulate matter are low in the rivers and greater in the mixing zone of the Kara Sea. As for Laptev Sea, $(Hg_T)_D$ in Kara Sea waters represents the major fraction of Hg (average 68%), according their low SPM load.

The deep marine water samples exhibit quite variable Hg concentrations. However, $(Hg_T)_D$ represents always more than 85% of the total Hg in these samples. The relatively high SPM content of some deep samples indicates that the marine end-member is probably not unique and sea-water masses of different age or/and origin may reach the mixing zone.

4.4. RELATION OF HG WITH PHYTOPLANKTON AND OTHER PARTICULATE ORGANIC MATERIAL

The Hg enrichment in particulate matter measured both in the Laptev Sea and in the Kara Sea is due to the well known affinity of Hg to organic matter. The significant positive correlations found between $(Hg_T)_P$ and POC (Fig. 4) are consistent with similar observations made in other marine environment (Lindberg and Harriss, 1974; Bartlett and Craig, 1981; Rae and Aston, 1982).

In the Kara Sea, where chlorophyll was measured, the significance level of the correlation between $(Hg_T)_P$ and chlorophyll is better than with POC considered as a whole (Fig. 5). At the time of sampling, the chorophyll content of riverine particles was low; we can conclude that Hg concentrations in SPM are mainly controlled by the mixing of a Hg-poor river material, probably dominated by inorganic components, with a Hg-rich marine organic material consisting of autochthonous phytoplankters.

Albeit the incorporation of Hg into particles due to biological uptake would usually result in low dissolved fraction in water, we observed an enrichment of the dissolved Hg fraction (Fig. 3c). This enrichment of dissolved Hg in the mixing zone may result from the input of Hg-rich organic material by the rivers floods and the melting of the ice sea-cover during the warmer season.

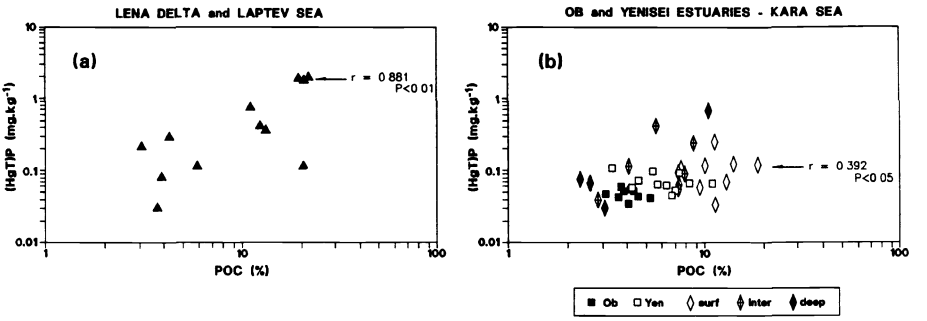

Fig. 4. Relationships between $(Hg_T)_P$ and POC (a) Laptev Sea; (b) Kara Sea.

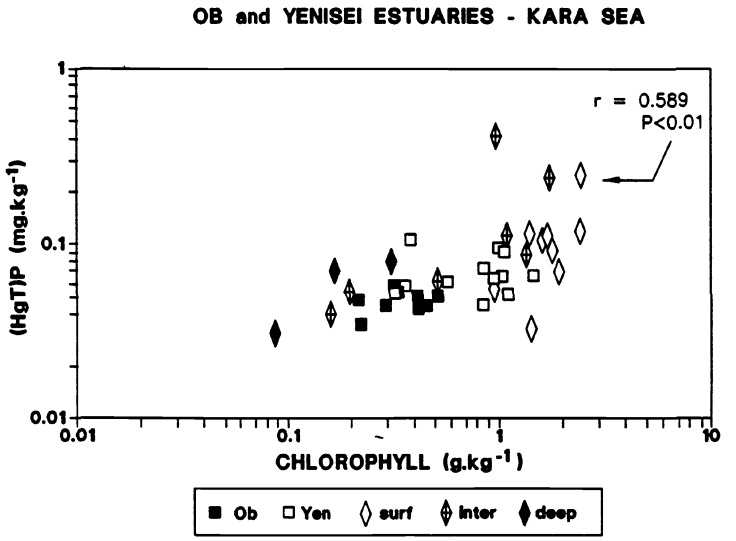

Fig. 5. Relationship between $(Hg_T)_P$ and total chlorophyll in the Kara Sea.

During the flood, the steep increase of water discharge takes place due to the melting of snow and to atmospheric precipitation. Large amounts of dissolved and colloidal humic substances as well as POC reach the river waters from surrounding forests, tundra, bogs and lakes (Telang *et al.*, 1991). It is possible that the water masses from the spring flood enriched in organic matter and in Hg (dissolved and particulate) are temporarily trapped in the mixing zone and still influence the carbon and Hg levels at the time of sample collection. Actually, the presence of such "old" water masses, enriched in organic carbon, was shown previously in the southern part of the Laptev Sea by Létolle *et al.* (1993).

4.5. Mercury Fluxes to the Arctic Shelf

Inputs of Hg from the Lena, Ob and Yenisei Rivers to the Arctic Shelf were calculated based on the average Hg concentrations measured in freshwaters in the present study and on the average annual water and SPM discharges recently re-evaluated (Gordeev *et al.*, 1993). Results of the calculation are shown in Table IV. These estimations of the gross particulate Hg inputs are based on the assumption that our Hg measurements, from September 1991 in the Lena and September 1993 in the Ob and Yenisei, are representative of the yearly Hg concentration averages. For the dissolved fluxes, we took into account the large difference in Hg concentrations between the flood and the dry season. During the period from August to April, we calculated the dissolved Hg fluxes assuming that the water discharge constitutes 40% of the total annual discharge; taking for $(Hg_T)_D$ the average of our measurements in the rivers. For the flood period (May-July), which flushes about 60% of the total water discharge, $(Hg_T)_D$ concentrations used in the calculations for the three rivers were taken as three times those of the dry period. This estimation was based on the extrapolation to zero salinity of the dilution line between Hg concentration and salinity (7.1 - 32.6) obtained in the Laptev Sea (Fig. 3a).

TABLE IV

Mercury fluxes to the Arctic Shelf

	$(Hg_T)_D$ (10^3 kg a^{-1})	$(Hg_T)_P$ (10^3 kg a^{-1})	Hg Total (10^3 kg a^{-1})
Lena River	1.15	2.9	4.0
Ob River	0.53	0.82	1.3
Yenisei River	0.41	0.31	0.7
Total Laptev Sea *	1.6	4.1	5.7
Total Kara Sea *	1.3	1.7	3.0
Total Eurasian Arctic Rivers *	3.9	11.3	15.2
Atmospheric deposition **			
Laptev Sea			2.0
Kara Sea			2.6

* Extrapolations on the basis of Hg fluxes of Lena, Ob and Yenisei rivers and average total annual water and SPM discharges from Eurasian Arctic rivers (Gordeev *et al.*, 1993).

** Surface areas: 662 10^3 km^2 for the Laptev Sea and 883 10^3 km^2 for the Kara Sea (Gorshkov, 1983).

Results were extrapolated to estimate the gross Hg inputs to the Laptev and the Kara Sea, and the total Hg flux from all Eurasian Arctic rivers which reaches 15.2 10^3 kg a^{-1}.

The direct Hg atmospheric deposition to the Laptev Sea and the Kara Sea was estimated using the lowest wet deposition rates of total Hg recently measured in northern Norway (3 μg m^{-2} a^{-1}) (Iverfeldt, 1991). Direct atmospheric inputs of Hg appear to be of

the same order of magnitude as those from the rivers (Table IV). Mercury evasion from sea surface remains to be assessed.

Mercury concentrations measured in summer in these three Siberian rivers are among the lowest ever measured in freshwaters. However, according to the elevated Hg concentrations measured in the mixing zones, Hg concentrations in the rivers during flood are probably much higher. These Arctic estuarine systems are influenced by anthropogenic inputs originating from atmospheric deposition; most of the Hg being released during flood time.

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METHYLATED AND ELEMENTAL MERCURY CYCLING IN SURFACE AND DEEP OCEAN WATERS OF THE NORTH ATLANTIC

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Abstract. Biogeochemical cycling of mercury (Hg) in the ocean and air-sea exchange are integral parts of the global Hg cycle. Ionic Hg (i.e. reactive Hg-Hg^0) is converted in ocean surface waters to elemental Hg (Hg^0) with the subsequent loss, via gas evasion, of the Hg^0 to the atmosphere. During a recent cruise in the North Atlantic Ocean, Hg^0 in surface waters was a substantial fraction of the reactive Hg (85%, on average) and there was a relationship between photosynthetic pigment concentration and Hg^0. In addition, there was evidence of Hg bound to "collodial" material (of greater than 1,000 molecular weight). Ionic Hg concentrations were around 0.15 pM, similar to the average colloidal Hg concentration of 0.2 pM. Methylated Hg compounds, both dimethylHg (DMHg) and monomethylHg (MMHg), were found in the deeper waters with DMHg being the predominant methylated species. This contrasts with freshwater lakes where MMHg is the principal species and no DMHg has been found. Preliminary modelling, using estimated rate constants for the formation and decomposition of DMHg and MMHg, predicts an enhanced stability of DMHg in ocean waters relative to fresh water. Deep ocean waters, formed by sinking of surface waters, can preserve DMHg that was produced in the more productive surface regime.

1. Introduction

The ocean is a significant source and sink for atmospheric Hg and air-sea exchange is an important feature of the global biogeochemical cycle of Hg (Mason et al., 1994a; Fitzgerald, 1989; Gill and Fitzgerald, 1987a; Mason et al., 1992). Elemental Hg, a major dissolved gaseous Hg species in surface ocean waters is usually present at saturated concentrations, and thus most aquatic systems are a source of atmospheric Hg due to volatilization at the air/water interface (Kim and Fitzgerald, 1986; Vandal et al. 1991; Fitzgerald et al., 1991; 1994). A number of studies (Mason et al., 1994c; Fitzgerald et al., 1994) suggest that direct reduction of ionic Hg is the predominant source of Hg^0 in the mixed layer, while demethylation is the principal source of Hg^0 in low oxygen waters (Mason and Fitzgerald, 1993). In natural waters, methylation, reduction and particulate scavenging are the three main processes consuming ionic Hg. As ionic Hg supply is typically limiting, these processes compete for the available ionic Hg, leading to rapid depletion of ionic Hg from the water column (Hudson et al., 1994; Hurley et al., 1991; Fitzgerald et al., 1994).

The aquatic chemistry of Hg is unusual compared with that of other trace metals because Hg can exist as dissolved and particulate ionic species, as organic complexes, as dissolved gaseous Hg (dimethylmercury (DMHg) and Hg^0), and as dissolved and particulate monomethylmercury (MMHg). Most contemporary investigations of the Hg distribution in the open ocean (Gill and Fitzgerald, 1985, 1987a, 1988; Gill and Bruland, 1987; Dalziel and Yeats, 1985; Olafsson, 1983; Brugmann et al., 1981; Cossa et al., 1992) and coastal waters (Dalziel, 1992; Cossa and Martin, 1991) have measured only reactive and total Hg. Our recent investigations

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have focussed on the Hg speciation in the equatorial Pacific Ocean (Kim and Fitzgerald 1986; 1988; Kim, 1987; Mason and Fitzgerald 1993; 1991; 1990; Mason et al. 1994b). Cossa and Martin (1993) measured Hg speciation at stations in the Mediterranean. DimethylHg was found in the deep waters of both the equatorial Pacific and the Mediterranean Sea. In freshwaters, MMHg is the predominant methylated Hg compound and studies indicate that high MMHg concentrations are found in low oxygen or anoxic environments (Bloom et al., 1991). DimethylHg has not been detected in temperate lakes (Vandal et al., 1991; Cossa et al., 1994). Methylation occurs both in the sediment and in the water column with sulfate reducing bacteria being the principal methylating organisms in both freshwater and estuarine environments (Gilmour and Henry, 1991).

There have been previous investigations of Hg in the North Atlantic (Olafsson, 1983; Gill and Fitzgerald, 1988; Dalziel and Yeats, 1985; Cossa et al., 1992), but no speciation measurements were made. We report here preliminary speciation data from a cruise in August 1993 in the North Atlantic as well as a model for MMHg and DMHg formation and preservation in ocean waters.

2. Methods

Sampling was conducted during the Intergovernmental Oceanographic Commission (IOC) Baseline Trace Metal cruise aboard the Canadian research vessel Hudson in the North Atlantic in August, 1993 (Figure 1). Collections were made at 9 stations, with additional surface samples between stations. Samples were analyzed on-board for reactive Hg and dissolved gaseous Hg (DGHg; Hg^0 and DMHg). Surface samples, in some instances, were analyzed for colloidal Hg (after acid digestion). Samples were frozen for later analysis of MMHg and total Hg and, when possible, water was filtered and samples stored for particulate Hg determination. Samples were also collected for the determination of photosynthetic pigments. Photosynthetic pigment analysis was performed by Jim Hurley at the University of Wisconsin (see Hurley and Watras, 1991 for analytical methods).

The analytical methods used have been discussed in detail elsewhere (Mason and Fitzgerald, 1991; 1993; Mason et al., 1993a). It is generally accepted, based principally on studies by Gill and Fitzgerald (1987b), that most of the Hg in open ocean waters (>80%) is reactive (i.e. reducible by $SnCl_2$ or DGHg). This is in direct contrast to coastal, estuarine and freshwater environments where a large fraction of the dissolved Hg (i.e. < 0.4 μm) is not "easily reducible" (Bloom et al., 1991; Mason et al., 1993a). Previously, reactive Hg was defined as that fraction of the Hg in natural waters that was reducible by $SnCl_2$ when the analysis was completed within 48 hours of acidification (Gill and Fitzgerald, 1987b). Bloom (1994), however, showed that Hg is often released within hours of acidification in freshwater and that analysis of unacidified samples provided a more accurate estimation of the labile inorganic Hg fraction, which the reactive Hg determination is thought to represent (Mason and Fitzgerald, 1990). Unacidified samples were analyzed for reactive Hg on the 1993 North Atlantic cruise.

Dissolved gaseous Hg species were determined by purge and trap techniques of the unamended sample. A 2 L aliquot was stripped of DGHg and the volatile Hg trapped on a gold trap for the estimation of the total DGHg fraction (Mason and Fitzgerald, 1991; Vandal et al., 1991). A further 2 L was degassed and trapped on a Carbotrap column for the DMHg determination. The Hg^0 fraction was determined as DGHg-DMHg (Mason and Fitzgerald, 1993). Methylmercury was determined by liquid extraction with methylene chloride prior to ethylation, gas chromatographic separation and atomic fluorescence detection (Bloom, 1989).

Reactive Hg was determined by addition of 1 mL of a acidic 10% $SnCl_2$ solution to 500 mL of unacidified seawater (Mason et al., 1993a). For total Hg analysis on board, a 1 L subsample of seawater was acidified with 1 mL of a 6 N HCl solution (Seastar^R) and allowed to digest for at least 72 hours prior to analysis by $SnCl_2$ reduction. For the determination of colloidal Hg, a 20 L surface seawater sample (prefiltered through a 0.4 μm filter) was subjected to cross-flow ultrafiltration using a 1,000 molecular weight cutoff membrane (Guentzel et al. (submitted)). The retentate and filtrate were collected and analyzed 72 hours after acidification, along with a sample of the feedwater, using $SnCl_2$ reduction.

3. Results and Discussion

3.1 WATER MASSES AND CIRCULATION IN THE SUBPOLAR NORTH ATLANTIC

The region of the North Atlantic covered during the cruise was that of deep water formation. Dense (cold and more saline) seawater from the Greenland and Norwegian Seas spills over sills on each side of Iceland, sinks to the bottom and flows southward (McCartney, 1991). Stations 7, 11, 13, and 14 sampled these waters before and after bottom water formation (Figure 1). By the time these waters reach Station 4, the station chosen here for detailed discussion, the deep waters are greater than 50 years old, and have increased in nutrient concentration due to inputs via particulate dissolution (Figure 2). Water age was determined based on known circulation patterns (McCartney, 1991) in this region and on preliminary results from Freon 11 and carbon tetrachloride measurements made during the cruise (Yeats, pers. comm.; Smethie, 1993). At Station 4, the deep waters formed by surface water sinking are beneath the northeast flowing intermediate waters (600-2100 m). At mid-depth, the overall flow is clockwise within the subpolar region (McCartney, 1991). Although the differences are small, it appears that the intermediate waters at Station 4 consist of two distinct regions - a lower oxygen (170 μM), higher salinity (35.0 ‰) zone above a higher oxygen (195 μM), lower salinity (34.88 ‰) region (Figure 2). The mixed layer was less than 50 m at Station 4 and the upper waters (100-600 m) - counterclockwise circulating subpolar waters - are less than ten years old. Overall, the nutrient profiles show an increase with depth, with the thermocline and the deep waters being the major regions of concentration increase.

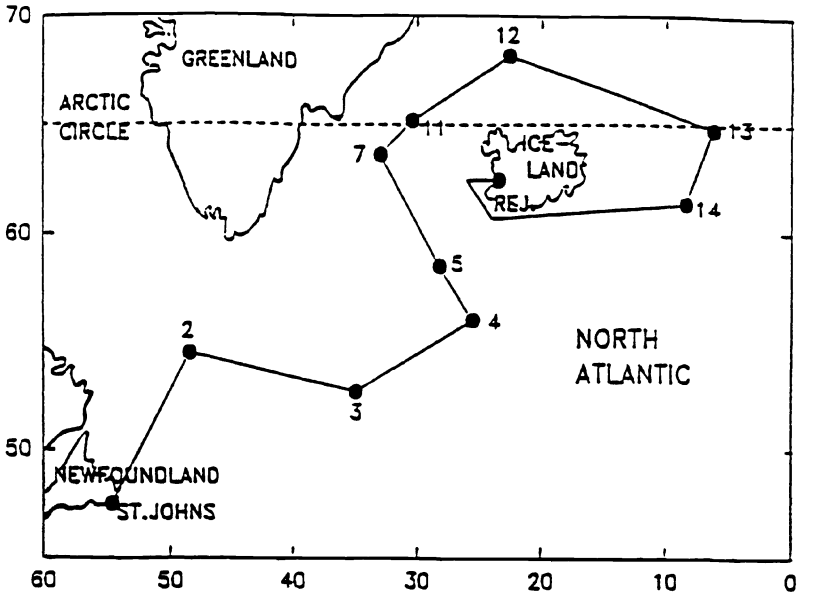

Fig. 1. The cruise track of the Hudson in the North Atlantic in August 1993.

3.2 TOTAL, REACTIVE AND ELEMENTAL MERCURY

Total Hg was measured on board, after 72 hours of acid digestion, at Stations 4, 5, 7 and 11. The mean concentration, 2.36 $\pm$ 1.6 pM (n=27), includes two higher values (5.55 pM at 50 m at Station 4 and 7.22 pM at 25 m at Station 7). Both these high values coincided with the bottom of the mixed layer/thermocline region and could reflect the presence of high particle densities. No information on other trace metals measured during the cruise, nor of particulate concentration, is available at present to support this assertion, however. Higher concentrations were also found in the thermocline of the equatorial Pacific (Mason and Fitzgerald, 1993) and other oceanic regions (Gill and Fitzgerald, 1987; 1988; Cossa et al., 1992).

Overall, there was less than a factor of two difference in the average concentration (the high values excluded) among these four stations (2.16 $\pm$ 0.86 pM at Station 4; 1.16 $\pm$ 0.36 pM, Station 5; 1.93 $\pm$ 1.0 pM, Station 7 and 3.06 $\pm$ 1.44 pM at Station 11). Station 11 was relatively shallow (1400 m), being in the Greenland Basin, and consisted entirely of $<$10 year old water. This trend of higher total Hg in "younger water" is also reflected in the profile at Station 4. Further, the Station 4 profile suggests that the older waters have a higher relative percent reactive Hg than the intermediate waters (Figure 2; Table 1), a reflection of particulate remineralization releasing reactive Hg and sedimentation removing particulate Hg.

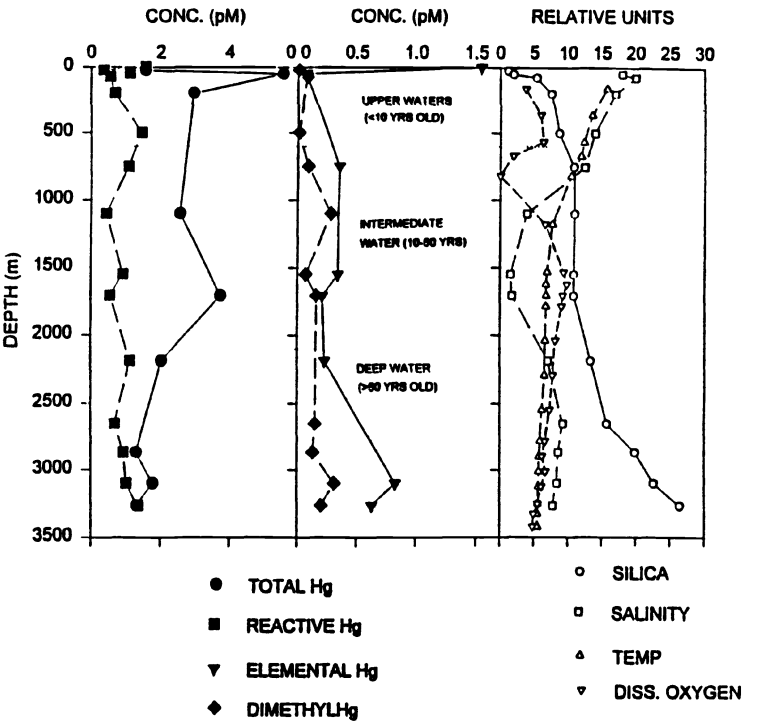

Fig 2 Concentration of mercury compounds and fraction (total and reactive Hg, dimethylmercury and elemental mercury) and hydrographic data for Station 4 (56 03°N, 25 53°W)

TABLE I
A summary of the mercury concentrations and speciation in the different water masses found at Station 4 (56 0° N, 25 5° W)

WATER MASS	MIXED LAYER	THERMOCLINE	INTERMED WATER	DEEP WATER
TOTAL Hg	1 55	4 25 ± 1 85	3 15 ± 0 83	1 70 ± 0 37
REACTIVE Hg	0 95 ± 0 85	0 94 ± 0 41	0 75 ± 0 31	1 03 ± 0 25
ELEMENTAL Hg	0 89 ± 0 91	0 07	0 30 ± 0 08	0 56 ± 0 31
DIMETHYLHg	<0 01	0 05 ± 0 05	0 15 ± 0 09	0 20 ± 0 08
%Hg°/REACT	94	8	40	54
%REACT /TOTAL	61	22	24	61

Reactive Hg concentrations varied between the detection limit (0.35 pM) and 2.05 pM. The concentration increased slightly with age for all samples, from 0.71 ± 0.41 pM for <5 year old water to 0.86 ± 0.35 pM for >50 year water. This lack of a distinct increase was evident at Station 4 (Figure 2; Table 1) as well, in contrast to the increase in nutrients in the deeper waters. Thus, remineralization alone is not controlling the deep water profile, suggesting that particulate scavenging or conversion of reactive Hg to other Hg species is important. Prior to the cruise, there was little information concerning the concentration and distribution of Hg in high latitude ocean waters. Olaffson (1983) measured a mean reactive Hg concentration of 8.5 ± 3.5 pM and total Hg of 11.1 ± 3.9 pM for the waters sampled during the current investigation; values significantly higher than the data presented here (Figure 2). A study by Brugmann et al. (1981) measured concentrations ranging from 0.5 to 5 pM for the region around the Faroe Islands. These values are more comparable to those found during this study. Concentrations found by other investigators, in various ocean regions are also similar to the present values, with somewhat higher concentrations being found in less remote regions of the world ocean.

There was a general increase in reactive Hg concentration from north to south. Stations 12 and 13 had the lowest concentrations (0.41± 0.11 pM and 0.54 ± 0.34 pM, respectively) while the more southerly stations had concentrations about a factor of three higher (0.91 ± 0.47 pM at Station 2; 1.23 ± 0.48 pM at Station 3). Surface water concentrations generally decreased northward from 0.79 pM near Station 2 to the detection limit at Station 12, before increasing in the vicinity of the last two stations, which were again further south. Elemental Hg was a significant fraction of the reactive Hg for all surface water samples (85% overall; 0.84 ± 0.45 pM Hg^0, 0.98 ± 0.9 pM reactive Hg), as found for Station 4 (Figure 2). For the mixed layer at Station 4, 94% of the reactive Hg was attributable to Hg^0 while in the deeper waters the fraction Hg^0/reactive Hg decreased (Table 1). Even in these deeper waters, however, Hg^0 is a much higher fraction of the reactive Hg than found in the equatorial Pacific where the Hg^0 was 15% of the reactive Hg, on average, for the mixed layer samples. The higher reduced Hg concentrations in the surface waters likely reflect the reduced inputs to the region via atmospheric deposition (little precipitation) during the cruise, and the productive nature of the waters. Under these conditions of limited input of reactive Hg, reduction consumes most of the input and the reduction rate is controlled by the rate of supply of reactive Hg to the mixed layer.

There is a strong correlation between the concentration of Hg^0 in the surface waters and the concentration of chlorophyll a, except at Stations 5, 7 and 11 (Figure 3). These stations were occupied after a storm with gale force winds had passed over the ship, and the cruise track between these stations. Substantial degassing of the mixed layer of Hg^0 at these stations as a result of this storm could account for the low Hg^0 concentrations, which are lower than would be expected based on the relationship between Hg^0 concentration and chlorophyll a for the other stations. A correlation between chlorophyll a and Hg^0 prpoduction has been shown for lakes and microorganism-mediated reduction of Hg(II) has been demonstrated with both pure cultures and with field samples (Mason et al., 1994c).

Some surface water samples were ultrafiltered (1,000 molec. wt. cutoff) by Rodney Powell of Bill Landing's group from Florida State University. Analysis

suggests the presence of colloidally-bound Hg (Hg_c) in surface waters (Guentzel et al., in prep.). Colloidal Hg ranged from <0.05 pM to 0.35 pM. These results are striking when one considers that, on average, about 85% of the reactive Hg (0.98 ± 0.9 pM) in the surface waters of the North Atlantic was actually Hg^o i.e. ionic Hg concentrations were about 0.15 pM, on average. In addition, as discussed in detail in Guentzel et al. (in prep.), there was a correspondence between the amount of colloidal Hg and the presence of photosynthetic pigments. Highest concentrations of colloidal Hg coincided with the highest concentrations of pigments while the sample taken after Station 12 has both the lowest colloidal Hg concentration and the least pigments. This correspondence suggests that processes associated with primary productivity could be the source of the complexing colloidal fraction. This notion is in agreement with the suggestion by Bruland et al. (1991) and others that phytoplankton are the source of the metal complexing capacity of the marine water column.

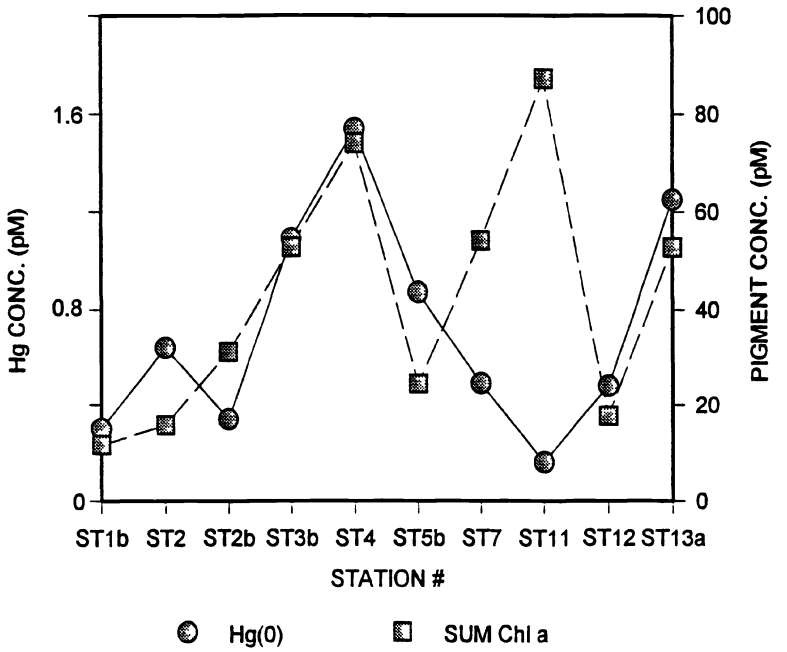

Fig. 3. Relationship between measured elemental mercury concentration and chlorophyll a.

3.3 DIMETHYLMERCURY AND MONOMETHYLMERCURY

Concentrations of DMHg ranged from the detection limit (10 fM) to 0.31 pM. The highest concentrations were found in the deeper waters at most stations (Figure 2; Station 4). The water column in the North Atlantic is well ventilated and oxygen concentrations are never suboxic. However, DMHg was found at all stations. Thus, our results suggest that low oxygen conditions are not a prerequisite for the presence of DMHg in ocean waters - as we had concluded from our previous work in the equatorial Pacific (Mason and Fitzgerald, 1990; 1991). Cossa and Martin (1993) also found DMHg in oxygenated sub-thermocline waters in the Mediterranean - in the Alboran Sea and Strait of Gibraltor, where oxygen concentrations were above 150 μM. No DMHg was detected, however, in the mixed layer of the North Atlantic; in agreement with previous results (Mason and Fitzgerald, 1993; Cossa and Martin, 1993). In addition, while DMHg has been found in deeper older ocean waters, it has not been found in the water column of lakes or estuaries (Vandal et al., 1991; Fitzgerald et al., 1994; Mason et al., 1993a). Quevauviller et al. (1992) reported the presence of DMHg and methylated tin species in anoxic mangrove sediments.

The presence of DMHg in deep ocean waters could result from *in-situ* production or from advective transport from other regions. Modelling calculations for the equatorial Pacific, and laboratory stability experiments (Mason and Fitzgerald, 1993; Mason, 1991), infer *in-situ* formation. Significant production of methylated Hg compounds in oxygenated waters does not, however, concur with the current literature which deals primarily with freshwater and estuarine environments (e.g. Gilmour and Henry, 1991; Winfrey and Rudd, 1990; Compeau and Bartha, 1985; Gilmour et al., 1992). These studies indicate that low oxygen conditions are the primary site of formation and that sulfate-reducing bacteria are the main methylating organisms, producing primarily MMHg in freshwater lakes and in estuaries. There have been some reports of DMHg in freshwater and estuarine systems but the results are somewhat inconsistent with the overall body of data. Studies by Fagerstrom and Jernelov (1972) and Craig and Bartlett (1978) suggest that DMHg can form in alkaline anoxic sediments and that the formation of DMHg is via the disproportionation of MMHg in the presence of sulfide, i.e.:

$$2\ CH_3Hg^+ + S^{2-} \rightarrow (CH_3Hg)_2S \rightarrow (CH_3)_2Hg + HgS.$$

Baldi et al. (1993) found that resistance to μg/L concentration of MMHg by *Desulfovibrio desulfuricans* was related to the transformation of the MMHg to DMHg via the dimethylmercury sulfide intermediate, resulting in the formation of DMHg, methane and HgS. Given the presence of sulfide even in oxygenated seawater (Cutter and Oats, 1987), this reaction could account for the presence of DMHg in deeper ocean waters. Otherwise, another pathway besides methylation by sulfate reducers (with DMHg formation via reaction with sulfide) is producing DMHg in ocean waters.

3.4 SOURCES AND SINKS FOR DIMETHYLMERCURY

The lack of DMHg in surface waters is likely due to the enhanced decomposition of DMHg in the presence of light (Mason, 1991) and the additional potential loss of DMHg via gas exchange at the water surface. We had previously hypothesized, based on the equatorial Pacific data (Mason and Fitzgerald, 1993), that DMHg formation was slow and that it slowly accumulates with time in deeper waters, the concentration being a function of both the rate of formation and the rate of decay:

$$d[DMHg]/dt = k_1.[Hg(II)] - k_2.[DMHg]$$

where k_1 is the rate constant (assumed to be first order) for the formation of DMHg from reactive Hg (considered here to be Hg(II)) and k_2 is the rate constant for the decay of DMHg to MMHg.

If the concentration of DMHg increases with time, this should be reflected in the North Atlantic samples. The water samples were therefore categorized on the basis of the time since the water was at the surface (i.e. 0-5 years; 5-10 years; 10-50 years and > 50 years) based primarily on halocarbon concentration (Yeats, pers. comm.). The average DMHg concentration for the time spans were:

0-5 yrs: 0.03 $\pm$ 0.04 pM (n=23; half of the samples were below the detection limit (DL));

5-10 yrs: 0.06 $\pm$ 0.03 pM (n=16, 2 samples below the DL);

10-50 yrs: 0.12 $\pm$ 0.07 pM (n=22, no samples below the DL) and

> 50 yrs: 0.13 $\pm$ 0.08 pM (n=9, no samples below the DL).

If accumulation of DMHg begins after waters leave the mixed layer, then the concentration of DMHg at any time is given by:

$$[DMHg] = (k_1/k_2).[Hg(II)](1-\exp(-k_2.t))$$

and the maximum concentration, at steady state, is:

$$[DMHg]_{max} = k_1.[Hg(II)]/k_2.$$

The DMHg data collected during the cruise suggests that steady state (i.e. $\exp(-k_2.t)$ _ 0) is reached in the order of 50 years. Thus, k_2 (the rate of DMHg decomposition) is about 0.07 yr^{-1} (2 x 10^{-9} s^{-1}; 0.02% day^{-1}), assuming that equilibration occurs within 5 half-lives. Also, taking $[DMHg]_{max}$ to be 0.13 pM, k_1 (the rate of DMHg formation) is 0.018 yr^{-1} (0.5 x 10^{-9} s^{-1}; 0.005% day^{-1}) at 0.5 pM Hg(II). These rates are somewhat smaller than those estimated from mass balance considerations and laboratory stability experiments for the deeper waters of the equatorial Pacific (Mason and Fitzgerald, 1993). These calculations suggest that the formation rate of DMHg is an order of magnitude less than its decay and that a long residence time is required for the concentration to build to detectable levels. At the surface, if formation of DMHg is occurring, the increased degradation rate and loss due to gas exchange result in no detectable accumulation of DMHg. At the formation and decay rates estimated here, a minimum residence time of deep waters of about 5 years is required for DMHg to build up to detectable levels. Thus, DMHg is detected in the deeper waters of the ocean but not in dimictic lakes where mixing occurs annually.

In addition, as the decomposition rate of DMHg is higher in freshwater than in seawater (by about an order of magnitude in laboratory experiments; Mason, 1991), DMHg formation rates would have to be substantially higher for DMHg to accumulate in dimictic freshwater lakes, on the order of 0.05 to 0.1% day^{-1}. Further, in contrast

to MMHg which accumulates in anoxic waters (Bloom et al., 1991; Mason et al., 1993a; Cossa et al., 1994), the results of the various oceanic studies (Mason and Fitzgerald, 1983; Cossa and Martin, 1994; this work) suggest that DMHg formation occurs under suboxic/oxic conditions, as suggested by a number of laboratory studies (Wood et al., 1968; Fagerstrom and Jernelov, 1972; Compeau and Bartha, 1985). Further, these studies suggest DMHg formation under alkaline conditions. Thus, it seems that conditions conducive to DMHg accumulation do not typically occur in temperate lakes.

Preliminary results indicate that MMHg concentrations in the North Atlantic are low, around the detection limit of 50 fM. If MMHg is formed only by decomposition of DMHg, then we can estimate the MMHg decay rate in a similar manner to that used for DMHg above:

$$d[MMHg]/dt = k_2.[DMHg] - k_3.[MMHg]$$

where k_2 is the rate constant for the decay of DMHg and k_3 is the rate constant for the net removal of MMHg (demethylation and particulate scavenging and removal). Again, at steady state, taking [MMHg] as 50 fM:

$$[MMHg]_{max} = k_2.[DMHg]_{max}/k_3 = k_1.[Hg(II)]/k_3$$

and k_3, the MMHg removal rate constant, is 0.18 yr^{-1} (0.05% day^{-1}). This rate is similar to previous predictions and laboratory determined values for the demethylation of MMHg (Gilmour and Henry, 1991). Again, considering freshwater lakes, if the decomposition rate for DMHg, but not that of MMHg, is enhanced in fresh relative to seawater, as suggested by our mass balance estimations (Mason and Fitzgerald, 1993), then DMHg would not accumulate to detectable levels in freshwater lakes even if the residence time of deep waters was greater than 5 years.

These calculations suggest that the presence of DMHg in seawater but not in freshwater is consistent with the idea that the enhanced stability of DMHg in seawater, coupled to the long residence time of waters away from the surface mixed zone, allows DMHg to accumulate in the ocean to detectable levels. In addition, acidification of freshwater lakes results in more rapid decomposition of DMHg (Mason, 1991). Further, one cannot conclude, based on the absence of detectable DMHg in lakes, that DMHg is not formed nor what is the predominant pathway of MMHg formation. Our ocean studies, and the calculations presented here actually suggest that DMHg forms directly from Hg(II) and is decomposed rapidly to MMHg in freshwater systems and, as a result, DMHg never accumulates to detectable levels. The production of DMHg by microorganisms would be advantageous as DMHg is lipid soluble but does not accumulate within cells (Mason et al., submitted), thereby providing an effective detoxification mechanism.

4. Conclusion

The results of the North Atlantic cruise, while preliminary, suggest similarities and differences compared to the distribution and speciation in the equatorial Pacific. Methylated Hg species are again a distinctive feature of the profiles, and Hg^0 is a higher fraction of the reactive Hg in the North Atlantic. The ultrafiltration experiments suggest the presence of organic complexes of Hg in surface seawater. This has been

suggested by the high complexation of other trace metals by organic chelates in seawater, and because Hg forms very strong complexes with sulfur compounds. This aspect of the oceanic chemistry of Hg requires further investigation.

Elemental Hg was a large fraction of the surface reactive Hg suggesting that the production of Hg^0 is limited by the rate of supply of ionic Hg. Dimethylmercury is found in the deeper waters and the initial results suggests that DMHg is relatively stable in the cold, deep waters of the North Atlantic. Overall, the results of the North Atlantic cruise provide further evidence of the mechanisms for the formation of Hg^0 and methylated Hg species put forward after the 1990 equatorial Pacific cruise. Methylated Hg production and Hg^0 formation are limited by the rate of supply of ionic Hg and methylated Hg species tend to accumulate in deeper waters while Hg^0 formation is primarily a mixed layer phenomenon. Also, as found in other ocean regions, DMHg is the dominant methylated Hg compound, in contrast to freshwater environments where MMHg predominates.

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A Preliminary Mercury Budget for Narragansett Bay (Rhode Island, USA)

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Abstract

The distribution of total Hg (Hg_T) and reactive (Hg_R) in Narragansett Bay, fresh water tributaries and point source discharges was determined during a synoptic survey, carried out in April, 1986. A Hg budget which includes fluvial inputs and atmospheric Hg deposition was constructed and the estuarine behavior of Hg assessed.

1. Introduction

There is little information regarding the distribution, reactivity and fate of Hg in estuarine environments. Flocculation and coagulation of trace metal (e.g.,Fe, Mn, Cu) and organic colloids dissolved in freshwater can occur under conditions of increasing ionic strength (Sholkovitz, 1978) and may result in removal of dissolved constituents during estuarine mixing. Thus, estuaries can serve as traps for riverborne material by way of sediment deposition. Conversely, remobilization of metals bound to particulate matter can occur with increasing salinity. For example, a maxima in dissolved Hg at low salinity (ca. 5 ppt) has been observed in several estuaries, perhaps due to remobilization from particles under turbid conditions. In the Gironde Estuary total dissolved Hg (determined following oxidation with bromine) covaried with turbidity; solubilization of Hg from particles in the turbidity maximum was hypothesized as the source of an upper estuary dissolved Hg maxima (Cossa and Noel, 1987). A similar distribution for dissolved Hg was observed in the Rhône Estuary (Cossa and Martin, 1991). Furthermore, a general decrease in the partition coefficient between particulate and dissolved Hg with increasing salinity provided additional evidence of Hg remobilization from particles. In contrast, removal of total dissolved Hg was observed in the Saint Lawrence Estuary and attributed to adsorption onto solid phase in the turbidity maximum and/or coagulation and of organic colloids (Cossa et al., 1988). Mercury removal within the estuarine mixing zone was also indicated in a study of the Connecticut River Estuary (Gill, 1980). Mercury covaried with dissolved Fe, Hg coprecipatation with Fe was suggested. Here we report the distribution of Hg in Narragansett Bay and its fresh water tributaries determined during a synoptic survey, carried out in April, 1986. A Hg budget which includes fluvial inputs and atmospheric Hg deposition was constructed and the estuarine behavior of Hg assessed.

2. Methods

A map of the sampling sites is given in Figure 1. Narragansett Bay is located on the north-eastern coast of the United States. It is a well flushed estuary with an average residence time for water of 24 days. The highly industrialized city of Providence is at the head of the bay. Twelve stations in Narragansett Bay were sampled to cover a salinity gradient from 7 to 32 ppt.

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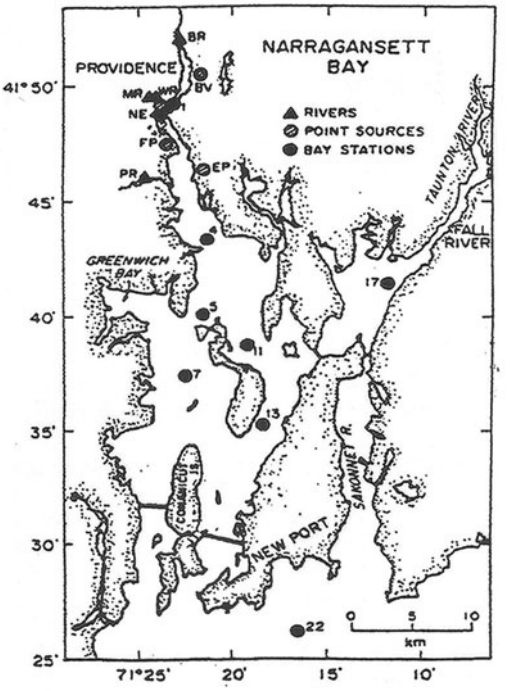

Fig 1 Narragansett Bay is located on the north-eastern coast of the United States Sampling locations included six stations within the bay (4,5,7,11,13,17) at two depths (0 3 and 13m) and two in the Providence River (1,2) Four rivers which flow into the estuary (Blackstone[BR], Woonasquatucket [WR], Moshassuck [MR], Pawtuxet [PR]) and four point sources (Blackstone Valley Wastewater Treatment Facility (WTF) [BV], Field's Point WTF [FP], East Providence WTF, Narragansett Electric cooling water [NE]) were also sampled

Collections were made using trace metal clean techniques and a teflon pumping apparatus Acid-labile Hg (Hg_R) was determined in filtered (combusted, 0 4 μm GFF filter) and unfiltered samples which were acidified to 0 5% HNO_3 The analysis ($SnCl_2$ reduction, preconcentration on Au with detection by CVAAS, Gill and Fitzgerald, 1985) was conducted following a 1 month acid digestion period Total Hg was measured on unfiltered fresh water and upper estuary collections following bromine monochloride oxidation (Bloom and Crecilius, 1983) Strongly bound Hg was defined as the difference between Hg_T and Hg_R Atmospheric deposition of Hg to Narragansett Bay was estimated from average Hg rainwater and atmospheric particulate concentrations measured at Groton, CT (Gill, 1980)

3. Results

The speciation of Hg in the tributaries is given in Figure 2 River waters Hg levels were elevated relative to the saline waters Unfiltered Hg_T concentrations ranged from 36 to 150 pM for these urban impacted waters while Hg_R values were lower (8 to 29 pM) Strongly bound Hg forms were a major fraction of the fresh water Hg Point source Hg_T concentrations ranged from 42 to 346 pM of which >50% was strongly bound Strongly bound comprised 25% of the total Hg, in

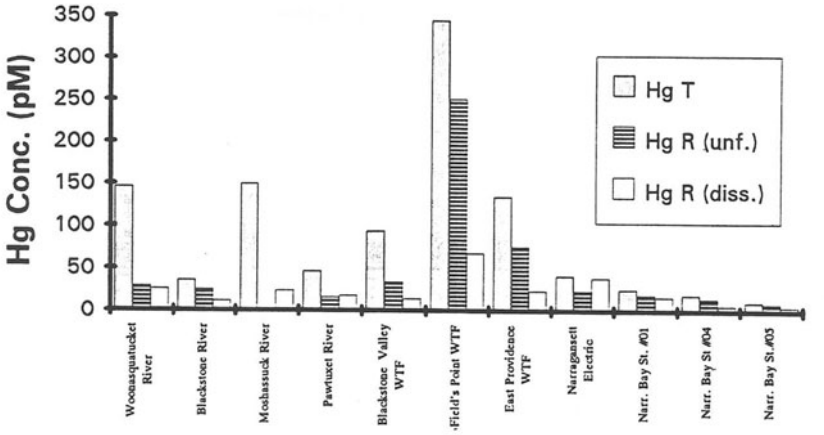

Figure 2. The speciation of Hg in the tributaries and upper bay stations (Stations 1, 4 and5).

the upper bay collections (Stations 1, 4 and 5) indicating loss of this component in the upper estuary. A mean Hg_R concentration for the fresh water end-member was estimated based on the measured Hg_R concentration for each source multiplied by it discharge rate at the time of this study. The flow-weighted mean Hg concentrations are used to assess the behavior of the Hg fractions across the salinity gradient. Within the estuary unfiltered Hg_R in was highest at the head of the estuary (18.5 pM) and decreased seaward (5.5 pM); removal at low salinity (ca.7ppt) was indicated. The role of suspended matter in Hg transport is supported by the strong correlation of Hg_R in unfiltered collections with turbidity (r=0.99) and total suspended load (r=0.96). Dissolved Hg_R ranged from 2 to 17 pM and covaried inversely with salinity suggesting conservative mixing.

4. A Preliminary Budget

A Hg budget for Narragansett Bay was developed from this limited data set and is presented in Figure 3. The Taunton River flux was approximated assuming a Hg_R concentration of 95 pM, the average of the four rivers sampled. Fluvial inputs contributed 61 g d^{-1}, equivalent to 69% of the total Hg flux into Narragansett Bay. The flux from point sources was 18.5 g d^{-1} (21%). Atmospheric deposition was estimated at 10 g d^{-1} (10%) assuming an average rain concentration of 50 pM (Fogg and Fitzgerald, 1979); 328 km^2 for the are of the bay (Pilson, 1985); and 100 cm of rain per year. Tidal exchange removes approximately 49 g d^{-1}. This calculation is based on 406 x 10^6 m^3 as the volume of the tidal prism[2]; the concentration of the inflowing water is taken as 5.5 pM (Station 22); and a fresh water entrainment rate of 1% per tidal cycle results in elevation of the outgoing water to 5.8 pM. A balanced budget requires a flux to the sediment of 40 g d^{-1}. In summary, approximately 50% of the Hg entering the bay is exported by tidal exchange and 50% retained within the estuarine sediments.

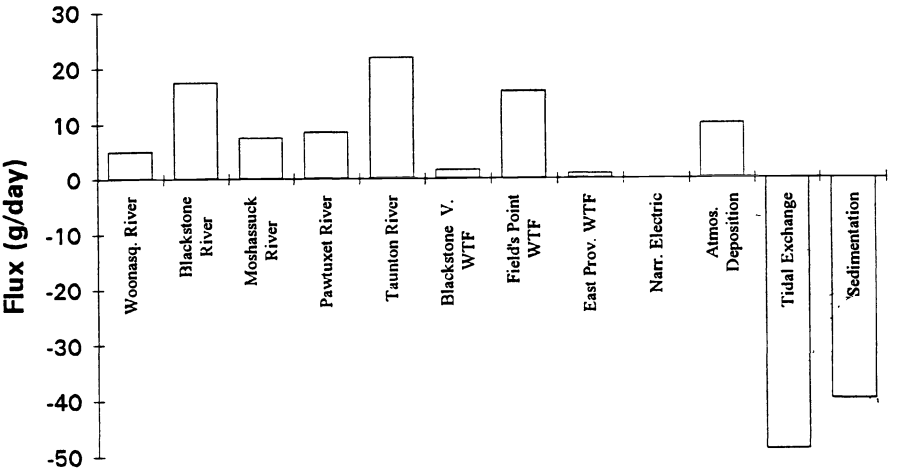

Figure 3. A preliminary Hg budget for Narragansett Bay.

5. Conclusions

A strongly bound form of Hg was evident in river and point source collections. This component was absent from saline waters and appeared to removed at the salt water interface. Dissolved Hg_R mixed conservatively along the salinity gradient. However, removal of Hg_R associated with suspended material at low salinities was suggested. A preliminary budget was constructed for Narragansett Bay Rivers contribute the principal Hg flux to the bay followed by point source discharges and atmospheric deposition. Our calculations indicate that 50 % of the Hg entering the estuary is deposited and 50% is exported via tidal flushing.

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ARCTIC MARINE MAMMALS AS INTEGRATORS AND INDICATORS OF MERCURY IN THE ARCTIC

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Abstract. Mercury concentrations were determined in liver, kidney and muscle of belugas, narwhal, white-beaked dolphins, pilot whales, ringed seals, harp seals and walrus. Tissue collections and analyses were performed largely over the past 10 years. Sampling sites ranged across the Canadian Arctic from the Mackenzie Delta and Banks Island in the west, Grise Fjord in the north, the Atlantic coast in the east and south. High Hg levels in the liver of ringed seals from the western Arctic, collected in 1987 and 1988 were similar to previously-reported values for ringed seals collected in 1973 and 1972 from the same area. Comparison among different marine mammal species showed substantial inherent differences in Hg levels among different species. White-beaked dolphins and walrus had much less Hg than pilot whales. A comparison of Hg levels in ringed seals from locations across the Arctic and Hudson Bay showed that Hg was generally higher in ringed seals from the western than the eastern Arctic, indicating a possible influence of the different geological settings in the eastern and western Arctic. The effect of age was considered in these comparisons. A similar, but less pronounced effect was noted for belugas, with some possible anthropogenic influence on animals in Hudson Bay. The spatial trend in Hg levels in animals appeared to be largely present-day background concentration reflecting geological differences between the eastern and western Arctic. Higher Hg concentration were present in surficial sediments and coastal waters in the western Arctic than the eastern Arctic in accord with the Hg trend observed in seals and belugas.

1. Introduction

Delineating the sources of trace metals such as Hg found in marine mammals is a difficult problem, because many factors influence the concentration of Hg in these animals. Knowledge about the anthropogenic component is important because this component is potentially under the control of man and can be reduced or mitigated over time, but the natural background component is equally important as it may be the major source of Hg in some areas. We have concentrated on two Arctic marine mammal species, beluga and ringed seals, as these are year-round residents of the Arctic. Ringed seals especially are deemed to be good Arctic indicator species at the top of the food chain that can provide an integrated response for areas in the Arctic as they are less migratory than some other marine mammals (Smith, 1987). We have also analyzed tissue samples from other marine mammals from locations across the Canadian Arctic and the Atlantic coast of Canada.

For more than ten years we have investigated metal contaminants in tissues of marine mammals, largely from the Canadian Arctic, the southern Hudson Bay and northeastern Atlantic, with a view to determining spatial and temporal trends and present-day background concentrations of metal contaminants. This paper presents an overview of some of these findings largely for two Arctic marine mammals species, ringed seals and beluga, and new information on Hg in ringed seals. It focuses on the abnormally high background concentrations of Hg in the tissues of some animals and

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the factors that may influence this, such as inter-species differences, tissue-type differences, and spatial changes in the level of Hg in belugas and ringed seals and temporal Hg changes in ringed seals and walrus.

2. Methods and Materials

The prior treatment of tissue samples and the determination of Hg in marine mammal tissues in this laboratory have been described extensively elsewhere (Wagemann *et al.*, 1983; Wagemann and Armstrong, 1988; Wagemann and Stewart, 1994). Essentially, the well-established cold-vapour atomic absorption method for determining mercury with prior wet-digestion of tissues was used. Tissues of marine mammals were obtained in all cases in conjunction with Native subsistence hunts except for dolphins from the coast of Newfoundland, where tissues were obtained from dead stranded animals.

The assessment of abnormal levels of pollutants always begins with the determination of the contaminant in the tissues and blood of the animals of concern, and can then proceed by a number of stratagems, as shown below:

1. Comparison of tissue levels of the contaminant in animals from the test area with previously established levels under controlled conditions (laboratory) that had produced no discernable effects in other animals.
2. Comparison of tissue levels of Hg in test area animals with levels in animals from pristine or reference areas.
3. Comparison of tissue levels of Hg in animals from different geographic areas.
4. Comparison of tissue levels of Hg in animals harvested at the same location but in successive time intervals.

3. Results and Discussion

In any assessment or comparison of metal concentrations in tissues, biological and non-biological factors that can have a bearing on tissue levels must be taken into account. Ordinarily, different sampling and measuring techniques would also be included, but all results being compared here were determined in the same laboratory using the same measuring and sampling techniques. The following factors were taken into account: intra-species differences; the age of the animals; the gender of animals; different tissue types (liver, kidney, muscle etc.) which differ in their affinities for particular metals; and geological and sedimentary differences in coastal regions frequented by the animals.

3.1 INTRA-SPECIES DIFFERENCES

Significant differences in Hg concentration among species do exist (Figure 1),

and are likely to be principally the result of dietary differences among species,

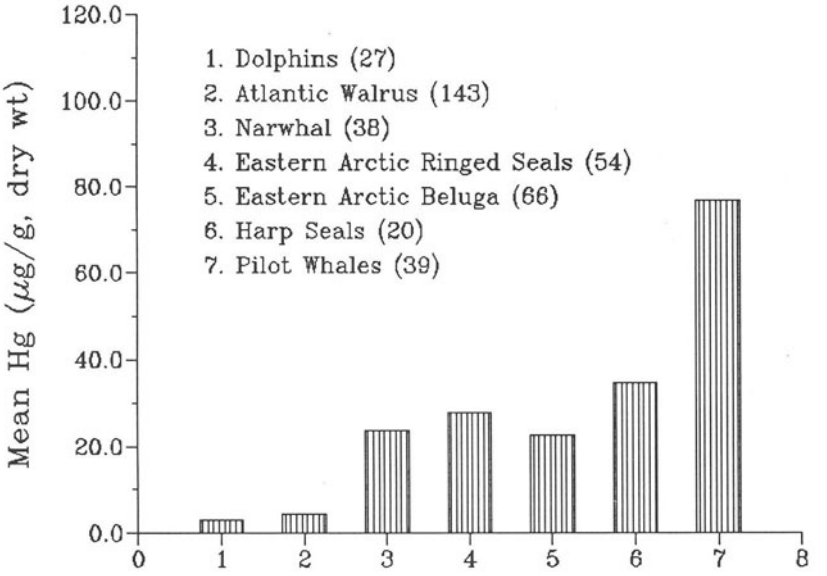

Fig. 1. Mean Hg concentrations, μg/g dry wt, in liver of groups of marine mammals (n) from different locations in the eastern Arctic and Canada's Atlantic coast (dolphins, pilot whales). Bar graphs are based on data of Muir *et al.* 1988 (1,7); Wagemann and Stewart, 1994 (2); Wagemann *et al.* 1983 (3); Wagemann, 1989 (4); Wagemann *et al.* 1990 (5); Wagemann *et al.* 1988 (6).

although differences in metabolic rates (excretion and accumulation, biological half-life of Hg) may also be factors, but this information is largely unavailable for marine mammals, however, the general diet of the different species is known (Ridgeway, 1972). Each bar graph (Fig. 1) represents a mean derived from of 20 to 143 animals from the eastern Canadian Arctic and the eastern Atlantic, the former area consisting largely of the Canadian Shield. Significant differences in Hg levels occur principally between dolphins and pilot whales, and between walrus and pilot whales. The data were not age-corrected, but mean age differences among groups of hunted animals are generally not great.

3.2 AGE AND GENDER

The relationship between age and Hg concentration (Table I) in marine

TABLE I

Associations† among metals in liver, kidney, and muscle, and between metals and age and gender of ringed seals from Sachs Harbour (1987, 1988 combined) at $0.90 \leq P < 0.95$, $0.95 \leq P < 0.99$ (underlined), and $0.99 \leq P$ (doubly underlined).

Gender & No. of Samples	Dependent Variables	Independent Variables		
		Liver	Kidney	Muscle
Common to males and females (123)	Se	+Age, +Hg	---‡	---
	Cd	+Zn	+Cu, +Zn	---
	Zn	+Cu	---	---
	Hg	---	+Age	-Cu
Females only (60)	Hg	-Age	---	+Cd
	Cd	+Age, +Se	+Age	+Age
	Cu	---	-Age	-Age
	Se	---	---	+Pb, +Zn
Males only (63)	Cd	-Pb	---	+Pb
	Zn	---	+Hg, +Cu	+Pb
	Cu	---	-Age	+Se
	Se	---	---	Age, +Hg

† signs associated with chemical symbols indicate positive (+) and negative (-) correlations.

‡ --- no associations found at the indicated confidence level.

mammal tissues, has also been well established by other investigators (Arima and Nagakura, 1979; Honda *et al.*, 1986; Muir *et al.*, 1988; Wagemann *et al.*, 1988; Hansen *et al.*, 1990; Wagemann *et al.*, 1990; Paludan-Müller *et al.*, 1993; Wagemann and Stewart, 1994). Age, among other variables, when strongly correlated with Hg, is an important variable for the assessment of Hg pollution, but any such analysis has to be based on a sufficienly large sample. The analysis reported here (Table 1) encompassed a relatively large sample, 123 ringed seals (60 females, 63 males), collected in 1987 and 1988 at Sachs Harbour N.W.T. Canada (western Arctic). Age was significantly, positively correlated with mercury in the kidney in the combined sample containing both genders but not in males or females separately, even though mean ages and age ranges were very similar for males and females. The association between Hg and age in marine mammals occurs most frequently in liver and kidney. Gender is generally not a factor that governs the level of trace metals in marine mammals. Although gender was initially included as a variable, it was subsequently omitted as it did not significantly influence trace metal levels.

3.3 TISSUE TYPE

The pattern of site distribution of metals within the organism is tissue specific and metal specific. Of the three tissues analyzed, Hg was mostly concentrated in the liver, with kidney and muscle having successively lower concentrations (Table II). This pattern prevails in most marine mammals. The concentration of total Hg is usually

TABLE II

Mean concentration (μg/g) ratios of total Hg in liver (L), kidney (K) and muscle (M) for different marine mammal species from the eastern Canadian Arctic and the Atlantic coast of Canada, and the number of animals (samples) in each group.

Species	L/K	L/M	K/M	Samples
Eastern Arctic Beluga	2.1	7.6	3.7	66
Dolphins	2.9	1.8	0.64	25
Narwhal	3.0	8.0	2.3	38
Walrus	3.3	11	3.3	112
Ringed Seals	5.1	27	5.2	35
Harp Seals	9.8	26	2.7	20
Pilot Whales	11.6	550	49	15

a factor of 3 greater in the liver than in the kidney, but can be significantly higher than that for some marine mammals. On the other hand, the concentration ratio of liver/muscle is generally higher and more varied than the liver/kidney ratio. The listed ratios are specific for total Hg and are generally quite different for other metals. The concentration of methylmercury relative to total Hg, was low in the liver of ringed seals (15 to 30 %; Wagemann, 1994). In view of the high total Hg and relatively low methylmercury concentration in liver, and because methylmercury was considered not to be a good indicator of geological influences on biota, liver was deemed to be most suited for monitoring geological influences on mercury in biota.

3.4 GEOGRAPHIC SITE-SPECIFICITY

The delineation of spatial trends of Hg in animals requires a large consistent data base over broad geographic areas. Of all the trace metals, Hg has been determined and reported most assiduously in the past. Nevertheless, systematic information on Hg concentrations has only relatively recently become available for ringed seals and beluga. Similar information on Hg in other marine mammals of the Canadian Arctic, such as harbour seals and bearded seals is still very limited or nonexistent. This study encompasses a sufficiently broad distribution of sampling sites for two species (ringed seals and beluga) across the Canadian Arctic to make possible a comparison of background concentrations in these animals throughout the Arctic. The comparison takes into account the factors listed namely, species, tissue type, and age of animals. In order to assess the impact of global Hg pollution on these animals, it was necessary to determine firstly whether or not Hg levels were aberrantly high in some animals after other factors known to influence Hg levels in biota were taken into consideration. Contrary to expectation, the results that were obtained were not spatially uniform across the Arctic (Figure 2). Ringed seals from the western Arctic had a significantly higher concentration of Hg than those from the eastern Arctic. The comparison was made on the basis of Hg concentration per mean unit age so as to account for the somewhat different mean ages of the groups from different sites. A similar pattern emerged for belugas as for ringed seals (Figure 3), with higher concentrations in the western than the eastern Arctic, except for an aberrantly high concentration in the group from the east side of Hudson Bay, possibly due to cumulative impacts from hydroelectric installations in the Hudson Bay drainage.

It is difficult to determine to what extent atmospheric, global pollution has pervaded biota, and if so, is it attributable to global, anthropogenic pollution? Based on various published reports, an increase in the Hg concentration in lake sediments (Lockhart *et al.*, 1994), the atmosphere (Slemr and Langer, 1992), and in Greenland ice (Weiss et al., 1974), global Hg pollution has increased in the inanimate environment. There is also some evidence from human and polar bear mummies (Wheatley and Wheatley, 1988) that it has increased over time in biota.

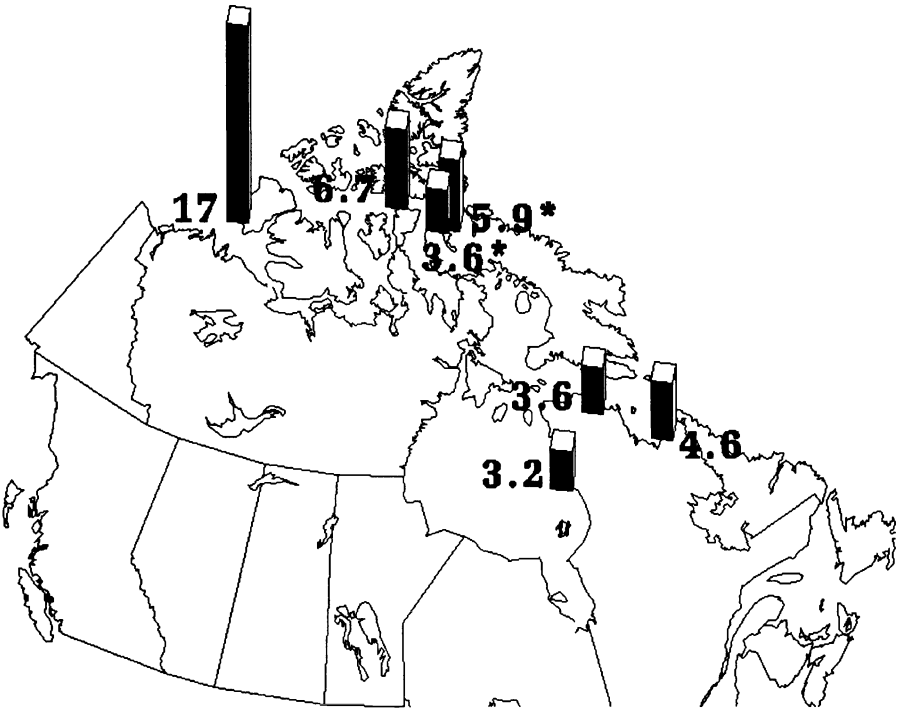

Fig. 2. Mean Hg concentrations, μg/g dry wt, per unit age (at the base of each bar) in liver of groups of ringed seals at locations across the Arctic; from west to east: Sachs Harbour, Resolute bay, Strathcona Sound and Admiralty Inlet, Inukjuak (eastern Hudson Bay), George River and Wakeham Bay. The marked data "*" are from Wagemann, 1989.

The concentration of Hg in ocean water, on the other hand, shows no indication of any increase and has remained relatively low and within, 1-15 ng/L, not surprisingly because oceans have a large capacity to absorb inorganic pollutants before any increases could be expected to be detected. However, coastal waters can show elevated Hg levels, be it from industrial and domestic outfalls or run-off from more cinnabarniferous drainages. The latter situation appears to pertain more to the western than the eastern Arctic. A very generalized geological map of Canada (Figure 4) shows that the Precambrian Shield (igneous and metamorphic rock) covers a very large part of the the eastern and central Arctic while the western Arctic consists largely of post-Cambrian, unmetamorphosed rock and volcanic and sedimentary rock. It would be very difficult to characterize generally, in terms of Hg concentration, the large geologic formations (Fig. 4). These large areas are not entirely homogenous but contain smaller

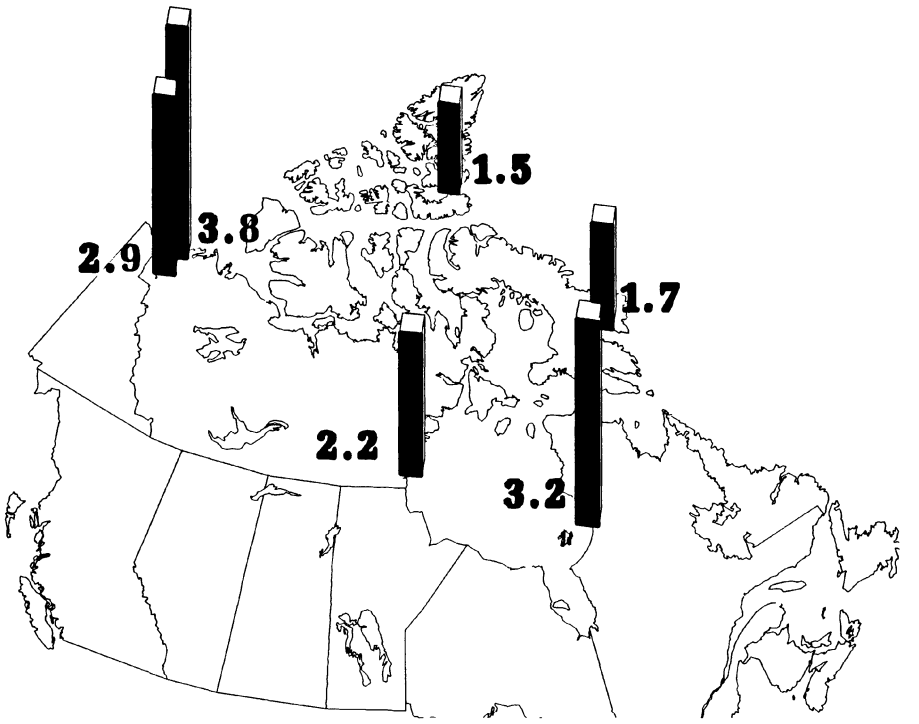

Fig. 3. Mean Hg concentrations, μg/g dry wt, per unit age (at the base of each bar) in liver of groups of beluga at locations across the Arctic; from west to east: Mackenzie Delta and East Whitefish, Grise Fjord, (most northerly), Eskimo point (western Hudson Bay), Nastapoka (eastern Hudson Bay) and Pangnirtung. Based on data from Wagemann *et al.* (1990).

regions of different types of associated rocks and mineralized areas when viewed on a finer scale. Nevertheless, differences in Hg appeared to be reflected in the surficial coastal bottom sediments and waters of the eastern and western Arctic (Table III). The relatively high concentration of Hg in ringed seals from the western Arctic and the relatively low concentrations in seals from the eastern and central Arctic corresponded to the different geological settings and the different Hg concentrations in the sediment and water in the eastern and western Arctic.

3.5 TEMPORAL TRENDS

Systematic studies of temporal variations of metals in marine mammals are understandably sparse because of the time involved and the consistency of analysis required. We have examined two relatively short-term temporal data bases for walrus and ringed seals. The mean concentration of Hg in liver of ringed seals collected in 1987-88 at Sachs Harbour (123 animals) was 107 μg/g (dry wt). Ringed seals collected in 1971-72, in the same vicinity (80 animals) had a mean concentration of Hg in the liver of 85 μg/g (dry wt) (Smith and Armstrong, 1975), not significantly different

(α=0.05) from the mean for the animals collected 16 years later. Both the earlier and later samples were analyzed in the same laboratory. Unfortunately, ages of the animals collected earlier were not available. The comparison, therefore, did not take into account age differences among the two groups. The difference in mean age between these two groups was deemed to be small as the groups were relatively large, and the the animals were obtained by hunting. Walrus, collected at Igloolik (western Hudson Bay) in 1982 to 1988, were examined for temporal variations by Wagemann and

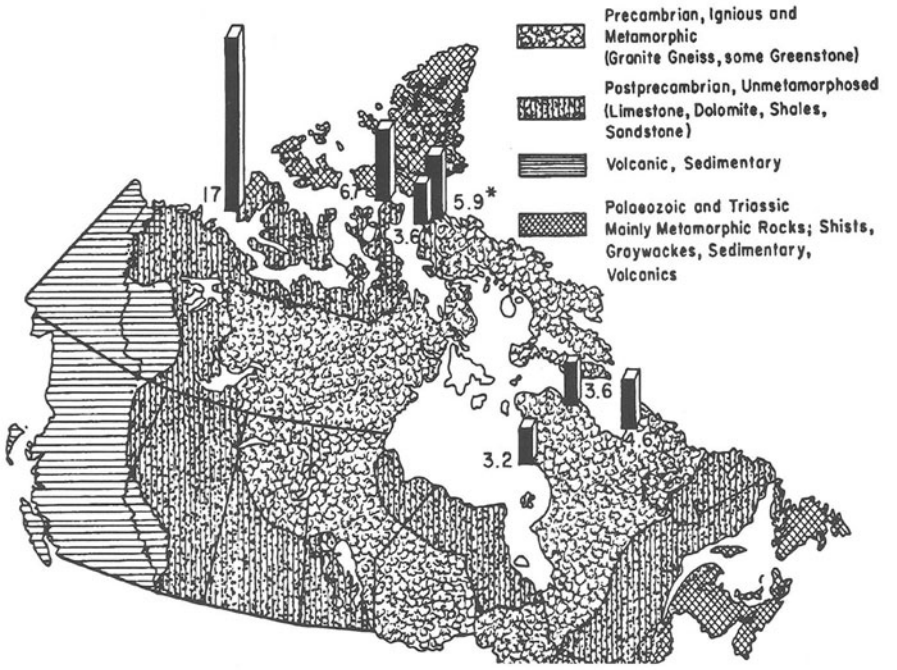

Fig. 4. Generalized geological map of Canada (based on Geological Survey of Canada map #1250), with bar graphs of the Hg concentration (μg/g dry wt) in the liver of ringed seals superimposed.

Stewart (1994). The annual means for Hg (similar mean ages) did not differ significantly at α=0.05. Over the short term at least, temporal increases in the Hg concentration in marine mammals from the Canadian Arctic have not been detected. In the longer term, however, such increases are indicated by analyses of human and marine mammal hair and tissues from mummies in the Arctic (Wheatley and Wheatley, 1988; Hart-Hansen *et al.*, 1991).

TABLE III

Mean Hg concentration ranges, spanning different sampling locations, in surficial coastal marine bottom sediments[‡] in the western and eastern Arctic and surficial or near-surficial waters of the Arctic.

Region	Sampling Locations	Hg in Sediments ng/g, dry wt	Hg in Water ng/L
Western Arctic	South Beaufort Sea & Alaskan North Slope	68-243[†]	11-29[§]
Eastern Arctic	Lancaster Sound, Jones Sound, Baffin Bay	40-60[††]	3.7[§§]

‡ Grab samples; mercury concentration ranges encompass a range of particle size frequency distributions, textures and compositions.
† Data from: Thomas, et al. 1982.
†† Data from: Loring, 1984.
§ Southern Beaufort Sea water, data from: Weiss, et al. 1974.
§§ Arctic Ocean water, data from: Schmidt and Freimann, 1984.

4. Conclusions

Species differences, age and other influences on Hg levels were taken into account to arrive at the present-day natural background concentration in animals in the area under study. Mercury concentrations in ringed seals and beluga from the Canadian Arctic, though they differed widely between the eastern and the western Arctic, were seemingly at present-day background concentrations reflecting the different geological settings of the eastern and central Arctic, and the western Arctic. Atmospheric transport probably did contribute some Hg assimilated by the animals, but it has not been possible to quantify this component in marine animals because of lack of data. Information on the spatial distribution of depositional fluxes and their relationship to uptake of Hg by biota is unavailable. It is even more difficult to quantify the anthropogenic component since Hg is not introduced into the environment exclusively by man. No temporal increase in the Hg concentration was detected, in the short-term at least, in ringed seals and walrus in the Canadian Arctic. The existing, inherent differences in tissue Hg levels between different marine mammal species seem to derive largely from dietary differences.

Acknowledgments

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PART VIII

MERCURY METHYLATION AND REDUCTION PROCESSES

SOURCES OF METHYL MERCURY TO FRESHWATER ECOSYSTEMS: A REVIEW[2,3]

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[2] Plenary address to the International Conference on Mercury as a Global Pollutant
[3] Publication #10 of the Experimental Lakes Area Reservoir Project (ELARP).

Abstract. The recent development of sensitive analytical techniques for the determination of MeHg concentrations in water has resulted in a rapid advancement in our understanding of MeHg production and transport in lake and reservoir systems. Results from three recent whole-ecosystem studies have shown that there are three important sources of MeHg to aquatic systems - precipitation, runoff from wetlands, and in-lake methylation. Data from these three studies are used to construct a simple model that illustrates how the relative importance of these sources can vary with rates of atmospheric deposition of MeHg, lake type, percentage of wetlands in the terrestrial catchment and the percentage of water surface area that covers flooded terrain.

1. Introduction

Until quite recently, it was generally believed that the only source of MeHg to freshwater ecosystems was internal (in-lake) production of methyl Hg (MeHg). However, we now know that wetlands can be important external sources of MeHg to lakes (Rudd et al. 1992; St. Louis et al., 1994). This likely explains why fish in brown-water lakes, which receive significant inflow from wetlands, often have high concentrations of MeHg (e.g. Driscoll et al., 1994). The atmosphere may be another important external source of MeHg to some lakes. For example, Hultberg et al., (1994) concluded that atmospheric deposition is an important source of MeHg for drainage lakes located in heavily polluted regions of southern Sweden. The recent recognition of the importance of external sources of MeHg to freshwater ecosystems followed the development of a highly sensitive technique for the determination of MeHg in water (Bloom, 1989; Horvat et al., 1993).

In this paper, I attempt to summarize and synthesize the present understanding of the relative importance of sources of MeHg to lakes and reservoirs (atmospheric, terrestrial and internal). This will be largely done by drawing information from three recent whole-ecosystem studies: Little Rock Lake, WI. (Watras et al., 1994); Lake Gardsjon, southern Sweden (Hultberg et al., 1994); and from studies of MeHg in flooded and unflooded boreal catchments that are being carried out as part of the Experimental Lakes Area Reservoir Project (ELARP), northwestern Ontario. A primary goal of the ELARP is to improve the understanding of the causes of elevated Hg concentrations in fish taken from hydroelectric reservoirs (e.g. Hecky et al. 1991)

Water, Air, and Soil Pollution **80**: 697–713, 1995.

2. Materials and Methods

2.1. SAMPLE COLLECTION

For the three studies discussed in this paper, rainwater and surface-water samples were collected using the stringent clean-hands-dirty-hands protocol described in St. Louis et al., (1994a), Hultberg et al., (1994) and Watras et al., (1994). It is assumed that estimates MeHg in deposition obtained by event rainfall collectors and bulk (IVL) collectors are equivalent. This assumption is based on year-to-year similarity of MeHg deposition rates measured at the same location using rain collectors and bulk collectors (H. Hultberg pers. comm., Hultberg et al., 1994).

2.2. ANALYTICAL

The MeHg data discussed in this paper are comparable. For all three studies, MeHg concentrations were analyzed by GC-CVAFS following aqueous phase ethylation of MeHg (Bloom, 1989, Horvat et al., 1993). The labs analyzing all of these samples (IVL, Brooks-Rand Ltd., Frontier Geosciences and Flett Research Ltd.) have recently successfully participated in an international inter-comparison exercise (Bloom and Horvat, 1995).

3. Results and Discussion

3.1. SOURCES OF MeHg TO FRESHWATER ECOSYSTEMS

Three sources of MeHg to freshwater ecosystems will be considered. Two of the three sources (terrestrial runoff and direct atmospheric deposition onto the lake surface) are external to freshwater systems. The third source is internal and is comprised of MeHg produced in the sediments, the water column and in the intestinal contents of fish.

Atmospheric Deposition:

To evaluate the relative importance of external vs. internal sources of MeHg, atmospheric inputs of MeHg must be accurately quantified. Deposition of MeHg has been measured at several sites in the northern hemisphere and has been found to vary considerably from one region to another. In Table I, the data are arranged in order from lowest to highest deposition rate. There is a ten fold range between the lowest (0.39 mg ha^{-1} yr^{-1}, ELA, northwestern Ontario) and highest deposition rates (1.9-4.0 mg ha^{-1} yr^{-1}, southern Sweden).

TABLE I.

MeHg in wet/bulk deposition collected in several regions of the northern hemisphere[1].

Region	Wet/Bulk Deposition mg ha^{-1} yr^{-1}	Reference
ELA NW Ontario	0.39	St. Louis et al., (this issue)
N. Sweden	0.70	Munthe and Iverfeldt, (1994)
Wisconsin	0.88	Fitzgerald et al., (1991)
S. Finland	1.1	M. Verta pers. comm.
E. Sweden	2.0	Munthe and Iverfeldt, (1994)
W. Sweden	2.9	Munthe and Iverfeldt, (1994)
S. Sweden	1.9-4.0	Munthe and Iverfeldt, (1994) Hultberg et al., (1994)

[1] Adapted from St. Louis et al. (this issue).

MeHg deposition in the equatorial Pacific is likely even lower than at ELA. Although an annual deposition rate was not reported, concentrations of MeHg at three sampling locations in the equatorial Pacific average <0.01 ng/L (below the analytical detection limit, Mason et al., 1992). For comparison, average MeHg concentrations at ELA are 0.04 ng/L (St. Louis et al., 1995).

At the present time, the origin of MeHg in deposition is not known but may be directly or indirectly related to industrial activity. For example, the two most remote sites listed in Table I (ELA and northern Sweden) have the lowest deposition rates, while the highest rates are in southern, western and eastern Sweden which are relatively close to industrialized areas of Europe. The intermediate sites (northern Wisconsin, southern Finland), while not remote, are somewhat removed from heavily industrialized areas. The undetectable concentrations of MeHg in equatorial Pacific rain suggest that the source of MeHg in rainfall is terrestrial.

In addition to the amount of MeHg measured in rainfall and bulk collectors (Table I), MeHg inputs via litterfall (i.e MeHg attached to fallen needles, leaves and twigs) may also be important. Hultberg et al., 1994 reported that MeHg deposition via litterfall is equal to wet/bulk deposition in the Lake Gardsjon area of southern Sweden. However, the source of MeHg in litterfall is not known. It could be atmospheric in origin or it could be produced on the surface of leaves and needles. It is also possible that the MeHg in litterfall is not all newly produced or deposited but is instead recycled from soil emissions or by root translocation. If the latter are true, it would not be correct to include litterfall in estimates of deposition. On the other hand, if MeHg in litterfall is of atmospheric origin, then present wet/bulk loading estimates (Table I) are underestimates of total MeHg deposition and this could lead to over estimates of rates

of MeHg production in lakes and wetlands by mass-balance calculations.

Terrestrial catchments as sources/sinks for MeHg:

Terrestrial catchments that contain wetlands have been identified as important sources of MeHg to downstream aquatic systems (Rudd et al., 1992; St. Louis et al., 1994a). Wetland areas of catchments at the ELA contributed 26 to 79 times more MeHg per unit area to downstream water than did purely upland areas of catchments that contained no wetlands (saturated organic soils, St. Louis et al., 1994a). This finding appears to be of general importance as wetlands have also been identified as important sources of MeHg by recent studies in Wisconsin and northern Sweden (Bishop et al., 1994: Hurley et al., 1994; Krabbenhoft et al., 1995). Also, Driscoll et al., (1994) reported a significant relationship between the percentage of near-shore wetlands in Adirondack lake catchments and the MeHg concentration of lake water.

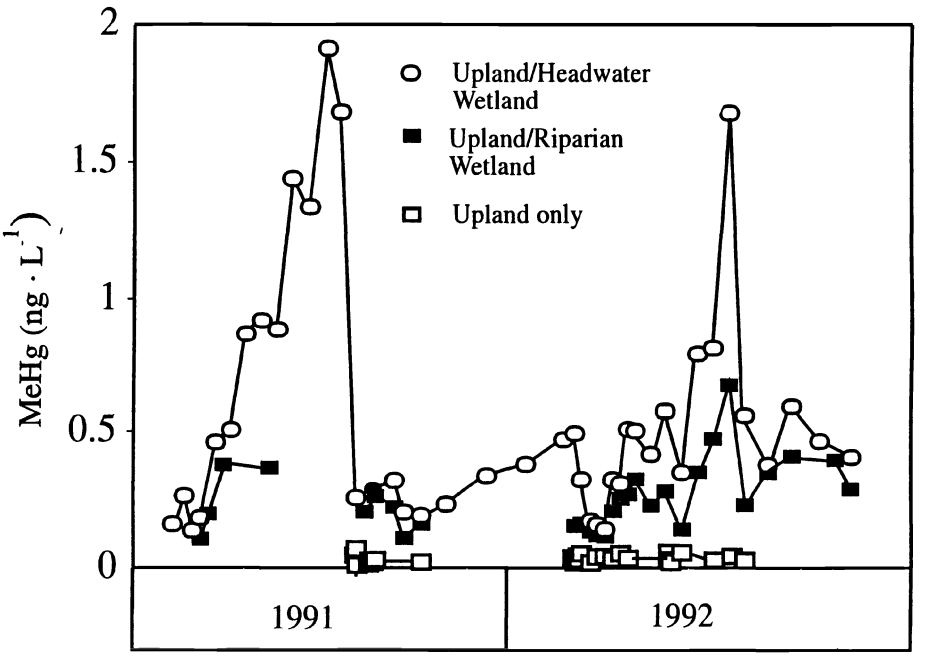

Figure 1. Concentrations of MeHg in stream water exiting three types of terrestrial catchments at the ELA, northwestern Ontario.

The ELARP is intensively studying the production, storage and export of MeHg in wetlands (Fowle et al., 1994; Heyes et al., 1994; Moore et al., 1994). The project is also studying, at the subcatchment level, the transport of MeHg from uplands (Allan et al., 1994, St. Louis et al. 1994a). Figure. 1 shows that the conclusions of St. Louis et al., (1994a), which presents data from the first year of the ELARP study, have

been consistent on the longer term. That is, concentrations of MeHg from a purely upland catchment are uniformly low (<0.1 ng L^{-1}). Concentrations of MeHg are intermediate in value (0.1-0.6 ng L^{-1}) in a stream draining a catchment that is composed of upland terrain and stream-side wetland areas (riparian wetlands) that receive water from the uplands. MeHg concentrations are very high in a stream draining a catchment that is composed of uplands and a large (4.3 ha) continuous area of headwater wetland (0.1-1.9 ng L^{-1}, Figure 1).

TABLE II
MeHg export from three types of terrestrial catchments at the ELA, northwestern Ontario.

Catchment	Per Cent Wetland	1991 (mg ha^{-1} yr^{-1})	1992 (mg ha^{-1} yr^{-1})
Upland	0	0.07	0.08
Upland/ Riparian Wetland	14	0.32	0.87
Upland/ Headwater Wetland	16	0.96	1.14

The export of MeHg from these catchments follows a similar pattern to concentration, with the purely upland catchment consistently exporting about ten fold less MeHg per hectare than catchments that contain wetlands (Table II). The export of MeHg also depends on the seasonal distribution of precipitation. MeHg concentrations in runoff from wetland containing catchments are highest during mid-summer (Figure 1; St. Louis et al. 1994a). Thus, stream flow during midsummer, which can be quite variable depending on the timing and quantity of precipitation, is very important. For example, in the combination upland/riparian wetland catchment, stream flow was interrupted during midsummer 1991 by a prolonged drought and annual export during 1991 was less than half of the 1992 export when stream flow was continuous (Table II). In contrast, in the catchment containing the large headwater wetland, storage of water sustained stream flow during the dry summer, and export of MeHg was only slightly lower in 1991 than in 1992.

This pattern of MeHg concentrations and export in runoff from three different types of catchments (purely upland, upland/riparian wetland, upland/headwater wetland) is consistent at least within the ELA area. Very similar MeHg concentrations and export have also been found in the outflow from two other purely upland catchments, two other catchments that are combinations of uplands and riparian wetlands and one other catchment with a large area of continuous wetland (St. Louis et al. 1994b). This predictability means that it is possible to begin to model, for other boreal locations with similar atmospheric inputs, MeHg output from terrestrial surfaces using knowledge of the type and percentage of wetlands in upland terrain, the seasonal precipitation and predicted runoff (see later discussion).

Average annual input-output budgets for the three types of catchments for 1991-93 (Table III, St. Louis et al., 1994) show that catchments containing wetlands exported MeHg because they were net MeHg producers. The capacity of wetlands for producing MeHg can be fully appreciated by estimating the rate of MeHg production per hectare of wetland. For example, the combination upland/riparian wetland catchment consists of 86% upland terrain and 14% wetland area adjoining the stream that drains the catchment. If the whole catchment receives MeHg in precipitation at a rate of 0.39 mg ha^{-1} yr^{-1} and the upland area of the catchment exports MeHg at a rate of 0.07mg ha^{-1} yr^{-1} (Table III), then the wetland area must be producing MeHg at a rate of 4.7 mg ha^{-1} yr^{-1} to sustain the annual export from the catchment of 0.78 mg ha^{-1} yr^{-1}. Even if it is assumed that input from wet precipitation should be doubled by including litterfall (Hultberg et al., 1994), the wetland areas would still need to produce MeHg at a rate of 4.4 mg ha^{-1} yr^{-1} to support the measured export. This MeHg production rate is comparable to the estimated rate of MeHg production in ELA lake sediments (5.0 mg ha^{-1} yr^{-1}, see later discussion).

TABLE III

Average annual production of MeHg by terrestrial catchments at the Experimental Lakes Area, northwestern Ontario during 1991-1993 (ranges in parentheses). All values are in (mg ha^{-1} yr^{-1}).

Catchment	Wet Precipitation	Export	Production
Upland	0.39 (0.32 to 0.41)	0.07 (0.06 to 0.08)	-0.32 (-0.26 to -0.35)
Upland/ Riparian Wetland	0.39 (0.32 to 0.41)	0.78 (0.32 to 1.14)	0.39 (-0.09 to 0.82)
Upland/ Wetland Headwater	0.39 (0.32 to 0.41)	1.9 (0.96 to 2.4)	1.48 (0.55 to 2.11)

TABLE IV

Retention or demethylation of MeHg in upland catchments. All values are in (mg ha^{-1} yr^{-1})

Catchment	Wet Precip.	Wet + Dry Precip.	Export	% Retention or Demethylation
Gardsjon Upland	4.0[1]	8.0	2.0	75
ELA Upland	0.4[2]	0.8[3]	0.07[2]	91

[1] Hultberg et al. (1994)
[2] St. Louis et al. (1994)
[3] Assuming wet equals dry deposition as in Hultberg et al. (1994)

In contrast to wetlands, the ELARP study (St. Louis et al., 1994a; Allan et al., 1994) and other research (Hultberg et al., 1994; Lee et al., 1994) have demonstrated that uplands are sinks for MeHg in precipitation (Table III, IV). The fate of MeHg retained in uplands is unknown. Some is stored in soils (Lee et al., 1994). Feather mosses, which contain very high concentrations of MeHg (Moore et al., 1994), may also be important upland storage sites (although production of MeHg in these mosses may also explain these high concentrations). It is also possible that some of the MeHg "retained" by uplands is demethylated rather than stored in the soils or mosses but demethylation in upland soils has not been studied.

Even though a large percentage of MeHg is retained and/or demethylated in upland terrain (75% at Lake Gardsjon, southern Sweden, and about 91% at ELA, Table IV), runoff of the residual MeHg from uplands may be an important source to lakes in regions where atmospheric inputs are very high. For example, at Lake Gardsjon, MeHg runoff from an upland catchment is about 30 fold greater per unit area than at ELA (because of higher precipitation inputs and lower percentage retentions, Table IV). Also in contrast to ELA, runoff of MeHg from purely upland areas appears to be an important source of MeHg to lakes in southern Sweden. Hultberg et al. (1994) found that the amounts of MeHg entering Lake Gardsjon from upland runoff and direct precipitation were of equal importance (Figure 2). It was estimated that together these two inputs are sufficient to account for all MeHg accumulated by fish on an annual basis (Figure 2).

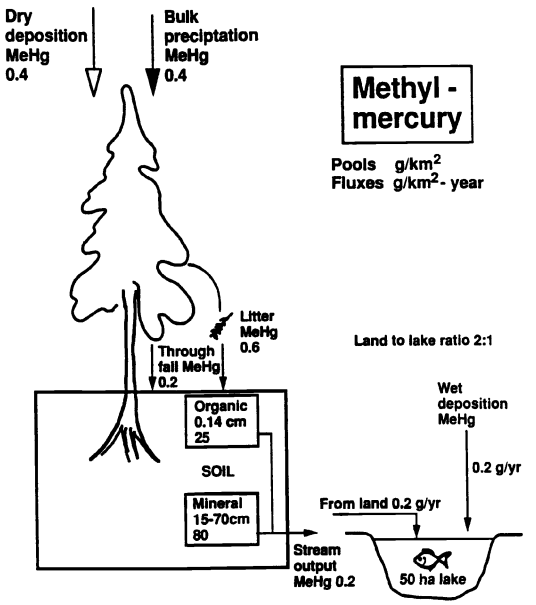

Figure 2. Pools of MeHg and inputs of MeHg to a 50 ha lake in southern Sweden with a 100 ha watershed. Inputs from direct wet deposition (0.2g/yr) and runoff were 0.2g/yr were sufficient to account for annual MeHg bioaccumulation by fish. From Hultberg et al. (1994).

In-Lake Production of MeHg:

Originally it was thought that all MeHg in freshwater ecosystems was produced internally and that methylating bacteria active in the sediments were the only source of internal MeHg production (e.g. Jensen and Jernelov, 1967). Later it was found that internal production also occurs in the water column (Furutani and Rudd, 1980; Parks et al., 1989), in the external slime layer of fish (Jernelov, 1972) and the intestinal contents of fish (Rudd et al., 1980). More recently, flooded terrestrial surfaces have been shown to be important internal source of MeHg to reservoirs (Hecky et al., 1991). While there is no doubt that methylation occurs in these sites, quantitative determinations of the rates of methylation and of the relative importance of these internal sources has eluded researchers for decades (Winfrey and Rudd, 1990).

The reason that our understanding of internal MeHg production is so vague is that there no methods for the measurement of natural rates of Hg methylation or demethylation. Isotopic methods that have been used for many years, only determine relative rates of methylation and demethylation and the ratios of methylation to demethylation (M/D, Furutani and Rudd 1980; Ramlal et al., 1986). While these methods are useful in determining sites of methylation and factors influencing rates of methylation and demethylation (e.g. Bodaly et al. 1993), for two reasons they do not give quantitative rate information (Winfrey and Rudd, 1990). First, high specific activity isotopes ($^{203}Hg^{2+}$ and $^{14}CH_3Hg^+$) have not been available, necessitating the addition of high concentrations of cold carrier Hg^{2+} or CH_3Hg^+. Second, methods have not been developed for the determination of the proportion of the isotope that is available to the methylating or demethylating populations. Thus the specific activity of the Hg or MeHg isotopes that the microbes use is unknown. For the measurement of methylation, Stordall and Gill (1994) have recently made progress on the first shortcoming by developing techniques that reduce the amount of Hg^{2+} carrier that is added to a sample. However, completion of a quantitative isotopic assay awaits development of methods for the measurement of the bioavialability of the added Hg^{2+}. To date, there has been no attempt to develop a quantitative isotopic method for the measurement of demethylation rates.

A second approach that is under development is to determine natural rates of net methylation in sediments using wet chemistry. For this approach, the net methylation rate is the sum of two separate measurements: 1) the flux of MeHg across the sediment-water interface and 2) the accumulation of MeHg on solid sediments with time. Methods for the flux measurement have been developed Sellers et al. (1994) but determination of rates of MeHg accumulation on the solid sediments is difficult because of the large background pool of MeHg that is attached to the sediment particles (P. Sellers and C. Gilmour pers. comm.). Probably some combination of the isotopic and wet chemistry approaches will be used in the future to obtain natural rates of methylation and demethylation.

Even though the quantitative methods for sediment methylation are not yet available, it is possible to obtain whole-lake estimates of net methylation rates using a mass-balance approach. For example, in the English/Wabigoon system, where large amounts of Hg were added from a chlor-alkali plant, an annual net methylation rate of 22 mg ha^{-1} yr^{-1} for the entire river-lake system was estimated using input-output budgets (Parks et al., 1989). More contaminated reaches of the system were estimated

to have annual rates about 10 fold higher than for the whole-ecosystem. A second whole-ecosystem methylation rate was obtained for a seepage lake (the treatment basin of Little Rock Lake, Wi.; Watras et al., 1994) using measured inputs of MeHg to the lake, as well as sediment trap fluxes and sediment accumulation of MeHg. In this case, the rate of 30 mg ha^{-1} yr^{-1} was considered to be a maximum estimate because it may have included some recycling of MeHg from particulate sedimentation to the water column (Figure 3).

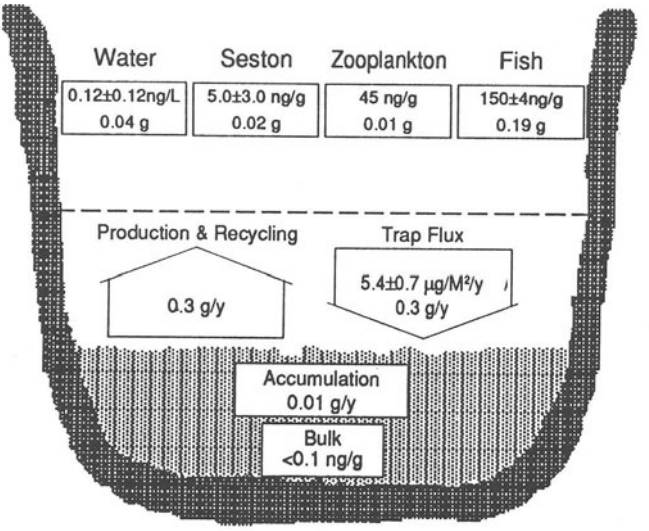

Figure 3. MeHg budget for the treatment basin of Little Rock Lake, WI. From Watras et al. (1994).

The mass-balance approach is also being used by the ELARP study to determine whole-ecosystem rates of Hg methylation before and after flooding of a 14.3 ha wetland. Input-output budgets and production and transport of MeHg within the experimental wetland were studied for two years prior to flooding (1991-92) and will be followed for at least 3 years after flooding in 1993.

Prior to flooding, MeHg concentrations in the outflow of the 2.4 ha central pond in the experimental wetland averaged 0.1 ng/L (0.05 to 0.28 ng/l). After 1 month of flooding, MeHg concentrations increased dramatically and peaked at a concentration of 2.3 ng/L (about 20 fold above preflood values, Rudd et al. in prep.).

TABLE V

Inputs to the model used to estimate the relative importance of direct atmospheric precipitation, terrestrial runoff and in-lake production as sources of MeHg to freshwater systems. Watershed and lake areas are in ha, MeHg inputs from all sources are in mg ha^{-1} yr^{-1}.

Simulation Lake/Reservoir	Lake Area (ha)	Watershed Area (ha)	% Wetland in Watershed	% Flooded	Direct Precip.[1]	Upland Runoff[2]	Wetland Runoff[3]	In-Lake Production[4]	Flooded Production[5]
Lake (Fig. 4a)	50	5, 100 or 500	0-100	0	0.4	0.1	3	5	-
Lake (Fig. 4b)	50	5, 100 or 500	0-100	0	0.4	0.1	3	30	-
Lake (Fig. 5a)	50	5-505	15	0	0.4, 0.9 or 4	0.1, 0.22 or 1.0	3	30	-
Lake (Fig. 5b)	50	5-505	15	0	0.4, 0.9 or 4	0.1, 0.22 or 1.0	3	5	-
Reservoir (Fig. 6a,b)	50	500	15	0-80	0.4, 0.9 or 4	0.1, 0.22 or 1.0	3	5	130

[1]Direct precipitation inputs are taken from measured values obtained at ELA (St.Louis et al., this issue), Wisconsin (Fitzgerald et al., 1991), and in southern Sweden (Hultberg et al., 1994). [2]It is assumed that upland runoff equals 25% of precipitation because uplands at ELA retained or demethylated 75% of MeHg in rain (Table IV).

[3]The mid range of export of MeHg from ELA catchments that contain wetlands (St. Louis et al., 1994).

[4]In-lake production rate of 5 mg ha^{-1} yr^{-1} is the average MeHg flux from undisturbed cores taken from wetland ponds at ELA (ELARP unpub. data). The 30 mg ha^{-1} yr^{-1} value is from Watras et al., 1994.

[5]The rate of MeHg production from flooded terrestrial areas (26 times flux of undisturbed ELA cores) was estimated from the minimum increase in MeHg flux observed after flooding of wetland 979 at ELA.

Annual input-output budgets show that there was a 26 fold increase in outflow of MeHg from the experimental catchment after flooding during the summer of 1993 (Rudd et al. in prep.). Early (first summer) post-flood data suggest that the large increase in loss of MeHg from the experimental catchment was the result of increased methylation and was not due to leaching of MeHg from plants and peat after flooding. This was concluded because the mass of MeHg in flooded plant tissues increased after flooding rather than decreasing, as would have been expected if leaching had been important (Heyes et al., 1994). MeHg also appears to be increasing in peat after flooding (unpub. ELARP data). Hence the estimated 26 fold increase in MeHg outflow is a minimum estimate of the increase in net methylation because a portion of the newly produced MeHg was bound by the plant tissues and peat. A more accurate estimate of the increase in methylation rate following flooding will be determined after further sample analyses. These results substantiate Hecky et al. (1991) who concluded, using indirect data, that there was a large increase in net methylation following flooding by reservoir development in northern Manitoba.

3.2. MODELLING THE RELATIVE IMPORTANCE OF MEHG SOURCES TO AQUATIC ECOSYSTEMS

Using the data from the three whole-ecosystem studies, a simple mathematical model was developed to examine the relative importance of atmospheric, terrestrial and in-lake sources of MeHg to lakes and reservoirs. With the limited amount of data presently available, this modelling exercise is useful primarily for evaluating differences in the relative importance of MeHg sources to lakes, and for establishing directions of future research (i.e. the model is not a predictive tool).

Inputs to the model included lake area, watershed area, and percent wetland in the watershed. Other inputs were fluxes of MeHg from direct precipitation to the lake surface, runoff from uplands, runoff from wetlands, and in-lake production.

Importance of watersheds as sources of MeHg:

Simulations of the relative importance of the watershed as a source of MeHg to lakes were made by manipulating three inputs to the model: 1) percent wetland in the watershed, 2) the ratio of watershed to lake area, 3) in-lake rate of MeHg production. For this exercise, fixed inputs to the model were the rate of direct precipitation onto the lake surface, and the areal rates of MeHg runoff from purely upland catchments and from wetlands. The values for all of these model inputs were measured values. The rationale for their choice are given in Table V.

Figure 4a gives simulations for three lakes that are 50 ha in area, which have in-lake methylation rates of 5 mg ha^{-1} yr^{-1} and are located in a region of low atmospheric precipitation (0.4 mg MeHg ha^{-1} yr^{-1}). One of the lakes is a seepage lake with a 5 ha watershed the other two lakes are drainage lakes with 100 and 500 ha watersheds. For the drainage lake with a 500 ha watershed, when only 15% of the watershed area was wetland, about 50% of the MeHg input to the lake originated from the watershed. This percentage of wetland is common to many catchments in Canadian the boreal forest. In contrast, for a seepage lake (5 ha watershed, 50 ha lake) only 6% of total MeHg input originated from the watershed even if 100% of the watershed was

composed of wetland (Figure 4a). This simulation is consistent with Watras et al. (1994) who concluded that in-lake production of MeHg was the major source of MeHg for Wisconsin seepage lakes

In Figure 4b, all factors are the same as in Figure 4a., except that in-lake methylation was set at 30 mg ha^{-1} yr^{-1} (Watras et al., 1994). In this case, the relative importance of the watershed as a source of MeHg to seepage lakes was extremely low even if 100% of the watershed was wetland. For a 500 ha:50 ha drainage lake, if the watershed was 15% wetland, about 18% of total MeHg inputs was from the watershed and if 100% of the watershed was wetland, 55% of total input was from the watershed. For this drainage lake situation, where in-lake methylation rate was high and atmospheric input was low, this simulation suggests that both the watershed and internal production were important sources of MeHg.

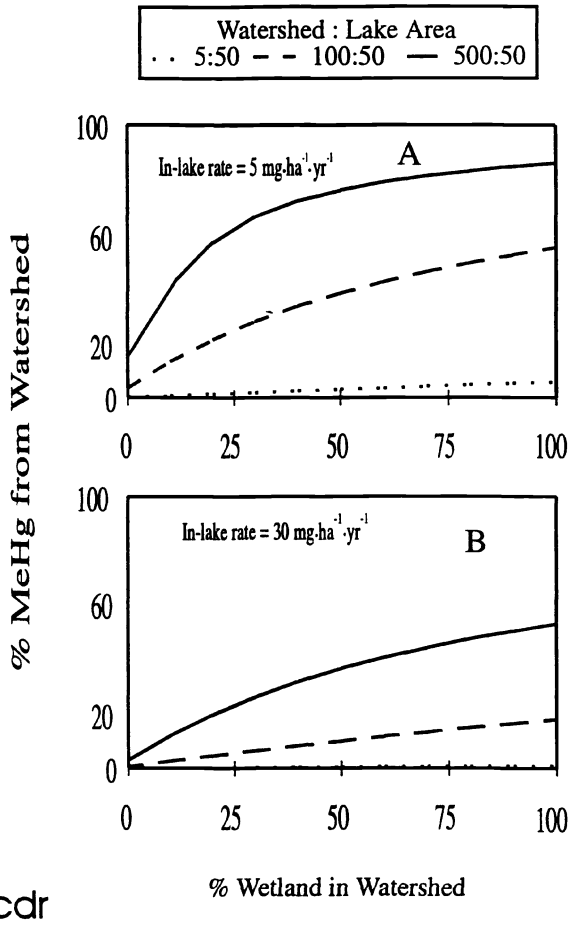

Figure 4. The relative importance of the watershed as a source of MeHg as a function of the watershed:lake area ratio, the % wetland in the watershed, and the in-lake methylation rate.

Importance of atmospheric precipitation as a source of MeHg:

Simulations of the possible importance of precipitation as a source of MeHg to lakes were made by manipulating the following inputs to the model: 1) watershed: lake area ratio, 2) rate of direct precipitation onto the lake, 3) rates of internal methylation. For this exercise, fixed inputs to the model were the percentage wetland in the watershed (15%) and the flux of MeHg from wetland areas 3 mg ha^{-1} yr^{-1}. It was assumed that 75% of the MeHg present in precipitation was retained or demethylated in upland watersheds (Tables IV,V).

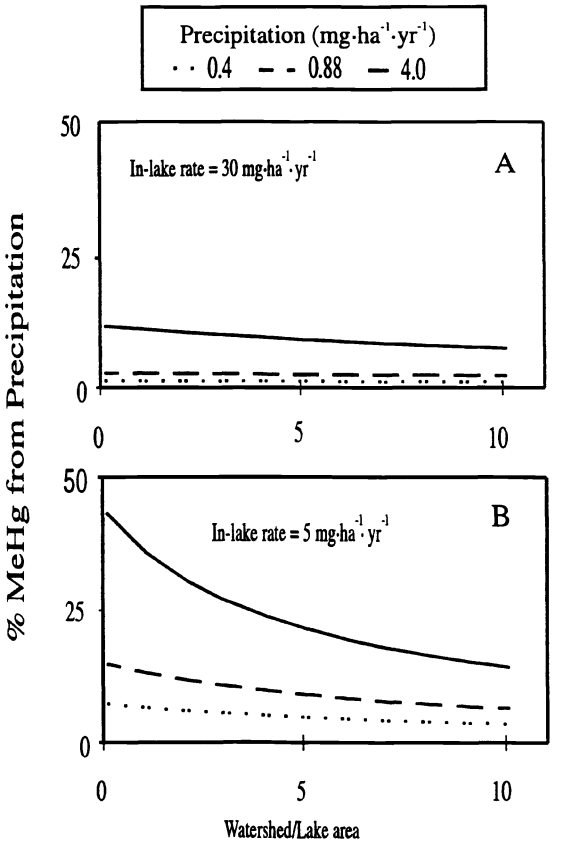

Figure 5. The relative importance of precipitation onto to the lake surface as a source of MeHg as a function of the watershed:lake area ratio, the MeHg precipitation rate, and the in-lake methylation rate.

Figure 5a gives simulations for three 50 ha lakes with internal methylation rates of 30 mg ha^{-1} yr^{-1}. At all three levels of MeHg in precipitation (Table I,V), inputs of MeHg to the lake surface would be of minor importance for both seepage and drainage lakes. This simulation is consistent with Watras et al. (1994) who concluded that input of MeHg from precipitation was of minor importance to a seepage lake (Little Rock Lake, WI). The simulations shown in Figure 5b suggest that if the internal methylation rate is reduced to 5 mg ha^{-1} yr^{-1}, that in regions of high MeHg in precipitation, direct

inputs of MeHg to the lake surface could be important for seepage lakes (up to 40% of total input) and significant for drainage lakes (>14%). If the total impact of the high precipitation rate is considered (by summing the direct inputs to the lake surface plus the elevated export from upland watersheds), the importance of precipitation could be >24% of total input for drainage lakes with a watershed: lake area ratios greater than 10:1 (simulation not shown). In general, these simulations support Hultberg et al. (1994) who concluded that precipitation can be an important input of MeHg to drainage lakes as well as seepage lakes in high precipitation areas. However, the simulations also predicted that at least 25% of MeHg was produced internally even in the extreme case of the low level of internal methylation rate (5 mg ha^{-1} yr^{-1}) and high MeHg deposition rate (4 mg ha^{-1} yr^{-1}). This is contrary to Hultberg et al. (1994) who concluded that internal methylation was unimportant in southern Swedish drainage lakes because MeHg inputs from precipitation and runoff equal annual uptake of MeHg by fish (Figure 3). Assuming there is significant internal methylation in southern Swedish lakes, as the model suggests, total MeHg inputs must be higher than annual fish uptake. This suggests that there must be significant internal demethylation in the southern Swedish lakes which would be necessary to balance the MeHg input-output budgets.

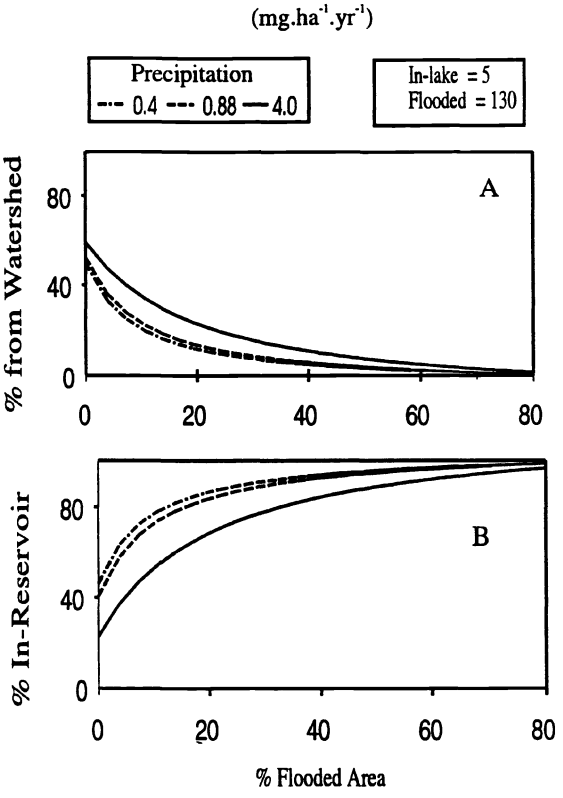

Figure 6. The relative importance of the watershed (a) and the in-reservoir production (b) as sources of MeHg to a reservoir as a function of the percentage of reservoir surface area that is flooded and MeHg input via direct precipitation.

Importance of flooded areas as sources of MeHg:

Simulations of the importance of flooded areas as sources of MeHg were made by manipulating two inputs to the model: 1) the percentage of reservoir surface area that was flooded terrain, and 2) the level of atmospheric deposition of MeHg (Table V, Figure 6). For this exercise, fixed inputs to the model were, the flux of MeHg from the former lake sediments (5 mg ha^{-1} yr^{-1}) and from flooded areas (130 mg ha^{-1} yr^{-1}), the areas of the watershed and former lake surface, the export of MeHg from wetland areas, and the percentage catchment area that is wetland (Table V).

The simulations are plotted as percentage of total MeHg input from the watershed (Figure 6a) and from internal reservoir production (Figure 6b). Both ways of looking at the reservoir situation show that the most important source of MeHg to a reservoir is internal production if the % flooded area of a reservoir surface exceeds about 10% of the reservoir area. The amount of MeHg in precipitation does not change the situation markedly because of the importance of internal production. Even in the extreme situation (simulation not shown), where 100% of the reservoir catchment is wetland and only 10% of the reservoir surface is flooded terrain, internal production is still equal in importance to watershed input.

These modelling exercises, which are based on measured MeHg fluxes in three systems located at three geographic locations, are consistent with data obtained in other independent studies of MeHg. For example, Driscoll et al. (1994) found a significant relationship between concentrations MeHg and DOC in lake water. They concluded that wetlands are important sources of both MeHg and DOC to lakes and this observation is consistent with the modelling results (Figure 4). Model simulations were also consistent with present understanding of MeHg fluxes in reservoirs. For example, Hecky et al. (1991) found large (2-3 fold) increases in the Hg concentrations of pike following flooding of Southern Indian Lake, Manitoba even though the surface area was increased only 20% by flooding (Newbury et al. 1983). They conclude that flooded terrain is the most important source of MeHg, which is also consistent with the model (Figure 6). The success of this model in generally simulating the results of recent studies indicates that the straightforward modelling approach used here is adequate to model sources of MeHg to freshwater systems.

4. Conclusions

Recent research has shown that there are three important sources of MeHg to lakes - internal production, inputs from watersheds that contain wetlands, and atmospheric inputs. Modelling of data from three recent whole-ecosystem studies demonstrates that under different circumstances each of the three sources can be important for lakes. For reservoirs, the model indicates that internal production of MeHg is always very important .

The success of the modelling exercise also demonstrates that with further research it should be possible to predict accurately MeHg inputs using the straightforward approach described here. Most urgently required are field studies that quantify fluxes of MeHg under different environmental circumstances. For example,

studies are needed:

1) to improve knowledge of total rates atmospheric deposition of MeHg at different geographic locations (i.e. is MeHg in litterfall important component of atmospheric deposition?)

2) to determine if MeHg export from wetlands is higher in regions of high atmospheric deposition than regions of low atmospheric deposition (i.e. is export from wetlands internally controlled?)

3) to develop methods that accurately determine rates of methylation in lakes and wetlands.

4) to develop methods that accurately determine rates of mercury demethylation in uplands, wetlands and in lakes.

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IS TOTAL MERCURY CONCENTRATION A GOOD PREDICTOR OF METHYL MERCURY CONCENTRATION IN AQUATIC SYSTEMS?[4]

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[4]Contribution No. 11 of the Experimental Lakes Area Reservoir Project (ELARP).

Abstract. Methyl mercury (MeHg) concentrations were compared to total mercury (THg) concentrations in a variety of types of aqueous samples collected at the Experimental Lakes Area during 1991 through 1993. In several streams, an experimentally flooded wetland, and peat pore water, there was no relationship between MeHg and THg concentrations. %MeHg (compared to THg) ranged from <1% to over 90%. In three ELA lakes, as in groups of lakes from other regions, a linear relationship between MeHg and THg concentration was found. However, these relationships differed by a factor of three from one region to another. This study shows that THg inputs and/or concentrations are not very useful in predicting MeHg concentrations, and that factors within ecosystems are very important in controlling MeHg concentrations.

1. Introduction

In aquatic environments, MeHg is the Hg species that is most toxic and that bioaccumulates most efficiently. Microbial methylation, rather than chemical methylation (Berman and Bartha 1986), is likely the most important origin of MeHg in watersheds and aquatic systems, except in areas that have very high MeHg in precipitation (Hultberg *et al.*, in press; Rudd, this issue). Diverse bacteria are known to methylate Hg in culture, but certain evidence from natural environments (sediments) and pure cultures suggests that sulfate reducers are especially important methylators (e.g., Gilmour and Henry 1991).

One pathway of methylation, demonstrated to occur in a culture of *Desulfovibrio desulfuricans* (Berman *et al.*, 1990; Choi and Bartha, 1993), is methyl transfer from cobalamin (vitamin B_{12}) to Hg^{2+}. Because Hg^{2+} is one of the reactants in the methylation reaction, the concentration of Hg^{2+} in a system might be expected to have an effect on the rate of formation, and the concentration, of MeHg. A linear relationship between amount of Hg^{2+} added to lake sediments and rate of formation of MeHg was shown in laboratory experiments (Rudd *et al.*, 1983), demonstrating that in a system where all else remained constant, methylation was first order with Hg concentration. On a larger scale, point source contamination of Hg from chlor-alkali paper plants also resulted in increased MeHg in the receiving river system (Parks *et al.*, 1989). In contrast, additions of Hg^{2+} to experimental enclosures in a reservoir did not enhance uptake of MeHg into fish (Hecky *et al.*, 1991).

The nature of the relationship between Hg^{2+} and MeHg is particularly important

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when considering the increasing content of Hg^{2+} in atmospheric deposition (estimated to be a factor of 2-5 since preindustrial times; Anon., 1994). While the examples referred to above suggest that a predictive relationship between MeHg and inorganic Hg might exist, these data are from systems where inorganic Hg concentrations were increased above background by over an order of magnitude. In this paper we will examine the relationship between MeHg and THg in a wide variety of aqueous samples taken from the Experimental Lakes Area (ELA), northwestern Ontario. THg is primarily inorganic in most samples, except for some wetland streams (e.g., Watras *et al.* in press; St.Louis *et al.*, 1994), and is the parameter most commonly measured in Hg studies.

The ELA receives no point source contamination, and is relatively removed from atmospheric effects of industrial activity, e.g., acid precipitation (Linsey *et al.*, 1989). THg and MeHg in precipitation are 4.04 $\pm$2.54 and 0.052 $\pm$.046 ng/L, respectively (St.Louis et al., this issue). The types of water sampled included streams, a lake, two wetland ponds and interstitial water from a peatland. We will also present data from a wetland pond and surrounding peatland that were experimentally flooded in 1993.

2. Methods

2.1 SITE DESCRIPTIONS

The Experimental Lakes Area is located near Kenora, Northwestern Ontario (93°30'-94°00'W, 49°30'-49°45'N). Streams or direct runoff draining four different headwater catchments were sampled. One upland catchment (114IF) was 5.7 ha, with young forest growth (following logging in 1976) and no wetland areas. A second upland catchment (224SIF) also had no wetland areas, but the forest was much older (>100 years), and the ground cover consisted mostly of feather mosses. One upland/wetland combination catchment (239EIF) was 170 ha, with young growth following a burn in 1980, and a riparian wetland along the drainage stream. A second upland/wetland combination catchment (979EIF) was 55 ha and very similar in vegetation and wetland distribution as the first. A headwater wetland catchment (632OF) was 40 ha, most of which was upland, but which contained a 3.5 ha wetland through which all runoff flowed before exiting at the outflow weir of the wetland. There was a central, 0.86 ha pond (Pond 632) in this wetland. A shield lake outflow was sampled that drained a 723 ha watershed containing 6 lakes and several wetlands, with Lake 240 (44 ha) being the last in the series. A second wetland pond (Pond 979) was sampled. It was 3 ha in area prior to experimental flooding and 10 ha after flooding on June 29, 1993. All of these sites, except the old growth upland catchment, are described in detail in St.Louis *et al.* (1994)

2.2. SAMPLE COLLECTION

All sample collection was as described previously in St.Louis *et al.* (1994), using the stringent clean-hands-dirty-hands protocol. Streams and ponds were sampled weekly during high spring flow, biweekly during the low-flow summer period, and monthly during winter at sites that had flow. All stream and lakes data reported here were from unfiltered samples.

2.3. ANALYTICAL

THg concentrations were determined by cold vapour atomic fluorescence (CVAFS), following oxidation with bromine monochloride (BrCl), reduction with $SnCl_2$, and purge and trap of the resulting Hg^o onto gold (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988). MeHg concentrations were analyzed by GC-CVAFS following distillation and aqueous phase ethylation of MeHg (Bloom, 1989; Horvat *et al.*, 1993).

The labs analyzing all of these samples (Brooks-Rand, Frontier Geosciences and Flett Research) recently successfully participated in an international intercalibration exercise (Bloom and Horvat, this issue). For Flett Research, who carried out most of the analyses shown here, analytical precision was $\pm$ 5% for THg, and $\pm$ 0.015 ng/L for MeHg. There are no certified standards by which to determine accuracy for low level aqueous samples. In lieu of this, comparison was made with the "consensus" value obtained in the international interlab comparison held recently (Bloom and Horvat, this issue). Flett Research results were within 9% and 12% for THg and MeHg, respectively.

3. Results and Discussion

In runoff water draining the purely upland, new growth (<20 years) watershed (Figure 1A), THg concentrations ranged from 4.6 to 16.3 ng/L and MeHg from 0.01 to 0.11 ng/L. THg concentrations were higher than in precipitation (Table I, due to evaporation, but MeHg concentrations were lower, due to retention and/or demethylation (Lee and Hultberg, 1990; St.Louis *et al.*, 1994). There appeared to be some year to year trends, with THg concentrations highest in 1991, and MeHg concentrations highest in 1993. There was no significant relationship between MeHg and THg concentrations during this three year period (r^2 = 0.0066, n = 38). It appeared that in 1992 and 1993 both MeHg and THg increased during each year, but the relationship was still not significant when each year was examined separately.

In a stream that drains a watershed containing both upland area and a riparian wetland (Figure 1B), THg concentrations were mostly between 7 and 14 ng/L, with a few lower values, and MeHg concentrations were between 0.11 and 0.47 ng/L. As in the upland catchment (Figure 1A), there appeared to be some year to year trends, with THg highest in 1991, and MeHg highest in 1993. There was no significant relationship between MeHg and THg concentrations over time (r^2 = 0.012, n = 44).

In the outflow stream of a headwater wetland (Figure 1C), THg concentrations were generally lower (2.2-7.4 ng/L) than in runoff water from the two upland catchments above, while MeHg concentrations were higher (0.16 to 2.7 ng/L). There was one period in the summer of 1991 when MeHg concentrations increased as Hg_T increased (Figure 5), but in the fall the two concentrations diverged completely and continued to show different patterns in the following two years. There was no relationship between MeHg and Hg_T concentrations over time (r^2 = 0.0064, n = 61).

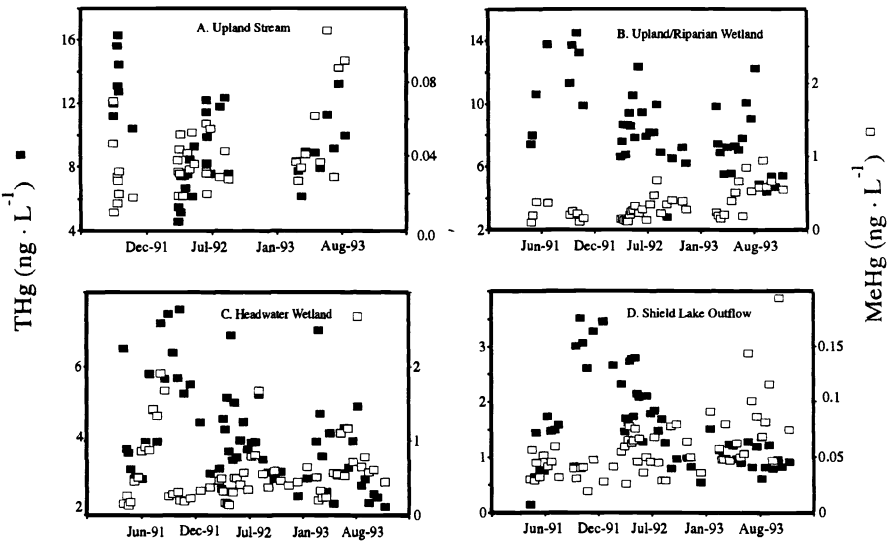

Fig. 1. Concentrations of MeHg and THg during 1991-1993 in, (A) a stream draining a new growth upland catchment, (B) a stream draining a combination upland/wetland catchment, (C) a stream draining a headwater wetland, (D) the outflow of a Canadian Shield lake.

The high MeHg concentrations in this and other wetland outflows (St.Louis *et al.*, 1994; Krabbenhoft *et al.*, this issue; Bishop et al., this issue) are likely related to high MeHg production in wetlands (St.Louis *et al.* 1994). Within peat porewater, % MeHg ranged from 1.2 to a very high 31% in depth profiles at two sites (Figure 2). This suggests that methylation rate was high at certain locations, but was not related to THg concentrations.

As in all of the ELA streams and runoff waters, the relationship between MeHg and THg in other streams is also highly variable with time (Bishop *et al.*, 1994; Krabbenhoft, this issue), so this variability appears to be a common characteristic of streams. Compared to streams, the concentrations of both THg and MeHg in the shield lake outflow (Figure 1C) were more uniform over the three year period (THg was 0.6 to 3.5 ng/L and MeHg was 0.02 to 0.19 ng/L). There was a slight seasonal pattern in the lake outflow, with lower values of MeHg in the winter and higher values in the summer (relative to THg), but with quite a few exceptions. There was no relationship over time between MeHg and THg concentrations (r^2 = 0.039, n = 58).

When all of the stream, runoff, and lake data were grouped together (Figure 3), there was some seasonal pattern in %MeHg, with the highest values occurring in the summer. Temperature is a factor that has been shown to influence methylation in the

absence of change in inorganic Hg inputs (e.g., Winfrey and Rudd, 1990; Ramlal *et al.*, 1993; Bodaly *et al.*, 1993). The effect of temperature is difficult to separate from other seasonal changes, such as increased primary production in summer months, but these seasonal patterns do illustrate that factors controlling MeHg within an ecosystem changed with time. While the summer period does not *necessarily* produce high MeHg concentrations, it is the period in which the highest values are possible (Figure 3).

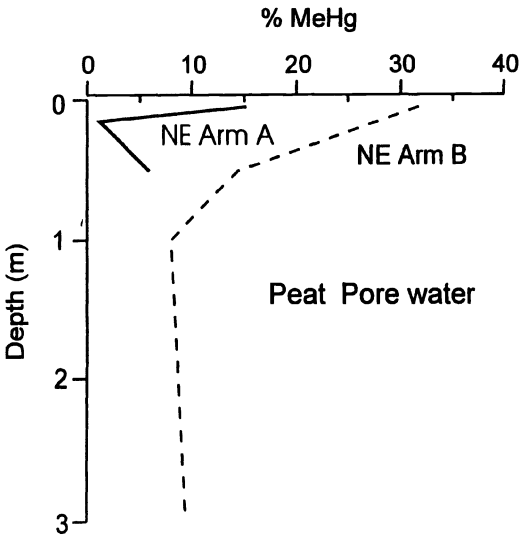

Fig. 2. % MeHg in the porewater of the experimental wetland, at two sites, collected after flooding in September, 1993.

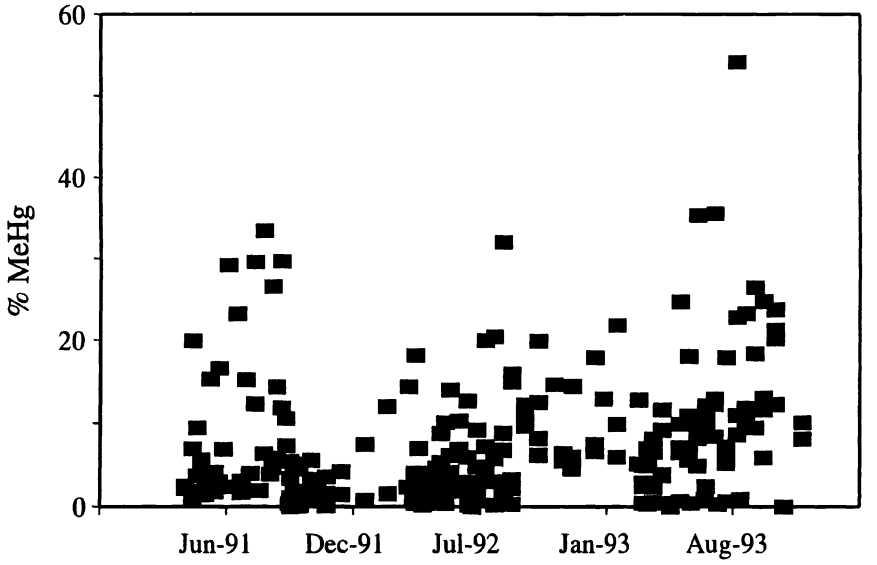

Fig. 3. Seasonal trends in % MeHg in stream, runoff and lake water, during 1991-1993.

In addition to looking at the relationship of MeHg to THg over time within each site, another way to look at these data is over the long term, and to ask whether sites that were generally higher in THg were also generally higher in MeHg. To do this, average MeHg and THg concentrations were calculated for each sampling site, using all data from the three year period (Table I).

TABLE I.

Average concentrations of THg and MeHg, and average % MeHg (±1 standard deviation) for samples collected 1991-1993 at the Experimental Lakes Area.

Site	Average THg ng/L	Average MeHg ng/L	Average % MeHg
Upland, new growth (114IF)	9.7 ± 3.0	0.04 ± 0.02	0.46 ± 0.25
Upland, old growth (224SIF)	2.3 ± 0.54	0.03 ± 0.03	1.3 ± 1.1
Upland/wetland (239EIF)	10.5 ± 4.0	0.21 ± 0.09	3.0 ± 3.4
Upland/wetland (979EIF)	8.4 ± 2.6	0.39 ± 0.42	4.7 ± 4.4
Shield lake outflow (Lake 240)	1.5 ± 0.81	0.06 ± 0.03	5.1 ± 4.1
Headwater wetland (632OF)	4.1 ± 1.4	0.6 ± 0.5	15.5 ± 10.6
Pond 632	3.3 ± 1.2	0.24 ± 0.07	8.1 ± 4.2
Pond 979 (preflood)	2.6 ± 1.5	0.09 ± 0.04	4.4 ± 2.5
Pond 979 (postflood)	4.5 ± 1.7	1.38 ± 0.51	31 ± 18
ELA precip. (St.Louis *et al.*, this issue)	4.04 ± 2.54	0.052 ± 0.046	1.0

There was no relationship between average THg and average MeHg concentrations at the different sites (Figure 4). One of the highest THg sites had one of the lowest MeHg averages (a new growth upland catchment). The old growth, upland catchment had similar low MeHg concentrations, but also very low THg concentrations (Table I). The three streams draining upland/wetland combination catchments showed a negative relationship between MeHg and THg (Figure 4).

In contrast to the overall picture (Figure 4), however, if only the lake and the two ponds are considered, there was a linear, positive correlation (Table II). Positive, and significant, correlations between MeHg and THg were found in other studies where the

data set included lakes only (with no stream or runoff data) and where lakes with anoxic hypolimnia were excluded (Table II).

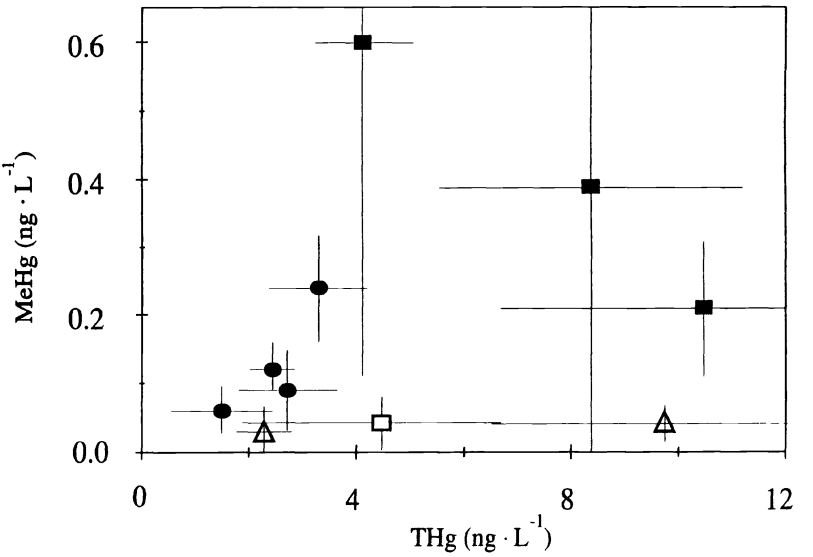

Fig. 4. Average concentrations of MeHg, with 1 standard deviation shown, plotted against the average concentration of THg for all the sampling sites. Data taken from Table I. Triangles are upland streams, squares are combination upland/wetland streams, and circles are ponds/lakes at ELA.

Table II.

The relationship between MeHg and THg concentrations in four sets of lakes located in different geographic locations.

LAKES	Regression Equation	r^2	n	P<0.01
E.W.[1]	MeHg = 0.06 THg_T + 0.05	0.83	8	yes
ELA	MeHg = 0.09 THg_T - 0.09	0.72	3	no
NY[2]	MeHg = 0.1 THg_T - 0.03	0.84	16	yes
WI[3]	MeHg = 0.2 THg_T - 0.1	0.81	7	yes

[1] English-Wabigoon, Parks *et al.*, 1989
[2] New York, Driscoll *et al.*, 1994
[3] Wisconsin, Watras *et al.*, in press

These studies suggest that THg might be a good predictor of MeHg concentrations for a particular set of lakes, once the relationship has been determined, and sites with anoxia are considered separately. However, the slopes of the lines relating

MeHg to THg in each lake set varied from 0.06 to 0.2 (Table II), meaning that a predictive relationship determined in one region may not be useful in another. Some possible explanations for regional differences are 1) different regions tend to have lakes with longer (e.g., Wisconsin seepage lakes) or shorter (e.g., English-Wabigoon system) water residence times, 2) different mineral and clay assortments could cause more or less binding of Hg^{2+}, and 3) different productivity levels in different regions could support different rates of microbial (methylation) activity.

An important question is *why* do lakes show linear relationships between MeHg and THg when streams, which are important inputs of MeHg and THg to most lakes, do not (either over time, or from one stream to another)? This implies an important role for internal (in-lake) processes in modifying the ratio of MeHg to THg, and that there is some common factor in lakes within one geographic area.

An example in which internal processes are obviously important in modifying the relationship between MeHg and THg is in reservoirs, where fish have elevated MeHg even though there has been no change in external inputs of inorganic Hg (e.g., Hecky *et al.*, 1991; Johnston *et al.*, 1991). In the Experimental Lakes Area Reservoir Project (ELARP; Kelly and Rudd, 1993; Rudd, this issue) both MeHg and THg were measured in water before and after flooding of a pond and its surrounding peatland. Flooding had a relatively small effect on average THg concentrations (the average concentration increased about 2-fold, from 2.6 $\pm$ 1.5 ng/L preflood to 4.5$\pm$ 1.7 ng/L postflood), but a very large effect on average MeHg concentrations (over 10-fold, from 0.09 $\pm$0.04 to 1.4 $\pm$0.5 ng/L; Rudd *et al.*, in prep.). There was also a dramatic increase in %MeHg in the surface water, from about 8% preflood to a high of 92% in August, 2 months after flooding (Figure 5).

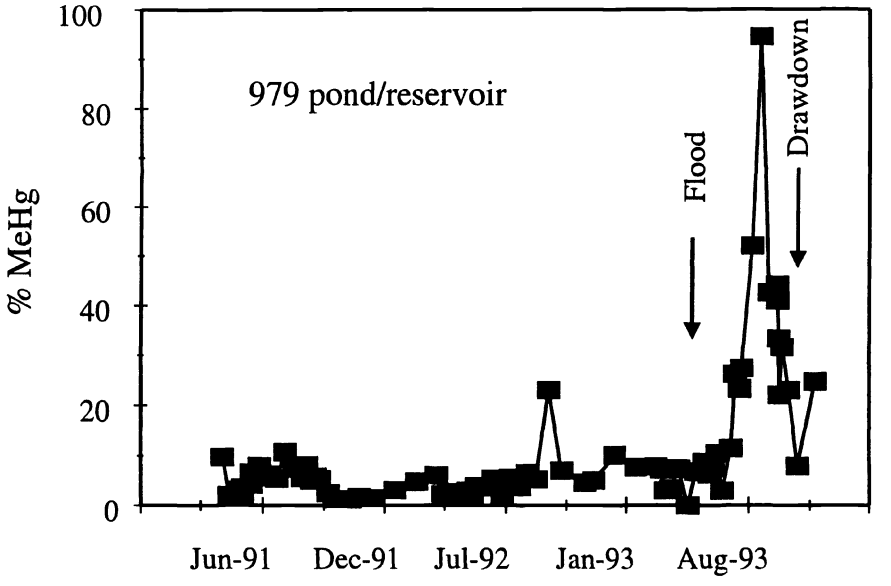

Fig. 5. Concentrations of MeHg and THg in the experimental wetland pond, before and after flooding on June 27, 1993.

The flooding example illustrates how a change in environmental conditions can mean that measurement of THg concentrations during this change would have very little predictive value for MeHg concentrations. Increased MeHg in reservoirs is thought to be linked to increased microbial activity, as flooded material is decomposed (Hecky *et al.*, (1991). Decomposition of dead organic material is probably analogous to experiments in which additions of bacterial substrate to sediments result in enhanced methylation activity without the addition of new Hg^{2+} (Furutani and Rudd, 1980).

The extremely high percentage of MeHg in the experimental reservoir following flooding (31% on average, and a high of over 90%; Figure 5) suggests that almost all of the inorganic THg in the water column, regardless of whether it was complexed or attached to particles, was available for methylation (which probably mostly occurred at the flooded peat surface (Rudd *et al.*, in prep). This is an important concept for modelling, indicating that methylation rate, rather than chemical speciation of inorganic Hg, might be the more important parameter to quantify and to use in predicting MeHg concentration in water and fish.

In summary, THg concentration was not a good predictor of MeHg concentration in stream water or in lakes in general, but it appeared to be a good predictor for lakes within individual geographic areas. The range of ratios of MeHg to THg was very large from one system to another, and changed dramatically following experimental flooding. Because THg was not a good predictor in many circumstances, this means that it must not be the overriding factor determining concentrations of MeHg in aquatic systems. This might lead one to conclude that there is no point in controlling Hg emissions to the atmosphere because factors within ecosystems are more important in determining the amount of MeHg that is produced. On the other hand, laboratory addition experiments and point source releases of inorganic Hg show that increased Hg^{2+} usually leads to increased MeHg. Obviously, *both* Hg^{2+} inputs and changes in environmental conditions within ecosystems are important in determining MeHg concentrations. Most importantly, we need to study MeHg itself in order to understand its production in the environment.

Acknowledgments

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DETERMINATION OF MERCURY METHYLATION RATES USING A 203-HG RADIOTRACER TECHNIQUE

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Abstract. A radiotracer method for the determination of mercury (Hg) methylation rates in bulk water and water overlying intact sediment cores has been developed. A sediment core with overlying water is collected in a core tube, the overlying water is spiked with high specific activity 203-Hg radiotracer, and the core is incubated at ambient temperature. Aliquots of the overlying water are removed, the Hg is extracted from the sample, and the activity in the extract is measured. A 10-25 fold sample preconcentration is achieved using a dithizone-chloroform extraction technique and a sodium nitrite back extraction step to separate inorganic Hg(II) from monomethylmercury (MMHg). The use of this technique, in conjunction with high specific activity 203-Hg, has allowed for spiking concentrations in the overlying water of approximately 1 ng Hg/L. This spiking level is about the same concentration as the ambient water overlying the core, thus not significantly perturbing the system. Our technique is a significant improvement over previous methodologies which used 203-Hg spike additions of 1 μg Hg/L or higher. The technique was used to measure Hg methylation rates at the Experimental Lakes Area (ELA) in Ontario, Canada during August of 1993 and at an extensively studied estuarine site in Gulf Breeze, Florida, USA during September, 1993 and June, 1994. Multiple cores were collected and spiked with a range of 1 to 11,800 ng Hg (as 203-Hg) into the overlying water. MMHg production at the ELA site indicated rates of 0.25 to 3.7 pg/cm^2/day (0.08 to 2.5 % methylation/day). Results from Gulf Breeze were significantly higher at 1.5 to 425 pg/cm^2/day or 0.06 to 18 % methylation/day. These rates are one to three orders of magnitude greater than previously measured "specific rates" in bulk water samples and sediments. A direct comparison of rates with previous sediment methylation assay techniques is not possible, however, because of the significant differences between our methodology and previous assay protocols.

1. Introduction

The various chemical forms or species of an element in natural waters can behave differently thereby controlling its biogeochemical behavior and toxicity to organisms. In the case of mercury (Hg), the element's chemistry in aquatic systems is very complex because a thermodynamically predictable interaction does not exist between solution complexes of inorganic Hg(II) and organo-Hg compounds, such as monomethylmercury (MMHg). It is now well established that MMHg in natural waters and sediments is principally produced by bacteria from inorganic Hg that is naturally present in the ecosystem and from Hg that is added from exogenous sources. The partitioning of Hg between these two pools is kinetically controlled by the net effect of the production (methylation) and destruction (demethylation) of MMHg by biologically mediated processes. The relative abundance of methylated Hg species in aquatic systems is of particular concern since these compounds are highly toxic, they are the major form of Hg accumulated in fish tissues, and can enter the food chain by direct uptake from solution (Westoo, 1973; Huckabee *et al.*, 1979; Cappon, 1984; Stokes and Wren, 1987).

In recent years, considerable research has been conducted on the factors controlling methylation and demethylation of Hg in aquatic systems. Extensive

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background on this subject for low pH lakes can be obtained from recent reviews by Winfrey and Rudd (1990) and Gilmour and Henry (1991). Much of this work has been conducted using Hg radiotracer additions to natural water column or sediment core samples to monitor the Hg methylation or demethylation process. While presently available radioisotopic assay methods (e.g. Furutani and Rudd, 1980; Gilmour *et al.*, 1992) enable researchers to study the factors controlling MMHg production by bacteria and to use this information in developing predictive models, we are presently not able to quantitatively measure the rate at which inorganic Hg atoms are converted to MMHg molecules in natural environments hereafter referred to as "true" *in situ* rates of MMHg production. Rather, the rates that have been obtained are reported as "specific rates" because the assay techniques require the addition of Hg at levels that often greatly exceed ambient concentrations (Ramlal *et al.*, 1986). In fact, researchers caution that this information should only be used for relative comparisons within a given system of the effects of particular environmental condition on methylation and demethylation rates (Xun *et al.*, 1987).

The major goal of this research was to develop a radioisotopic method so that "true" *in situ* rates of Hg methylation can be assayed in the water column and at the sediment-water interface. Two basic changes were made to current radiotracer assay methods to work at "environmentally realistic" spike levels of added radiotracer. First, enhanced sensitivity in counting radioactive decay was achieved by switching from liquid scintillation counting (the most common method currently being used) to gamma counting using a NaI detector. This change achieved between a 10- and 100-fold enhancement in sensitivity for comparable counting times. Additional reductions (~10-fold) in added radiotracer spike have been achieved by obtaining a higher specific activity (20 to 30 mCi/mg) radiotracer.

2. Materials and Methods

2.1 SEDIMENT CORE AND BULK WATER INCUBATIONS

Sediment cores were obtained by pushing a 10 cm diameter by 17 cm or 35 cm length Teflon cylinder into the sediment to a depth of approximately 7 to 15 cm. Sediment was removed from around the outside of the core to allow placement of a threaded Teflon cap below the core tube prior to removing from the sediment. Upon removal from the sediment, a polyethylene cap was placed on the core top and the core was placed in a clean polyethylene bag for transport to the lab. Water samples for incubations were collected directly into 2 L Teflon sample bottles using trace metal clean protocols for collection and handling (Gill and Bruland, 1990).

Sediment core incubations were conducted by adding 203-$HgCl_2$ radioisotope to approximately 500 mL to 1L of water overlying an intact core. Bulk water samples were similarly spiked. Temperature was controlled by using an incubation chamber set to the temperature of the sediment during the time of collection. The cores and bulk water samples were typically incubated for 12 to 48 hours with at least 4 subsamples collected for analysis during this period. A "time zero" aliquot was taken immediately after

This sample extraction procedure achieved several desirable features necessary for conducting low level radioisotopic assays of Hg over the previous technology. First, a preconcentration of analyte of approximately 5 to 10-fold was achieved. Second, the final volume is small (typically 10-20 mL) which is necessary for introduction of the whole sample to the detector for counting. Third, the technique is compatible with trace element clean handling practices and protocols; a necessary requirement for working at trace levels. And fourth, the procedure is simple; the reagents used are minimal, they have a low Hg blank, and the recovery is high.

The gamma detector cosisted of a well-type NaI crystal (5 1/4", Harshaw Chemical) interfaced to a multi-channel analyzer (NaI-plus board, Canberra) installed in an IBM compatible PC. The liquid scintillation detectors that have been used previously have very high efficiencies, however, the sample must be mixed with a scintillation medium (cocktail), therefore only a fraction of the sample can be counted. Thus, the dilution by the cocktail raises the detection limit and increases the amount of total Hg that must be added at the beginning of the experiment.

We conducted several laboratory tests of the extraction methodology to confirm the separation efficiency reported by Schintu *et al.* (1989). Initially, the back extraction into $NaNO_2$ was performed only twice. This did not always separate all the inorganic from organo-Hg. Repeating the extraction two more times for a total of four extractions resulted in consistent background results for the organo-Hg fraction. This extended procedure was used for the June, 1994 samples. The initial extraction step was better than 98% efficient with distilled de-ionized water, and our local estuarine seawater (Table I). The back extraction step also had a similar extraction efficiency for these matrices. The procedure was also tested for the extraction of radiolabelled MMHg (Table I). The procedure was approximately 90% efficient for D.I. water but only 79% efficient for estuarine water.

Table I
Extraction efficiencies for 203-Hg spikes.

Fraction	D.I. #1	D.I. #2	D.I. #3	Estuarine
Extraction efficiency for inorganic mercury spikes:				
Organic	99%	99%	98%	---
Inorganic	99%	98%	95%	99%
Extraction efficiency for organic mercury spikes:				
Organic	92%	86%	88%	79%
Inorganic	---	---	---	---

2.3 DETECTION LIMIT

We define the "detection limit" as the minimum detectable amount of MMHg production that can be achieved in a MMHg assay. MMHg production can be expressed as a percentage of the amount of initial spike added or as total pg of Hg methylated per unit time (e.g. pg MMHg/ cm^2/ per day). The amount of total Hg added in each experiment can be estimated from the specific activity (mCi of radioactive Hg per mg of stable Hg). Because of the high specific activity of the Hg, we were able to spike 1 ng into the overlying water yielding a concentration of 1-2 ng Hg/L. The spike concentration was verified through direct analysis by the methods of Gill and Bruland (1990). We estimated detection limits for each set of experiments by dividing twice the activity associated with the background counts by the activity (in counts per minute) of the spike added. These radioactivity determinations were then converted to stable Hg levels using the initial specific activity of the 203-Hg radiotracer supplied by the manufacturer. All results were also corrected to the activity level at the time the experiment was conducted using the half-life of the Hg radioisotope (46.6 days). Factors which affect the detection limit include: the specific activity of the Hg radioisotope, the amount of Hg spike added in the assay, the volume of sample taken for an assay, the amount of decay that occurs between the experimental manipulation and isotope counting, and the separation efficiency of the radioisotopic MMHg produced from the original inorganic spike. For core assays, we estimate a detection limit between 0.2 to 0.8 pg/cm^2/day or 0.06 to 0.3% methylation per day.

2.4 FIELD EXPERIMENTS

Sediment cores and water samples were collected from a number of study sites in the development of this methodology. During the summer of 1992, we did not have the high specific activity spike and were limited to spiking at relatively high concentrations (250-700 ng/L). We visited a number of sites including the Experimental Lakes Area (ELA), Ontario; Lake Barco, Florida; Offatts Bayou, Texas and in the Gulf of Mexico. Cores and water samples were collected at all these sites with only one core showing any results. In 1993, experiments were performed using the higher specific activity Hg radiotracer at ELA and at a site in Gulf Breeze, Florida where methylation had been successfully and repeatedly measured by others. These experiments were repeated and extended in June, 1994 at Gulf Breeze, Florida.

2.4.1 *Experimental Lakes Area*

Samples were collected from ELA in August, 1993 after the flooding of Lake 979 in July (to simulate hydroelectric operations). Eight sediment cores with approximately 800 mL of overlying water were collected by diver using a 2L Teflon cylinder and were returned to a shore based laboratory for isotopic spiking. The overlying water was spiked with a total amount of Hg equivalent to 1 , 5, and 20 ng. Incubation of the cores was conducted at the lake temperature of 20°C inside a controlled temperature chamber. The samples were slowly rotated on a special mount to mimic the conditions at the sediment water interface. Subsampling (100-250 mL aliquots) occurred over intervals of 3 to 8 hours.

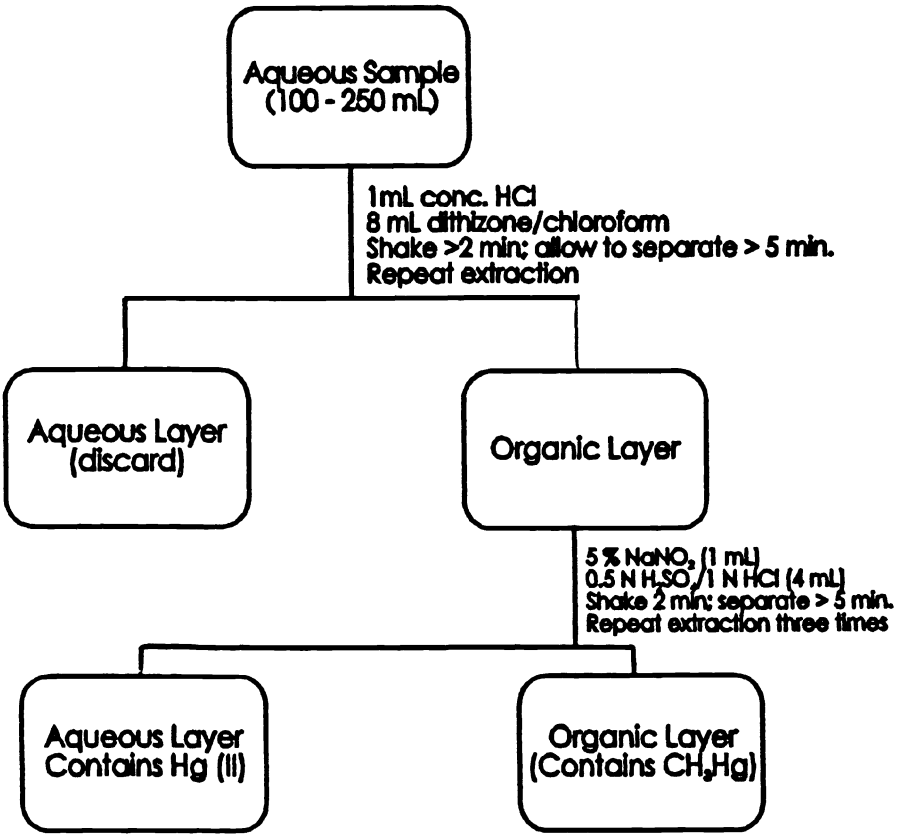

Fig. 1. Determination of mercury Methylation Rates using a 203-Hg Radiotracer Technique.

2.4.2 *Gulf Breeze, Florida*

A total of twelve cores were collected from a shallow, brackish water environment near the EPA lab in Gulf Breeze, Florida in September, 1993. The overlying water was spiked with 1, 5, and 20 ng of total Hg. The Teflon containers were smaller (1L) than the containers used at ELA. Because of the sandy bottom, the cores were "built" by placing some of the sand and plant material in a core that already had the bottom screwed on. Water was then placed on the top. The cores were allowed to equilibrate for at least eight hours at a temperature of 30°C before spiking. Subsamples were taken approximately every 3 to 4 hours over a 24-hour period. Additional core incubations were conducted in June, 1994 at this same location. The overlying water was spiked with a broader range of concentrations from 2 to 11,000 ng total Hg. The cores were subsampled every 3 hours for a period of 12 hours. One core was incubated at 5°C to determine whether the incubation temperature would affect the methylation rate. A water sample was collected and spiked at a level of 20 ng/L to examine the methylation without sediment.

3. Results and Discussion

Results from cores collected at ELA and Gulf Breeze in which methylation appeared to be occurring at measurable rates are reported in Table II. As mentioned earlier, this represents only a fraction of all the cores collected. The difficulty in finding sites where measurable methylation is occurring is indicative of the heterogeneity of the Hg methylation process. The successful sites had a significant amount of degrading organic matter and the presence of hydrogen sulfide indicating a reducing environment. The Gulf Breeze samples were from a sandy site. Methylation rates were measurable at one site in the Florida Everglades where the sediment was also sandy. Core 13 collected from Gulf Breeze in June, 1994 was incubated at 5°C rather than 30°C. The reduction in temperature significantly lowered the methylation rate when compared to cores 6 and 11, which were spiked at the same level. The initial concentration of total Hg added to the overlying water for each core is given in Table II. Analysis of filtered lake water from ELA indicated a concentration of 2.5 ng total Hg/L. Unfiltered water from Gulf Breeze had 4.2 ng total Hg/L in the overlying water. The water sample collected at Gulf Breeze in June, 1994 had an initial positive signal for MMHG that decreased to a background level within six hours indicating that demethylation may be occurring in the water column.

Time course data for six cores reported in Table II are shown in Figure 2. In all cases, there was a significant increase between the initial measurement and the first sampling at 3 hours. This rapid production was followed by a general decrease in net production over the rest of the time period. We interpret this as indicating that demethylation was significant, especially when coupled with the demethylation observed in the water sample from Gulf Breeze. Some other process such as adsorption onto sediments could also be causing the reduction in MMHg in the overlying water. A minimal gross methylation rate was estimated from the slope of the line between the initial point and the first data point. We emphasize that this rate is only approximate since it appears that intensive subsampling is required during the first six hours to get a

Table II
Summary of methylation rates from select cores.

Core Number	Amount Spiked (ng)	Water Volume (ml)	Hg Conc. Initial (ng/L)	Methylation Rate ($pg/cm^2/day$)	Methylation Rate (% /day)
ELA 8/93:					
8	1	660	1.5	0.25	1.3
1	5	910	5.5	0.54	0.6
2	5	910	5.5	1.7	2.5
6	20	950	21	3.7	1.3
7	20	650	31	0.54	0.08
Gulf Breeze 9/93:					
12	1	900	1.1	1.5	14
13	5	650	7.7	8.2	12
14	20	580	34	22	8.5
15	20	580	35	32	12
Gulf Breeze 6/94:					
7	2.2	540	4.1	2.4	8.6
6	22	710	31	50	18
11	22	600	37	44	16
13*	22	620	36	1.2	0.44
8	64	510	130	36	4.4
9	580	600	970	200	2.8
12	580	610	950	430	5.7
14	11,400	500	22,800	82	0.06
* - incubated at 5 °C					

more detailed picture of the true rate before demethylation or adsorption become significant contributors. Methylation rates *vs.* initial concentration in the overlying water are shown in Figure 3 as both $pg/cm^2/day$ and % methylation/day. The rate reported as % methylation/day shows a general decrease as the concentration added increases indicating that there is a limiting factor other than the amount of mercury added. At high concentrations, the amount of MMHg formed depends on the amount of methylating agent available in the system. The methylation rate reported as $pg/cm^2/day$

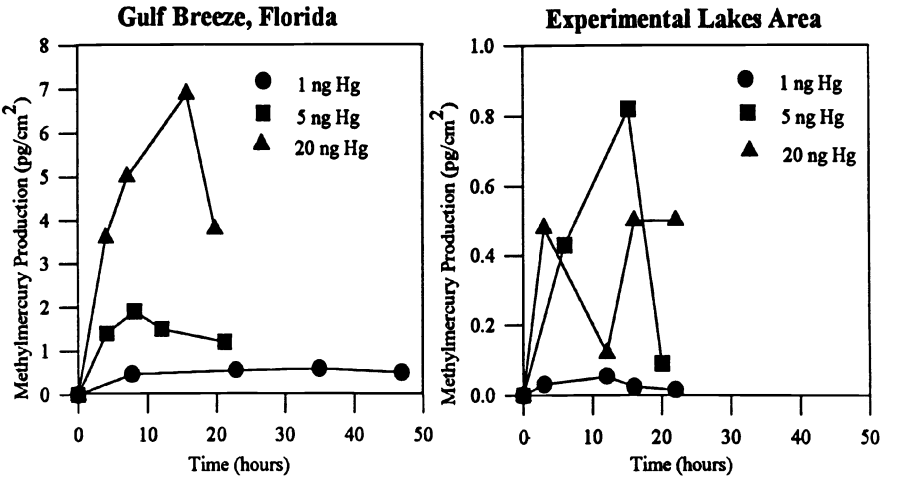

Fig. 2. Time course of MMHg production in water overlying a sediment core using three different spike levels.

indicates an increase with increasing concentration and shows a spike at the 1 μg concentration level. Additional data are required to interpret this spike.

A conceptual model of the speciation and exchange process that may be occurring in the core is given in Figure 4. Our methylation assays measure the amount of MMHg in the water column above the core and do not include any MMHg that may be adsorbed onto the sediments at the sediment-water interface. Each data point reflects a balance between methylation, demethylation, and the flux or exchange between the water and sediment. One possible scenario is that the inorganic Hg is being removed to the sediment-water interface, methylation is occurring at this interface by microbial activity, and the MMHg diffuses back into the water column. However, by our assay technique, we cannot distinguish between methylation occurring in the water column, methylation occurring in the sediments and "true" *in situ* methylation by specific microbes.

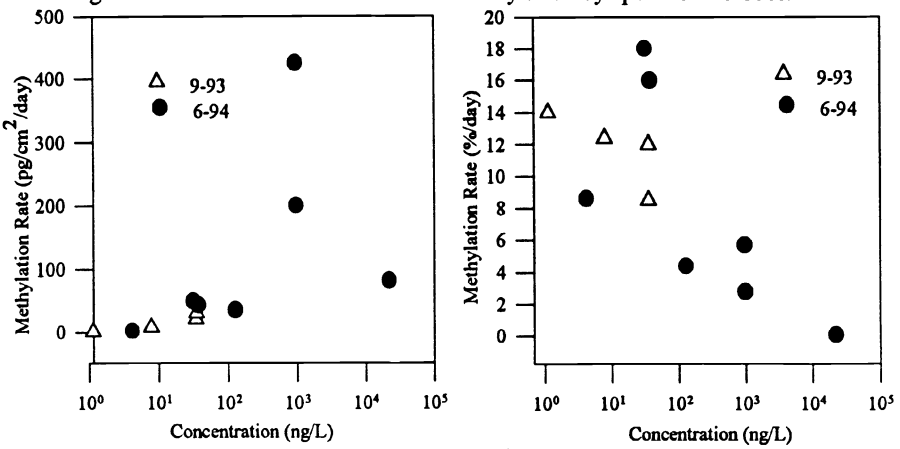

Fig. 3. Comparison of Hg methylation rates reported as pg/cm²/day and % methylation/day for the same cores.

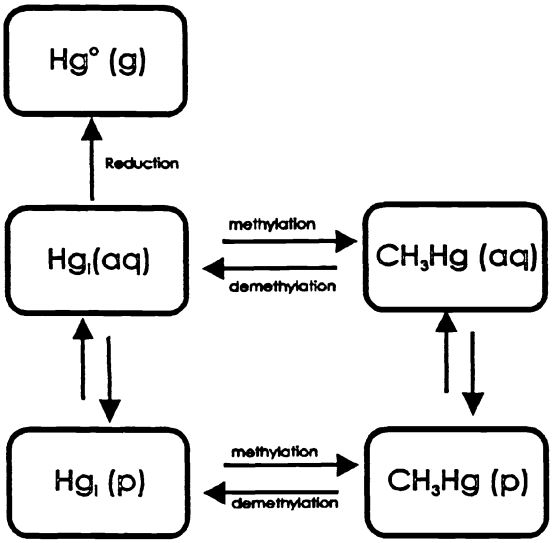

Fig. 4. Model of mercury methylation in core.

Measurement of both bulk water samples and water overlying sediment was tried in several of our investigations. The water sample collected from Gulf Breeze in June, 1994 indicated net demethylation in the water column, although other water samples have indicated a small net methylation. From our observations, both methylation and demethylation may be occurring within the water column, however it is not as significant in the short term as the methylation occurring when sediment is present.

Analysis of the water fractions for most of the cores indicated a steady decrease in the amount of radioactive inorganic Hg in the overlying water. Over 60 % was observed to be lost during the initial 24-hour period. The dithizone-chloroform extraction was attempted on the sediment but it appears that the majority of the Hg cannot be removed from the sediment by this method. This would indicate that removal of the inorganic Hg is a part of the process.

4. Conclusions

The goal of measuring methylation using a tracer with spiking concentrations near natural levels was achieved. The separation chemistry appears to work well. Results show significant and readily measurable methylation occurring at ELA and Gulf Breeze on short time scales (hours). Modifications need to be made in the sampling intervals since it appears that demethylation is very significant and starts to measurably reverse the process within the first 12 hours. Now that the method has been shown to work, the procedure can be extended to other areas and we can study the affects of variations in environmental conditions. A significant drawback is the short half-life, which requires most experiments to be done within the first few months of obtaining the spike, if low levels are required for the procedure.

For future work, the following areas should be addressed: 1) measure demethylation rates with a high specific activity MMHg radiotracer to compare with methyltion rates and determine whether demthylation is the primary removal process; 2) measure the production of radioactive elemental Hg, if it is being formed; 3) expand the technique to examine MMHg produced that is not released into the water column; and 4) measure other parameters at sites where methylation is readily occurring to understand why the process is heterogenous within the environment.

Acknowledgements

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METHYLMERCURY PRODUCTION IN THE ANOXIC HYPOLIMNION OF A DIMICTIC SEEPAGE LAKE

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Abstract. Experimental results and field data indicated that methyl-Hg was produced within a layer of bacterioplankton near the top of the anoxic hypolimnion of Pallette Lake. In situ incubations at ambient Hg concentrations indicated that the net flux of methyl-Hg from the layer was between 50 and 100 pmol/m^2*d. This input was sufficient to account for the summer accumulation of methyl-Hg in the entire hypolimnion and it exceeded atmospheric inputs by 2 orders of magnitude. Maximum rates of net methylation occurred in the same region of the water column where we observed maximum rates of sulfate reduction. The measured rates were: 100 fmol methyl-Hg/L*d and 90 nmol SO_4/L*d. Sulfate reducing enrichment cultures isolated from the hypolimnion were also able to methylate Hg in the laboratory. Sulfate reduction did not occur in anoxic profundal sediments during summer and we infer from ancillary data that methylation in profundal sediments was also low. Whole-lake rates of sulfate reduction in the hypolimnetic layer and shallow sediments were roughly equivalent, but we cannot yet compare methylation rates at these sites due to large uncertainties in the littoral flux of methyl-Hg. We propose that zones of Hg methylation and SO_4 reduction follow the oxic/anoxic boundary in both the watercolumn and sediments. The relative importance of watercolumn and sediment processes will depend on the physical and chemical structure of a given lake.

1. Introduction

Mass balance studies have shown that external loading is not sufficient to account for the methyl-Hg accumulating annually in the biota of several Wisconsin seepage lakes (Watras et al., 1994). This observation suggests that in-lake methylation is an important component of the Hg cycle in these lakes. However, there are large uncertainties in present estimates of in situ rates of methyl-Hg formation. Due to methodological constraints, it has not been possible to directly measure Hg methylation under natural conditions.

In 1988, the accumulation of methyl-Hg in the anoxic hypolimnion of Little Rock Lake was first observed (Bloom and Watras, 1989). Hypolimnetic increases in Hg and methyl-Hg followed Fe during summer anoxia but not in winter, suggesting that factors other than shifting redox conditions were the cause (Hurley et al., 1991; Bloom et al., 1991). Fine-scale vertical profiles in three stratified lakes later showed that the seasonal development of a methyl-Hg rich region paralleled the development of bacterioplankton layers below the oxic/anoxic boundary (Watras and Bloom, 1994). These data suggested that methyl-Hg was formed de novo within plankton layers. The seasonal time-course of methyl-Hg build-up indicated net methylation rates of 50 to 100 ng/m^2*d in the anoxic watercolumn.

In saline and freshwater sediments, Hg methylation has been linked to the activity of sulfate reducing bacteria (SRB) (Compeau and Bartha, 1987; Gilmour et al., 1992). In Wisconsin lakes, watercolumn profiles have indicated that hypolimnetic zones of methyl-Hg enrichment were also transition zones for sulfate and sulfide concentrations (Watras and Bloom, 1994). Bacteriochlorophylls indicated the presence of phototrophic sulfur bacteria (PSB) and the sharp

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depletion of sulfate suggested the presence of SRB. Consortia of these sulfur-cycle microbes are known to exist in stratified Wisconsin lakewaters (Parkin and Brock, 1981).

Here, we report the results of field studies on Hg methylation in the watercolumn of a remote lake in northern Wisconsin. We monitored seasonal changes in the depth distribution of waterborne Hg species and we measured net rates of Hg methylation using in situ incubations at ambient Hg concentrations. The objectives of these studies were: 1) to directly measure net rates of methyl-Hg formation in the watercolumn; 2) to determine the potential importance of watercolumn methylation on the seasonal dynamics of methyl-Hg in the lake; and 3) to compare Hg methylation rates with the rates of other biogeochemical processes (such as sulfate reduction, bacterial production, and photosynthesis) at specific depths in the watercolumn.

2. Methods

Pallette Lake is a pristine 70 ha, clear-water seepage lake with a maximum depth of 18 m (Watras et al, 1994). Anoxia develops in the hypolimnion to a depth of roughly 12m by late summer. Layers of planktonic algae and bacteria occur in both the oxic and anoxic portions of the stratified watercolumn (Watras and Bloom, 1994).

During 1992, we sampled the lake monthly from June - September using a vertical profiling system that measures several bio-optical and physical variables at a spatial scale of 1 - 2 cm throughout the watercolumn (Watras and Bloom, 1994). At specific depths relative to the observed location of plankton layers, we collected discrete water samples for chemical and biological analyses. Detailed methods for these analyses are given by Watras et al. (1994), Watras and Bloom (1994) and Craig (1987). Using clean technique, we also collected discrete water samples for Hg speciation (Watras and Bloom, 1994). Analytical methods for Hg species followed Bloom and Fitzgerald (1988) and Bloom (1989).

Incubation experiments were conducted during July and August. Water samples were collected to determine net rates of Hg methylation (using unamended whole-water samples), sulfate reduction (using $^{35}S\text{-}SO_4$: Jorgensen, 1978; Gilmour et al., 1992), heterotrophic bacterial production (using ^{3}H-thymidine incorporation: Fuhrman and Azam, 1982) and photosynthesis (oxygenic and anoxygenic using $^{14}C\text{-}H_2CO_3$ with and without DCMU: Steenbergen and Korthals, 1982; Craig, 1984). In the sulfate reduction assays, acid-volatile $^{35}S\text{-}HS^-$ was distilled from water samples using a non-radioisotopic sulfide carrier to improve recovery. In the bacterial production assays, tritiated thymidine additions were made to 10 nM.

Samples for incubation were collected in glass bottles by the overfill technique used for Winkler determinations of dissolved O_2. Ambient redox conditions were thus guaranteed to within at least 0.1 umol O_2 - the detection limit of our Winkler titrations. The bottles were sealed and resuspended in clear plastic bags at their original depth for the specified incubation period.

Clean technique was followed during all phases of the Hg methylation experiments. Bottles

were rigorously cleaned and blanked prior to deployment. Incubation blanks consisted of bottles filled with low-Hg laboratory water. The experimental bottles containing lake water were not amended with any substrate. Bottles were retrieved from depth at t = 0, 3, 7, 10 and 17 days during July and at t = 0, 10, 17 and 24 days in August. Net rates of methylation were calculated from the change in methyl-Hg concentration along this time-course using a simple linear regression model.

Laboratory experiments were conducted to test the ability of SRB to methylate Hg by inoculating samples from the layers and littoral sediments into modified Widdel medium (Henry et al., 1994) buffered with 10 mM MOPS, reduced with 30mM sulfide and containing either 10 mM acetate or lactate as a C source. After turbidity and sulfide production indicated SRB growth, the enrichment cultures were inoculated into new media containing 50 ug/L $HgCl_2$. The methyl-Hg concentration in unfiltered medium was assayed after growth to stationary phase. Uninoculated medium spiked with $HgCl_2$ was used as a control.

3. Results and Discussion

3.1. Watercolumn Stratification

Pallette Lake became thermally stratified soon after ice-out in spring. Strong biological and chemical gradients were evident in the watercolumn by mid-summer (Figure 1). Layers of photosynthetic algae or sulfur bacteria developed in the hyperoxic metalimnion or anoxic hypolimnion, as evidenced by the Chl-a and BChl-e distributions (Figure 1a,c,e). The algal and bacterial layers were photosynthetically active.

The distribution of carbon and sulfur species paralleled the distribution of the two biotic layers (Figure 1b,d,f). A mid-water increase in DOC corresponded spatially to the metalimnetic algal layer, perhaps due to organic matter released from cells. A sulfide/sulfate transition zone developed below the oxic/anoxic boundary near the layer of sulfur bacteria. This transition zone suggests the joint activity of sulfide-oxidizing and sulfate reducing bacteria, as observed in other Wisconsin lakes by Parkin and Brock (1981).

Unlike the other constituents, the distribution of methane appeared simply to follow Fickian diffusion from sediments with an oxidation sink near the O/A boundary (Figure 1f).

3.2. Mercury Distribution in the Watercolumn

Concentrations of total Hg (HgT) and particulate Hg (HgP) increased in both the oxic and anoxic plankton layers (Figure 2a-c). Earlier studies on lakes in this region have shown that eolian Hg inputs are scavenged by settling particulate matter and remineralized at depth (Watras et al., 1994). Increases in HgT and HgP within deep plankton layers support the hypothesis that remineralized Hg is reaccumulated by particulates in the metalimnion and hypolimnion (Watras and Bloom, 1994). The observed decrease in Hg near the sediment/water interface is consistent

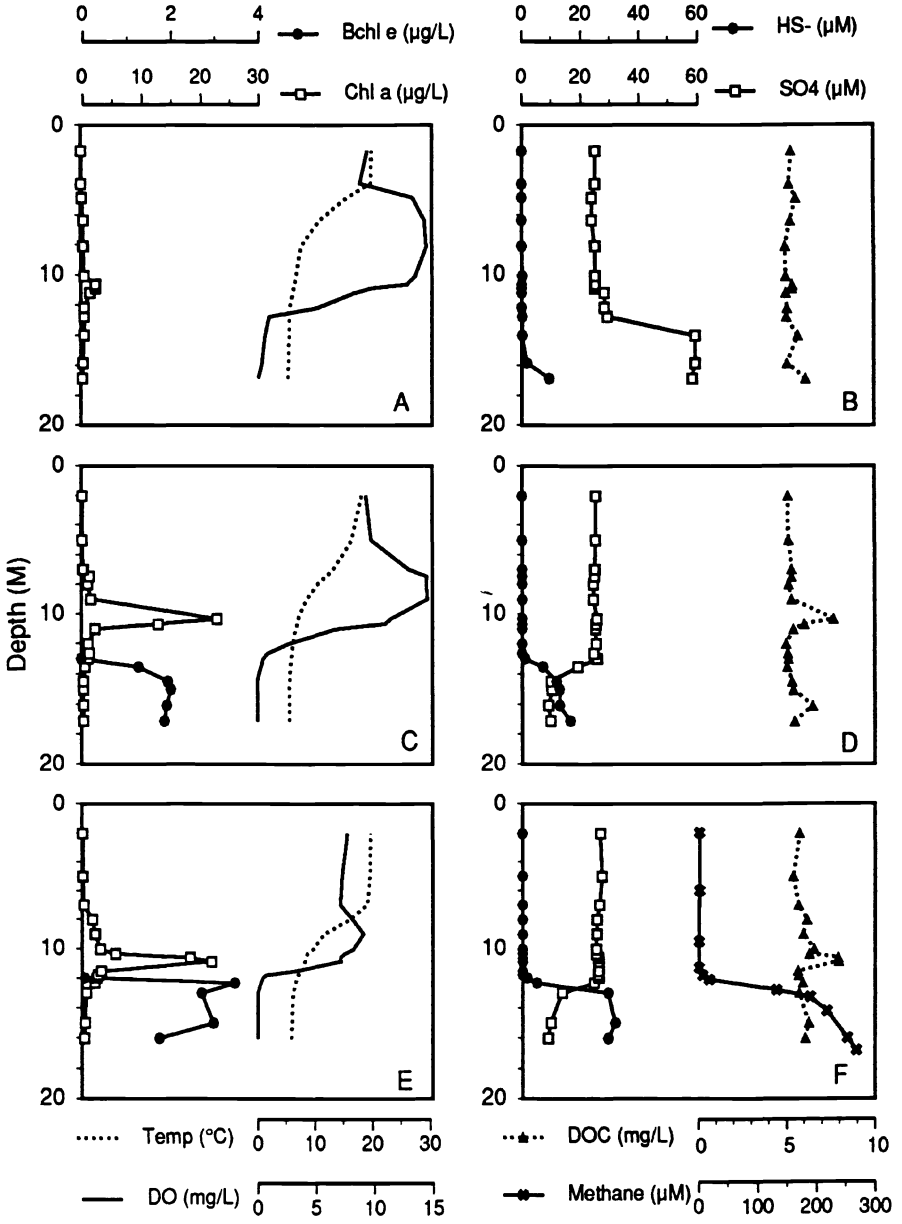

Fig. 1. Seasonal changes in the depth distribution of chlorophyll-a, bacteriochlorophyll-e, temperature, dissolved oxygen, sulfide, sulfate, dissolved organic carbon and methane in Pallette Lake. June, A and B. July, C and D. August, E and F. Note all data from 1992 except methane 1993.

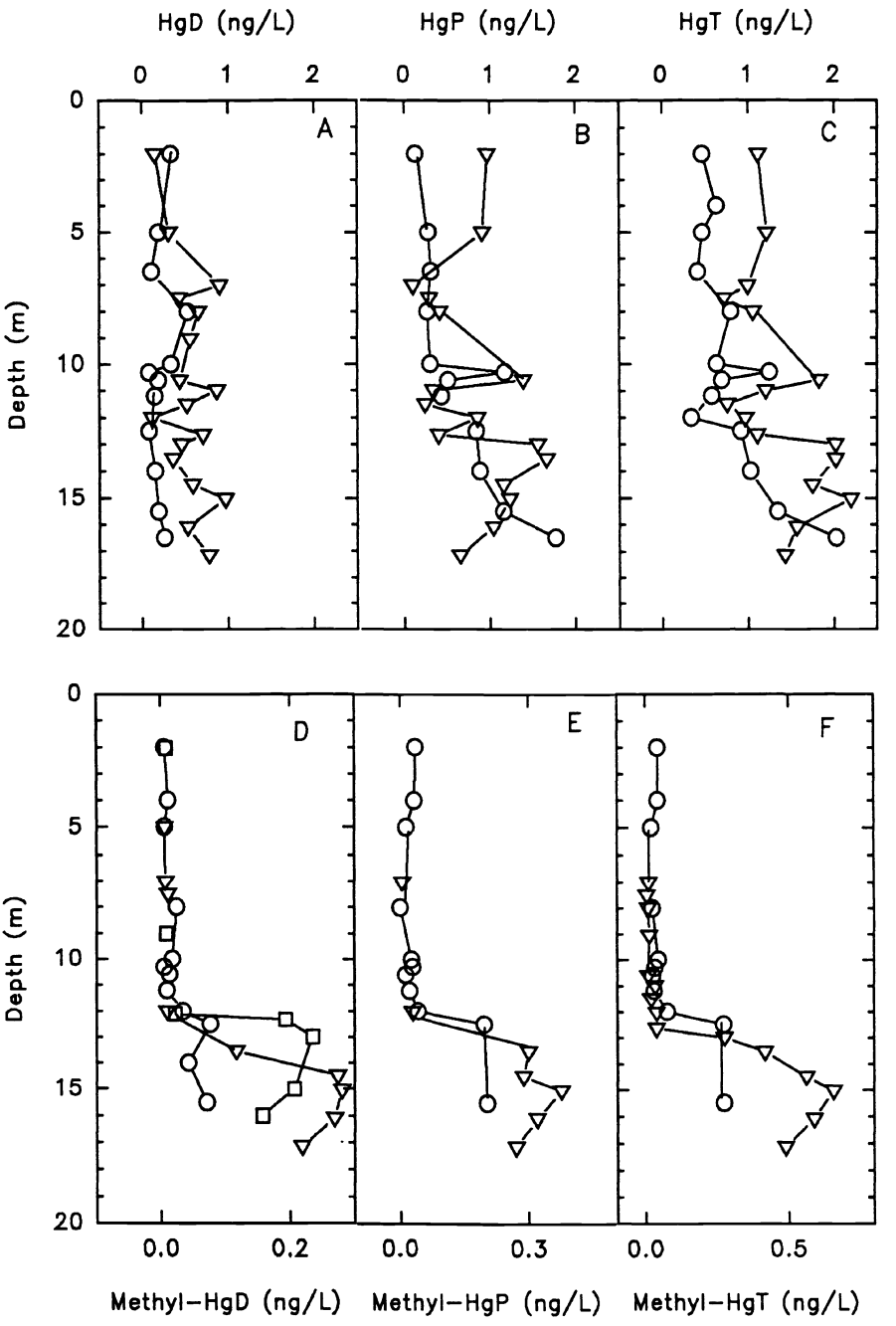

Fig. 2. Seasonal changes in the depth distribution of mercury species in Pallette Lake. June, circles. July, triangles. August, squares. D, dissolved; P, particulate; T, total.

with this hypothesis (Figure 2b,c). Ultimately, sediment burial or evasion back across the air/water interface is the fate of most atmospherically derived Hg in these lakes (Watras et al., 1994).

Methyl-Hg concentrations increased only in microbial layers below the O/A boundary (Figure 2d-f). At the methyl-Hg maximum, roughly 70% of the methyl-Hg was in the particulate fraction and methyl-HgT constituted 20% to 30% of the HgT. No seasonal accumulation of methyl-Hg was observed in oxic waters and methyl-HgT constituted 5 to 10% of the HgT there. As seen with Hg, methyl-Hg concentrations also decreased near profundal sediments. These observations are consistent with data from earlier studies on this lake (Watras and Bloom, 1994).

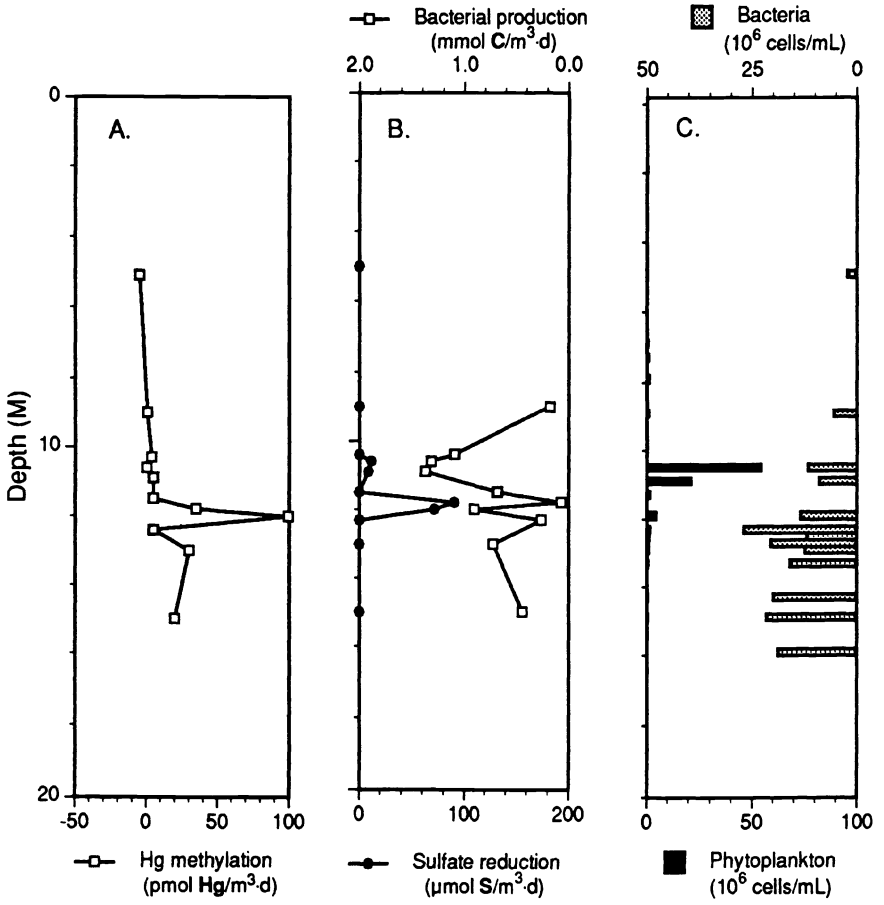

Fig. 3. Biogeochemical process rates and microbial abundances from in situ incubations in Pallette Lake.

3.3. Biogeochemical Process Rates

During July and August, we measured net rates of methylation ranging from -0.01 to 0.02 ng/L*d using unamended incubation bottles in the water column. Maximal rates of methyl-Hg formation were measured in anoxic waters near the region where maximum concentrations of methyl-Hg were observed. These measured rates were 0.01 ng/L*d in July and 0.02 ng/L*d in August. The August incubations clearly showed that methyl-Hg formation was restricted to a narrow zone in the watercolumn (Figure 3a). Similar results were obtained in July, although the measured rates were lower by roughly 2-fold. Assuming that the zone of methylation spanned a layer that was 0.5m to 1.0 m thick, net methylation rates on an areal basis ranged from 10 to 20 ng/m^2*d within the layer. These areal rates agree well with estimates of net hypolimnetic methyl-Hg production calculated by integrating the seasonal depth profiles shown on Figure 2: 8 ng/m^2*d (Table I).

TABLE I.

Net rates of methyl-Hg formation estimated from incubation experiments and from sequential depth profiles in Pallette Lake.

Method	Net Methylation Rate (ng/m^2*d)
Incubation Experiments	
July	10
August	20
Seasonal Depth Profiles	
June-July	8

Lakewide, we estimate that the net methyl-Hg flux from the hypolimnetic layer was between 3.4 and 6.8 mg/d as Hg (17 to 34 umol/d), but we cannot yet place this flux in full biogeochemical perspective (Table II). The hypolimnetic flux is considerably larger than our estimate of atmospheric methyl-Hg deposition to the lake (10.5 ug/d, based on 1% methyl-Hg in deposition and a net HgT depositional rate of 10 ug Hg/m^2*y: Watras et al., 1994). And we infer from ancillary data that profundal sediments are a weaker source of methyl-Hg than the hypolimnetic layer. The depth-distribution of methyl-HgD indicates a diffusive gradient going towards rather than away from deep sediments (Figure 2d). The low methyl-Hg content of these sediments (ca. 1% methyl-Hg, Gilmour, Watras and Bloom, unpublished data) is consistent with

the hypothesis of low profundal methylation. However, there are still large uncertainties in estimates of methylation in shallow sediments and these estimates are further complicated by variability in the advective flow of groundwater. In areal extent, the hypolimnetic bacterial layer and the region of non-profundal sediments (<12M) are roughly equivalent. But given the uncertainties in shallow sediment flux, we are unable to estimate the relative importance of these methyl-Hg sources with any reasonable degree of confidence.

Ancillary incubation experiments indicated that rates of sulfate reduction and bacterial production were elevated in the region where high methylation rates were measured (Figure 3b,c). Bacterial production was maximal near both the oxic and anoxic layers, however, there was a distinct minimum at the depth of maximum sulfate reduction (Figure 3b). This most likely reflects the inability of SRB to take up and incorporate exogenous thymidine (Gilmour et al., 1990).

Enriched cultures of bacteria from the sulfate reducing layer in the watercolumn and in sediments were able to reduce sulfate and methylate Hg under laboratory conditions. Enrichments grown on acetate from the watercolumn layers produced up to 8.7 ng/L methyl-Hg, but lactate enrichments did not methylate the added Hg(II). Sediment enrichments produced up to 42 ng methyl-Hg/L on acetate and 3 ng/L on lactate. Sulfate reduction did not occur in the lower portion of the hypolimnion or in profundal sediments, presumably because sulfate concentrations were below threshold levels (Gilmour et al., 1992). Rates of sulfate reduction in the hypolimnetic layer and in sediments underlying oxic waters were estimated to be roughly equivalent (Table II).

TABLE II.

Rates of Hg methylation and sulfate reduction in water and sediments of Pallette Lake

Region of Lake	Hg Methylation Rate		Sulfate Reduction Rate	
	Areal ($pmol/m^2*d$)	Whole Lake (umol/d)	Areal ($umol/m^2*d$)	Whole Lake (mol/d)
Hypolimnion	50 - 100	17 - 34	40	14
Sediments (<12M)	NA	NA	10 - 50	3.5 - 17.5
Sediments (>12M)[1]	~0	~0	0	0

1. see text for methylation rate estimate

These data support the hypothesis that sulfate reduction and Hg methylation are linked

biogeochemically (Compeau and Bartha, 1987; Gilmour and Henry, 1991). Moreover, they support the notion that parallel process occur in microbial layers below the O/A boundary in anoxic hypolimnia and littoral sediments (Figure 4; Watras and Bloom, 1994). The observed distribution of methane does not suggest tight linkage between methanogensis and Hg methylation (Figure 1f).

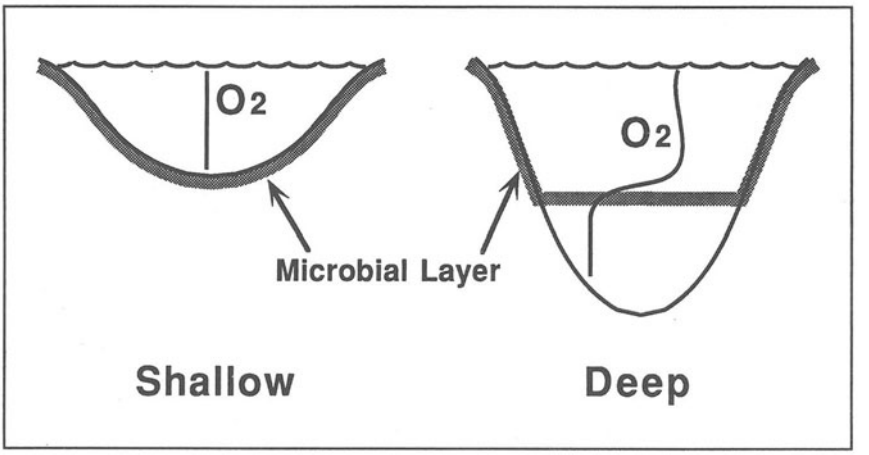

Fig. 4. Location of biogeochemically active microbial layer in shallow, well-mixed and deep, stratified lakes.

3.4. Alternative Hypotheses

Alternative explanations for the observed methyl-Hg maximum include: 1) co-precipitation with Fe and Mn (Cossa et al., 1994), 2) diffusion into the microbial layer from above or below, 3) downward transport on settling particulate matter (Verta et al., 1994) and 4) extracellular or abiotic methylation (Parkman et al., 1994; Weber, 1993).

Since the accumulation of methyl-Hg occurs well below the depth at which Fe and Mn oxyhydroxides are precipitated, geochemical control via sorption by solid-phase Fe or Mn seems unlikely. However, the accumulation of HgP within the oxycline may be controlled both geochemically and biologically by co-precipitation and phytoplankton uptake or adsorption.

The diffusion of methyl-Hg into the anoxic microbial layer seems unlikely because concentrations of dissolved and particulate methyl-Hg are both highest within the layer. Methyl-Hg scavenging in the epilimnion and downward transport on settling algae or fecal pellets is not consistent with data on seston methyl-Hg burdens. Particle enrichment (ug methyl-Hg/g particulate matter) increased by an order of magnitude within the anoxic microbial layer and decreased again toward sediments (Watras, unpublished data).

We cannot definitively separate biotic from abiotic methylation in this study, but the close association between the microbial layer and methyl-Hg accumulation argues strongly for a biological basis. Parkman et al. (1994) observed that most of the methyl-Hg accumulating below the O/A boundary in Framvaren Fjord was dissolved and that Hg methylation occurred in filtered and unfiltered water samples when incubated with added Hg(II). They concluded that Hg methylation was not directly biological but rather was indirectly stimulated by bacterial exoenzymes. This pathway seems less likely in Pallette Lake because most of the methyl-Hg at depth was in the particulate phase (Figure 2d,e).

4. Conclusions

We tentatively conclude that methyl-Hg is produced within anoxic microbial layers, whether in hypolimnetic waters or in sediments underlying oxic water. Field data showing the occurrence of a methyl-Hg maximum within the sulfate depletion zone of Pallette Lake and incubation experiments showing Hg methylation and sulfate reduction co-occurring strongly suggests that sulfate reducing bacteria are involved in methylation. The relative importance of physical sites as sources of methyl-Hg should depend, in part, on the distribution of such microbial activity. In lakes with small anoxic hypolimnia, sediments may be the dominant site for Hg methylation. But in lakes with extensive waters below the O/A boundary, hypolimnetic contributions to the total flux of methyl-Hg may be substantial.

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Measurement of Hg Methylation in Sediments Using High Specific-Activity ^{203}Hg and Ambient Incubation

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Abstract. Two methods were developed for estimating the rate of in situ methylmercury (MeHg) formation in sediments. One method is based on incubation of intact sediment cores without added Hg over a period of days. The second method uses $^{203}HgCl_2$ with a specific activity high enough to be used as a tracer (relative to bulk Hg). Use of high-specific activity $^{203}HgCl_2$ allowed measurement of methylation rate in hours at ambient total Hg concentrations. $^{203}HgCl_2$ was pre-equilibrated with pore water before injection into intact cores, to allow complexation with dissolved ligands. Methylation rates were measured with $^{203}HgCl_2$ additions as low as 0.02 μCi and 1.2 ng Hg per g wet weight sediment. These methods were tested in epilimnetic and littoral sediments of two pristine seepage lakes in Northern Wisconsin, and found to compare well. In situ methylation rates in Pallette and Little Rock Lake sediments ranged from 0.1 to 0.4 ug/m^2 d. Use of ^{203}Hg gave lower errors with shorter incubation times than the ambient incubation method. A method for extraction of $Me^{203}Hg$ from bulk sediments is given.

1. Introduction

Estimates of ambient gross and net Hg methylation rates in aquatic sediments have not been made and are critical to modelling the behavior of Hg in aquatic systems. The specific activity of commercially available ^{203}Hg is not sufficient to be used as a tracer in natural waters or in uncontaminated sediments. Rates estimated using highly enriched Hg concentrations may not reflect rates at ambient Hg concentration and speciation (Winfrey and Rudd, 1990; Gilmour and Henry, 1991).

One potential solution is to make ^{203}Hg of high enough specific-activity to act as a tracer or near-tracer. In short-term experiments, this should provide gross methylation rates (Xun et al., 1987). Another solution is longer-term incubation of sediments without Hg addition. This method requires longer incubation times in order to measure changes in MeHg against the variability in the ambient MeHg concentration, and most likely reflects net MeHg production.

In this paper we describe development of both methods, give examples of their use in remote pristine lakes, and show how the methods compare when used at the same site. In particular we focus on the concentration dependence and time course of methylation of added $^{203}HgCl_2$. In all cases, methylation rates were measured within intact sediments, in order to preserve redox gradients critical to biogeochemical processes. We also chose to measure methylation within sediments based on the repeated observation that MeHg production in aquatic systems (generally estimated in the past using lower-specific activity ^{203}Hg or non-radioisotopic spikes) is maximal in sediments (Korthals and Winfrey, 1987; Regnell, 1990;

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Ramlal et al., 1993). In addition, MeHg concentrations (Andren and Harriss, 1973) and methylation rates are generally maximal at or within a few cm of the sediment surface (Gilmour et al., 1992), often at the redox interface.

2. Materials and Methods

2.1 SAMPLING SITES

Pallette and Little Rock lakes are pristine seepage lakes in the Northern Highlands District of Wisconsin. The biogeochemistry of Hg in both lakes has been studied extensively, (e.g. Weiner et al., 1990; Rada et al., 1993; Hurley et al., 1994; Watras et al., in press). Little Rock Lake was partitioned in 1984 and one basin acidified with sulfuric acid over 6 years, ending in 1991 (Brezonik et al., 1993). At the time of this work in 1993, surface water sulfate concentrations were approximately 50 μM in Little Rock Treatment; 25 μM in Little Rock Reference and 30 μM in Pallette Lake.

Estimates of methylation by ambient incubation were made in Pallette Lake littoral sands, in a groundwater outflow zone, in July 1992; and in Little Rock Reference basin epilimnetic muck in June 1993. Methylation was measured using high specific-activity ^{203}Hg at two littoral and one epilimnetic sediment sites in Pallette Lake, and in one epilimnetic site in each basin of Little Rock Lake, in August 1993. The time course and concentration dependence of methylation were also examined in replicate, intact cores in the littoral groundwater inflow zone of Pallette Lake in May, 1994. Sediment characteristics are given in Table I. Macrophytes were present at all sites samped except the Pallette groundwater outflow site. The hydrology of the littoral sediments in Pallette Lake strongly affects microbial activity within sediments (Gilmour et al., unpublished data). A description of Pallette Lake hydrology and its affect on the Hg cycle is given in Krabbenhoft and Babierz (1993). For this study, sediments were sampled by hand, using divers in deeper waters.

Table 1. Characteristics and Hg and MeHg content of sediments examined in Pallette and Little Rock Lakes, WI. Sediment concentrations are per gram dry weight.

Site	depth m	date	% dry weight	LOI[a]	Hg, ng/g x	Hg, ng/g SD	MeHg, ng/g x	MeHg, ng/g SD	n	%MeHg
Little Rock										
Treatment basin	3	6/93	6.4	29	140.5	5.6	10.4	0.5	3	7.4
		8/93	10.9		83.3	4.4	3.1	02	2	3.7
Reference basin	2	6/93	9.5		82.4	21.2	4.6	0.3	3	5.7
		8/93	10.3		76.5	10.7	3.7	0.5	2	4.6
Pallette Lake										
Grdwtr. inflow	0.5	9/92	75	0.4	1.13	0.56	0.06	0.04	4	5.9
Grdwtr. outflow	2	8/92	75	0.3	1.67	1.04	0.01	<0.01	4	1.6

[a] Loss on ignition

2.2 HIGH SPECIFIC ACTIVITY ^{203}Hg

The goal of this method is to use ^{203}Hg of specific activity sufficient to act as a tracer in natural sediments and waters. For a <10% Hg spike, this can mean addition of <1 ng Hg/g sediment in clean sands, and of less than 100 pg/L in most waters. Generally delivered at <1 mCi/mg, ^{203}Hg produced commercially cannot be detected at sub-ng concentrations. High specific-activity $^{203}HgCl_2$ was produced for this work by custom synthesis from ^{202}Hg obtained from Oak Ridge National Labs. Isotope processing was performed by the Buffalo Materials Research Center, Buffalo, NY. Two batches were used in this work, with specific activities of 27.9 mCi/mg (Aug. 1993) and 16.7 mCi/mg (May 1994).

Methylation within sediments was estimated by injection of ^{203}Hg into intact sediment cores at 1 cm depth intervals. This method is analogous to the mthod used for sulfate-reduction rate measurements described by Jorgensen (1978). The ^{203}Hg was pre-incubated with sediment pore waters for an hour before injection into cores, to allow formation of dissolved Hg complexes. Sealed cores were incubated in situ for a period of hours to 2 days, then cut with depth into 2.5 cm slices, and immediately frozen. Injections of ^{203}Hg were generally made to 10 cm depth. MeHg extractions were done on aliquots of 2.5 cm depth sections, giving methylation rates for four sediment depths.

MeHg was extracted from aliquots of thawed sediment by an amended version of the method described in Gilmour et al., (1992). This procedure is a variation on the Longbottom et al., (1973) and Westoo (1968) methods, including a number of back-extraction steps. Approximately 10 g of homogenized sample was weighed into a 50 mL Teflon Oakridge tube. The following reagents were added: 4 mL of 4 M urea; 2 mL of 0.5 M $CuSO_4(5H_2O)$; 8 mL of 6N HCl; and 10 mL toluene. The sample was then vortexed for 2 min., and shaken for 30 min. at 250 rpm on an orbital shaker. This step was repeated and the toluene layers combined in another 50 mL Teflon Oakridge tube. Sodium thiosulfate (14 mL of 0.01N) was then added to the combined toluene layers, vortexed 2 min and shaken for 30 min. The top layer (toluene) was removed to waste and 7 mL of 2 M $CuCl_2$ $(2H_2O)$ added. The sample was again vortexed 2 min. and shaken 30 min. Toluene (7 mL) was added, vortexed 2 min., and shaken 1 h. The sample was centrifuged if necessary to separate layers. The toluene was then removed to a glass scintillation vial.

Gamma emissions were assayed using a 3 inch NaI-well detector. Appropriate precautions were taken, including performance of all steps in a fume hood, precautions for using gamma emitting radioisotopes, and storage of extracts in glass to prevent evaporation of toluene. The ambient methylation rate was calculated by multiplying the fraction of added ^{203}Hg methylated per day by the ambient total Hg concentration in the horizon of interest. This calculation assumes that ^{203}Hg is added as a tracer, and that the speciation and sediment/water partitioning of added Hg mimic that of ambient Hg. In some cases where ^{203}Hg additions were non-tracer (e.g. concentration dependence experiments), methylation was calculated by multiplying the fraction of ^{203}Hg methylated by the total (ambient + added ^{203}Hg) concentration.

2.3 AMBIENT INCUBATION

Incubation of intact sediment cores without added Hg can allow estimation of net methylation rate at ambient Hg speciation and concentration. The net methylation rate is estimated by the average MeHg concentration in sediment cores after incubation, compared to the ambient MeHg concentration in sediments at the beginning of incubation. Methylation rates can be estimated separately for multiple sediment horizons by determining the MeHg concentration at various depths. The success of this method depends on quantification, and minimization, of spatial and analytical error among sediment samples. A prior estimate of the spatial heterogeneity of MeHg can be used to estimate the number of replicates cores needed for incubation.

To estimate net methylation in the Wisconsin Lakes, at least triplicate intact sediment cores were taken, sealed and incubated over a period of days in situ. Sediments were sampled directly into clear PVC tubes. All gear was rigorously acid-leached before use to minimize Hg contamination, and non-contaminating sample handling and storage techniques were used (e.g. Gill and Fitzgerald, 1987). Core tubes were about 3.5 or 4.5 cm in diameter and about 30 cm in length. At least 10 cm of sediment was sampled with overlying water. Tubes were sealed on both ends with rubber or silicone stoppers, and placed back in the lake for incubation, preserving ambient temperature and light conditions.

After incubation, cores were sectioned and immediately frozen. For the measurements reported here, the top 4 cm of sediments was removed and homogenized. Net methylation rate was calculated by subtracting the average ambient MeHg concentration in at the beginning of incubation, from the average MeHg at the end of incubation. Rates were then corrected to per day estimates. The heterogeneity in ambient MeHg concentrations among cores was generally the largest associated error with this measurement.

In both Pallette and LRR sediments, MeHg concentrations were also measured in cores after incubation with added molybdate, a specific inhibitor of microbial sulfate reduction, or with added sulfate. Sodium molybdate was injected into cores at 1 cm depth intervals, through small ports drilled into the core tubes and filled with silicone seal. The final calculated molybdate concentration in pore waters was 40 mM, based on previous measurements of porosity.

2.4 Hg AND MeHg ANALYSIS

Analyses were performed either at the Academy of Natural Sciences or by Frontier Geosciences, Seattle, WA. Methods were comparable in both laboratories. MeHg in sediments was separated via distillation (Horvat et al., 1993) and analyzed via ethylation/CVAF (Bloom, 1989). In our laboratory, during the time these samples were analyzed, MeHg spike recoveries (200 pg spike per 10 g sediment) averaged 96.4 ± 7.9%. Recovery of SRM DOLT was 89.5 ± 9.7%. The detection limit for these samples was 2 pg/g, based on 3 times the standard error of distillation blanks, and distillation of 10 g sediment.

Total Hg concentrations in sediments were measured by acid digestion and analyzed by CVAF (Bloom and Fitzgerald, 1988) with preconcentration on gold (Gill and Fitzgerald, 1987). Sediments were were digested with 10 mL of 7:3 concentratied HNO3: H2SO4, at 95°C for 4 h, and then diluted with 0.003 N BrCl solution prior to analysis. SRMs were routinely analysed. In our laboratory, spike recoveries averaged 104.4 ± 9.9 for sediments.

3. Results and Discussion

3.1 HIGH SPECIFIC ACTIVITY ^{203}HG METHYLATION

3.1.1. *Use of ^{203}Hg as a tracer.* Total Hg concentrations Pallette Lake sands are very low, and therefore represent a worst case for use of ^{203}Hg as a tracer in sediments. A summary of the Hg addition levels relative to ambient bulk and pore water Hg concentrations in the Wisconsin Lake sediments is shown in Table II. In the August 1993 measurements, ^{203}Hg additions increased the ambient Hg concentration about 250% in Pallette Lake sands and by 50% to 75% in Little Rock muck. However, methylation rate measurements made in August suggested that less ^{203}Hg could be used (see below). Therefore in May 1994, less total ^{203}Hg was added, even though the specific activity of the isotope produced in May, 1994, was lower than that made in August, 1993.

Table II also lists the measured Hg concentrations in sediment pore waters. The injection of ^{203}Hg into these pore waters constituted direction additions of 3 to 10 ng/mL, or approximately 1000X increases in Hg concentration. However, the use of ^{203}Hg to measure ambient methylation rates within sediments presupposes that added ^{203}Hg partitions onto sediment surfaces rapidly relative to the rate of methylation. We have not yet tested this hypothesis. Preincubation of ^{203}Hg with sediment pore waters allowed complexation with dissolved (< 0.2 μm) ligands, but not surfaces, before methylation measurements began.

Table II. Comparison of added ^{203}Hg concentrations with ambient Hg concentrations in lake sediments. Concentrations given are averages for the top 4 cm. The number of replicates (n) indicates the number of sediment cores analyzed. At least 4 depths from each core were analyzed. Sediment concentrations are per gram dry weight.

Site	Date	Ambient Hg		Added ^{203}Hg		
		bulk ng/g	pore water ng/L	bulk ng/g	pore water ng/mL	sp. activity μCi/g
Little Rock						
Treatment basin	8/93	82.4	5.0	62.5	4.8	1.72
Reference basin	8/93	76.5		36.7		1.02
Pallette Lake						
Grdwater inflow	8/93	1.13	3.5	2.7	1.1	0.07
	5/94		7.5	0.8	0.3	0.02

The detection limit for this method is determined by the carry-over of inorganic ^{203}Hg during MeHg extraction. At a total ^{203}Hg concentration ranging from 0.5 to 5 ng/g wet weight sediment, the fraction of Hg carried over during extraction averaged $5.6 \pm 2.8 \times 10^{-5}$. Using Pallette Lake sediment characteristics, and a sediment depth of 4 cm, this yeilds a detection limit for a one day incubation of 0.12 pg/cm^3 d or 0.005 ng/m^2 d. Assuming that added ^{203}Hg partitions rapidly onto solids, the specific activity achieved allows the use of ^{203}Hg as a tracer in all but the lowest Hg concentration sediments (e.g. Pallette Lake sands). Lower Hg additions or an increase in specific activity will allow use of ^{203}Hg as a tracer in all sediments. Methylation rates for the five sediments examined using this method are shown in Table III.

3.1.2. *Time Course.* In Pallette Lake sands, methylation of added ^{203}Hg was through 24 in the four depths examined (Figure 1). The linearity, and near-zero intercepts of the methylation time courses suggest that ^{203}Hg availabilty does not change over that time, e.g. that ^{203}Hg injected into cores is no more available immediately after injection than after many hours. This suggests that partitioning of added ^{203}Hg onto sediments is very rapid. Measurements taken here up to 24 h probably represent gross methylation.

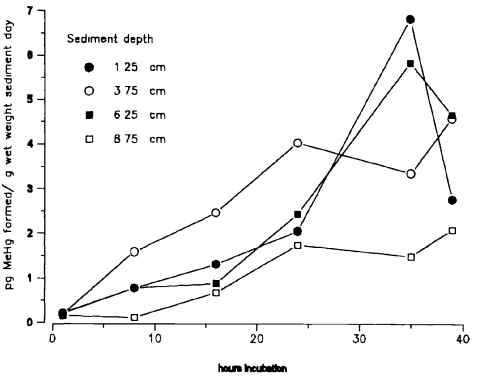

Figure 1. Time course of MeHg production from $^{203}HgCl_2$ in Pallette Lake, WI, littoral sands, May 1994. Methylation rate was calculated based on the fraction of the label methylated times the ambient bulk Hg concentration.

After 34 h, methylation rates decreased in two of the cores sections, possibly indicating net demethylation after this time. At this stage of development of this method, the time course of methylation needs to be examined for each site before an incubation time can be chosen for gross rate measurements.

Table III. Comparison of gross methylation rate estimates for the top 4 cm of sediment using the tracer-level ^{203}Hg and ambient incubation methods in lake sediements. The number of replicates (n) represents the number of cores examined. Standard deviation is among cores. Multiple depths were examined within each core for methylation rates based on ^{203}Hg. For ambient incubation, homogenized 0-4 cm sediment sections were examined. See text for a discussion of methylation rate calculation and error using the ambient incubation method.

Site	Methylation rate, $\mu g/m^2/d$						
	^{203}Hg				ambient incubation		
	x	SD	n	date	x	n	date
Liitle Rock							
Treatment basin	0.29	0.02	2	8/93			
Reference basin	0.09	<0.01	2	8/93	0.19	3	6/93
Pallette Lake							
grdwater inflow	0.35	0.02	2	8/93			
	0.16	0.06	6	5/94			
grdwater outflow	0.35	0.17	2	5/94	0.09	6	6/92
12 m	0.18	0.03	2	8/93			

3.1.3 *Concentration dependance.* The Hg concentration dependance of methylation was examined by added between 0.4 and 3.7 ng ^{203}Hg/gram wet weight to intact Pallette Lake sand cores. Methylation rates were calculated as the product of the fraction ^{203}Hg methylated and the total Hg concentration, in this case the sum of the ambient total Hg and the added ^{203}Hg. At added ^{203}Hg concentrations within 0.4 to 1.7 ng added ^{203}Hg, calculated methylation rates were fairly constant (Figure 2). However, the calculated methylation rate increase more rapidly above 2 ng/g added Hg in most of the sediment horizons examined. This suggests that the fraction of total Hg available for methylation increased with added Hg concentration, possibly due to saturation of sorption sites in these very low organic carbon-content sands.

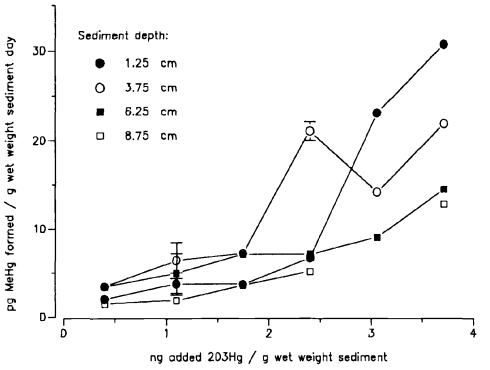

Figure 2. Concentration dependance of $^{203}HgCl_2$ methylation, same time and site as Figure 1. Each point represents an individual core. Error bars are given for replicated samples and represent the error between two cores.

3.2 AMBIENT INCUBATION

The ambient MeHg concentration in Pallette Lake littoral sands in groundwater outflow zones was extraordinarily low (Table I), <0.01 ng/g. Incubation of 16 cores for 5 days did not yield MeHg concentrations significantly different from ambient MeHg concentration (11 ± 1 pg/g). However, the average concentration of MeHg in unamended cores after incubation (9.7 ± 4 ng/g, n=16) was significantly (α <0.05) greater that in cores incubated with molybdate (4.8 ± 2.6 pg/g, n=4), in which MeHg concentrations decreased. If the assumption is made the molybdate blocks the bulk of methylation activity, an estimate of gross methylation can be made from the difference in concentration in unamended and molybdate amended cores. This value is given for gross methylation rate in Table III. An estimate of the error in this measurement can be

gained from the variability in MeHg concentration among cores, which yeilds a coefficient of variation of 10-40%. Although molybdate appears to block or inhibit methylation in sediments in most cases (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Kerry et al., 1991; Gilmour et al., 1992; Regnell, 1994) there are exceptions (e.g. Maitilanin, this volume). The addition of up to 800 μM sulfate to water overlying Pallette Lake cores did not affect MeHg concentration in cores after incubation. However, neither did sulfate stimulate sulfate-reduction in these organic carbon-limited Pallette Lake sands (Gilmour, unpublished data).

In LRR, net demethylation appeared to occur in the top 4 cm of sediment (Figure 3); MeHg concentrations in unamended cores decreased during incubation. As in the Pallette Lake experiment, the change in MeHg concentration was less than the variability in MeHg concentration. However, addition of 60 to 240 uM sulfate to water overlying cores resulted in MeHg concentrations significantly above ambient variability in MeHg. MeHg concentrations in cores amended with molybdate decreased more than MeHg concentrations in unamended cores, but the difference was not significant. The estimated value for gross methylation reported in Table III is the difference between the decrease in MeHg concentration in unamended and molybdate amended cores.

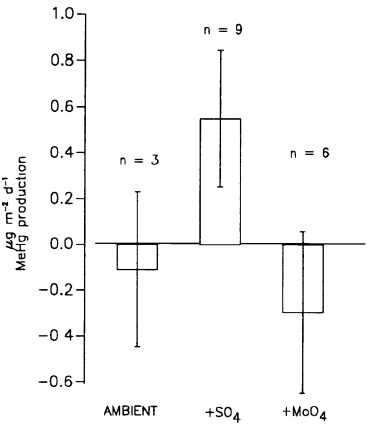

Figure 3. MeHg production in 0-4 cm LRR sediments after 13.5 days incubation. Ambient = unamended cores; +SO4 = cores incubated with 60 to 240 μM SO_4 added to overlying water; + MoO_4 = cores injected with Na_2MoO_4 to a final concentration of 40mM in pore water.

The LRR sediments sampled contained extensive submerged aquatic vegetation with roots well below 4 cm. Unlike Pallette lake sands, where sulfate reduction and MeHg production appear to be organic carbon-limited, sulfate stimulated both sulfate reduction MeHg production in LRR sediments. Sulfate reduction appears to be sulfate-limited at this site in LRR, based on our experiments showing stimulation of sulfate reduction by added sulfate (Gilmour, unpublished data), and consistent with more extensive studies of sulfate reduction in LRL (Urban et al., 1994).

4. Conclusions

Methylation rate estimates using the high-specific activity ^{203}Hg and ambient incubation methods were quite similar (Table III). The similarity in results from two very different techniques suggests

these values for MeHg production are reasonable estimates of ambient methylation rates.

The ^{203}Hg technique is relatively fast, and similar to radiotracer techniques used routinely for many biogeochemical assays. It is an extension of the the method described by Furutani and Rudd (1980) and Xun et al., (1987) for measurement of Hg methylation and methylation/demethylation ratios, with the major changes here being addition of Hg at tracer levels, measurement of methylation rate within intact sediment cores, an improved MeHg extraction method and use of a gamma counter for increased sensitivity. At the specific activity described here, ^{203}Hg can be used as a tracer or near-tracer in all sediments. Drawbacks include the cost and trouble of custom ^{203}Hg synthesis (about $1800/mCi), working with a gamma-emitting radioisotope, and radioactive hazardous waste production from extractions. However, the fairly short half-life (47 days) should allow laboratories to hold waste for decay.

Before this method can be used routinely, a number of issues need to be addressed. One potential problem is that speciation of added ^{203}Hg may not mimic in situ speciation in a short time frame relative to the time of incubation. Pre-incubation of the radioisotope with sterile ambient pore waters allows complexation with at least dissolved ligands prior to methylation rate measurement. Although the linear time course of methylation shown in Figure 2 suggests that there is not a large pulse of relatively available ^{203}Hg immediately after injection into cores, the kinetics of Hg sorption to particles in many sediments needs to be examined. Second, the time course over which gross and net methylation are being measured needs to be tested in a larger number of sediment types. In Pallette Lake, it appears that gross methylation is being measured through about 24 h. This is comparable to the appropriate incubation time for measurement of sulfate reduction within sediments (Jorgensen, 1978).

Relative to the radioisotopic method, the ambient incubation method is more time consuming and is subject to much greater variability. Ambient incubation may be better suited for net methylation measurements at this time, due to the unavailability of radioisotopic (either ^{14}C of ^{203}Hg) MeHg at specific activity high enough to be used as a tracer. However, there is often very high error associated with looking for small changes in large numbers, and many replicates will generally be needed. In the case of the sediments examined here, net methylation was not significant usng the ambient incubation. Nevertheless, estimates of gross methylation (and potentially gross demethylation) could be derived by comparing changes in MeHg in unamended cores relative to changes in MeHg in cores hwere methylation was at least partially blocked by molybdate. Addition of molybdate to sediment cores before incubation resulted in decreased MeHg concentrations at both sediment sites examined.

Estimates of MeHg production in and efflux from sediments are critical missing rates in current models of Hg cycling. The methods described here provide some of the first estimates of in situ gross methylation rates.

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INVOLVEMENT OF BACTERIA IN METHYLMERCURY FORMATION IN ANAEROBIC LAKE WATERS

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Abstract. The potential net MeHg formation in water bodies and surface sediments was investigated. The radiochemical method was applied to the methylation assays performed *in situ* The role of sulfate reducing bacteria and overall bacteria activity in the methylation process was examined by molybdate and formaldehyde addition, respectively The impact of light conditions was tested by light and dark incubations. Low but detectable methylation was found in the oxic epilimnion of all lakes. The rates were affected neither by molybdate nor by formaldehyde. The highest rates were observed in the hypolimnion within the sulfide maxima. Near the sediment surface the rates again declined. Usually, the methylation rates in sediments were of the same level as the rates the anoxic water. Formaldehyde prevented methylation in the anoxic water and sediment. Molybdate inhibited methylation in sediments but in the sulfidic waters the inhibition was only partial or the methylation process was stimulated by molybdate No significant differences in methylation activity were found between the natural light and the dark bottle incubations. The highest methylation rates were not always concomitant with the highest MeHg concentrations, the highest concentrations more likely to be found in the particle rich water layers The results show that MeHg in sulfidic waters was formed biotically by sulfate reducing bacteria which were competing with methanogens for acetate and hydrogen under sulfate limiting conditions

1. Introduction

The mechanism and bacterial groups involving in mercury (Hg) methylation to monomethylmercury (MeHg) has been of interest of many research groups in recent decades. MeHg concentrations are higher in oxic/anoxic (O/A) boundary and sulfidic layers than mixed layers of stratified lakes and estuaries (Bloom *et al.*, 1991; Verta *et al.*, 1994; Watras *et al.*, 1994; Mason *et al.*, 1993; Parkman *et al.* 1993). Sulfate reducing bacteria (SRB) are important Hg methylators in anoxic sediments (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Gilmour *et al.* 1992). Hg methylation by extracellular enzymes may take place in environments with high decomposition of organic material (Parkman, 1993). Methylcobalamine, a vitamin B_{12}-derivate produced in many organisms, is capable of spontaneous Hg methylation in aqueous solution (e.g. Imura *et al.*, 1971). Although MeHg is formed in different conditions, in biotic and abiotic processes, there may be a linking factor between them. The aim of the study presented here was to measure the *in situ* Hg methylation rates and the ambient Hg and MeHg concentrations in lake watercolumns and surficial sediments during summer stratification. In addition, the role of SRB and overall bacterial activity on methylation process was examined by inhibitor tests.

2. Materials and methods

Four forest lake profiles and surficial sediments were studied for net Hg methylation and for concentrations of Hg, MeHg (see Verta and Matilainen, 1994), sulfide, sulfate, oxygen, Fe, Mn and chlorophyll *a* in late summer 1993. The study lakes, polyhumic

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drainage lakes, Keskinen Hakojärvi (Keha, epilimnetic pH 5.5) and Hakojärvi (Hako, pH 6.3), and limed (L) and control (C) basins of an oligo-mesohumic seepage lake Iso Valkjärvi (Iva, pH 6.7 and 5.9, respectively) are situated in southern Finland. The lake characteristics are discussed in more detail by Verta *et al.* (1994). The sampling was performed with a peristaltic pump thin layer sampler with ultraclean teflon tubing from the lake deeps.

Potential Hg methylation rates with and without bacterial inhibitors were measured *in situ* using the modified radiochemical method of Furutani and Rudd (1980). The $^{203}HgCl_2$ and inhibitors were sterile-filtered (0.2 μm), N_2-gassed and stored in sterile syringes. The solutions were injected to the bottom of the incubation tubes (75 ml, Nalge 3118) filled with sample water or sediment. For methylation assays, duplicate samples were spiked with $^{203}HgCl_2$ (15-17 kBq [0.38 μg Hg · 0.2 ml]$^{-1}$). One molybdate-treated, one formaldehyde-treated, and one darkened sample without inhibitors per depth were also included. Na_2MoO_4, a specific inhibitor of dissimilatory sulfate reduction, and formaldehyde, a broad-spectrum inhibitor, were added prior to the $^{203}HgCl_2$ spikes as final concentrations of 2.7 mM and 1 %, respectively. Every sample was handled individually and capped quickly. The samples were kept in cool and dark until the whole set was immersed to the original depths for 24 h in transparent acrylic tubes (wall thickness 2 mm). Incubation was terminated with 1 ml of 4 M HCl. The formed $Me^{203}Hg$ was extracted with 15 ml of toluene and the extract was dried twice with Na_2SO_4. An aliquot of 5 ml was mixed with 10 ml of scintillation cocktail (Lumagel, Lumac; The Netherlands) and the radioactivity was measured with a liquid scintillation counter (Wallac 1411). The net Hg methylation rates are expressed as percentage of added $^{203}HgCl_2$ methylated per day in the sample volume of 75 ml. The blank values (0.03-0.04 %/d; $^{203}HgCl_2$ extracted without incubation) were not subtracted from total values because the method gives possibility only for comparison between different sites, not for measurement of actual rates. In comparison with natural Hg concentrations in waters and sediments the added Hg was 625-4400-fold and 2-10-fold, respectively.

Chlorophyll *a* in 95 % ethanol (75 °C, 5 min) was determined spectrofotometrically at a wavelength of 665 nm (SFS 5772: ISO 10260). The same extracts were used to record the absorption spectra between 300 and 850 nm in order to control the shifts of the absorption peak positions due to the phototrophic bacteria chlorophyll. Sulfide was determined with a colorimetric method modified from the standards of ISO 10530:1992, ISO/TC147/2:1993 and SFS 3038:1977. Briefly, the samples were taken to 120-ml borosilicate glass bottles with conical shoulder and ground glass stopper. The following reagents were added on the shore by injecting and shaking the samples completely after each reagent: (1) 5 ml of 20 % [$Zn(CH_3COO)_2 \cdot 2\ H_2O$]; (2) 10 ml of 0.2 % N,N-dimethyl-1,4-phenyl diammonium chloride in 20 % (v/v) sulfuric acid; (3) 2 ml of 10 % [$NH_4Fe(SO_4)_2 \cdot 12\ H_2O$ in 2 % (v/v) sulfuric acid. Absorbance was measured at 665 nm. Sulfate was determined ionchromatographically (ISO 10304-1), and concentrations of Fe and Mn by inductively coupled plasma (ICP) by the National Board of Waters and the Environment.

3. Results and discussion

3.1. METHYLATION IN OXIC ZONES

Methylation rates were low (<0.1 %/d) in the mixed zones and O/A boundaries of the watercolumns (Figs. 1-4). Differently treated samples yielded practically similar low methylation rates indicating that the process in oxic layers was not microbial. More likely, methylation was determined by Hg binding to particulate matter and demethylation. In polyhumic lakes Keha and Hako methylation was slightly lower than in oligo-mesohumic lake Iva (C) where formaldehyde stimulated epilimnetic methylation (Fig. 3). These results support our earlier findings from the epilimnetic waters of the same lakes that aerobic MeHg formation was abiotic and suppressed by humic compounds and particulate matter, and that formaldehyde stopped the demethylation but not methylation (Matilainen and Verta, 1994; submitted). In L. Iva formaldehyde probably caused a leaching of methylating agents from phytoplankton cells (Lee and Fisher, 1992). Mason *et al.*, (1993) reported that Hg^0, an end-product of MeHg demethylation, was formed principally in the mixed zone and the highest concentrations were found in the region of low oxygen region of an stratified estuary. The methylation minima in the O/A transition zone with high content of pigmented particles, especially in L. Iva, was a likely result from both the binding of the added Hg to particles and demethylation of heterotrophic bacteria.

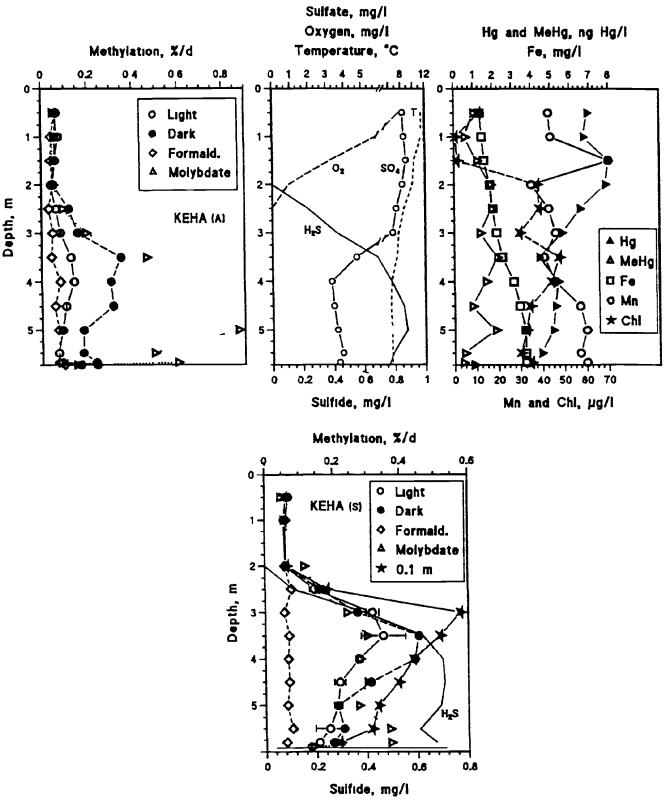

Fig 1 Hg methylation rates in Lake Keha watercolumn and surficial sediment (5.75 m) without inhibitors (formaldehyde and molybdate) in the light and dark, and with inhibitors in the light in 30 August 1993 (A) Vertical distribution of sulfate, oxygen, temperature, sulfide, total Hg, MeHg, Fe, Mn and chlorophyllous pigments (Chl) is also shown The methylation experiment was repeated in 7 September (S) with a supplementary incubation of a sample set at 0 1 m depth In September the sediment methylation (5 9 m) was examined only with and without molybdate in the light (Light mean ± s d , n=2, others n=1)

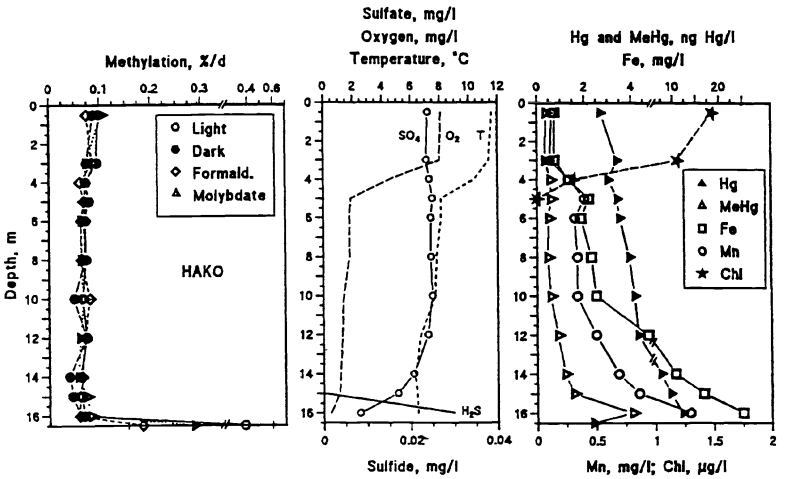

Fig. 2. Hg methylation rates in Lake Hako in 6 September 1993. Dark incubation of the sediment (16.5 m) was not assayed. Note the Mn scale in mg/l. See the caption of Fig. 1.

3.2. METHYLATION IN HYPOLIMNION

As shown in Figs. 1-4, Hg methylation increased with increasing sulfide concentration and was microbial. The *in situ* methylation experiment in L. Keha in 30 August was repeated a week later (Fig. 1). The low methylation in the light samples of August in comparison with the parallel experiment in June (data not shown), and the uncertainty if the samples in transparent tubes were exposed to light for too long time, were the reasons for the experiment in 7 September. The increased temperature stimulated methylation in L. Keha hypolimnetic samples that were incubated near the water table (0.1 m; Fig. 1). The stimulation was most pronounced at 3-3.5 m where also the light and dark methylation rates were high. Formaldehyde prevented the methylation completely in the sulfidic layers and surficial sediments of lakes Keha and Iva (C) (Figs. 1 and 3). In L. Hako some oxygen was found as deep as 16 m, below which traces sulfide was detected. Methylation maxima lay in the surface sediment and formaldehyde inhibited methylation more effectively than molybdate (Fig. 2).

Molybdate clearly stimulated Hg methylation especially in the lower hypolimnion of lakes Keha and Iva (L) (Figs. 1 and 4). In June (data not shown) and 30 August, the stimulative effect of molybdate in L. Keha was highest at 5 m, and in September at 5.5-5.7 m (Fig. 1). Molybdate had no effect on methylation in water of L. Iva (C) but the inhibition was complete in the surficial sediment (Fig. 3). Generally, the methylation rates in sediments without inhibitors were of the same level as in the sulfidic water layers.

3.3. MICROBIAL METHYLATION

The occurrence of the green sulphur bacteria changes the shape of the absorption spectrum of the total cell extraction (Eloranta, 1985). The shift of the red absorption peak (Fig. 5) was from 663-665 nm at 0.5 m depth to 656-657 nm in the layers of chlorophyllous pigment maximum of the lakes Keha and Iva (Figs. 1, 3 and 4). Also, the absence of the carotenoids that was seen as a relative decline of the curves between 450 and 480 nm indicated the presence of the phototrophic bacteria in the upper limit of the hypolimnion.

In lakes Keha, Iva (C) and (L) the chlorophyllous pigments within the O/A boundary were most evidently caused by phototrophic sulfur bacteria. In the mixed water layers the pigments originated from phytoplankton. Methylation rates, however, were usually lowest within O/A boundary where the levels of chlorophyllous pigment, Hg, MeHg, Fe and Mn began to increase (Keha 2 m, Iva/C 3.75-4 m, Iva/L 4-4.5 m). Sulfide was not detected, and sulfate concentration was as high as, or higher than in the mixed layer. It seems that there was no active Hg methylation by microbial or spontaneous processes in this zone. More likely, the elevated MeHg concentrations at O/A transition zone are caused from settling of particle bound Hg and MeHg from epilimnion (Mason *et al.* 1993; Watras and Bloom, 1994; Verta and Matilainen, 1994). Due to the high binding affinity of Hg to particulate organic material the added Hg was not available for methylation (bacterial or spontaneous). If any Hg methylation took place during the incubation the formed MeHg was quickly demethylated by heterotrophic bacteria.

In all profiles studied methylation maxima occured in the sulfidic water layers with lowered sulfate concentration. In these layers formaldehyde stopped the methylation effectively, whereas, molybdate stimulated or had no effect on MeHg formation.

The stimulatory effect of molybdate on methylation process may be due to the competition between SRB and methanogens for H_2 and acetate. Inhibition of methanogenesis was found to stimulate SRB activity and Hg methylation in sediments (e.g. Compeau and Bartha, 1985), and SRB were able to outcompete methanogens in sulfate limited freshwater sediments (Lovely and Klug, 1983). In the experiments with Blelham Tarn profundal sediments by Jones and Simon (1984) (see also Gelwicks *et al.*, 1994), methanogenesis from CO_2 decreased during late summer, whereas acetogenesis and acetoclastic methanogenesis increased over the same time period. Furthermore, addition of molybdate to these sediments stimulated methanogenesis suggesting the precence of metabolically active population of acetate-utilizing SRB. Whether those acetate-utilizing SRB, e.g. *Desulfotomaculum* spp., or other bacteria capable of using acetate and Hg methylation became the dominating members of the population in sulfate-limited sulfidic waters remains unknown. Because the methylation rates and sulfide concentrations were associated to each other it is evident that SRB play a role in MeHg formation. Until proved otherwise, it is possible that releasing of methylating agents, e.g. similar to methylcobalamine from lysing cells, or exoenzymes from living cells to surrounding water cause a spontaneous Hg methylation in the presence of mercuric ion.

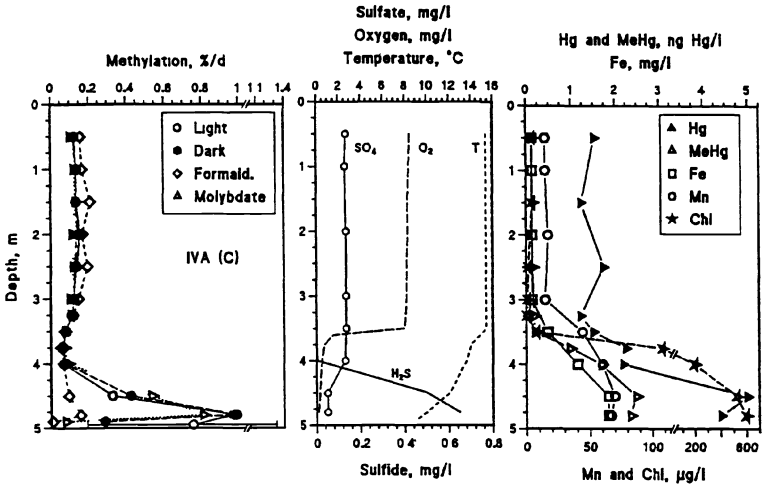

Fig 3 Hg methylation in Lake Iva control (C) basin in 25 August 1993 The deepest points in the methylation profile represents surficial sediment (4 9 m) See the caption of Fig 1

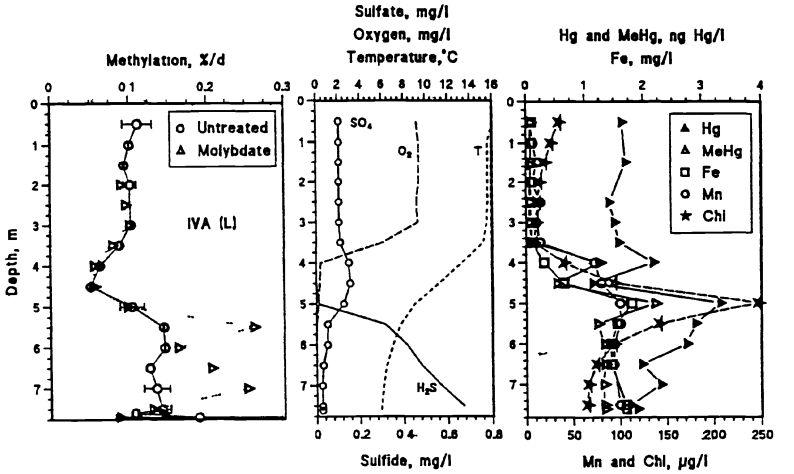

Fig 4 Hg methylation in Lake Iva limed (L) basin in 25 August 1993 Formaldehyde and dark incubations were not assayed Sediment surface lies at 7 7 m See the caption of Fig 1

3.4. METHYLATION AND METHYLMERCURY

Hg^{2+}, as Cd^{2+} and Ag^{+}, are classified as inessential toxic metals with low electronegativity, high polarizability and tendency towards covalent bonding to ligands (Gadd, 1992). Thus, if Hg behaves like Cd, Se and Zn in association with decomposing planktonic debris (Lee and Fisher, 1993), it should generally follow the fate of organic carbon and protein release, and be biologically recycled and have longer residence time in surface waters than the more particle-reactive metals. In L. Iva, the distributions of Fe, Mn, Hg and MeHg were closely associated with pigmented particles (Figs. 3 and 4). In the polyhumic lakes Fe, Mn, Hg and MeHg were distributed more equally in the watercolumn (Figs. 1 and 2), and in L. Hako, the concentrations increased toward the sediment. Usually higher fraction of the Hg and MeHg in hypolimnion and above the sediment surface was in particulate form (Verta and Matilainen, 1994). This indicates the Hg scavenging from epilimnion both in biotic particles and probably in minerogenic material, as Mn oxide matrix (Lee and Fisher, 1993).

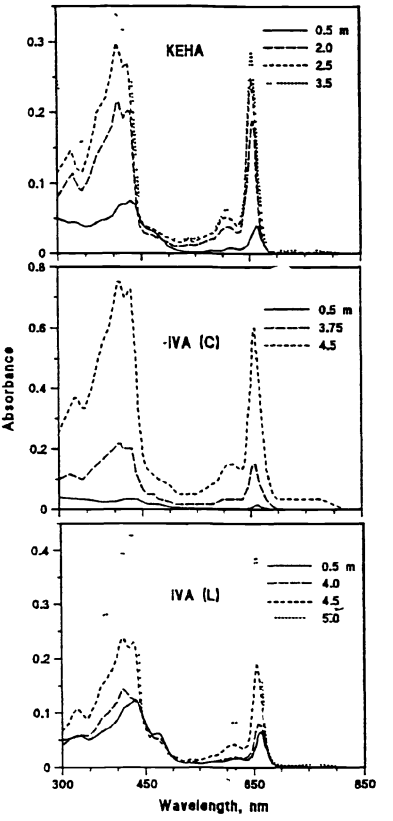

Fig 5 The absorption spectra of the total pigment extracts (94 % ethanol) in the samples taken from 0 5 m and the layers with maximum chrorophyll (665 nm) concentrations in lakes Keha and Iva (C = control,L = limed)

4. Conclusion

Microbial Hg methylation was obvious in sulfidic hypolimnion and surficial sediment The acetate-utilizing SRB were suggested the main methylators under sulfate limiting conditions in late summer. The methylation rates in surficial sediments were lower than, or at the same level as the hypolimnetic waters. Low methylation rate in the oxic layers and within O/A boundary was a common feature for all lake profiles

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METHYLMERCURY PRODUCTION IN FLOODED SOILS: A LABORATORY STUDY

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Abstract. The effect of soil flooding on methylmercury (MeHg) production was studied by placing humus and peat with water in 40 liter vessels. Total mercury (Tot-Hg), MeHg, nutrients, total organic carbon (TOC) and color were measured in water. Potential mercury methylation and demethylation rates in water and in flooded soils (humus and peat) were measured using radiochemical methods under aerated and non-aerated conditions during a period of 117 days.

In general, the potential methylation in humus and peat were one order of magnitude higher than in the water phase. During the experiment, methylation increased in humus and in peat but decreased in water. Demethylation decreased in all compartments. Anoxis increased methylation in soils but not in the water phase. On the other hand, demethylation was clearly higher in anoxic conditions. Tot-Hg increased more rapidly than MeHg in the water of the vessels, and a more rapid MeHg increase was observed in peat vessels than in humus vessels. Highest concentrations of MeHg (5.42 ng/L peat, 7.98 ng/L humus) were measured in non-aerated vessels.

Water color correlated negatively with methylation in water but positively with MeHg concentrations, indicating that humic substances are the main MeHg carriers but are not active methylating agents. Methylmercury fluxes to water (3.6-44 ng/m^2*d) were of the same order of magnitude as those measured in field experiments in Canada and in a beaver lake in Finland but were notably higher than those fluxes from unflooded catchmets.

The results indicate that increased net methylation in flooded humus and peat soils, especially in anoxic conditions, is the main reason for increased MeHg concentrations in reservoirs.

1. Introduction

Elevated levels of methylmercury (MeHg) were found in fish living in newly built reservoirs in the 1970's in Canada and the USA and in 1980's in Finland (Potter *et al.* 1975, Abernathy & Cumbie 1977, Bodaly & Hecky 1979, Meister *et al.* 1979, Bodaly *et al.* 1984, Alfthan *et al.* 1983, Lodenius *et al.* 1983, Verta *et al.* 1986). According to the literature cited above, two main processes are hypothised for the increased accumulation of MeHg: (1) Inorganic Hg is released from flooded soil, thus increasing its availability and (2) microbes decompose the flooded organic matter and methylate the inorganic Hg attached to it. Increased microbial methylation caused by released nutrients and organic compounds from soil and vegetation has been suggested as a major source of MeHg (Bodaly *et al.* 1984, Hecky *et al.* 1987).

The latest observations of MeHg levels in rain water, soil and runoff waters and Hg methylation in soil indicate that soil has an important role in MeHg production (Mucci *et al.* 1994, St. Louis *et al.* 1994, Morrison & Thérien 1995, Lee *et al.* 1995). The release of the MeHg produced or stored in soil may be an important source of MeHg for reservoirs. Studies of this source of MeHg are lacking. However, observations of the effect of a beaver dam on the MeHg budget of Lake Keskinen Hakojärvi (KEHA), in southern Finland as well as experimental flooding of Lake 979 in Experimental Lakes Area (ELA) in Ontario, Canada, support this hypothesis (Verta *et al.* 1993, St. Louis *et al.* 1994a). As a result of the flooding, MeHg concentrations in the water of these lakes have been increasd by an order of magnitude.

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The objective of this study was to investigate MeHg production in flooded soils. In a laboratory experiment we tested the ability of humus and peat to methylate mercury and determined how the oxic conditions affect rates of mercury methylation and demethylation, and release of Tot-Hg and MeHg from the soils.

2. Material and Methods

Humus soil and peat were taken from two sites located in southern Finland (61°N 25°W). The humus soil was obtained at a depth of 5-10 cm from a dry *Calluna*-type Scots pine (*Pinus sylvestris*) forest. The peat was removed at a depth of 10-25 cm from a *Myrtillus*-type spruce swamp. The soil was sieved (mesh sizes: 2.8 mm for humus and 4.7 mm for peat) and frozen at -18 °C. The samples were thawed, tempered and put in 45 L polyethylene vessels; and a nylon net (mesh size 1 mm) was placed over the soil. Finally, 40 L of water (lake water from Lake Päijänne, southern Finland) were poured into each vessel. The experiment consisted of five test units: two vessels with humus and water (aerated and nonaerated), two with peat and water (aerated and nonaerated), and a control vessel containing only water. The water was aerated by two aquarium pumps 20 cm above the humus or peat. The vessels were allowed to stabilize for 24 h before the first sampling. The experiment was carried out in the laboratory at 14 ± 1 °C in the dark.

Water samples were transferred to sample bottles with siphons. Oxygen and temperature were measured in situ with a Marvet AJ 90 probe (Top Solutions Inc.). Conductivity and pH were measured, and methylation and demethylation samples were incubated immediately after sampling. Water quality (alkalinity, color, Tot-N, NO_2-N, NO_3-N, NH_4-N, Tot-P, Fe and Mn) was determined a day after each sampling. The Tot-Hg, MeHg and TOC samples were frozen in acid-washed polyethylene bottles until analysed. Samples from the flooded soil were taken by vaccuming soil into a 100 mL syringe.

The rates of methylation and demethylation were determined by incubating the samples for 24 h at + 14 °C after labelling with $^{203}HgCl_2$ and $^{14}CH_3HgI$, respectively. Incubation doses ranged from 22.6 to 131 kBq per 5 g Hg in methylation assays, and from 0.82 to 0.99 kBq per 0.33 Hg in demethylation assays. Each test consisted of duplicate samples. The amount of methylmercury ($CH_3{}^{203}Hg+$) formed was determined using a modification of the method developed by Furutani and Rudd (1980), and the products of demethylation ($^{14}CO_2$ and $^{14}CH_4$) were measured by a method developed by Ramlal *et al.* (1986). Radioactivity was measured with a liquid scintillation counter (Racbeta, LKB-Wallac, Finland). A more detailed description of the methods is presented by Matilainen *et al.* (1991). Rates are expressed as the percentage of the added mercury methylated or demethylated per day and per 2 g of soil (dry weight).

Tot-Hg and MeHg in water were analysed as described by Bloom (1989), Bloom & Fitzgerald (1988), Bloom & Crecelius (1983), and Horvat *et al.* (1993).

3. Results

3.1. Methylation and demethylation rates in flooded soil

In general, the potential methylation rates in humus and in peat were one order of magnitude higher than in the water phase. In aerated humus the rates remained low during the whole experiment. After a lag period of about 20 d, the methylation rates in humus started to increase and were clearly higher in the non-aerated vessels (Fig. 1a). A much shorter lag period (about 4 d) occurred in peat, and again at the end of the experiment the rates were higher in non-aerated vessel (Fig 1b).

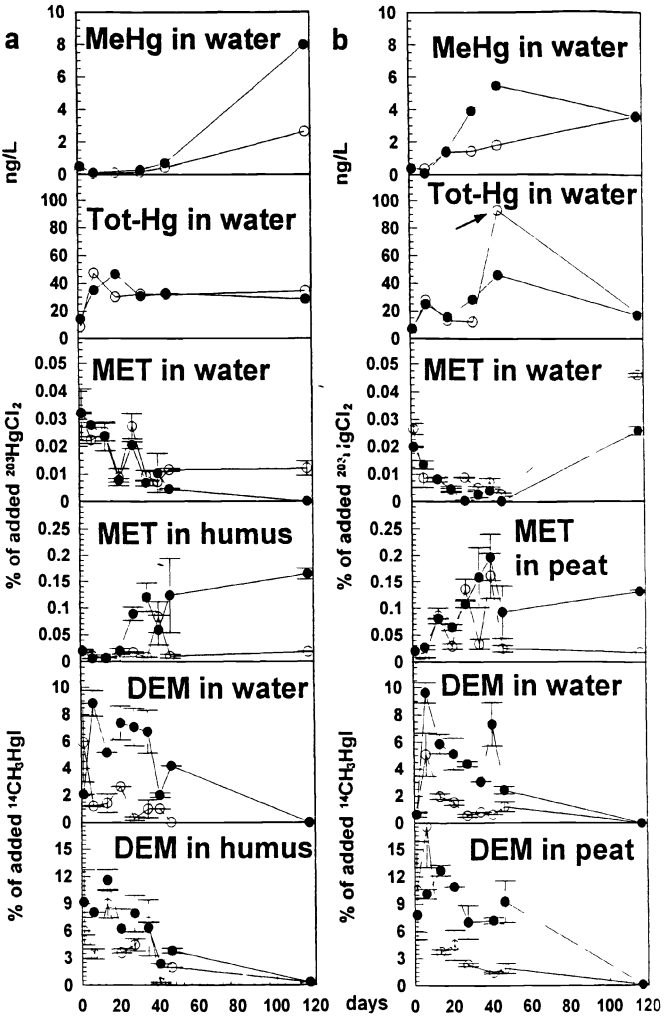

Fig. 1. MeHg and Tot-Hg concentrations in water, and methylation and demethylation rates in water and in soil plotted against time The humus vessels (a) are presented on the left and the peat vessels (b) are on the right. Solid dots indicate the non-aerated vessels and the open cirles are the aerated vessels. An arrow (in aerated peat vessel) indicates probably contaminated Tot-Hg observation.

Demethylation decreased during the experiment and almost no demethylation was measured in vessels after 117 days of incubation (Fig. 1). In peat the decrease was more rapid in the aerated conditions.

3.2 METHYLATION AND DEMETHYLATION RATES IN WATER

In water the methylation rates decreased during the first 46 days of the experiment and the methylation rates were higher in the the humus vessels than those in the peat vessels (Fig. 1). In peat, however, the methylation rates in the vessels increased at the end of the experiment .

Parallel to the rates in soils, the demethylation rates in water decreased during the experiment. Demethylation rates were generally higher in nonaerated vessels (Fig. 1).

3.3 TOT-HG AND MEHG AND OTHER DISSOLVED SUBSTANCES

The Tot-Hg concentrations in water increased during the first week in all vessels (Fig 1). In peat vessels a further increase was observed between days 19 and 45.

Methylmercury concentrations increased more rapidly in the peat vessels than in the humus vessels (Fig. 1). This increase was most pronounced in non-aerated peat. Concentrations in the others, especially in the humus vessels, increased at much lower rates. However, due to the late increase of MeHg concentration, the nonaerated humus vessel reached the highest concentration (7.98 ng/l) at day 117.

Water color and TOC increased in all vessels throughout the experiment (Fig 2). The same trend was also true for Total-N-, NH_4-N-, Total-P- and Fe-concentration in water (Table I). On the contrary, NO_3-N concentrations decreased in all vessels.

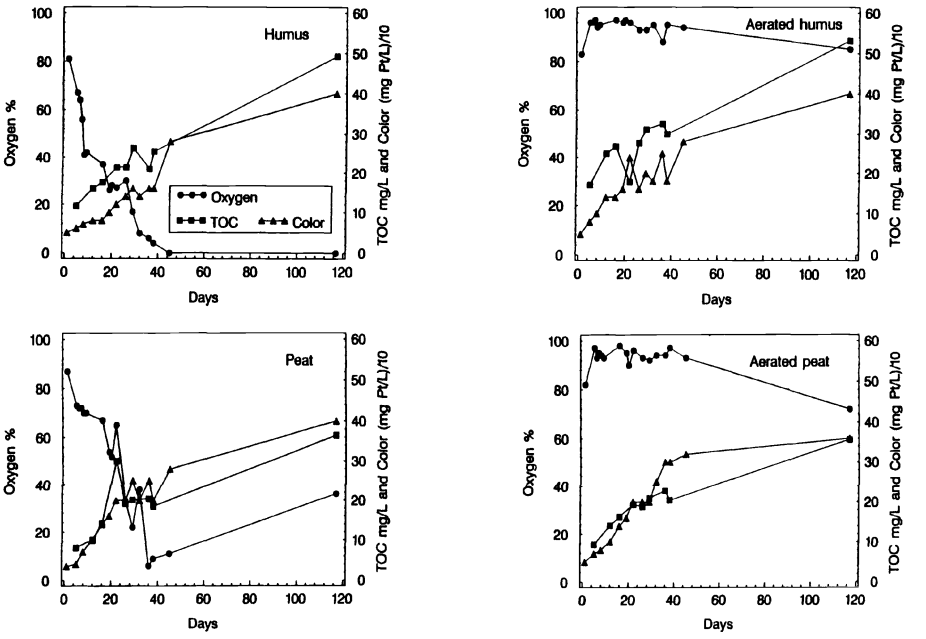

Fig. 2. Percentage oxygen, TOC and color in water of different vessels.

TABLE I
Water quality of different vessels during the 45 days of the experiment. Values after 1 day and 45 days from the start of the experiment are shown.

VARIABLE	HUMUS	AER. HUMUS	PEAT	AER. PEAT
pH	5.90-5.35	5.95-5.22	6.42-5.98	6.29-4.47
Conductivity (mS/m)	65.5-74.4	65.5-66.3	69.4-63.8	69.7-61.5
Alkalinity (mol/L)	0.09-0.04	0.09-0	0.18-0.12	0.16-0
Tot-N (μg/L)	760-1700	750-1700	690-1300	770-1300
NO_2-N (μg/L)	0-2	0-0	0-6	0-2
NO_3-N (μg/L)	300-18	300-29	340-31	350-48
NH_4-N (μg/L)	0-280	0-750	0-620	0-660
Tot-P (μg/L)	20-720	25-640	12-370	16-370
Fe (μg/L)	82-1100	110-780	85-1300	100-1100
Mn (μg/L)	31-50	36-39	16-16	20-13

To test the effect of organic matter on MeHg production, several correlations were calculated. Water color correlated negatively with methylation in water but positively with MeHg concentrations (Fig 3). TOC, on the other hand, revealed only a weak positive correlation with MeHg concentrations ($r=0.54$, $p<0.01$, $N=23$).

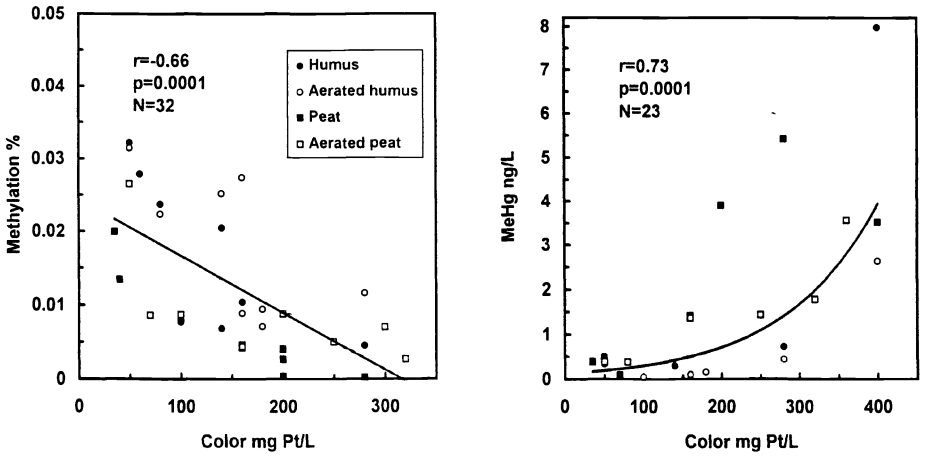

Fig. 3. Methylation rates in water (during 46 days) plotted against water color (left) and MeHg concentrations in water (during 117 days) plotted against water color (right).

4. Discussion

The water in the vessel with humus soil reached total anoxia 46 days after flooding and remained oxygen-free to the end of the experiment. There was a significant drop in oxygen in the nonaerated peat vessel, but total anoxia in the water was not reached. The same result has also been found in other experiments (Verta *et al.* 1986, Morrison & Thérien 1995).

The methylation rates in flooded humus and peat without aeration exceeded those in aerated vessels. These results agree with those of studies on flooded soils from reservoirs (Hecky *et al.* 1987, Jackson 1987). In those limnocorral experiments increased rate of Hg methylation resulted principally from utilization of organic substrates as nutrient substrates by methylating microbes, and creation of anaerobic or oxygen-poor conditions.

For humus, Tot-Hg release clearly differed from the release of MeHg. At first, the release of Tot-Hg was rapid but remained at the same level. The increase in MeHg concentrations was much slower. For peat, Tot-Hg behaved similarly to humus, but the release of MeHg started much earlier parallel to methylation.

The high MeHg concentrations in the water of the non-aerated humus vessel at the end of the experiment agree well with the high methylation activity in humus (Fig. 1a). The maximum MeHg concentration (5.42 ng/L) was also recorded in the non-aerated peat vessel at the time of maximum methylation in peat. The increasing concentrations of MeHg during the experiment and the positive correlations of MeHg with humic substances (color) indicate significant net methylations in flooded soils. Aeration clearly decreased methylation in humus, but also in peat. This negative effect was not seen in methylation in the water phase, which was expected, since anoxia was generally not reached during the first 46 d.

The potential methylation and demethylation rates measured here cannot be regarded as actual rates. They were achieved with isotope additons that greatly exceed natural levels. The living plant material was removed and the soil was sieved before flooding, which obviously affected the potential methylation and demethylation rates. The rate of decomposition of different plant material varies (Brinson *et al.* 1981, Webster & Benfield 1986, Rochefort *et al.* 1990) and subsequently the methylation potential varies for different plant species (Morrison & Thérien 1995). Nonetheless, the results indicate that net methylation in submerged nonliving humus and peat material can cause extensive changes in water MeHg concentrations, and that these changes can (at least partly) be explained by increased methylation in the flooded soils.

In the humus vessels, methylation in water decreased while TOC and color were increasing, regardless of the positive correlation between MeHg/TOC and MeHg/color. In the peat vessels the decreasing trend for methylation in water and the increasing trend for TOC and color were also true during the 46 days of the experiment. This outcome is in agreement with the results of methylation studies on waters with humus additions (Miskimmin *et al.* 1992) and those on natural epilimnetic waters (Matilainen & Verta 1994). The results of such studies suggest that humic substances probably act as MeHg carriers, not as active methylation agents. Contrary to the results for humus vessels, the water phase methylation in peat vessel was at its highest at the end, simultaneously with

high TOC and water color. An explanation for this could be that the methylating microbe populations in those vessels may have adapted to high concentrations of organic matter in water.

In order to compare fluxes of MeHg from flooded soils with fluxes from the different catchment areas, MeHg production was calculated during the first 46 days and during the whole experiment (Table II). The MeHg fluxes in the experiment were 1.1 to 61 times higher for humus and 3.4 to 107 times higher for peat than those from podzols and peat soils in natural catchments situated in Canada, Sweden and Finland (St. Louis *et al.* 1994b, Lee *et al.* 1995, Verta *et al.* 1993), but 2.3 to 28 times lower than measured by Verta *et al.* (1993) in Lake KEHA one year after it was dammed by beavers (Table II). The daybase fluxes from those catchments were transposed from fluxes that were orginally calculated on a yearly base.

TABLE II

Output fluxes of MeHg to water from the flooded soil at different catchments and in this study.

Vessel/catchment soil type	Location	Output flux ng/m^2*d MeHg
Humus	this study	5.8 (45 d) 25 (117 d)
Aerated humus	this study	3.6 (45 d) 8.2 (117 d)
Peat	this study	44 (45 d) 11 (117 d)
Aerated peat	this study	14 (45 d) 11 (117 d)
Former wetland (Reservoir 979)	southwestern Ontario, Canada	3.2
Headwater wetland	southwestern Ontario, Canada	0.41
Podzol	Gårdsjön, southwestern Sweden	0.55
Podzol/peat	Padasjoki, southern Finland	0.62
Podzol/peat (Lake KEHA)	Padasjoki, southern Finland	100

5. Conclusions

The results clearly indicate an increase in net MeHg production after flooding of humus or peat soils. Methylation is stimulated if anoxic conditions are achieved in inundated soils. The MeHg release from humus soil may be as important or even greater than that from peat soil. The increased net methylation in flooded humus and peat soils may be the main reason for elevated concentrations of MeHg in reservoirs.

Acknowledgements

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THE ROLE OF MICROORGANISMS IN ELEMENTAL MERCURY FORMATION IN NATURAL WATERS

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Abstract. Gas evasion of elemental Hg (Hg^0) from the open ocean plays a prominent role in the global mercury cycle. Elemental Hg is formed primarily by reduction of ionic Hg in the mixed layer of aquatic systems. By culturing phytoplankton in defined media, and by incubating natural seawater and freshwater samples, we have demonstrated that Hg^0 is produced by microorganisms, with formation rates (0.5 to 10% d^{-1}) similar to those estimated from mass balance studies. Our results also suggest that <3 μm microorganisms are the primary Hg reducers in natural waters. Eucaryotic phytoplankton are capable of reducing ionic Hg to Hg^0 but the rate of reduction is insufficient to account for the observed reduction rates found in incubated field samples. Bacteria are thus the more likely Hg reducers. In seawater, cyanobacteria such as *Synecococcus* may account for much of the mercury reduction, while in the eutrophic, polluted Upper Mystic Lake north of Boston other procaryotic microorganisms are contributing to the overall Hg reductive capacity of the medium. By reducing ionic Hg, microorganisms play a pivotal role in the aquatic biogeochemistry of Hg, not only by enabling evasion to the atmosphere, but by directly decreasing the amount of ionic Hg available for methylation.

1. Introduction

Elemental mercury (Hg^0) plays a fundamental role in the global Hg cycle. The exchange of Hg between surface waters and the atmosphere is rapid as a result of the formation of Hg^0 in natural waters, and its subsequent evasion, (Mason *et al.*, 1994a). In the atmosphere, which is responsible for most of the global Hg transport, about 98% of the Hg is gaseous Hg^0. In the oceans, which are a major source and sink for atmospheric Hg, 10 to 30% of the dissolved Hg is Hg^0 (Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1993); the situation is similar for freshwaters (Vandal *et al.*, 1991; Xiao *et al.*, 1991). As Hg^0 formation removes reactive Hg from the water column where it could otherwise be methylated (Fitzgerald *et al.*, 1994), this process plays an important role in the biogeochemical cycling of Hg in aquatic systems.

However, the mechanisms whereby reactive Hg species are reduced to volatile Hg^0 are poorly known. The reduction appears to be chiefly biological, as suggested by field studies in the equatorial Pacific Ocean (Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1993) and in freshwater and estuarine environments (Kim, 1987; Vandal *et al.*, 1993; Mason *et al.*, 1993a). The inverse correlation between Hg^0 concentration and primary productivity evident from the results of these field studies suggests a casual relationship. There is, however, also evidence for the abiotic reduction of Hg (Alberts *et al.*, 1974; Winfrey and Rudd, 1990; Xiao, 1994). Mass balance calculations suggest

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that reduction rates in the open ocean and in freshwater lakes are in the vicinity of 0.5 to 10 x 10^{-7} s^{-1} (0.5 to 10% d^{-1}; Vandal *et al.*, 1991; Mason *et al.*, 1994b). A recent study in an estuarine mesocosm (Kim, 1987) showed that while there was some relationship between primary productivity and Hg^0 concentration there was no strong association between production of Hg^0 and phytoplankton species composition. The role of bacteria was not investigated.

Studies of Hg reduction by procaryotic microorganisms at high Hg^{2+} concentrations have demonstrated that some bacteria can convert Hg(II) to Hg^0 using a plasmid-encoded enzymatic pathway (the *mer* gene; Belliveau and Trevors, 1989; Robinson and Tuovinen, 1984; Summers and Silver, 1978). Whether this detoxification mechanism is induced at the picomolar Hg concentrations found in natural systems, which are typically 5 to 6 orders of magnitude lower than those used in the laboratory induction experiments, is not known. However, recent studies indicate that microbial reduction of Hg(II) can occur by other mechanisms than the *mer* gene pathway (Oremland *et al.*, 1991; Barkay *et al.*, 1989).

Barkay *et al.* (1989) found that mercury-resistant microorganisms, isolated from lake and estuarine water by culturing at μM Hg concentrations, were able to reduce Hg at rates of 1 to 10% per hour. This study showed that most of the biotic reduction in the isolate from the estuary was due to bacteria (the isolation procedure killed the eucaryotes in the sample) and that other pathways beside the *mer* gene were involved. In contrast, in the freshwater isolate, most of the biotic reduction was due to the *mer* gene pathway. Oremland *et al.* (1991) have shown that demethylation of MeHg, which produces Hg^0, can occur via an oxidative pathway, and that this mechanism could be important in natural waters. Water column demethylation has been demonstrated in freshwater lakes (Xun *et al.*, 1987; Winfrey and Rudd, 1990) although estimated rates of demethylation are less than the estimated rates of Hg^0 formation in the same systems (Vandal *et al.*, 1991; Fitzgerald *et al.*, 1994).

Eucaryotic microorganisms can also reduce Hg (Ben-Bassat and Mayer, 1987, 1988; Bentz, 1977). The algae *Chlorella* reduced Hg in culture when exposed to μM Hg (Ben-Bassat and Mayer, 1977, 1978) although the rate of formation was slow, being on the order of 0.01% of the added Hg per day. These investigators found that the formation of Hg^0 decreased in concert with the inhibition of photosynthesis. Several studies have also shown that phytoplankton can externally reduce Cu(II) and Fe(III) and other metals by cell surface enzymatic processes (Price and Morel, 1990; Jones *et al.*, 1985, 1987). Three reduction pathways were identified for the diatom *Thalassiosira weissflogii*: reduction by organic compounds released into the medium, by cell wall components, and via a plasmalemma enzymatic pathway. Enzymatic reduction was the principal pathway and was inhibited by metabolic inhibitors. Reduction rates were proportional to concentration at low μM concentrations of copper, being about 2% day^{-1} for 10^6 cells/L (1 fmol $cell^{-1}$ hr^{-1} μM^{-1} copper added). We hypothesize that Hg(II) is reduced by algae by a similar mechanism.

Since there is little direct evidence in the literature for biotic reduction of Hg(II) by natural communities of microorganisms exposed to low Hg concentrations, we investigated Hg reduction in laboratory studies with natural samples and phytoplankton cultures. We report here the results of the monoculture experiments and laboratory incubations of field samples which suggest that microorganisms play an

important role in the production of Hg^0 in both freshwater and marine environments.

2. Methods

Cultures were maintained in acid-cleaned polycarbonate bottles, and were spiked from μM $HgCl_2$ standards. Natural samples were collected in acid-cleaned bottles from a depth of about 5 m using a peristaltic pump and acid-cleaned teflon tubing; seawater from the ocean side of Martha's Vineyard, Massachusetts, and freshwater from the Mystic Lakes in Boston (Aurilio *et al.*, 1994). Control (abiotic) samples were either prepared by microwaving the samples until boiling (approx. 6 minutes per liter of sample) or by 0.2 μm filtration. Artificial seawater with added nutrients, trace metals/EDTA and vitamins (Aquil; Price *et al.*, 1989) was used for the culture experiments. As Hg is not significantly complexed by EDTA in the presence of 0.5 M chloride, Hg was added at required concentration, and was not buffered in the solution.

Incubation experiments involved either continuous bubbling of the sample for 3 to 5 hours after Hg addition or 18 to 24 hours batch exposures where samples were not continuously bubbled (Mason *et al.*, 1993b). During initial studies it was found that there could be significant formation of Hg^0 at the start of an experiment. After addition of the Hg spike there was a rapid formation of Hg^0 within the first 20 minutes followed by a slower abiotic production. Other investigators have noted a similar initial production of Hg^0 after addition of Hg (Xiao, 1994) and other trace metals (Jones *et al.*, 1987). This initial abiotic formation, which presumably results from the presence of reductants either in solution or on the container walls, occurs even in distilled water. To remove this initial production of Hg^0, samples were sparged continuously with Hg-free air, and the gaseous Hg was collected periodically after addition. Alternatively, for batch cultures that were not continuously sparged, samples were degassed with air an hour after the addition of the Hg spike to remove any gaseous Hg formed due to the initial reduction. All cultures were maintained under constant fluorescent light (150 μEinstein m^{-2} s^{-1}; Price *et al.*, 1989) at 25°C.

Mercury analyses relied on atomic fluorescence quantification of Hg^0 (Bloom and Fitzgerald, 1988). To determine Hg^0, samples were purged unamended and the volatile Hg trapped on gold columns. For the determination of reactive Hg, tin chloride was used to convert labile Hg species into Hg^0. All sample manipulation and degassing was done under clean room conditions. Details of the analytical techniques are contained in Bloom and Fitzgerald, 1988; Gill and Fitzgerald, 1987; Mason *et al.*, 1993a).

3. Results and Discussion

3.1 ABIOTIC REDUCTION

A number of experiments performed at nM concentrations of Hg showed that abiotic reduction rates in distilled water were higher than in seawater (Table I), as suggested by other investigators (Xiao, 1994; Barkay *et al.*, 1989). Amyot *et al.* (1994) found that light was necessary for Hg^0 formation in an acidic oligotrophic lake.

Addition of hydrogen peroxide, a reducing agent, did not, however, enhance Hg^0 formation suggestive of photosynthetically-mediated Hg^0 production in this lake. Our measured rates in distilled water (1.1% day^{-1}; 1.2 x 10^{-7} s^{-1}) are somewhat lower than those found by others (Alberts *et al.*, 1974; Winfrey and Rudd, 1990). Abiotic reduction rates in artificial seawater were only 40% of the distilled water rates. Further, abiotic formation rates in microwaved lakewater were similarly greater than the rate measured in microwaved seawater (Table I). Because Hg^0 formation rates are also typically lower in seawater (Mason *et al.*, 1994b; Table III) than in freshwater (Vandal *et al.*, 1991, 1993; Table IV) the relative importance of abiotic formation is similar in both systems, from 10 to 30% of the total formation rate.

TABLE I

Abiotic formation rates for elemental Hg in different media under batch culture conditions. Spike concentrations of inorganic Hg were either 0.5 or 0.6 nM.

SAMPLE	Hg^0 (%/day)
DISTILLED WATER	1.1
DISTILLED WATER WITH AQUIL TRACE METALS (ATM)	1.1
MICROWAVED MYSTIC LAKEWATER	1.1 ± 0.6
ARTIFICIAL SEAWATER WITH ATM	0.44
MICROWAVED SEAWATER	0.28 ± 0.2

3.2 MERCURY PRODUCTION BY MARINE MICROORGANISMS

The results of field studies in the equatorial Pacific Ocean (Mason and Fitzgerald, 1993; Mason *et al.*, 1994b) and in the North Atlantic (Mason *et al.*, 1994c) indicated that reduction rates range were between 0.2 and 1% day^{-1} for the open ocean, while higher conversion rates were estimated for the Pettaquamscutt estuary, Rhode Island (Mason *et al.*, 1993a). A number of marine phytoplankton cultures were therefore studied to assess their ability to reduce inorganic mercury to Hg^0 at rates similar to those estimated from field data. Previous studies with *Thalassiosira weissflogii* had shown that this organism could reduce copper at rates of 1 to 10 fmol $cell^{-1}$ hr^{-1} when exposed to 1 to 10 μM Cu(II) (Jones *et al.*, 1987). If reduction rates were similar for Hg, then rates around 0.5 amol $cell^{-1}$ hr^{-1} would be expected at the 0.5 nM exposure concentrations used in the Hg experiments. Our studies with a variety of marine microorganisms showed that the diatom, *T. weissflogii* and the green alga, *Dunaliella tertiolecta* and *Pavlova lutheri*, reduce Hg(II) to Hg^0 at similar rates (0.1 to 0.5 amol $cell^{-1}$ day^{-1}; Table II) while the coccolithophore, *Pleurochrysis caterae*, and the cyanobacterium, *Synecococcus bacillaris*, produced Hg^0 at a slower rate. Preliminary results suggest that *Prochlorococcus*, an abundant open ocean cyanobacteria, also reduced Hg(II) at a rate similar to *Synecococcus*. The formation rates found in these experiments are an order of magnitude lower than those predicted from the experiments with *T. weissflogii* and copper. Because of the low concentration

of Hg relative to other trace metals in the Aquil mixture (Price *et al.*, 1989), competition for reduction sites could account for the slower rates of reduction of Hg, compared to copper, found in the monoculture experiments.

TABLE II

Production of elemental Hg by cultures of marine microorganisms. All production rates are corrected for abiotic production. For the continuous bubbling experiments, abiotic production was 1.3% d^{-1}; for batch exposures, 0.75% d^{-1}. 500 mL samples were spiked to 0.5 nM mercury.

SPECIES	CELLS/L	pg/CELL Chl a$	Hg^0 (%/day)	Hg^0 (amol $cell^{-1}$ d^{-1})	Hg^0 (pmol μg^{-1} Chl a d^{-1})
T.W.	7.7×10^7	1.8	3.0	0.29	0.16
T.W.	7.5×10^6	1.8	0.40	0.48	0.25
D.T.	1.9×10^8	0.5	2.3	0.12	0.25
P.L.	2.4×10^8	0.2	9.7	0.41	2.05
SYN	1.0×10^9	0.01	6.6	0.067	6.6
CCII#	1.3×10^8	0.11	0.35	0.027	0.25

NOTE: T.W. *Thalassiosira weissflogii*, D.T. *Dunaliella tertiolecta*, P.L. *Pavlova lutheri*, SYN *Synecococcus bacillaris*, CCII *Pleurochrysis caterae*.

Batch experiment.

$ Chlorophyll a concentrations per cell were estimated using the general relationship between chlorophyll concentration and cell volume derived by Montagnes et al. (1994).

The production rate of Hg^0 was a function of cell size. *S. bacillaris* is less than 1 μm in radius and its rate of production was highest of the organisms tested on a surface area basis (Mason *et al.*, 1993b) or when normalized to chlorophyll a (Table II). Production rates, in pmol μg^{-1} chl a day^{-1}, were comparable for all the phytoplankton except *Pavlova* and *Synecococcus* which both produced Hg^0 at a higher rate, with the rate for *Synecococcus* being about 30 times greater than the rate for *T. weissflogii*. The cell densities used in these experiments were substantially higher than those found in natural waters, except perhaps for *Synecococcus*. For example, to obtain a conversion rate of 1% day^{-1} with *T. weissflogii* would require a cell density of 10^7 cells/L. At typical oceanic abundances for cells of this size (10^5 cells/L or less) conversion rates would be less than 0.1% d^{-1}; i.e. less than abiotic formation rates. Algae would not be important reducers even at rates of reduction similar to those measured for *P. lutheri*. In contrast, a cyanobacterium such as *Synecococcus*, present at abundances of $> 10^8$ cells/L, could convert Hg at rates comparable to those measured in natural samples (>0.6% day^{-1} for *Synecococcus*). For the phytoplankton, therefore, it is probable that the smaller cyanobacteria are the important Hg reducers in ocean waters.

A preliminary investigation of Hg^0 production by natural populations of marine microorganisms was conducted using water collected from the ocean off Martha's Vineyard, Massachusetts. Water was pumped into acid-cleaned bottles and transported back to the laboratory for the incubation studies. Subsamples of the water were filtered

and/or amended with additions of trace metals and nutrients and the resultant Hg^0 formation measured (Table III). Distilled water blanks and microwaved samples showed low Hg^0 production (Table I) while the formation rate (corrected for abiotic formation) was 2.3 % day^{-1} for the unamended seawater sample. Addition of trace metals (the normal Aquil mixture; Price *et al.*, 1989) to the culture caused a decrease in the production rate for Hg^0. If Hg and other trace metals are reduced by the same mechanism, then this decrease could be accounted for by the competition between Hg and other reducible trace metals for the available reducing sites.

TABLE III

Formation of elemental mercury in coastal seawater amended with 0.6 nM inorganic Hg and incubated overnight. Formation rates are corrected for abiotic production which was 0.28 ± 0.19% day^{-1}. The chlorophyll a concentration of the sample was 3 μg/L. Samples were incubated in 500 mL polycarbonate bottles.

SAMPLE	Hg^0 (%/day)	Hg^0 (pmol day^{-1})	Hg^0 (pmol μg^{-1} Chl a day^{-1})
UNFILT.	2.3	6.9	4.6
UNFILT. PLUS ATM*	1.3 ± 0.6	3.9 ± 1.8	2.6 ± 1.2
3 μm FILT.	2.3	6.9	4.6
1 μm FILT	1.1	3.3	2.2

NOTE: * This average includes exposure to three different concentrations of Hg (0.3, 0.6 and 0.9 nM)

Filtration of the sample followed by incubation allowed a preliminary assessment of the size class of the Hg(II) reducing organisms. The >3 μm organisms were clearly not responsible for the reduction (Table III), as suggested by the laboratory culture experiments. The reducing capacity was split between the 1-3 and 0.2-1 μm fractions. The rate of Hg^0 formation for the unamended sample, on a chlorophyll a basis, was similar to that found for *Synecococcus*, suggestive of the role of the cyanobacteria in Hg(II) reduction in ocean waters. Although the data are limited, the results of the laboratory monoculture experiments and the field study indicate that while most marine phytoplankton are capable of reducing Hg(II) to Hg^0, only *Synecococcus* and possibly other cyanobacteria produce Hg^0 at rates comparable to those estimated from field measurement.

3.3 MERCURY REDUCTION IN AN EUTROPHIC LAKE

Elemental Hg formation rates in freshwater lakes have been previously estimated, based on mass balance calculations, to range between 1 and 10% day^{-1} (Vandal *et al.*, 1991; Fitzgerald *et al.*, 1991). Our studies with water collected from the Upper Mystic Lake in Boston over a year and incubated under laboratory conditions, confirm this range in formation rates (Table IV). The Upper Mystic Lake is eutrophic, with blooms of diatoms in the spring and fall and a predominance of cyanobacteria and green algae through the summer (MDC, 1978). The lake has been

historically polluted with high concentrations of arsenic, chromium and other trace metals (Aurilio *et al.*, 1994). Further, there are high concentrations of coliform bacteria (up to 10^5/L) and other heterotrophic bacteria in this lake (Cassidy, 1971). Total Hg concentrations in the Upper Mystic Lake range between 10 and 25 pM with reactive Hg concentrations of 5 pM or less. Elemental Hg concentrations vary throughout the year, ranging from 200 fM to 1.2 pM for the surface waters (Figure 1). Concentrations typically decrease with depth suggesting that the epilimnion is the principal region of Hg^0 formation, as found by Vandal *et al.* (1993). Based on the average reactive Hg concentration (2 pM) and Hg^0 concentration (0.6 pM), conversion rates of 2 to 4% day^{-1} are required to balance the estimated evasional fluxes of 200 to 400 pmol m^{-2} day^{-1}. The Hg^0 formation rates found during the incubation experiments (up to 8% day^{-1}) are generally higher than those estimated for open ocean waters (0.2 to 1% day^{-1}; Mason *et al.*, 1994b; Mason *et al.*, 1994c) but agree with the overall mass balance estimates.

TABLE IV

Formation of elemental Hg in surface water collected throughout the year from the Upper Mystic Lake, Boston. Rates are corrected for abiotic formation. Samples were incubated in 500 mL bottles spiked with 0.5 nM Hg. Chlorophyll a concentrations were measured by HPLC.

DATE	μg/L Chl a	Hg^0 (%/day)	Hg^0 (pmol day	Hg^0 (pmol μg^{-1} Chl a day^{-1})
APRIL 93	7.0*	7.9	20	5.7
MAY	0.35	2.3	5.8	33
JUNE	0.18	0.7	1.8	20
JULY	0.99	5.4; 3.8#	13.5; 9.5	27; 19
SEPTEMBER	0.14	3.4 ± 0.5$	8.5 ± 1.3	120 ± 19
OCTOBER	5.4	5.6	14.0	5.2
NOVEMBER	3.1	<0.5	<1.3	<0.84

NOTE: * The chlorophyll a concentration was determined for this sample by extraction and fluorescence measurement.

\# Samples collected one week apart.

$ Duplicate samples for the same day.

Elemental mercury concentration (Figure 1) and the rate of Hg^0 formation tracked productivity to some extent (Figure 2) with the highest reduction rates in the spring and fall. Both the reduction rate and Hg^0 concentration decreased with depth (Table V and Figure 1). There was also an increase in the Hg^0 reductive ability in July that coincided with an increase in chlorophyll a (Table IV). The correlation between chlorophyll a concentration and Hg^0 formation rate ($r=0.71$) is improved if the anomalous November sample (high chl a, low reduction rate) is ignored ($r=0.88$). Amyot *et al.* (1994) and Vandal *et al.* (1991, 1993) have also found similar relationships between Hg^0 concentration and photosynthetic indicators. While these correlation suggests that there is a link between productivity and reduction, they do not prove that phytoplankton are the primary reducers.

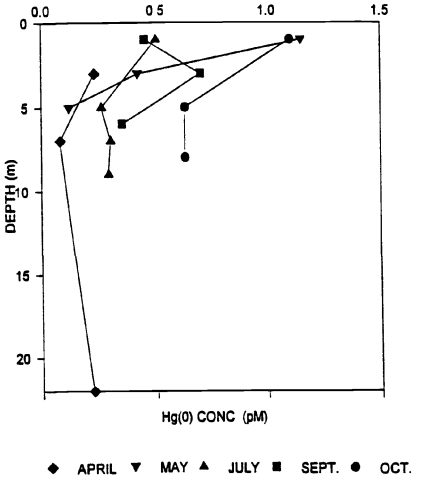

Fig. 1. Measured concentration of elemental Hg in the Upper Mystic Lake over the sampling period (March to November, 1993)

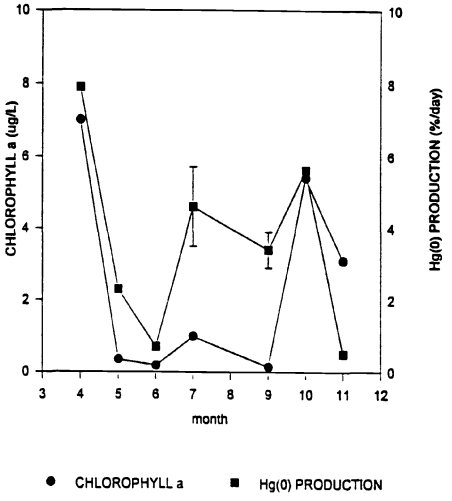

Fig. 2. Variation in chlorophyll a concentration and in the rate of elemental mercury formation for the Upper Mystic Lakes from March to November 1993.

TABLE V
Depth profile for July. Production of elemental Hg with depth in the Upper Mystic Lake. Experimental conditions are the same as in Table IV.

DEPTH (m)	μg/L Chl a	Hg°(%/day)	Hg° (pmol day^{-1})	Hg° (pmol μg^{-1} Chl a day^{-1})
1	0.99	3.8	9.5	19
5	1.75	3.1	7.8	8.9
7	3.36	2.0	5.0	1.3
9	7.19	1.1	2.8	0.8
19	7.84	<0.5	<1.3	0.3

The Hg° production rates, on a pmol μg^{-1} of Chl a basis, are much higher than those measured in the ocean samples or in the culture experiments (Tables II and III). Either the freshwater phytoplankton reduce Hg at a higher rate or other, non-photosynthetic microorganisms are contributing to the Hg° pool. Pigment analysis (Hurley, pers. comm.; Table VI) indicated that the May sample coincided with the end of a bloom (90% of the total chlorophyll a and derivatives was pheophytin a) and that there was little productivity in June. There was an increase in chlorophyll a and fucoxanthin (indicative of diatoms and chrysophytes) in July while the higher chlorophyll a concentrations in October and November coincided with the presence of fucoxanthin and pigments characteristic of cyanobacteria. The Hg° formation rates do not correlate with the presence (October and November) or absence of cyanobacteria. This is also true of a depth profile for Hg° production obtained in July (Table V). Overall, the rate of formation decreased with depth and did not coincide with the increasing chlorophyll a concentration with depth nor with the presence of cyanobacteria in the deepest sample.

Overall, the production rates, on a per chlorophyll basis, vary by at least two orders of magnitude, from <1 to 120 pmol μg^{-1} of chlorophyll a per day. The reduction rates are also, for the most part, higher than those found with the monoculture experiments (<3 pmol μg^{-1} of chlorophyll a day^{-1}) and in the sea water samples (<5 pmol μg^{-1} of chlorophyll a day^{-1}). These results suggest that while chlorophyll a concentrations provide some indication of the reducing ability of the Upper Mystic Lake waters, cyanobacteria and eucaryotic phytoplankton are not the only nor even the principal organisms reducing Hg in this lake.

Size fractionation experiments showed a similar trend to that found in the seawater samples. Most of the reduction was due to less than 3μm organisms (Table VII). In addition, inhibition experiments showed that while inhibition of photosynthesis (addition of DCMU or incubation in the dark) led to 20 to 30% decrease in the reduction rate, addition of the antibiotic ampicillin eliminated most of the reduction, typically an 80 to 90% decrease. These results strongly suggest that bacteria are responsible for most of the Hg° formation in the Upper Mystic Lake. Coupled with the lack of a correlation between Hg° formation and the presence of cyanobacteria, these results suggest that heterotropic microorganisms are the primary reducers in this eutrophic lake and are responsible for the high reduction rates even in the absence of phytoplankton production.

TABLE VI

Concentration of photosynthetic pigments (in nmol per liter) in waters taken from the Upper Mystic Lake. Concentrations determined by HPLC analysis (Hurley pers. comm.).

SAMPLE	fuco	allo	zea	chl b	B-caro	chl a	sum chl a
APRIL						7.7*	
MAY	0	0	0	0	0	0.39	3.97
JUNE	0	0	0	0.07	0	0.20	0.24
JULY	2.25	0	0	0	0	1.10	2.27
SEPT	0	0	0	0	0	0.16	0.33
OCT	0.51	0.33	0.33	0.45	0.86	6.00	7.51
NOV	1.68	0.27	0.27	0.30	0.33	3.47	4.91
JULY 5 m	0.68	0.08	0	0	0	1.92	2.89
JULY 7 m	1.80	0.12	0	0.59	0	3.73	4.81
JULY 9 m	0.45	0	0	0	0	7.98	8.65
JULY 19 m	0.24	0.11	0.26	0	1.23	8.62	8.97

NOTE: * Determined by acetone extraction and fluorescence measurement. Concentration calculated as 1 μg/L = 1.1nmol/L for chlorophyll a.

TABLE VII

Production of elemental Hg (% of added Hg reduced per day) by waters collected from the Upper Mystic Lake after filtration or after treatment with inhibitors. Experimental conditions are the same as in Table IV.

TREAT.	4/93	5/93	6/93	7/93	9/93	10/93	11/93
UNFILT.	7.9	2.3	0.7	5.4, 3.8*	3.4$\pm$0.5#	5.6	<0.5
3 μm FILT.	7.0	1.8	1.3			<0.5	
1 μm FILT.	3.9		1.2				
UNFILT +DARK				3.8, 2.6*	2.7		<0.5
+ DCMU				4.3	3.2	3.0	
+ AMPI.				0.7	1.7	0.7	<0.5

NOTES: * Samples collected one week apart

Duplicate samples from the same day

DCMU = 3-(3,4-dichlorophenyl)-1,1-dimethylurea, an inhibitor of photosynthesis, added at 10μM concentration

AMPI = ampicillin, a broad range antibiotic, added to 50μg/ml concentration

DARK = samples were wrapped in aluminum foil to exclude light

4. Mercury Reduction in Natural Waters

The results of the experiments with natural waters demonstrate that Hg is reduced, primarily by biotic means, at rates comparable to those estimated from mass balance estimates based on field measurements. Further, small organisms (typically < 3 μm in diameter) are the primary Hg reducers. The monoculture experiments and the incubations with seawater and freshwater samples suggest that while eucaryotic phytoplankton are capable of reducing Hg to Hg^0, the rate of reduction is insufficient to account for the observed reduction rates in the incubated field samples. Bacteria are thus presumably the more important Hg reducers.

In seawater, the evidence suggests that cyanobacteria such as *Synecococcus* could be important reducers but more studies with specific inhibitors and additional culture experiments are needed to clarify this observation. In addition, the role of heterotrophic bacteria in Hg reduction in seawater has not been studied. Further, it is not known whether the cyanobacteria reduce Hg by a cell surface mechanism or via a gene-encoded pathway. For the eucaryotes, Hg^0 production could involve cell surface reduction, similar to that found for other trace metals (Jones *et al.*, 1987) rather than a gene coded Hg resistance mechanism.

For the eutrophic Upper Mystic Lake, the results suggest that neither eucaryotic phytoplankton nor cyanobacteria are the main Hg reducers, implying that reduction by heterotophic bacteria is the predominant reduction pathway. A high concentration of coliform bacteria, which are known to reduce Hg at high exposure concentrations (Robinson and Tuovinen, 1984), could account for the difference between the seawater and freshwater samples. The results presented here are consistent with those of Barkay *et al.* (1989). These authors concluded that gene-encoded Hg reduction was the principal biotic reduction mechanism in freshwater, but not in estuarine waters.

In summary, the rate of reduction of Hg in a given aquatic system is a function of the nature of the microorganisms present, particularly the composition of both the autotrophic and heterotrophic procaryotes. Overall this study confirms the Hg^0 production rate estimates based on field data and has shown that biotic reduction of Hg is the primary route of Hg^0 formation both in seawater and in freshwaters. Further, this work also provides evidence for the role of procaryotic microorganisms in the reduction of Hg in natural waters.

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INFLUENCE OF HUMIC SUBSTANCES ON PHOTOLYSIS OF DIVALENT MERCURY IN AQUEOUS SOLUTION

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Key word index: Mercury, photochemistry, reduction, humic substances, environment, natural water, kinetic.

Abstract. Mercury (II) solutions were irradiated by a simulated sunlight in the presence of humic acid (HA) or fulvic acid (FA). Results show that, under the experimental conditions and the FA and HA chosen, less than 20% of the Hg in solution was photolysed with a rate of (1.63±0.29) x 10^{-2} s^{-1} (n=23) and the rest of (2.38±0.40) X 10^{-4} s^{-1} (n=23) depending on the substitutes of humic substances to which Hg were bond. The sunlight photolysis lifetimes were estimated to be 4 and 250 sunlight hours respectively under summer conditions at Stockholm latitude.

1. Introduction

Atmospheric mobilisation and air-water exchange are important features of biogeochemical cycling of mercury (Hg) in the environment. Two main forms of Hg exist in the environment, the elemental mercury Hg^0 and the divalent Hg (II). The predominant species (> 90 %) in the air is Hg^0 with the remaining fraction consisting of Hg(II). Atmospheric Hg is mainly deposited with precipitation in the water-soluble form of Hg(II) to the environmental surfaces, while volatile Hg species formed in the water body, mainly Hg^0, escapes into the atmosphere. This means that identifying the processes associated with cycling of elemental Hg between the atmosphere and natural water is of critical importance.

Mercury emissions from lakes (Schroeder and Fanaki, 1988; Xiao et al., 1991, Fitzgerald et al., 1991) and ocean water (Kim and Fitzgerald, 1986), probably in the form of Hg^0 and perhaps also $(CH_3)_2Hg$, have been measured. The volatile Hg species can be formed in sediments from Hg(II) both via biological or abiotic processes (Spangler et al., 1973; Steffan et al., 1988) or via a chemical reduction of mercuric ion in the presence of humic substances (Alberts et al., 1974). The latter process was enhanced when the solution was exposed light (Allard and Arsenie, 1991).

Investigations conducted in this laboratory (Xiao et al., 1994) show that a photoreduction in aqueous solution of Hg(II) to its elemental form is possible. In this experiment, pure $Hg(OH)_2$ solution was prepared in Milli-Q® water and kinetic data obtained can only be applied to relatively "clean" water bodies with low concentration of humic substances, chloride or other compounds that could coordinate to the mercuric ions. However, in most natural water system, Hg(II) is probably bound to different ligands, e.g. humic substances.

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Humic matter is known as heterogeneous copolymer of different chemical materials with different compositions and molecule weights depending on their sources and way of preparation. In aqueous systems such as surface water and shallow ground water, the concentration of dissolved humic matter generally is in the range of 1 to 10 mg l^{-1}. Humic substances are found to form complexes with many metal ions. Xu and Allard (1991) have shown that already in the presence of 1 mg l^{-1} of FA that almost all Hg (II) is bonded to FA. The complexing constant for Hg(II) and humic matter was estimated to be logK = 18-21 in a model natural freshwater with pH=7 and 21 ^{0}C (Munthe, 1991).

The aim of this investigation is to see the net effect of photolysis of Hg(II) in the presence of humic substances in aqueous solution. Mercury solutions together with humic substances were irradiated by a simulated sunlight under controlled conditions. Kinetic rate constants were obtained at different contents of humic substances and different concentrations of Hg both in Milli-Q and in natural waters. Finally the reactions half-lives under sunlight conditions were estimated.

2. Experimental

The experimental set-up is illustrated in Figure 1.

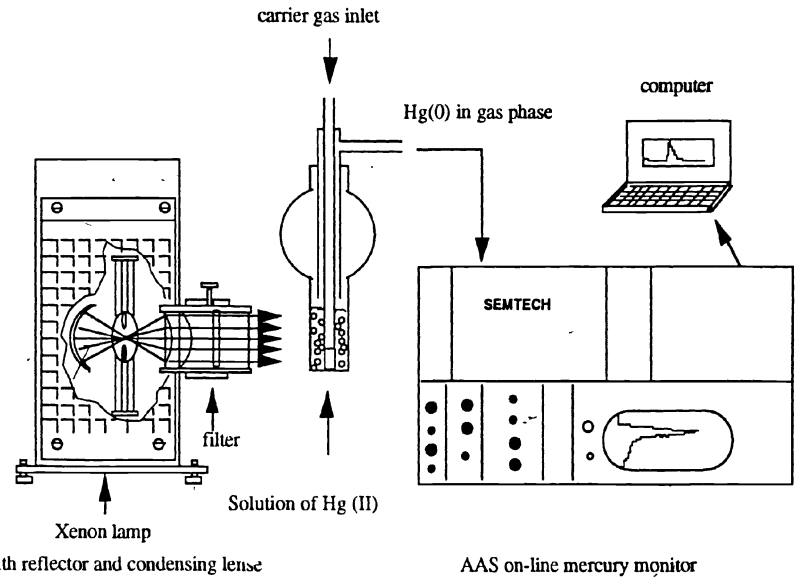

Figure 1. Experimental set-up.

A 400 W commercial xenon lamp, combined with a reflector and a condensation lens was used as a light source, which irradiates the reaction solution evenly at a horizontal direction. A colour filter was coupled to the system for cutting wavelength < 299 nm. A pyrex reaction bottle containing 20 ml solution was irradiated and the elemental mercury formed through photolysis was carried out by nitrogen. The flow rate

of the carrier gas was kept at 300 ml min^{-1} using a mass flow regulator. The changes of mercury concentration in gas phase were followed by Semtech® (Semtech Metallurgy AB, Lund Sweden), an instrument which can monitor Hg concentration directly and continuously. The working principle of this instrument is AAS with Zeem-effect. In order to eliminate the moisture influence, an extra washing bottle was placed between the reaction bottle and the Semtech. The concentration of Hg so measured was shown on the instrument screen directly and can also be collected by a personal computer for further data processing.

The light intensity of the xenon lamp was determined by a potassium ferrioxalate as a chemical actinometer (Xiao et al., 1994). A Shimadzu® UV-2100 UV-Visible Recording Spectrometer was involved in determining the exposed actinometer solution. It was also used to record the absorbency spectra of FA and HA solutions selected for this study, see Figure 2.

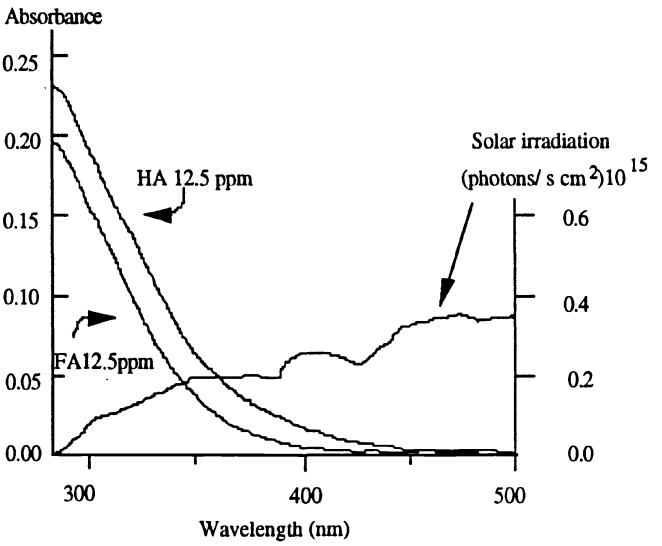

Figure 2. Absorption spectrum (pathlength of 1 cm) of FA and HA (12.5 ppm) solution and yearly maximum of daylight at 60°N (adapted from Svensson and Björndal, 1988).

Preparation of $Hg(OH)_2$ solution (pH = 7) has been described previously (Xiao et al., 1994). Diluted Hg working solutions were always prepared immediately prior to each experiment. $HgCl_2$ solutions were prepared from the neutral $Hg(OH)_2$ solution by adding NaCl (pro analyse grade) to make the chloride concentration 0.1 or 0.2 M. At this range of chloride concentration and pH, Hg is in the form of $HgCl_2$ (Benes and Havlik, 1979).

Some samples of humic (HA) and fulvic (FA) acids were isolated from the Göte River water in Gothenburg. The preparing procedures and characteristics concerning their elemental composition and molecular weight distribution etc. can be found in Plechanov (1983) under items FA-1 and HA-1 for fulvic and humic acid, respectively.

Fulvic was dissolved in Milli-Q water directly while humic acid was dissolved in 0.1 M NaOH. The resulting solutions were stirred with a magnetic bar for several hours at 25 ^{0}C and then centrifuged for one hour at 15000 rpm in a Philip centrifugation apparatus. The supernatant was then diluted to desired concentrations with Milli-Q water.

Reaction solutions with Hg concentrations of 20 and 40 ppb, FA or HA concentrations of 10 and 18 ppm were prepared for this study. The final pH's of the artificial solutions were between 5.0-5.2.

3. Results and Discussion

Figure. 3 presents the relative magnitudes of four different mercury solutions towards phtolysis under the same experiment conditions. The elemental mercury formed in gas phase was recorded in the concentration unit of $\mu g\ m^{-3}$.

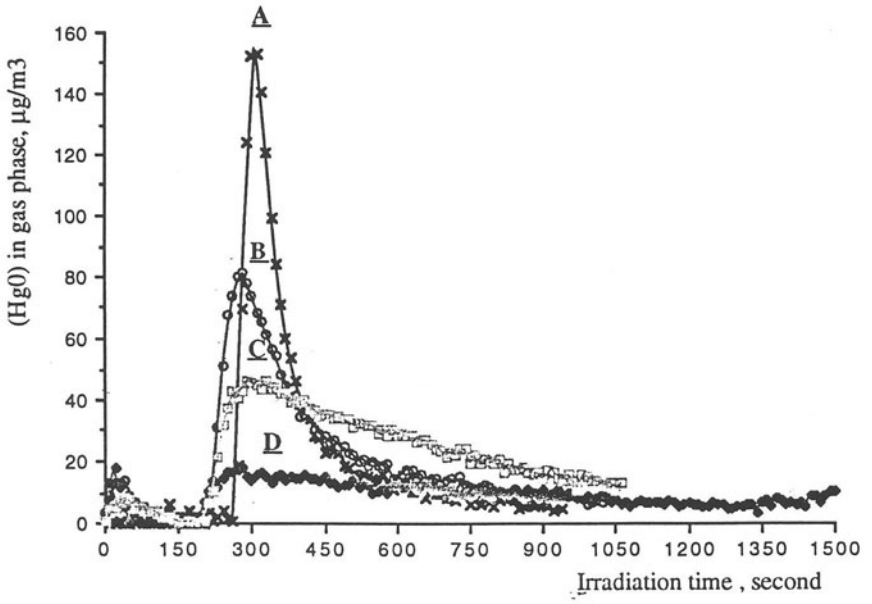

Figure 3. Relative magnitude of photolysis of divalent Hg in different solutions.. A. $Hg(OH)_2$ 20 ppb in Milli-Q water in the presence of 10 ppm FA (pH 5.2), B. $Hg(OH)_2$ 20 ppb in natural river water (pH 6.7), C. $Hg(OH)_2$ 20 ppb in Milli-Q water (pH 7.0) only , and D. $HgCl_2$ 20 ppb in Milli-Q water (pH 7.0) only.

It can be seen from Figure 3C that Hg(OH)2 can be photolysed directly, although its extinction coefficient of absorption at the wavelengths of interest is probably very small (Xiao et al., 1994).

Principally speaking, no HgCl2 could be photolysed in Milli-Q, due to the fact that it does not absorb light at wavelengths > 290 nm at all (Strömberg, 1990). The small amount of elemental Hg

formed, cf. 3D, when pure HgCl2 solution was irradiated may probably be the contribution from small quantity of $Hg(OH)_2$ which might exist in the $HgCl_2$ solution.

Water from the Göta River, which is used as the drain water sources for the city of Gothenburg, was sampled on January 1994. It was quite clean with concentration of Hg 3.1 ng L^{-1} and Total Organic Carbon (TOC) 5.0 mg L^{-1}. To this river water, 20 ppb $Hg(OH)_2$ was added before exposure to the xenon lamp. Elemental Hg formed in the gas phase cf. 3B, was much more than the same concentration of $Hg(OH)_2$ in Milli-Q water only.

Even more elemental Hg was formed when a 20 ppb mercury in Milli-Q water was irradiated in the presence of 10 ppm FA. This is illustrated by 3A, which shows the typical experimental result of the influence of humic substances on the photolysis of Hg(II) in aqueous solution.

Kinetic rate were evaluated by following the concentration decrease of the Hg(II) in solution. It was assumed that the elemental Hg formed through photolysis in solution was quantitatively transferred to the gas phase without losses in the system. Hence Equation (1) can be used:

$$[Hg^{2+}_{tot}]_t = [\,(n_{Hg^{2+}})_0 - (n_{Hg^0})_t\,] / V \qquad (1)$$

where $[Hg^{2+}_{tot}]_t$ is divalent Hg concentration in solution at time t, $(n_{Hg^{2+}})_0$ is the mass of divalent mercury in the solution at time zero, $(n_{Hg^0})_t$ is the mass of elemental mercury in the gas phase at time t, and V is the volume of reaction solution. $(n_{Hg^0})_t$ can be calculated from the concentration of Hg measured in the gas phase, $(n_{Hg^{2+}})_0$ and V are known.

At low concentration, photochemical reactions obey first order kinetics (Zepp, 1982), i.e. that the process can be described by Equation (2).

$$d[Hg^{2+}_{tot}]/dt = -k\,[Hg^{2+}_{tot}] \qquad (2)$$

In Figure 4a, $\ln[Hg^{2+}]$ as a function of time is plotted, for a typical experimental result in order to see whether the reaction is a first order one. However, the plot is definitely not a straight line, and the conclusion must be that it is not an ordinary first order reaction. Identical curves pattern would be obtained for all the experimental results conducted in the presence of humic substances.

The best fit of the experimental data were achieved when an assumption of "two-reaction processes" was made :

$$[Hg^{2+}tot]_t = [HgA^{2+}]_t + [HgB^{2+}]_t \qquad (3)$$

Where, $[Hg^{2+}tot]t$ is the total concentration of Hg in the solution calculated according to equation (1); HgA^{2+} and HgB^{2+} are assumed to be of Hg(II) bound to different substitutes A and B of humic substances. The A or B can either be one single function group or several function groups of humic matter with the same photolysis characters when expose to the xenon lamp. First order rate expressions were then, applied separately to both the reactions:

$$[HgA^{2+}]t = [HgA^{2+}]_0 E^{-k_A t}; \quad (4)$$

$$[HgB^{2+}]t = [HgB^{2+}]_0 E^{-k_B t} \quad (5)$$

The evaluation has been performed as follows: since one photolysis (the HgA) rate seems to be considerably higher than the other, almost no HgA will be left after a certain time interval, for example 200 seconds. Then, the contribution from $[HgA^{2+}]$ to $[Hg^{2+}tot]$ may become negligible (see Figure. 3A for the typical experimental result) and $[HgB^{2+}] \approx [Hg^{2+}tot]$. The concentrations of HgB^{2+} in the reaction solution from t=200 s to t=800 s can be calculated using Equation 1. By plotting $\ln[HgB^{2+}]t$ against reaction time t, the rate constant, k_B, and $[HgB^{2+}]_0$ can be obtained, see Fig. 4c.

By rearrange of equation (3), $[HgA^{2+}]_t = [Hg^{2+}tot]_t - [HgB^{2+}]_t$, the concentration of $[HgA^{2+}]_t$ in the reaction system can be calculated by using Equations (1) and (5). In the same way, k_A, and $[HgA^{2+}]_0$ can be obtained by plotting $\ln[HgA^{2+}]$ against reaction time t, see Fig. 4b. All the experimental results were treated in this way and the final results are summarised in Table 1.

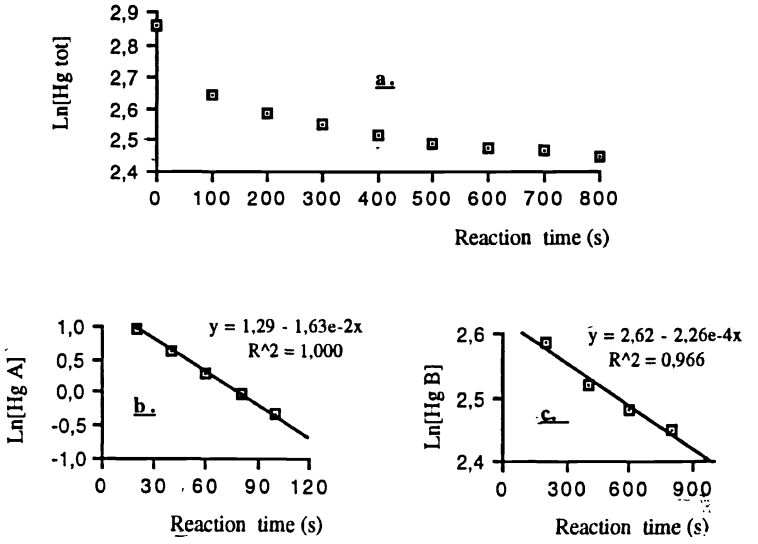

Figure 4. Typical calculating examples of first order plots. a. Ln[Hg $_{tot}$] against reaction time, b. Ln[Hg $_A$] against reaction time, and c. Ln[Hg $_B$] against reaction time.

The linearity in Figure 4b is quite good, but in Figure 4c one can perhaps see a slight "banana shaped" curve, although a considerable improvement has been achieved compared to Figure 4a. Even better fitting

was obtained if "three-reaction processes" was applied to the experimental data. Figure 5 presents the plot for the slowest process (corresponding to Figure 4c), when three types of complexes Hg(II) are assumed.

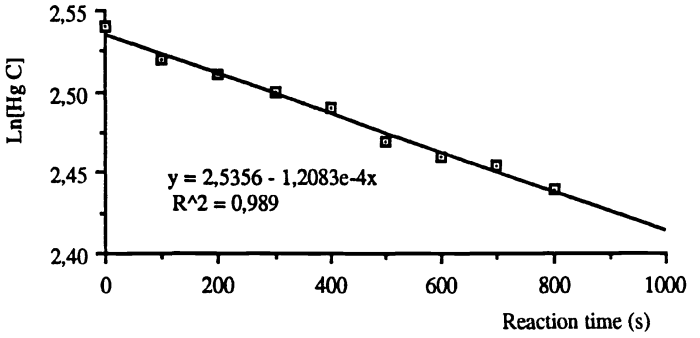

Figure 5. First order plot, Ln[HgC) against reaction time.

It is probable that Hg(II) is bonded to different types of sites of the very complex humic acid "molecule". Since, it has been shown that different Hg(II) complexes have different photolysis rates, see e.g. Xiao et al. (1994). It is not unlikely that a Hg(II) ion, bonded to one type of site of the humic acid has a photolysis rate that differs from a Hg(II) ion that is bonded to another type of site. This means that the photolysis of Hg(II) could very well be a sum of two or more photoreductions, which can be separately described by using ordinary first order reaction with their own reaction rates.

In Figure 5 the "banana shape" is disappeared. The third rate constants therefore, is obtained. An iterative method had to be used because at all times two fractions of Hg(II) were present. The new k_A was rather close to the k_A from Table I (2.3×10^{-2} s^{-1} compare to 1.6×10^{-2} s^{-1}). The "old" k_B is in between the new k_B and the new k_C, 2.3×10^{-4} s^{-1} respective to 4.1×10^{-3} s^{-1} and 1.2×10^{-4} s^{-1}. The Hg_A fraction obtained with three different Hg(II) forms was ≈17% (the old value ≈21 %) and the corresponding Hg_B and Hg_C fractions were calculated to be 11% and 72%. The difference of results obtained using two or three forms of Hg(II) assumption is not significant considering the extrapolation of the photolysis rate constants to the natural waters. Hence, only results treated by "two-reactions processes" were summarized in Table I together with the percentage of $[HgA^{2+}]_0/[Hg^{2+}{}_{tot}]_0$.

It can be seen that the larger photolysis rate is approximately $k_A \approx 2 \times 10^{-2}$ s^{-1}. This is a much larger constant than the one for $Hg(OH)_2$ (1.2×10^{-4} s^{-1}) reported previously (Xiao et al., 1994). The other rate constant, k_B, is approximately two magnitudes smaller, $\approx 2 \times 10^{-4}$ s^{-1}, which is in the same range as that of $Hg(OH)_2$. No significant difference between the experiments with HA and those with FA can be found. The HgA fraction varies between 10 to 23 % of the total Hg(II) with an average of ≈16 % in the artificial solution, the corresponding results are 9-17 and 14 % in the natural water.

When 20 ppb Hg was added to the Göte River waters, without the addition of FA or HA, the photolysis rate constants are $k_A=(1.3\pm0.3)\times10^{-2}$ s^{-1} (n=4) and $k_B=(1.8\pm0.1)\times10^{-4}$ s^{-1} (n=4), which are slightly lower than using the artificial FA and HA at a concentration level of 10-20 ppm.

Table I. Photolysis results of divalent mercury in aqueous solution with different content of humic substances

Experiment date	Reaction solution*	$k_B X10^4$ (s^{-1})	$k_A x10^2$ (s^{-1})	$(Hg_A)0/(Hg_{tot})0$ (%)
9311303	FA18+Hg20	2.24	1.39	10.00
9311305	-------	2.93	1.30	14.77
9312015	FA18+Hg20	3.22	1.15	19.55
9312016	-------	2.65	1.32	14.99
9312022	FA18+Hg20	2.52	1.79	15.44
9312024	-------	3.22	1.56	15.00
940131	FA18+Hg20	2.75	2.69	17.00
940131-1	-------	2.84	2.02	17.14
940201-16	FA18+Hg20	2.75	1.68	10.09
940201-17	-------	2.65	1.45	10.37
940131-12	FA18+$HgCl_2$ 20	2.13	1.96	22.90
940131-7	-------	1.92	2.53	23.30
9312025	FA10+Hg20	2.26	1.63	20.88
9312026	-------	2.60	1.54	20.95
940131-3	-------	1.53	1.65	11.05
940201-9	FA10+Hg40	1.92	1.68	17.19
940201-11	-------	2.68	1.61	11.35
9312027	HA18+Hg20	2.67	1.36	18.70
9312028	-------	2.26	1.44	21.50
940201-14	HA10+Hg20	2.08	1.67	14.66
940201-15	-------	2.13	1.69	13.21
940201-12	HA10+Hg40	2.10	1.56	12.89
940201-13	-------	2.04	1.54	12.63
940202-9	Hg20+GÄV	1.92	1.01	15.8
940202-10	-------	1.87	1.17	9.40
940202-7	$HgCl_2$ 20+GÄV	1.61	1.52	15.43
940202-8	-------	1.80	1.62	16.88

* Number are concentrations for HA , FA (ppm) and Hg (ppb). If not specified, Hg was artificial solution in the form of $Hg(OH)_2$. GÄV= natural water from the Göte River.

The xenon lamp in this study gives an artificial sunlight. The sunlight at 60° N (Stockholm's latitude) has been calculated to be approximately 400 times weaker than the xenon lamp used in this study. This is based on actinometer measurements (Xiao et al., 1994) and on a report by Svensson and Björndal (1988). This implies that the photolysis rate constant will be ≈ 400 times smaller at outdoor conditions. This gives a halflife of ≈4 sunlight hours for HgA^{2+} and 250 sunlight hours for HgB^{2+}, respectively. In these roughly calculated examples, the ground averages for all k_A and k_B in Table I were used, except for those obtained with the Göte River water. Such a short halflife means that photolysis definitely could have an influence on the evaporation of Hg from a lake surface (see also the reasoning in Xiao et al., 1994).

4. Concluding Remarks.

The photolysis of the Hg - HA/FA complex does not show an ordinary first order kinetics, but these data are possible to evaluate by assuming a sum of first order reactions, indicating that there is more than one type of Hg complex existing in the solution. This is not surprising, since humic and fulvic matter consist of complex "molecules" with many different functional groups to which the Hg^{2+} ions can bind.

The mechanism of the photolysis is still not clear, if the humic substances act as a photosensitizer to initialise the reaction through electron, energy transfer process (Cooper et al., 1989) or as a complexing agent with the photolysis occurring on the bond of the humic-Hg complex directly. When $HgCl_2$ was applied in this study, instead of $Hg(OH)_2$, both to Milli-Q water with humic substances and to the Göte River water, similar results were obtained as in the case of $Hg(OH)_2$, which implies that Hg-humic complex is formed first. The results of many attempts to elucidate structures of humic substances and to correlate them to photoactivity have up to now been unsatisfying (Kotzias et al., 1987). Hence, no efforts were done either in this investigation.

It should be pointed out that this is an experimentally determined rate constant, valid only under conditions similar to those of the experiments. In the real environment, situation may be quite different and much complicated, hence the magnitude of photolysis may vary significantly. However, there is no doubt that photolysis of divalent Hg in the natural water is an important process and the existence of humic substances in natural water does affect the distribution and mobility of Hg in the environment.

Further studies with improved methods to yield more accurate values for the rate constants are needed, for example, to find out if the rate constants discrepancies is influenced by the mass transfer of Hg^0 to the gas phase. In addition, different natural waters and wider ranges concentrations of Hg(II) and HA/FA should be tested.

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A Case Study of Mercury and Methylmercury Dynamics in a Hg-Contaminated Municipal Wastewater Treatment Plant.

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Abstract. A study of total Hg (Hg) and methylmercury (MeHg) was performed in a 40 mgd capacity municipal sewage treatment plant in which elemental Hg was used as a seal in 3 trickling filter center columns. Each seal contains several hundred kg of Hg. The seals have leaked repeatedly over time, prompting the current remediation study and ongoing replacement of the Hg seals with mechanical seals. A mass balance conducted three times while the seals were in place showed that the plant acted as a net source of both Hg and MeHg during normal operation. The average amount of Hg released in sludge plus effluent was 157 g Hg and 0.4g MeHg/d. Of this total, 138 g Hg and 0.3 g MeHg were in excess of influent wastewater, and were contributed by the WTP itself. About 95% of the total Hg was released in sludge, with only 6 to 7 g/d released to the receiving water body. However, on average, about 70% of the MeHg leaving the plant was released to the river. Effluent MeHg concentrations were 4-6 ng/L. The plant components that acted as the major sources of both total and MeHg within the plant were the trickling filters (TFs). Metallic Hg accidentally lost from the center column seals has accumulated in the rock filter media and underbedding of the tricking filters. MeHg production across the TFs was positively related to the Hg concentration in each of the TFs. A substantial fraction of the total Hg but not of MeHg was lost to sludge in each settling step. About 50% of the remaining MeHg appeared to be degraded during the tertiary aeration step.

1. Introduction

On January 20, 1993, the City of Reading, PA, signed a consent decree with the State of Pennsylvania agreeing to remove three mercury-filled trickling filter center column seals used in the Fritz Island Wastewater Treatment Plant (WTP). In conjunction with the replacement of the seals, the City also agreed to examine the extent of mercury (Hg) and methylmercury (MeHg) contamination within the plant, and in the receiving water body, the Schuylkill River.

The Fritz Island WTP is a currently a tertiary treatment facility with a 40 mgd capacity, operating routinely at about 15 mgd. Three of the six trickling filters within the plant employed Hg as a seal in the center column of the rotating distribution arms. The filters and columns were installed in 1954 and 1961, when the plant was upgraded to a secondary treatment facility, and have subsequently been used in both primary and secondary treatment. Each seal contains approximately 340 kg of mercury. Due to occasional excess pressure and equipment failures, Hg has been lost from these seals on numerous occasions. The seals were upgraded in 1986 to allow collection of Hg spills from the seals. However, Hg lost prior to 1986 escaped to the rock media and underbedding of the trickling filters (Entech Engineering, 1993).

In order to help determine the mobility and fate of the Hg contaminating the Fritz Island WTP, we conducted mass balance studies, in conjunction with Entech Engineering, of plant inflows and outflows on three dates in 1993, before plant remediation. We also examined the concentration and speciation of Hg in the inflow and outflow of individual plant components. The objectives of this work were 1) to determine the specific sources of Hg and MeHg contamination within the plant 2) to examine the production of methylmercury (MeHg) within the plant as a whole and in individual plant components and 3) to examine the mobility of the Hg contaminating the WTP, especially to sludge and to the receiving water body.

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2. Materials and Methods

2.1 SAMPLING

Four of six existing trickling filters (#1,3, 5 and 6) originally used Hg-containing center seals; one of these seals (#5) was replaced with a mechanical seal in 1984, and the rock media and underbed cleaned or replaced. The trickling filters (TFs) are 212 ft. in diameter and contain No. 4 trap rock to a depth of 7 ft. For the plant mass balance studies, triplicate discrete grab samples were taken at each sampling site directly into Teflon or glass sampling bottles using non-contaminating technique (e.g. Fitzgerald and Watras, 1989). Most of the sampling was carried out by personnel from ENTECH engineering, after training. For the study of Hg and MeHg releases from individual plant components, single, discrete samples were taken at the inflow and outflow of a number of individual components.

2.2 Hg AND MeHg ANALYSES

Samples were shipped overnight on ice to Frontier Geosciences, Seattle, WA, where all analyses were performed. Total Hg was analyzed by cold vapor atomic fluorescence (CVAF; Bloom and Fitzgerald, 1988) with preconcentration on gold (Gill and Fitzgerald, 1987). For total Hg, aqueous samples were digested using 10 mL of 0.2 N BrCl per 100 mL of sample, and exposure for 4-6 h to 75 watts of 253.7 nm irradiation. Sludge samples (1g) were digested with 10 mL of 7:3 HNO_3: H_2SO_4, at 95°C for 4 h, and then diluted with 0.003 N BrCl solution prior to analysis. Spike recoveries averaged 104.4 $\pm$ 9.9% for sewage and 97.2 $\pm$ 3.3% for water. MeHg was determined after distillation (Horvat et al., 1993a and b) by ethylation, isothermal GC and CVAF detection (Bloom, 1989). Recovery of spikes averaged 87.5 $\pm$ 9.5% for sewage and 86.1 $\pm$ 4.4% for water.

3. Results and Discussion

3.1. MASS BALANCE STUDIES

The WTP acted as a net source of both total Hg and MeHg, that is, the amount of both compounds released daily in sludge plus effluent was significantly greater that in the influent wastewater. Table 1 shows the concentration of Hg and MeHg in wastewater at two upstream inflow sites (the 6th St. pumping station and the grit chamber); the direct plant inflow (primary diversion box); the liquid effluent to the Schuylkill River (effluent weir) and sludge collected off the belt press, on each of the three sampling dates. There was surprisingly little variability in the concentration of total Hg and MeHg in influent and effluent over the 3 sampling periods. This is especially surprising since discrete rather than composite samples were taken.

Table 2 shows the mass balance calculation, based on the average of the sampling dates, for 1993. Mass balances for Hg and MeHg were calculated according to:

Input (ng/d) = ng Hg/L (primary diversion box) * inflow (L/d)

Gross output (ng/d) =[ng Hg/L (effluent weir) * outflow (L/d)] + [ng Hg/gww (sludge) * gww sludge/d]

Net output = gross output - input

Flows and sludge amounts were estimated from 1992 measurements for the same month.

Table 1. Total (unfiltered) Hg and MeHg concentrations in influent, effluent, and sludge at the Fritz Island WTP on three dates in 1993. All values represent triplicate samples.

		Hg, ng/L		MeHg, ng/L	
Inputs	Date	Avg.	SE	Avg.	SE
6th St. Pumping station	July 19	247	18	2.45	0.53
	Sept. 9	457	83	2.18	0.25
	Dec. 20	308	67	1.01	0.15
Grit chamber	July 19	233	33	2.20	0.26
	Sept. 9	173	65	3.15	0.08
	Dec. 20	92	25	1.41	0.33
Primary diversion box	July 19	185	58	2.45	0.20
	Sept. 9	556	130	1.91	0.13
	Dec. 20	333	61	1.36	0.11
Outputs					
Effluent weir	July 19	108	7	4.03	0.23
	Sept. 9	127	12	5.69	0.33
	Dec. 20	448	110	4.50	0.76
		μg/g wet weight		ng/g wet weight	
Belt Sludge	July 19	4.09	0.49	5.2	4.1
	Sept. 9	4.02	0.18	1.6	2.0
	Dec. 20	3.96	0.77	2.9	3.0

On average, 157 g total Hg were released from the plant per day, with >90% of this released as sludge. The strong partitioning of Hg into sludge is expected, based on the particle reactivity of Hg. Removal of a large fraction of total Hg to sludge is common is WTPs (e.g. Balogh and Liang, this volume). However, of the 157 g total Hg released from the Fritz Island WTP, only about 20 g/d was derived from wastewater, with the remainder generated inside the plant. This conclusion is supported by data from individual plant components (see below). While the concentration of total Hg in plant influent was similar to that measured for another municipal plant, the Metropolitan WTP in St. Paul, MN., the concentration of Hg in Reading sludge was about 10X higher than in St. Paul (Balogh and Liang, this volume).

About 0.4 g MeHg/d was released from the plant, with about 1/4 of this amount introduced from incoming wastewater and the rest generated inside the plant. However, only about 30% of the total amount of MeHg was removed as sludge, while 70% was released to the river in effluent. Again, the in-plant study also showed specific sources of MeHg within the plant.

Table 2. Average mass balance calculations for the Fritz Island WTP, 1993. Hg and MeHg values are derived from Table 1, flow and sludge data from Entech Engineering and the City of Reading.

	Hg, g/d		MeHg, g/d	
	avg.	SE	avg.	SE
Input	19.3	10.1	0.104	0.035
Effluent	12.8	10.6	0.269	0.048
Sludge	144	35.1	0.125	0.096
Gross output	157	33.7	0.394	0.061
Net output from STP	138	43.7	0.290	0.031
% of total from plant	88	10	74	5.4
% of total to sludge	92	6.5	32	28
% of total to effluent	8.2	6.5	68	19

Even before cleanup, the concentration of total Hg found in effluent water was below the NPDES permit level for this plant. There are currently no NPDES requirements for MeHg, although it is the more toxic and much more readily bioaccumulated species. The current total Hg permit levels (and the lack of a permit level for MeHg) reflect widely available analytical methods (and lack thereof for MeHg), and are likely to decrease as methods improve.

3.2 IN PLANT STUDY

Table 3 lists the concentration of Hg and MeHg in the influent and effluent from 1st and 2nd stage TFs, intermediate, tertiary and final settling tanks and aeration chambers. Primary settling occurs between the primary diversion box and the influent to the 1st stage TFs, although some recycling through the primary diversion box occurs. In general, the settling steps acted as removal processes for both Hg and MeHg to sludge, while the contaminated TFs acted as internal sources of both Hg and MeHg.

Table 3. Total Hg and MeHg concentrations in the influent and effluent of various components of the WTP, Aug. 17, 1993. Concentration change is the concentration in effluent divided by the concentration in influent, reflecting addition and removal processes within the plant. All values are for unfiltered liquid samples, unless sludge is noted.

Site	Hg ng/L	MeHg ng/L	% MeHg	Concentration change: Hg	MeHg
Plant influent	156	3.0	1.9		
1st stage TFs:					
Input	229	7.8	3.4		
Output, TF #1	5660	31.9	0.6	24.7	4.1
Output, TF #3	1540	24.0	1.6	6.7	3.1
Intermediate settling:					
Input	2670	29.4	1.1		
Output	215	13.0	6.0	0.1	0.4
Output, sludge	114000	71.0	0.1	42.5	2.4
2nd stage TFs:					
Input	215	13.0	6.4		
Output, TF #4	629	33.9	5.4	2.9	2.6
Output, TF #5	291	10.8	3.7	1.4	0.8
Output, TF #6	394	13.1	3.3	1.8	1.0
Tertiary settling:					
Input	288	9.1	3.2		
Output	167	11.1	6.6	0.6	1.2
Output, sludge	39600	287	0.7	138	31.5
Tertiary aeration:					
Input	167	11.1	6.6		
Output	148	4.7	3.1	0.9	0.4
Final settling:					
Input	148	4.7	3.2		
Output	76	6.9	9.1	0.5	1.5
Output, sludge	124000	205	0.2	838	43.6
Plant effluent	108	4.0	3.7		

On the date of sampling, August 17, 1993, the contaminated trickling filters were the major sources of both Hg and MeHg. In the worst case, the total Hg concentration in the effluent from TF #1 was about 25X higher than in influent, and the MeHg concentration was about 4X higher. The increase in Hg concentration across the TFs demonstrates that the elemental Hg contaminating this WTP is mobile through oxidation and solubilization of Hg(II) complexes. The increase in MeHg across the TFs also indicates additionally that MeHg is being formed from Hg(II) within the WTP.

Only TF s#1,3, and 6 had Hg seals at the time of this study. The release of Hg from TF #4 and #5 suggest that spilled Hg has moved around within the WTP. TF #5 was not a net source of either Hg or MeHg, probably because the Hg seal in this TF was replaced with a mechanical seal in 1984, and replacement or cleaning of the rock media and underbed was done at the same time. This also suggests that movement of Hg within the plant probably occurred before that date.

A large amount of total Hg was added to the wastewater in the first stage TFs, but at each subsequent settling step, a large fraction of this Hg was lost from the wastewater to sludge. More than 90% of the Hg in TF effluent was removed to sludge during intermediate settling. About 40%

of the residual was removed to sludge during tertiary settling, and 50% of that residual was removed during final settling. The net result, as described in the mass balance above, is that the concentration of Hg in final effluent was somewhat lower than in the influent. Most of the Hg added during passage of wastewater over the TFs left the plant as sludge.

MeHg behaved somewhat differently than total Hg within the plant (the analysis of total Hg includes the MeHg fraction, although MeHg generally represents less than 5% of the total Hg). The first stage TFs and TF#4 appeared to be the major sources of both total and MeHg within the plant. However, a smaller fraction of MeHg, relative to total Hg, was removed to sludge. MeHg production was roughly tied to the concentration of Hg in a given component, in that the most MeHg production occurred where total Hg concentrations were the highest. Our experience in natural waters and sediments (e.g. Gilmour and Henry, 1991; Gilmour et al., 1992) suggests that MeHg production in the TFs is primarily microbial, however, we did not test this hypothesis. MeHg was lost during tertiary aeration, probably due to chemical or microbial demethylation of MeHg to inorganic Hg during this step. We did not directly test whether sludge digesters were sources or sinks for MeHg.

4. Conclusions

This study shows significant *de novo* production of MeHg within a Hg-contaminated WTP. It also clearly shows that the elemental Hg contaminating this WTP is mobile via oxidation to and dissolution of Hg(II) compounds and via production of MeHg. The main site of MeHg production in this WTP was Hg-contaminated TFs, and production was related to total Hg concentration. Ongoing removal of Hg seals and clean-up of metallic Hg within the plant should substantially decrease this WTP's input of Hg and MeHg to the receiving water.

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DIMETHYLMERCURY AND DIMETHYLMERCURY-SULFIDE OF MICROBIAL ORIGIN IN THE BIOGEOCHEMICAL CYCLE OF HG

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Abstract: The transformation of MeHg under anaerobic conditions in axenic cultures of *Desulfovibrio desulfuricans* strain LS is compared to that in anoxic marine sediments contaminated by Hg of industrial origin. MeHg was added to cultures of *D. desulfuricans* strain LS and incubated at 28°C for two weeks. Significant amounts of dimethylmercury and metacinnabar were produced. These two Hg compounds were formed from the slow decomposition of the intermediate dimethylmercury-sulfide. Other collateral compounds, such as methane and ionic Hg, were also detected during the MeHg degradation process. On the other hand a sample of fresh sediment (1.5 g d.w.) was spiked with 10 μg of MeHg and 2 mmoles.ml^{-1} of pyruvate, as carbon source for sulfate-reducing bacteria. After 9 days of incubation at 28°C, significant amounts of dimethylmercury were produced. A lower content of this volatile species was found in a sub-sample of sediment supplemented with sodium molybdate, which is a strong inhibitor of sulfate-reducing activity. A kinetic study showed the disappearance of monomethylmercury from the sediment and the formation of dimethylmercury over the incubation period. The environmental significance of dimethylmercury and dimethylmercury-sulfide in the natural biogeochemical cycle of Hg is discussed.

1. Introduction

The microbial formation of monomethylmercury together with dimethylmercury has long been known (Wood *et al.*, 1968; Jensen and Jernelöv, 1969; Imura *et al.*, 1972; Bisogni and Lawrence, 1975). However, it became customary among researchers to convert dimethylmercury to MeHg by acid treatment and to determine total MeHg, as the sum of MeHg and dimethylmercury (Andren and Harris, 1973), because the method of Westöö (1966) based on gas chromatography with electron capture detection did not allow dimethylmercury to be measured. Today new methodologies (Ballantine and Zoller, 1984; Rapsomanikis *et al.* 1986; Bloom 1989; Filippelli, 1994) make it possible to determine many organic Hg species in the same sample. However, the 203-Hg radio tracer technique, which is very sensitive, does not discriminate between the two volatile species Hg(0) and $(CH_3)_2Hg$, and consequently fails to distinguish the processes of demethylation (cleavage of C-Hg bonds in organomercurials) and dimethylation (formation of dimethylmercury).

An increasing number of investigators have recently reported dimethylmercury of microbial origin in estuarine and mangrove environments (Compeau and Bartha, 1984, Quevauviller *et al.*, 1992). Other authors report dimethylmercury in the ocean in relation to

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lower concentrations of oxygen in water columns of the Pacific (Mason and Fitzgerald, 1993) and North Atlantic (Mason *et al.* 1994). Dimethylmercury has also been found in oxygenated sub-thermocline waters of the Alboran Sea and the Strait of Gibraltar (Cossa and Martin, 1993; Cossa *et al.*, 1994).

One of the principal species in the anaerobic conditions of marine and estuarine systems is hydrogen sulfide, which evolves from dissimulative reduction by sulfate-reducing activity. It is known to convert ionic Hg to metacinnabar (cubic HgS). Only in the eighties did it become evident that sulfate-reducing bacteria played a central role in Hg methylation. Axenic cultures of sulfate-reducing bacteria under low sulfate conditions methylated ionic Hg (Compeau and Bartha, 1984; Compeau and Bartha, 1985; Compeau and Bartha, 1987). Thus metacinnabar and MeHg are the two Hg compounds produced from ionic Hg in the presence of sulfate-reducing bacteria. It has been shown that methylcobalamine-like compounds could be responsible for Hg methylation by sulphate-reducing bacteria (Berman *et al.*, 1990; Choi and Bartha, 1993) and it was recently demonstrated that the methylation of inorganic Hg may be enzymatic (Choi *et al.*, 1994). This strain only converts 0.014 ± 0.0053 $\mu g.ml^{-1}$ to MeHg from 5 $\mu g.ml^{-1}$ of $HgCl_2$ (conversion factor 1:350), according to the mean value obtained in an intercalibration exercise (Padberg *et al.*, 1994).

On the other hand, other studies have demonstrated that MeHg was removed from solution (Rowland *et al.*, 1977) in the presence of H_2S and could be volatilized as dimethylmercury through the intermediate formation of a decomposable compound, dimethylmercury-sulfide (Wollast *et al.*, 1974; Craig and Bartelett 1978). This suggested that dimethylmercury might be formed from MeHg by sulfate-reducing bacteria (Wood and Yang 1983). Baldi *et al.* (1993) finally demonstrated that MeHg added to axenic cultures of *D. desulfuricans* strain LS is transformed to gaseous dimethylmercury and solid metacinnabar through the intermediate methylmercury-sulfide.

Dimethylmercury, as the final product, can also be synthesized from methylcobalamine and ionic Hg and from methylcobalamine and MeHg as a function of pH and temperature according to the Arrhenius equation (Filippelli and Baldi, 1993). Both mono- and di-methylmercury species were determined simultaneously, without solvent extraction, directly in the aqueous solution by purge-and-trap gas chromatography in line with Fourier transform infrared spectroscopy. Traces of dimethylmercury had previously been found in a similar experiment (Imura *et al.*, 1972).

The aim of this study was firstly to compare the results of MeHg transformation in axenic cultures of *D. desulfuricans* with those in natural Hg-polluted anoxic sediments, and secondly to demonstrate that MeHg is not stable under anaerobic conditions in the presence of hydrogen sulfide, but could be converted to other organic Hg species in pure microbial cultures and sediments.

2. Materials and methods

Experiments on the microbial transformation of MeHg were performed with *Desufovibrio desulfuricans*. The strain LS was kindly donated by Prof. R. Bartha and was cultured routinely in Postagate medium "C" containing per liter: 0.5 g of KH_2PO_4, 1 g of NH_4Cl, 4.5 g of $NaSO_4$, 0.06 g of $CaCl_2 . 6H_2O$, 0.06 g of $MgSO_4 . 7 H_2O$, 6 g of sodium pyruvate, 1 g of yeast extract, 0.3 g of sodium citrate, and 0.1 g of NaCl. The medium was finally adjusted to pH 7.8 with NaOH solution.

Dimethylmercury was detected in *D. desulfuricans* cultures at different times. The bacterial suspension was distributed in vials and kept anaerobic. Each vial (100 ml) was spiked with 100 $\mu g.ml^{-1}$ of CH_3HgCl as total Hg and incubated at 28°C. On different days, a vial was used to determine directly dimethylmercury in the sample by taking 10 ml of sample by syringe and transferring it to a 15 ml glass vessel without adding any chemical. The vessel was sealed to the purge-and-trap unit (Chrompack) and the sample was stripped with N_2 (60 $ml.min^{-1}$) for 5 min at 80°C as reported previously (Filippelli et al., 1992). Volatile dimethylmercury was trapped in a column at - 120°C, released by heating the column to 250°C and automatically injected into a gas chromatograph (Carlo Erba model HRGC) in line with a Fourier transform interferometer (Nicolet 20 SXB) equipped with an optical bench accessory. A CP-Sil 8 fused silica column (50 m by 0.53 mm; film thickness 2 µm; Chrompack) was operated isothermally at 100°C with a 10 $ml.min^{-1}$ N_2 flow rate. Dimethylmercury was identified by its retention time and infrared spectrum. Results were linear up to 100 µg, and the absolute sensitivity was 100 ng. The retention time and the peak area of dimethylmercury were also determined with a flame ionization detector. MeHg residues in *D. desulfuricans* cultures were quantified at different times. The sample was heated in the water-bath at 100°C for 10 min in 10 ml of 1 N HCl solution and the MeHg was extracted four times consecutively with 1 ml of toluene. The solvent layer was cleaned with anhydrous Na_2SO_4 and 1 µl was injected into a gas chromatograph (Carlo Erba model HRGC) equipped with an electron capture detector. The column (HP-1 Methylsilicone, 30 m by 0.53 mm (i.d.), film thickness 2.65 µm) was operated isothermally at 120°C (Filippelli, 1987). Five replicate analyses gave a coefficient of variation of 7.3%.

MeHg was converted to MeHg hydride by adding 0.1 ml of sodium boron hydride solution (20%) to 1 ml of sample in 5 ml of DDW and determining its spectrum with a purge-and-trap gas chromatograph in line with a Fourier transform infrared spectroscope as described previously by Filippelli et al. (1992).

Inorganic Hg was detected in *D. desulfuricans* cultures at different times after removal of 1 ml of sample and after four repeated extractions with 1 ml of toluene, the MeHg-free aqueous solution was mineralized with 1 ml of concentrated HCl for 1h at 80°C. The total

Hg was detected in 1 ml of sample by reduction to atomic Hg with 12% $SnCl_2$ in 1 N H_2SO_4 solution and detected by flameless atomic absorption spectrophotometry (Perkin Elmer 300S). Five replicate analyses gave a coefficient of variation of 5.3 %.

Metacinnabar was detected in two different batches of *D. desulfuricans*. One liter of microbial suspension was supplemented with 100 $\mu g.ml^{-1}$ of CH_3HgCl and the other with 100 $\mu g.ml^{-1}$ of $HgCl_2$. After 15 days of incubation the two cultures were centrifuged at 4,200 x *g* for 25 min and the precipitates dried under nitrogen flow. The solid material was ground and the powder analyzed by X-ray diffractometry (Siemens D500). Metacinnabar was identified from the highest peak of relative intensity .

Methane was detected in the headspace of *D. desulfuricans* cultures spiked with CH_3HgCl. An aliquot of 0.25 ml was taken with a gas sampling syringe and injected into a gas chromatograph (Hewlett Packard model 5890A) equipped with a flame ionization detector. The methane content was confirmed by PT/GC/FTIR analysis (Baldi *et al.*, 1993). Different volumes of 1% methane (Supelco) in nitrogen were diluted in a gas sampling flask (250 ml) and 0.25 ml of standard was injected to calibrate the method. Five replicates of the same sample gave a coefficient of variation of 3.1%.

Dimethylmercury-sulfide [$(CH_3Hg)_2S$)] was found when 10 μg of CH_3HgCl was mixed with 10 ml of a 2-day *D. desulfuricans* culture. The white precipitate that instantly formed was dissolved in 2 ml of chloroform, extracted with a separator funnel and concentrated to 1 ml. One microliter was injected into a gas chromatography in line with a mass spectrometer (HP 5895) equipped with a fused silica column (25m by 0.2 mm i.d.) coated with phenyl silicone (5%) (0.33 μm film thickness). The injection port was at 270°C and the analysis was performed with a temperature program from 100°C to 270°C at a rate of 25°C/min.

One kilogram of fresh anoxic superficial sediment was sampled in an industrial area near Ravenna (Italy) and stored at 4°C in a PVC bottle. Three grams of fresh homogenized sediment corresponding to 1.58 ± 0.15 g dry weight was distributed in vials (13 ml) under nitrogen. Four ml of sterile anoxic artificial sea water was added to the sediment leaving approximately 3 ml of headspace. The vial was closed with a rubber stopper and an aluminum seal. At the time of the experiment, the sample was supplemented by syringe with different compounds according to the type of experiment. For the control experiments, 200 g of a fresh sediment subsample was added to 200 ml of sterile artificial sea water with a final concentration of 20 mM of sodium molybdate. The sample was aerated for three days on a gyratory shaker at 140 r.p.m. at room temperature. The anoxic aerated sediment was transferred to vials as reported above.

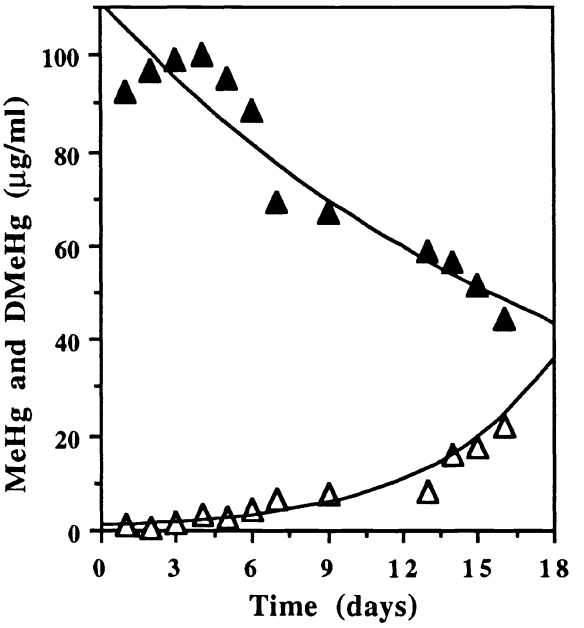

Fig. 1 - Conversion of 100 $\mu g.ml^{-1}$ of MeHg chloride (▲) to dimethylmercury (Δ) by *D. desulfuricans* strain LS in 16 days of incubation at 28°C.

An aliquot of 0.1 ml of an aqueous solution of MeHg containing 100 $\mu g.ml^{-1}$ Hg as MeHg chloride was added to the anoxic but aerated sediments. All the samples were amended with 20 mM of pyruvate as the sole carbon source for sulfate-reducing bacteria.

The speciation of Hg was also performed for low concetrations of Hg forms by extracting monomethylmercury and dimethylmercury with a methanol solution of 25% KOH, and heating the sample to 70°C for 10 min in sealed vials. An aliquot of 0.1 ml was added to 5 ml of distilled water and spiked with 0.1 ml of $NaBH_4$ solution (10%). The reaction flask was sealed to the purge-and-trap unit and purged with N_2 for 5 min. The gaseous organic Hg compounds were chromatographed and burned at the GC outlet in a quartz cell at 900°C. Organomercurials were detected as Hg(0) by an atomic absorption spectrophotometer in line with the gas chromatograph (Filippelli, 1994).

3. Results and discussion

The MeHg spiked in the *D. desulfuricans* culture tended to be transformed to dimethylmercury, as it was already reported by Baldi *et al.*; 1993, even at very high concentrations, such as 100 $\mu g.ml^{-1}$ (Figure 1). This concentration was halved in 15.5

days, with the formation of 22 $\mu g.ml^{-1}$ of dimethylmercury. This result was calculated from equations of figure 1 data:

$$MeHg = 111.28 \cdot 10^{-0.02246d}$$
$$R^2 = 0.889$$
$$DMeHg = 0.8972 \cdot 10^{0.0891d}$$
$$R^2 = 0.920$$

where MeHg is methylmercury, DMeHg is dimethylmercury and d = days. The amount of dimethylmercury expected from 50 $\mu g.ml^{-1}$ of MeHg was 25 $\mu g.ml^{-1}$ in relation to 1:1 disproportionation into dimethylmercury and metacinnabar. The experimentally determined concentration was 22 $\mu g.ml^{-1}$. The other half of MeHg formed metacinnabar which was detected by X-ray diffractometry from the characteristic peak of relative intensity at 26°35' theta. The conversion factor of monomethylmercury to dimethylmercury in the presence of H_2S was 1:2, and was much favorable than the conversion factor (1:350) of inorganic Hg to monomethylmercury yielded by the same strain (Padberg *et al.*, 1994; Choi *et al.*, 1994). The conversion factor of inorganic Hg to MeHg reported in literature for other microorganisms is generally less than 1:100 (Vonk and Sijpesteijn, 1973; Hamdy and Noyes, 1975). So

$$\overset{\text{I}}{Hg^{2+}} \rightarrow \overset{\text{II}}{CH_3Hg^+ + H_2S} \Rightarrow \overset{\text{III}}{(CH_3Hg)_2S} \Rightarrow (CH_3)_2Hg + HgS$$

In step I the conversion factor is two orders of magnitude lower than in step III°. The intermediate product dimethylmercury-sulfide (step II°) has already been observed in *D. desulfuricans* cultures (*Baldi et al.* 1993). Its retention time was 11.3 min, molecular weight was 464 and the compound contained Hg. The fragments were as follows: m/z 47 for $[CH3\text{-}S]^+$, m/z = 202 for $[Hg]^+$, m/z = 217 for $[CH3Hg]^+$, m/z = 249 for $[CH3\text{-}Hg\text{-}S]^+$, m/z = 264 for $[CH3\text{-}Hg\text{-}S\text{-}CH3]^+$, and m/z = 464 for $[CH3\text{-}Hg\text{-}S\text{-}Hg\text{-}CH3]^+$. The mass/charge ratio identified this species as dimethylmercury sulfide. This organic Hg form was previously observed (Craig and Bartelett, 1978) in an abiotic experiment. A similar organic Hg species, the MeHg methylsulfide ($CH_3\text{-}Hg\text{-}S\text{-}CH_3$) with a molecular weight of 264 was found in shellfish from Minamata Bay (D'Itri and D'Itri, 1977). This suggests that:

1) other methyl-sulfur Hg species are formed in the environment; 2) or other species of sulfur react with MeHg.

During incubation, methane was observed in the head space of *D. desulfuricans* cultures amended with MeHg chloride. In uninoculated controls spiked with MeHg, the methane was not observed. Ionic Hg was also determined in the aqueous solution after solvent extraction and both methane and inorganic Hg were correlated with the amount of dimethylmercury produced during growth (Figure 2). The microbial culture of *D. desulfuricans* lowered the pH from 7.8 to 6.2 when hydrogen sulfide was produced. Wollast *et al.* (1974) proposed that at acid pH, the species CH_3HgS^- formed methane and Hg sulfide as an alternative mechanism to the production of dimethylmercury and Hg sulfide. The CH_3HgS^- species should be formed from the reaction of $(CH_3Hg)_2S$ with S^{2-} (Schwarzenbach and Schellenberg, 1965). However this reaction in our study was of minor importance, since the final pH in cultures was not so acid (pH 6.2) and methane detected at pmoles/ml was <1% of the dimethylmercury production .

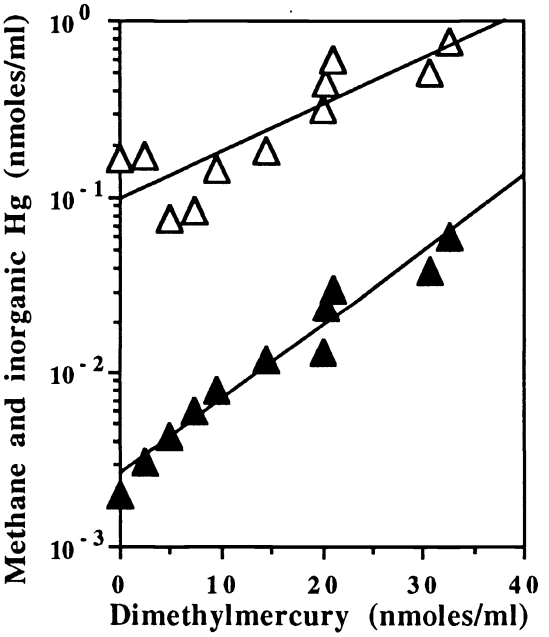

Fig. 2 - Correlation between dimethylmercury converted from 100 $\mu g.ml^{-1}$ of MeHg chloride versus methane (▲) and inorganic Hg (Δ) due to sulfate reduction activity of *D. desulfuricans* strain LS in 15 days of incubation at 28°C.

For the experiment with sediments, they were supplemented with MeHg chloride to demonstrate that MeHg is unstable not only in axenic cultures.

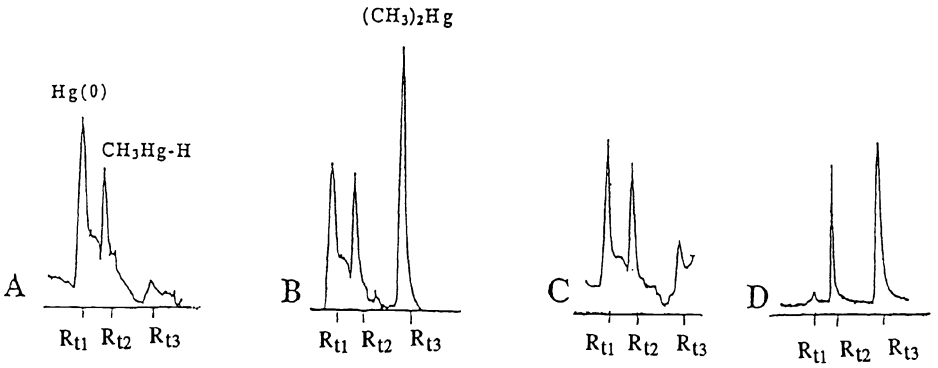

Fig. 3 - (A). Sample of natural anoxic sediment (1.5 g d.w.) without additions shows a peak of Hg(0) (R_{t1} = 1.2 min.) and MeHg-hydride (R_{t2} = 2.1 min.) formed after $NaBH_4$ was added to methanol-KOH extract. A doubtful peak, which could be dimethylmercury (R_{t3} = 4.1 min.) , was observed. (B) The same sediment was spiked with 10 µg of MeHg chloride, and after 9 days of incubation a significant peak of dimethylmercury was found together with Hg(0) and MeHg hydride.(C) When the same sediment was spiked with 10 µg of MeHg chloride plus 20 mM of sodium molybdate, a inhibitor of sulfate reduction activity, the peak of dimethylmercury was significatively reduced. (D) Standards of 6 ng of MeHg chloride converted to MeHg hydride by $NaBH_4$ and 5 ng of dimethylmercury were run.

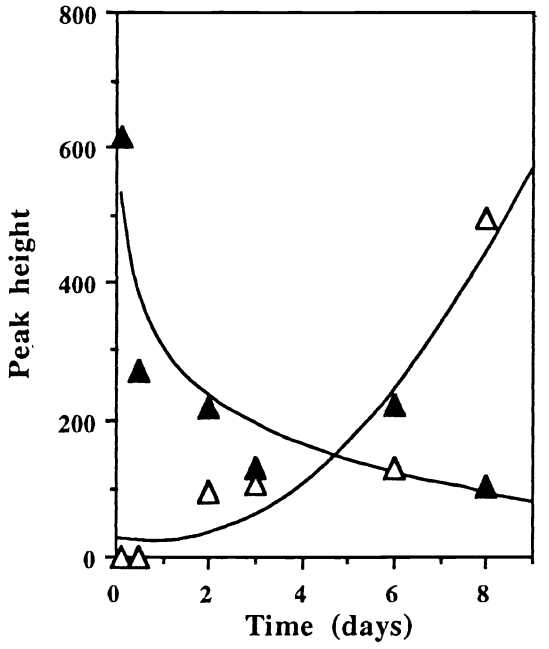

Fig.4. Kinetic studies to demonstrate that in the same anoxic sediment, incubated for 9 days at 28°C and spiked with 10 µg of MeHg chloride, dimethylmercury formed (Δ), whereas MeHg disappeared (▲).

Ten micrograms of MeHg chloride were added to fresh sediment (1.5 g d.w) and immediately disappeared in the time (2 min) it took to spike, open the vial and do the extraction with methanol solutions of KOH. From 10 μg spiked in the sediment, 1% (0.10 μg) was recovered as monomethylmercury and 0.30 μg was recovered from the anoxic sediment after aeration for three days and poisoning with molybdate. Where did the rest of the MeHg go? It is unlikely that a different method of extraction could explain the disappearance of 99% of the orgomercurial. Perhaps dimethylmercury sulfide forms, however we were unable to detect this species in the sediments with chloroform extractions. A method must be developed for this Hg species. Since dimethylmercury was found after 15 days of incubation of the sediment with pyruvate under anaerobic conditions at 28°C (Figure 3), we assume that it was formed from dimethylmercury-sulfide as in microbial cultures. The same sediment poisoned with molybdate showed lower concentrations of dimethylmercury.

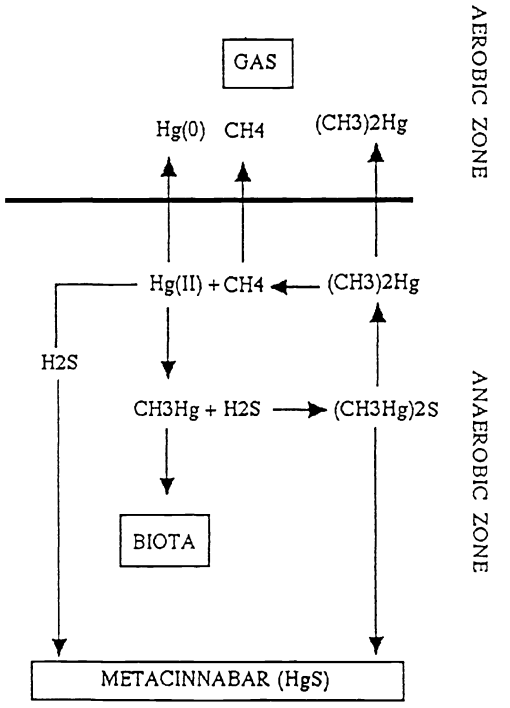

Fig. 5. Biogeochemical cycle of MeHg under anoxic conditions in the presence of H_2S as reactant, which renders it unstable and leads toproduction of other organic Hg species. In the end, MeHg is converted to metacinnabar and gaseous forms of Hg. A fraction of MeHg is immobilized in biota.

In a further experiment, MeHg disappearance was determine in the same sediment during 9 days of incubation at 28°C and after spiking with 10 μg of MeHg (Figure 4). Dimethylmercury was formed, but again dimethylmercury-sulfide was not detected.

In a system dominated by the presence of sulfate-reducing bacteria such as marine and estuarine systems, we suggest that MeHg is one of various organic Hg species. So not only demethylation, which commonly occurs in aerobic environments, but also dimethylation, which takes place with the formation of dimethylmercury tend to decrease the MeHg content of anaerobic systems. The suggested biogeochemical cycle of Hg (Figure 5) for such environments, predominantly buffered around neutral or lightly alkaline pH, involves the abiotic and/or biological formation of MeHg from inorganic Hg, and its rapid transformation by biological H_2S to the intermediate, dimethylmercury-sulfide; this in turn decomposes slowly to dimethylmercury and metacinnabar. Some dimethylmercury probably is lost by decomposition to methane and ionic Hg. The latter could be methylated again, or precipitated as metacinnabar, or volatilized as elemental Hg(0) (Baldi and Filippelli, 1994). In the end, MeHg is lost by degassing as dimethylmercury and Hg(0) or by precipitation as metacinnabar. This species accumulates in the Hg reserve pool. A fraction of MeHg is transferred from the geosphere to the biosphere by accumulation in biota, the only compartment in which it is stable.

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PART IX

MERCURY IN FISH AND WILDLIFE

CHANGES IN MERCURY LEVELS IN LAKE WHITEFISH (*Coregonus clupeaformis*) AND NORTHERN PIKE (*Esox lucius*) IN THE LG-2 RESERVOIR SINCE FLOODING

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Abstract. After flooding of the LG-2 reservoir in 1978-1979, it was noticed that Hg levels in fish rose dramatically In this study the Hg data have been examined on the basis of fish age for lake whitefish (Coregonus clupeaformis) and northern pike (Esox lucius), representing two different trophic levels Data were fit to Von Bertalanffy functions using non-linear regression analyses Reductions in error sums of squares indicated that differences among years were the major sources of variation, but that there were differences among stations within years For age profiles both species showed changes after flooding, whitefish increasing immediately and remaining similar until 8 years after flooding, with decreases afterward, while pike continued to increase until 8 years after flooding, remaining somewhat stable afterwards For whitefish, cohorts (year classes) from before flooding had similar concentrations, with maxima reached by around 1982, concentrations afterward remaining stable Subsequent cohorts reached plateaus at around 2-4 years of age, each successive cohort having a lower plateau For pike, Hg kept increasing in an almost linear fashion, cohorts from before flooding having similar concentrations Analyses indicated the very gradual return of whitefish to conditions present before flooding, while pike were remaining at much higher levels Inputs to older pike were therefore not decreasing, but younger pike may have been improving

1. Introduction

In reservoirs created in Labrador, Québec, and Manitoba within the last two decades, elevated levels of Hg have been found in fish as compared to levels present before flooding. It has been established that the presence of flooded vegetation is connected with elevated fish Hg (Hecky *et al.*, 1986; 1987), that flooded vegetation and soils contribute Hg directly to the water column immediately after flooding, and that the materials released from flooded vegetation favor methylation (Morrison and Thérien, 1991a;b). In spite of voluminous research on the accumulation of Hg in fish in these reservoirs, temporal aspects of this accumulation are still unclear. An understanding of the temporal aspects would provide a greater understanding of how Hg in the aquatic system has changed since reservoir creation, because fish act as integrators (directly and indirectly) of Hg in the aquatic system, and changes in Hg levels in water and lower trophic levels after flooding are not known.

In evaluating Hg levels in fish populations, researchers frequently establish linear relationships between Hg concentrations and fish weight or length, and a "standard" weight or length may be used to facilitate comparisons of different sites (e.g., Jones *et al.*, 1986). In systems not undergoing major changes in water quality, such relationships can be useful for establishing guidelines for consumption of fish, and changes in these relationships can signal new sources of Hg pollution. In a system undergoing change, such as a recently created reservoir, such relationships may still be useful in terms of guidelines for human consumption. However, fish growth rates are undergoing change

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in these systems, and thus comparisons of fish of equal lengths or weights among different years may be of limited value. Comparisons of Hg with age may be more useful because the evolution of Hg in cohorts can be followed and compared, but the relationship of Hg to age may not be linear. Log-log relationships may be useful for some comparisons, but induce an inverse weighting factor on errors and result in derivatives that are not intuitively simple.

Growth of fish has been frequently represented by the Von Bertalanffy expression, which has an asymptotic maximum size or weight (Ricker, 1975). Where Hg is related linearly to fish size, it should also be possible to represent Hg by a Von Bertalanffy-type function of age. Wakabayashi *et al.* (1987) applied it to bioconcentration of Hg in microcosm experiments.

The Von Bertalanffy equation as applied to Hg concentration is of the form:

$$Hg = Hg_{max} \cdot (1 - e^{-k \cdot age}). \quad (1)$$

The derivative with respect to age is:

$$\frac{d\,Hg}{d\,age} = Hg_{max}\, k \cdot e^{-k \cdot age} \quad (2)$$

$$= k\,(Hg_{max} - Hg). \quad (3)$$

Thus the constant k is the proportion of the difference between the asymptotic value (Hg_{max}) and the current value (Hg) that is added per unit time. Implicit in these expressions is the notion that losses are less than gains at young ages, but that losses increase proportionally faster than gains with age.

In this paper we examine the evolution of Hg levels of two species of fish: lake whitefish (Coregonus clupeaformis) and northern pike (Esox lucius). These species were chosen because the data on them were most complete, plus they represent two trophic levels. Lake whitefish feed on benthic and planktonic invertebrates, while northern pike are piscivorous. Concentrations are examined both as a function of age in individual years and within cohorts (year classes) over time.

2. Methods

The study site is the LG-2 reservoir in the James Bay area of northern Québec (54°N, 77°W), part of the La Grande hydroelectric development project. Flooding of this reservoir commenced in late 1978, and was completed by autumn 1979. The reservoir now covers an area of approximately 2800 km^2. Data were analyzed for five sampling stations.

Fish were collected in 1978 (the year before flooding), 1981, and then every 2 years from 1982-1992. In 1978 only 2 stations were sampled while in 1981 only 1 station was sampled, and only whitefish were collected. Since 1982, 5 stations have been sampled regularly. In total 847 whitefish and 850 pike were examined. La Société d'énergie de la Baie James and Hydro-Québec were responsible for sampling. Details on sample collection and chemical analyses as well as station descriptions can be found in Boucher *et al.* (1985), Messier and Roy (1987), and Verdon *et al.* (1991). The data were not as complete as would have been desirable, because for 1982-1986 there was some pre-

selection of specimens to be analyzed. This is common to reservoir Hg studies, because the notion of a "standard" size was widely used, and specimens were selected to have average sizes varying around this size. Thus not all samples include the full spectrum of ages. In addition, it proved very difficult to collect very young fish.

For each fish the weight, length, age, and muscle Hg concentration were measured. Hg analyses were done by cold-vapor atomic absorption spectrophotometry on tissue digests, the digestion being a hot acid-permanganate-persulfate oxidizing procedure.

The data were fit to the Von Bertalanffy expression by non-linear least squares (Draper and Smith, 1965) using the Marquardt technique (Marquardt, 1963). The NLIN procedure of SAS was used. The value of k was constrained to be less than 1.75, which corresponds to attaining at most 83% of the maximum value in 1 year.

As compared to linear least squares, non-linear least squares does not permit statistical testing of hypotheses (Draper and Smith, 1966), because statistical theory has been developed for linear systems only. F-test comparisons of variances can be made in a similar fashion as for linear systems, but no probabilities can be associated with the comparisons.

For each of the species, an expression was fit to all data together. Coefficient values found for this "GLOBAL" model were used as starting values to find a different set of coefficients for each year. The values for each "YEAR" model were then used as starting values to find a set of coefficients for each station within each year. Sequential improvements in error sums of squares were noted for each level - i.e., GLOBAL, YEAR, STATION(YEAR). The improvements attributed to the GLOBAL model are the reductions from total corrected sums of squares although a priori the GLOBAL models were only intended to provide starting values for the YEAR models. The model coefficients found for the YEAR models were subsequently used to estimate concentrations for various ages and cohorts.

3. Results

Variance tables for the 2 species are shown in Table I. The error sums of squares compare favorably with those coming from linear models for age with the same degrees of freedom. For whitefish the global model explained little variation (<1%), while for pike it explained much more (~20%). For both species separate models per year explained the most variation, an additional 23% and 43% for whitefish and pike respectively. The consideration of different models at stations within years explained an additional 13% and 6% respectively. Comparisons of observed and predicted values for YEAR models are shown in Figures 1 and 2.

The coefficient values found for each of the applications of the model are shown in Table II. There is considerable variation of coefficients within any particular year for both species, particularly for k. YEAR models exhibit marked trends. For whitefish, Hg_{max}-values stabilize at ~.55-.59 in 1982, while k-values show a decreasing trend. Only 1990 disrupts the pattern somewhat. For pike, Hg_{max} stays below 3 until 1988, when it starts a dramatic increase with a concurrent major drop in k-values.

Predicted concentrations as functions of age for ages 1 to 10 years are shown in Figure 3. Whitefish concentrations jumped dramatically shortly after flooding, but with some

TABLE I

Variance tables for both species for the Von Bertalanffy models.

WHITEFISH

SOURCE	df	SS	MS	F-ratio	Partial R-sq
TOTAL (U)	847	243 826			
TOTAL (C)	846	48 005			
GLOBAL	2	0 142	0 071	1 808	0 003
YEAR	14	10 785	0 770	19 676	0 225
STATION(YEAR)	50	6 387	0 128	3 263	0 133
ERROR	781	30 578	0 039		

PIKE

SOURCE	df	SS	MS	F-ratio	Partial R-sq
TOTAL (U)	850	5669 58			
TOTAL (C)	849	1251 67			
GLOBAL	2	243 57	121 79	240 35	0 195
YEAR	12	533 02	44 42	87 66	0 426
STATION (YEAR)	50	76 82	1 54	3 03	0 061
ERROR	786	398 26	0 51		

reduction 10 years after flooding Pike concentrations increased steadily for 8 years and remained relatively stable afterwards.

Predicted concentrations in cohorts are shown in Figure 4. Whitefish cohorts approach maxima at around 4 years, increasing little after. Successive cohorts have apparently decreasing maxima, although the year 1990 disrupts the pattern somewhat. In contrast, pike show successive cohorts following almost parallel trajectories.

4. Discussion

Hg concentrations both as functions of ages and in different cohorts showed early contamination followed by very slow recovery in whitefish. Successive cohorts have had decreasing concentrations. Pike, in contrast, worsened over the first 8 years, and then concentrations stabilized at the higher levels, and successive cohorts have not seemed to differ at the same ages.

A variant of the Von Bertalanffy expression is sometimes used for age-weight relationships where age is raised to the 3rd power. This gives an "S"-shaped curve similar to the curve for logistic growth. This function was also fitted to the Hg data, but generally gave worse fits than the original function. However, it gave better fits to the pike data starting in 1988. This is most likely due to lower Hg concentrations in young fish, which the "S"-shaped curve can better fit as compared to the "C"-shaped curve of

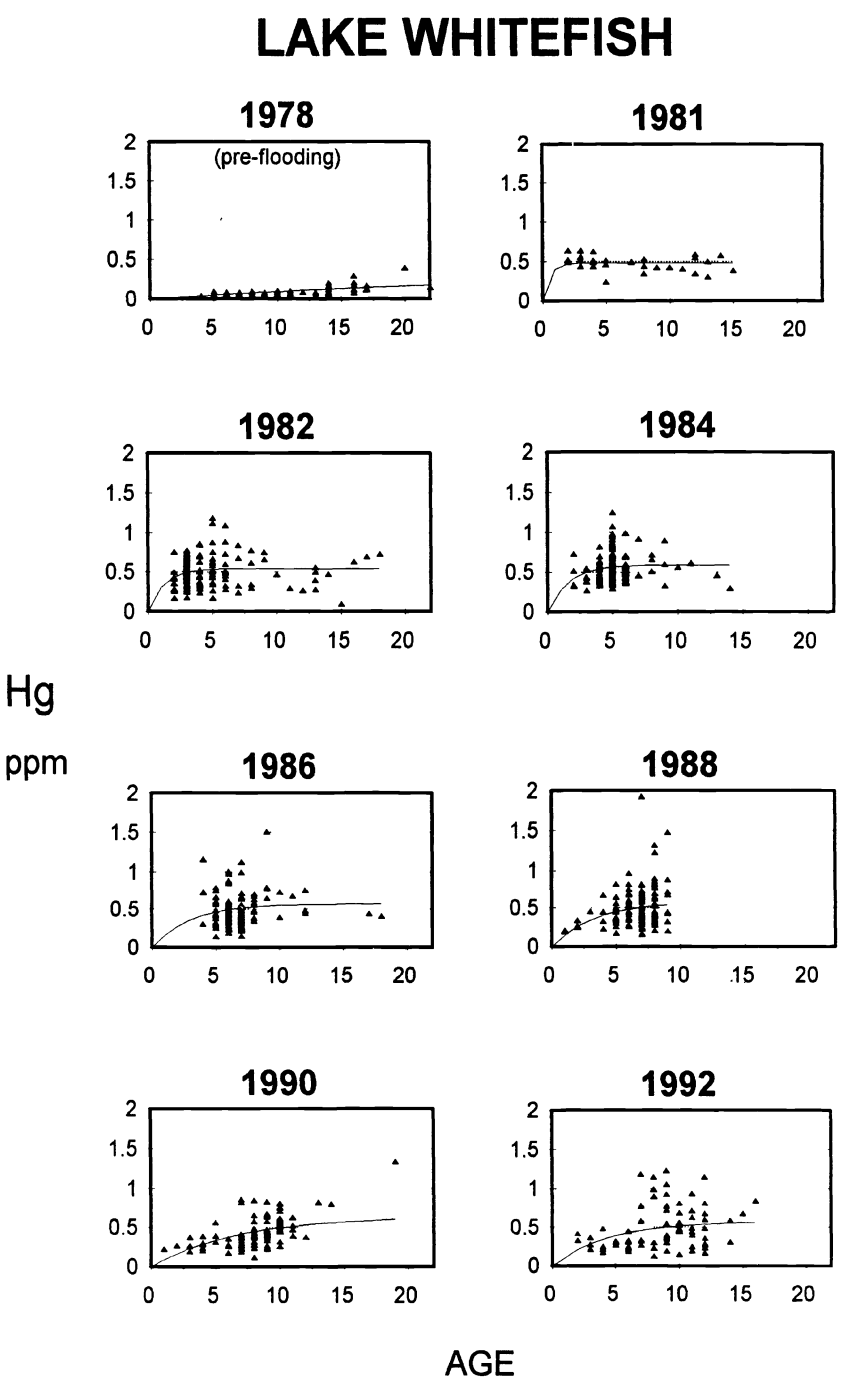

Fig. 1. Comparison of observed and predicted values for the YEAR models for Lake Whitefish

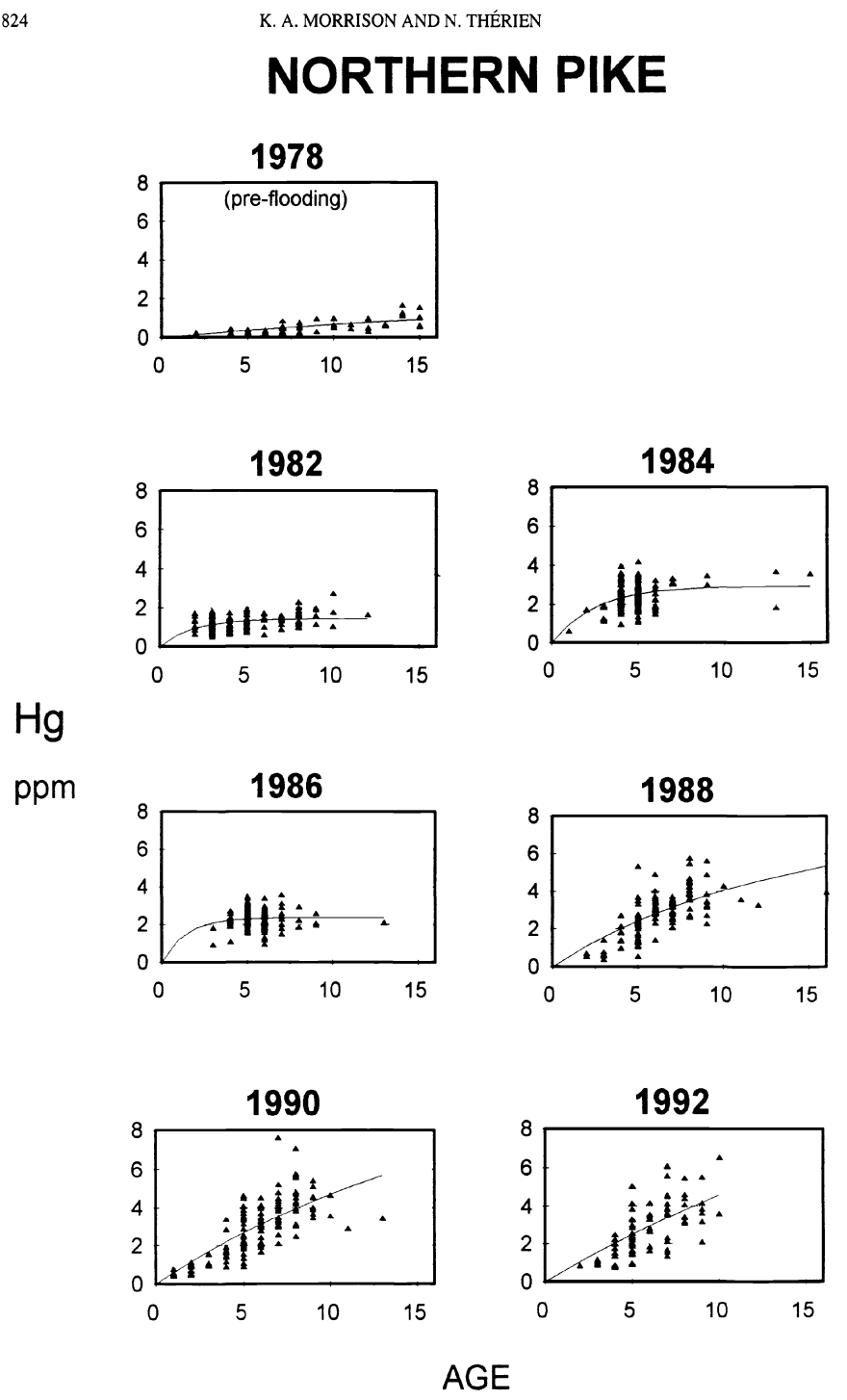

Fig. 2. Comparison of observed and predicted values for the YEAR models for Northern Pike

TABLE II

Coefficient values for the YEAR models and the STATION(YEAR) models

WHITEFISH

YEAR		1978	1981	1982	1984	1986	1988	1990	1992
	Hg max	0 368	0 484	0 543	0 591	0 572	0 587	0 643	0 579
	k	0 030	1 750	0 836	0 624	0 331	0 292	0 150	0 225
STATION(YEAR)									
Berezniuk	Hg max	0 329	0 484	0 495	0 500	0 522	0 677	0 843	1 157
	k	0 032	1 750	1 033	0 688	0 604	0 224	0 127	0 118
Coutaceau	Hg max	0 396		0 548	0 623	0 742	1 822	0 566	0 389
	k	0 030		0 671	0 417	0 248	0 057	0 304	1 265
LG-2	Hg max			0 391	0 826	0 806	0 458	0 799	0 919
	k			1 750	0 273	0 116	0 458	0 090	0 065
LG-3	Hg max			0 742	0 685	0 537	0 812	0 577	0 475
	k			0 578	0 539	1 750	0 237	0 170	1 750
Toto	Hg max			0 545	0 555	0 528	0 511	1 632	1 031
	k			1 110	1 750	0 317	0 365	0 036	0 074

PIKE

YEAR		1978	1982	1984	1986	1988	1990	1992
	Hg max	2 557	1 435	2 938	2 365	7 560	11 455	17 129
	k	0 030	0 542	0 393	0 706	0 077	0 053	0 031
STATION(YEAR)								
Berezniuk	Hg max	2 520	1 241	3 862	4 392	6 174	5 667	25 734
	k	0 030	0 937	0 270	0 164	0 100	0 080	0 018
Coutaceau	Hg max	2 680	1 812	3 421	2 311	6 723	6 245	23 769
	k	0 029	0 219	0 234	0 642	0 077	0 110	0 023
LG-2	Hg max		1 570	3 170	4 979	5 126	14 554	26 112
	k		0 752	0 538	0 141	0 154	0 041	0 016
LG-3	Hg max		1 094	2 369	2 201	11 250	16 929	14 074
	k		0 543	0 310	1 750	0 046	0 035	0 053
Toto	Hg max		1 631	2 537	2 373	6 395	5 900	21 722
	k		0 736	1 248	0 456	0 110	0 131	0 022

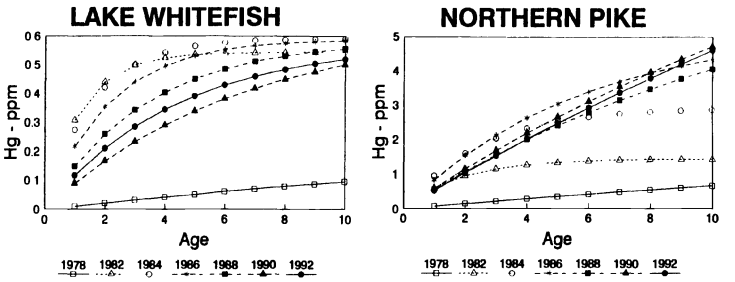

Fig. 3. Concentrations for ages 1-10 years estimated from the YEAR models

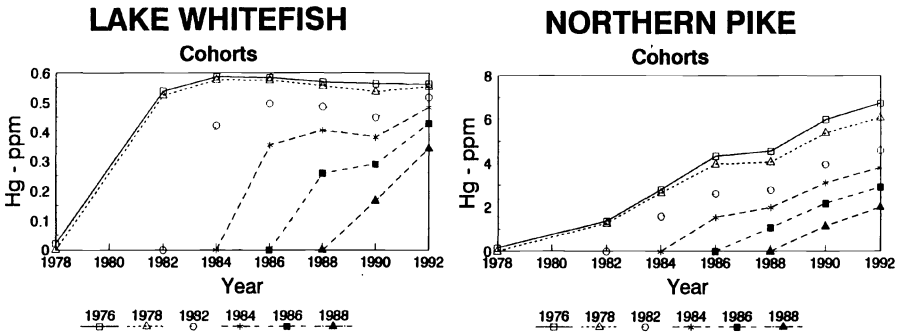

Fig. 4. Concentrations in various cohorts over time estimated from the YEAR models

the original Von Bertalanffy expression. There may thus be some signs of dropping levels in young fish while older fish remain heavily contaminated. This can be seen in the graphs for these years in Figure 2, where younger fish fall below the estimated line. For these same years the original function was estimated as having very low k-values and high Hg_{max} values, giving an almost-linear curve.

The whitefish data had more relative variation than the pike data. This is clearly demonstrated by the fits of the models. The complete models could only explain a total of 36% of the variation for whitefish, while they explained a total of 68% for pike. The differences among stations within years were also far more important for whitefish than for pike. Due to differences in soils and vegetation cover before flooding, the reservoir must been quite heterogeneous habitat after flooding. This could particularly affect benthic invertebrates, which would subsequently affect their predators. In contrast plankton could be expected to be somewhat more homogeneous. As the top aquatic predators, the pike would seem to average out the varying Hg concentrations in their food. This would suggest a hypothesis that variability of Hg concentration decreases as one moves up the food chain.

In examining the derivative of the Von Bertalanffy equation, it is evident that it is not a mechanistic expression - i.e., the negative term in the expression "-k·Hg" does not represent excretion or loss. The half-life of Hg body burden in fish has been estimated to be 100 to 500 days (Lockhart *et al.*, 1972; Sharpe *et al.*, 1977; Rodgers and Beamish,

1982) while for concentration a "half-life" value is 100 to 180 days. This latter range would correspond to a coefficient value for reduction of 1.4 to 2.5. Most k values that we found were below this range. In addition, the positive term in the equation ($k \cdot Hg_{max}$) would indicate a constant relative intake. Thus the parameter values reported here describe the data and not necessarily the underlying processes. However, this discrepancy can be resolved if one examines the equation:

$$\frac{d\,Hg}{d\,age} = \alpha \cdot Hg_{water} + \beta \cdot (1 - e^{-\delta \cdot age}) - \gamma \cdot Hg \qquad (4)$$

where α is a coefficient for an increase due to absorption from water, $\beta \cdot (1 - e^{-\delta \cdot age})$ is a term for increase due to food including dietary shifts, and γ is the coefficient for excretion, with a value between 1.4 and 2.5 as already mentioned above. This equation is more mechanistic than the Von Bertalanffy expression, and in fact reduces to it if:

$$\alpha \cdot Hg_{water} = k \cdot Hg_{max}, \quad \beta = (\gamma - k) \cdot Hg_{max}, \quad \text{and } \delta = k.$$

These equalities show how the coefficients are mutually dependent.

This equation provides another way to interpret the results from our analyses. For similar values of the product $k \cdot Hg_{max}$, the relative importance of food as a pathway increases with decreasing k, and vice-versa. Thus the relative importance of water as a pathway increases with increasing k. This is not surprising since a larger value for k means more rapid approach to the asymptotic maximum value, and equilibration with water via absorption should be relatively rapid as compared to accumulation from food. Bioaccumulation of methyl-Hg directly from water even with low concentrations (~1 ng L^{-1}) has been demonstrated to be rapid at pH's similar to those found in the reservoir (~6.3) (Ponce and Bloom, 1991).

For both species, k values were ~0.03 prior to flooding. After flooding the values increased for both species, but more so for whitefish than pike. Values for whitefish were generally greater than for pike, the exception being 1986. When values did drop, they dropped more markedly for pike than for whitefish. This is entirely consistent with their relative trophic positions. Before flooding, water was possibly negligible as a pathway for both species. Water Hg concentrations must have increased immediately after flooding (Morrison and Thérien, 1991a;b), and it may have become more important for both species, but due to the relative concentrations in respective food sources the effect would be more important for whitefish. Such a difference in relation to trophic position has been noted before (Phillips *et al.*, 1980). Later Hg in the water column would be gradually diluted due to water renewal. Thus by 1988 for pike the relative importance of water as a pathway could have dropped almost to pre-flooding levels, but with accumulation still higher due to food concentrations. For whitefish both water and food could continue to be important, but with the importance of water continually decreasing. It is unfortunate that no comparisons can be made between the fish data and water Hg concentrations. It is only since 1988 that suitable techniques have been used to permit total and methyl Hg measurements in water in the LG-2 reservoir. Since the major changes in water Hg would seem to have been during and shortly after flooding, the most important period was missed.

One situation that the Von Bertalanffy equation cannot express is decreasing Hg with age. Such a scenario could arise in 2 ways: an important change in diet with age to a

less contaminated source, or a sudden change causing faster increases in younger fish due to their higher relative growth rates. The former situation has been found for roach (Rutilus rutilus) in a humic acidic lake in Sweden (Lindqvist *et al.*, 1991). As for the latter situation, linear regression of the whitefish data for 1981 and 1982 indicated negative slopes, albeit insignificant, and Jones *et al.* (1986) found other such situations for reservoir fish data.

As already mentioned the data did not fully cover all ages. Nonetheless we consider the general observations valid. The use of the Von Bertalanffy equation for examining fish Hg patterns may permit better interpretations of existing data than the common linear or log-log covariance analyses that have been applied in the past.

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STORIES FROM OLD RESERVOIRS: SEDIMENT HG AND HG METHYLATION IN ONTARIO HYDROELECTRIC DEVELOPMENTS

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Abstract We sampled several Ontario Hydro reservoirs to determine the changes in mercury (Hg) and organic profiles of sediment cores with reservoir development. We also examined Hg methylation among reservoirs of different age and water chemistry In sediment cores from four Ontario reservoirs, reservoir (watershed) specific differences appeared to supersede general trends, with the differences between headpond and run-of river reservoirs particularly important. In general, the rate of Hg and organic accumulation appeared to increase with reservoir impoundment, but we were unable to discern consistent changes in concentrations of Hg or loss on ignition (LOI) with reservoir impoundment. We also observed significant positive correlations of sediment Hg with concentrations of chlorophyll derivatives and bacterial photopigments Our results are in agreement with earlier studies which indicated that an increase in Hg supply caused by erosion and release from flooded soils is central to the changes in Hg dynamics within reservoirs following impoundment Although Hg methylation activity of sediments from a series of reservoirs on the Mississagi River was positively correlated with organic content of the sediment, the observed rates were sufficiently variable that the potential effects of reservoir age or preparation methods could not be resolved Similarly, in our measurements of net methylmercury (MeHg) flux in two older reservoirs, the large range of variation in net MeHg flux observed among replicate samples obscured the potential effects of differences in geology and water chemistry Future studies should focus on resolving the underlying causes of this variability and in consolidating the 'microscale measurements obtained using sediment core incubation techniques and the 'macroscale values obtained by whole lake mass balance techniques

1. Introduction

Fish in reservoirs within many hydroelectric developments in Canada and the Northern Hemisphere contain mercury (Hg) at concentrations sufficient to trigger fish consumption advisories (Jones et al , 1986, OMEE/OMNR, 1993) Elevated Hg concentrations in fish may be a general, if not universal, effect of impoundment as they have been reported for reservoirs located over a wide geographic range, without known natural or anthropogenic sources of Hg (Jackson, 1988) Consequently, the potential for elevated Hg concentrations in fish has become one of the most significant issues in assessing the environmental impact of hydroelectric developments.

The general increase in Hg in fish following reservoir impoundment is thought to result from an enhancement of the mobility and bioavailability of Hg and methylmercury (MeHg) following flooding (Jackson, 1988) In part, at least, these changes appear to result from an increase in Hg supply caused by erosion of flooded soils and inundation of vegetation, with the suspension of the humic horizon of flooded soils particularly critical (Louchouarn et al , 1993) However, as the large majority of Hg accumulated by fish is MeHg (Huckabee et al , 1979, Bloom, 1992), changes in the dynamics of MeHg within reservoirs may also be critical to the increase in MeHg in reservoir fish following impoundment In particular, the decomposition of newly inundated vegetation and organic material in soils following flooding is thought to result in an elevation in the concentrations of dissolved and particulate organic material In turn, these elevated concentrations of organic material generally stimulate microbial activity, including MeHg production (Winfrey and Rudd, 1990) Despite this knowledge, the duration and extent of Hg elevation in fish from new reservoirs cannot be reliably predicted, and statistical models relating reservoir characteristics and fish Hg for one area may not apply to other regions (Johnston et al , 1991)

Existing reservoirs may provide useful information concerning the duration and extent of Hg elevation in fish from new reservoirs, particularly if, as in the case of Ontario Hydro's reservoirs, they encompass a wide range of age (< 30 to > 75 y), geology (particularly shield and non-shield), and flooded area (run of river to extensive flooding) Our studies focused on two main areas interpreting the history of Hg accumulation in sediments of selected reservoirs and determining Hg methylation rates in reservoirs In our analysis of sediment cores, we were particularly interested in determining if consistent changes in concentration or accumulation of Hg or organic material are associated with reservoir development Our Hg methylation studies were directed to evaluating potential differences in MeHg production or flux among reservoirs of different age and water chemistry

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2. Materials and Methods

We worked on six Ontario reservoirs - Lady Evelyn Lake on the Lady Evelyn River just above the Montreal River, Rocky Island, Aubrey and Tunnel Lakes on the Mississagi River, Eugenia Lake on the Beaver River, and Spence Lake off the South Muskoka River. Overall, the reservoirs encompassed a wide range of locations, dates of impoundment, storage volumes, drawdown and the degree of Hg contamination of fish (Table I).

2.1 Sediment Hg profiles

We located apparent depositional areas (depth > 15m) in Lady Evelyn (North and South Arms), Rocky Island, Aubrey and Tunnel Lakes, by using OMNR contour maps in conjunction with a boat mounted sonar depth recorder. At each site, several sediment cores were collected using a Kajak gravity corer (7 cm diameter). After carefully siphoning off the overlying water, each sediment core was extruded and sectioned at 1 cm intervals. For samples used in Hg analysis and ^{210}Pb dating, a 5 cm diameter plastic ring was used to take an inner subsample from each 7 cm diameter section, when the section was sufficiently solid to permit this subsampling. For our cores, the first samples with sufficiently low water content to permit subsampling were located at 3 - 5 cm. Samples were kept in individual plastic bags and refrigerated until frozen (-40°C). The two best cores from each site were then selected; one was analyzed for total Hg, loss on ignition (LOI) and dated by ^{210}Pb techniques, while the other was analyzed for organic pigments (chlorophyll derivatives, total carotenoids, oscillaxanthin and myxoxanthophyll).

The samples used for Hg and ^{210}Pb analysis were freeze dried, then ground and passed through a 60 mesh sieve, and the sieved sample then split for LOI determination, Hg analysis and ^{210}Pb dating. Normally, the sections from 0 - 5 cm were analyzed at 1 cm intervals, sections at 5 - 10 cm were analyzed at 1 - 2 cm intervals and sections from 10 - 40 cm were analyzed at 5 - 10 cm intervals. For each core, 10 samples were used for ^{210}Pb dating and 12 - 14 samples were analyzed for total Hg. Sediment LOI was determined gravimetrically following combustion to constant weight at 550°C, after drying (24 h) at 105°C. Total Hg was determined by cold vapour atomic absorption spectrophotometry (CVAAS) after acid and dichromate digestion of the sediment. For dating of the sediment cores, the samples were digested by a microwave technique and the alpha activity of the ^{210}Pb decay product, ^{210}Po, determined by alpha spectroscopy. The sediment cores were then dated using the constant rate of supply (CRS) model of Appleby and Oldfield (1978) by Atomic Energy of Canada Limited Research - Chalk River Laboratories.

The sediment samples used in determination of organic pigments were thawed and then extracted with four washes (20 ml) of 90% acetone at 4°C under low light conditions. The four acetone washes were combined, and made up to 100 ml. The extract was then subsampled and the concentrations of chlorophyll derivatives, total carotenoids, oscillaxanthin and myxoxanthophyll determined by spectrophotometer using methods described in detail by Han (1993).

2.2 Methylmercury production in existing reservoirs

2.2.a) ^{203}Hg methylation - Mississagi River reservoirs

Profundal samples from Rocky Island, Aubrey and Tunnel Lakes were collected by Kajak type gravity corer as described above. The sediment sample was then transferred to an acrylic tube (5 cm outer diameter - 75 cm m long) by gently pressing the tube into the sediment sample while it was in the corer. The tube was then filled with surface lake water, sealed with rubber stoppers and then maintained upright and refrigerated until the sample was used. Similar techniques were also used to collect littoral (depth < 5 m) samples from shallow bays which appeared to have reasonably stable sediments with a high organic content.

The refrigerated sediment samples were transferred to 10°C incubation chamber at least 4 days before the experiments. Sediment samples were processed in batches of four, with samples randomized so that only one sample from a given location and depth was included in each batch. The overlying water was siphoned to within ≈ 1 cm of the sediment surface and retained in an acid washed vessel. The top 3 cm of sediment from the core were extruded from the tube (3 - 1 cm extrusions) and the volume brought up to 350 ml by adding the siphoned water. The sediment/water mixture was mixed well to achieve a uniform consistency and 6 - 50 ml subsamples removed. Four of the subsamples were used for determination of Hg methylation and two were transferred to preweighed

crucibles for determination of dry weight and organic content. Dry weight of the sediments was determined gravimetrically after drying at 60°C for 24 h, after which organic content was determined by combustion at 550°C for 24 h.

Mercury methylation was estimated from the production of radiolabeled MeHg from $^{203}HgCl_2$ added to the sediment/water mixture (Furutani and Rudd, 1980; Korthals and Winfrey, 1987). The radionuclide, $^{203}HgCl_2$ (≈ 190 MBq/ mg Hg, Amersham Canada Limited), was diluted on receipt to 100 ml with 6 N HCl. For each determination of Hg methylation, 1.0 ml of the ^{203}Hg-labelled $HgCl_2$ was added to each of the four 300 ml Biological Oxygen Demand (BOD) bottles. In three of the four bottles, sufficient NaOH was added to adjust the pH to ≈ 6 before addition of the 50 ml of the sediment/water mixture. In addition, a sample of ≈ 2.5 x 10^8 bacteria from a mixed culture of sulphate reducing bacteria (SRB's - *Desulfovibrio desulfuricans* ATCC 29577, *D. gigas* TVA, *D. vulgaris* ATCC 29579, and *Halfnis alvei* TVA) were added to one of the three pH-adjusted samples. Thus for each sediment sample there was one acidified sample, two circumneutral samples and one circumneutral sample with SRB's. The BOD bottles were closed and the samples incubated without agitation at 22°C for 4 days, then the assay was terminated by adding 1 ml of 6 N HCl to each sample.

Methylmercury was separated from the sample by organic solvent extraction (Furutani and Rudd, 1980; Korthals and Winfrey, 1987) and the radioactivity of duplicate subsamples (250 µl) from the upper benzene layer determined by liquid scintillation counting. Results were expressed as activity - disintegrations per minute (dpm) corrected for background, quench and radioactive decay. Samples with activities which were less than 50% greater than their respective acid-killed control were considered inactive and were not included in the analysis. In total, 5 samples (of 39 total) were rejected by this criteria.

2.2.b) Net MeHg flux - Eugenia and Spence Lakes

Net MeHg flux of the sediment-water samples was determined from the difference in MeHg concentration in the water overlying the sediment core before and after incubation (Sellers et al., 1994). The method measures net MeHg flux, rather than production, as the observed change in MeHg is the net result of movement of existing MeHg from sediment to water, and MeHg production or loss through methylation and demethylation.

Samples were collected from Spence and Eugenia Lakes on August 16 and 23, 1993, respectively. Surface waters were ≈ 22°C in both reservoirs, but the water of Spence Lake was relatively soft (hardness 20 $mg \cdot L^{-1}$ as $CaCO_3$, conductivity 67 µS, pH 6.7), while the water of Eugenia Lake was relatively hard (hardness 176 $mg \cdot L^{-1}$ as $CaCO_3$, conductivity 334 µS, pH 8.2). The shoreline forests of both reservoirs are a mix of deciduous and coniferous trees. Both reservoirs had considerable recreational shoreline development; extensive agricultural activities were obvious only at Eugenia Lake. In Spence Lake, 'peat islands' with various successional stages of vegetation were prominent.

The sediment samples were collected at ≈ 1 m depth in an area of flooded soils, which had been forested prior to flooding. Samples were collected from a region free of visible obstructions, by pushing a teflon core tube (10 cm diameter and ≈ 30 cm long) by hand into the sediment to a depth of ≥ 10 cm. The teflon core tube used to collect the sediment water samples were immersed in plastic buckets filled with surface water at least two hours before samples were collected. The sediment and overlying water were withdrawn with minimal disturbance, closed, sealed and stored upright in plastic buckets containing surface water. Six replicate samples were collected from the same location in each reservoir.

The samples were transported to the laboratory (≤ 3 h), and then allowed to settle, with lids loosely on, for 2 - 4 h to enable re-establishment of chemical gradients (Sellers et al., 1994). Cores were incubated at 26 ± 0.5°C on a modified laboratory shaker which circulated the cores at ≤ 5 rpm, a rate of circulation which is sufficient to mix the overlying water, but does not mix the sediments or entrain sediments into the overlying water (Ramal et al., 1993; Sellers et al., 1994). After stabilization of the cores, an initial water sample (≈ 100 ml) was siphoned through teflon tubing into a pre-cleaned teflon bottle using 'clean' techniques (Sellers et al., 1994). The overlying water was drawn down to 3 or 6 cm from the sediment surface, the lid to the teflon tube closed and the sample incubated for ≈ 48 h. The final water sample was then withdrawn from the sediment core tube using the same methods. An intermediate sample was also collected at ≈ 24 h from one of the six samples from each reservoir (the tube with 6 cm of overlying water).

Water samples were frozen immediately after collection and analyzed for MeHg within 1 month of collection (Flett Research Ltd.) using the methods of Bloom (1989). The average recovery of spikes was 96.3% (range 90.4%

to 101.8%), while for the five samples measured in duplicate, the sum of low values was 88.7% of the sum of the high values. The net flux of MeHg was determined from the difference in initial and final MeHg concentrations and the volume of water above the sediment core.

After collection of the final water sample, the top 5 cm of sediment were extruded from the collection tube, into preweighed plastic bags, weighed and frozen. The sediments were then freeze dried to determine dry weight. The dry sediments were then sieved, and the sediments passing through the 0.6 mm sieve were pooled and the loss on ignition (LOI) of these fine sediments determined by combustion at 550°C for 24 h.

2.3. Statistical analysis

In the methylation studies, results were analyzed using the appropriate analysis of variance (ANOVA) or regression model. For ^{203}Hg methylation rates were log transformed as visual inspection of residual and normal probability plots indicated this was required to comply with statistical assumptions of normality and equality of variance. Cell means were compared using Tukey's tests (SAS, 1987), if the F-ratio of the effect was significant. Because of the small sample size and concerns with the statistical assumptions of normality and equality of variance, statistical tests with the sediment core and net MeHg flux data were conducted on both the measured variables and on these variables after transformation by ranking (Potvin and Roff, 1993). For the present data, generally similar levels of significance were obtained with both methods of analysis. A probability level of $P \leq 0.05$ was used as the criterion of significance in all statistical tests.

3. Results and Discussion

3.1 Sediment Hg profiles

The Hg concentrations in the sediments of the South Arm of Lady Evelyn Lake and Rocky Island Lake gradually decreased from 250 - 300 ng Hg/g (dry wt.) near the surface, to 100 - 150 ng Hg/g at depths of 15 - 20 cm and below (Figure 1). These profiles were generally similar to those reported for sediments of several small headwater lakes in South-Central Ontario (Evans, 1986) and Wisconsin (Rada et al., 1989). The sediment Hg profile for the North Arm of Lady Evelyn Lake, which was closer to the dam, was reasonably constant and at somewhat lower concentrations than the South Arm for much of the core (160 - 190 ng Hg/g), but there was a marked increase in Hg concentration (337 ng Hg/g) at a depth of 4 cm. On the basis of ^{210}Pb dating, this depth corresponds to the period immediately following the replacement of the original dam in 1972. For Aubrey Lake, Hg concentrations in sediments below 10 cm were very low (< 50 ng Hg/g), then increased rapidly to concentrations greater than 150 ng Hg/g at 6 cm and above. The Hg profile of sediments from Tunnel Lake was highly irregular with most concentrations between 150 - 250 ng Hg/g but extremely low concentrations observed at ≈ 6 cm (62 ng Hg/g) and ≈ 10 (29 ng Hg/g).

The profiles of LOI of were relatively constant for the North Arm of Lady Evelyn Lake (≈ 300 mg/g or 30%), and were slightly more variable but without consistent pattern for the South Arm of Lady Evelyn Lake (250 - 315 mg/g) and Rocky Island Lake (200 - 260 mg/g). For these reservoirs, changes in Hg concentration were largely independent of changes in LOI, and changes in Hg concentration per unit organic material (LOI) were largely driven by the much greater changes in Hg concentration (Figure 1). In contrast, LOI of sediments in Aubrey and Tunnel Lakes was generally low (<250 mg/g), and changes in LOI generally parallelled changes in Hg concentration. Consequently, concentrations of Hg per unit LOI reflected changes in both Hg and LOI. For Aubrey Lake, there was an abrupt change in sediment LOI, with values of less than 50 mg/g below 10 cm and values greater than 100 mg/g at depths of 6 cm and above. As observed with Hg, the LOI profile for Tunnel Lake was highly irregular with values ranging from less than 50 to greater than 200 mg/g, with inflections in LOI generally coinciding with those of Hg.

The estimated rates of Hg accumulation of the two basins of Lady Evelyn Lake varied much less than sediment Hg concentrations, with average rates of Hg accumulation (from 1930 to the present) of 34 and 31 ug/m^2/y, in the North and South Arms, respectively. These results thus suggest that the higher rate of sediment accumulation in the North Arm (≈ 170 g/m^2/y versus ≈ 120 g/m^2/y in the South Arm) diluted a relatively constant rate of Hg input, resulting in lower sediment Hg concentrations. The peak in Hg accumulation observed at 4 - 5 cm in sediments from North Arm of Lady Evelyn Lake (≈ 53 versus ≈ 31 ug Hg/m^2/y) reflected both the increase in Hg concentration

noted above and an increase in the rate of sediment accumulation. Estimated average Hg accumulation rates for Aubrey and Rocky Island Lakes over the period following impoundment were 43 and 55 ug/m^2/y, respectively. Average Hg accumulation rates for our reservoirs are roughly double the rates of 15 - 35 ug/m^2/y determined for seven headwater lakes in Minnesota and Wisconsin (Swain et al., 1992) and values of ≈ 20 ug/m^2/y reported for Precambrian Shield lakes in Ontario (Mierle, 1990). However, we have estimated accumulation on the basis of a single core in a deep depositional area within the reservoir, which tends to overestimate lakewide accumulation rates (Swain et al., 1992; Rada et al., 1993). In addition, our somewhat higher estimates of Hg accumulation rates in our reservoirs probably reflect both a higher rate of erosion in reservoirs as compared to natural lakes, and a higher ratio of terrestrial catchment to area in our reservoirs in comparison to small headwater lakes. Estimated Hg accumulation in Tunnel Lake was dominated by massive deposition of sediment at 5 - 7 cm (> 1500 g/m^2/y).

In general, profiles of Hg and LOI accumulation tracked each other (Figure 1). In the North Arm of Lady Evelyn Lake, Rocky Island, Tunnel and possibly Aubrey Lakes, the estimated rates of Hg and LOI accumulation appeared to increase at or around the time of impoundment. Although slight increases in sediment Hg concentration were also discernable for the North Arm of Lady Evelyn Lake, Rocky Island and Aubrey Lakes, at or around the estimated time of impoundment, these increases were small relative to the overall variation in sediment Hg concentrations. There were no distinct changes in Hg concentration of sediments from the South Arm of Lady Evelyn Lake around the time of impoundment, while sediment Hg concentration in Tunnel Lake, decreased at the estimated time of impoundment, likely a result of dilution by high accumulation rates at this period. Our results thus suggest that sediment Hg and organic accumulation rates may be more sensitive as indicators of the impact of impoundment than sediment concentrations, *per se*. Our results are also consistent with earlier studies of reservoirs in northern Manitoba and Quebec, which indicated that the increase in Hg supply caused by erosion of flooded soils, particularly the suspension of the humic horizon of flooded soils, was critical to Hg dynamics in reservoirs (Jackson, 1988; Louchouarn et al. 1993).

The correlations observed among the Hg concentrations of the sediment cores, pigment concentrations and LOI were generally similar for both raw and rank-transformed data. Sediment Hg concentration was most consistently correlated to LOI, with a significant positive correlation observed in all reservoirs but Rocky Island Lake. Sediment Hg concentration was also positively correlated with concentrations of oscillaxanthin (Lady Evelyn (North Arm), Aubrey and Rocky Island Lakes; chlorophyll derivatives (Lady Evelyn (North Arm) and Rocky Island Lakes); myxoxanthophyll (Aubrey Lake), and total carotenoids (Rocky Island Lake). In general, LOI was poorly correlated with pigment concentrations suggesting that the bulk of organic material contributing to LOI was allochthonous, which is also consistent with studies of reservoirs in northern Quebec (Louchouarn et al. 1993). The significant positive correlations between sediment Hg concentration and pigment concentrations suggest that for our reservoirs, sediment Hg concentrations are also positively correlated with reservoir productivity.

The story told by reservoir sediments thus appears to be highly contingent on the site specific features of the reservoir. For headwater reservoirs, created from large existing lakes, such as Rocky Island Lake and the South Arm of Lady Evelyn Lake, the sediment profiles were generally similar to those reported for headwater lakes, and appeared to be relatively undisturbed by impoundment. In contrast, the sediment profiles of the other reservoirs appeared to reflect varying degrees of disturbance associated with reservoir impoundment. The higher rate of sedimentation in the North Arm of Lady Evelyn Lake likely reflects greater shoreline erosion in this basin of the reservoir, which was closer to the dam. We are uncertain of the significance of the apparent increase in sediment Hg concentration and accumulation rate observed around the time of replacement of the original dam as the change in height of the dam was small (>1 m), and the construction was completed within one year. Sediment profiles of run-of-river reservoirs may be dominated by the activities related to impoundment and upstream development. In Aubrey Lake, it would appear that following impoundment, sedimentation at our sample site changed from the deposition of a material low in organic and Hg concentrations to a one with higher organic and Hg concentrations. These changes likely corresponded to the increased depth and decreased current velocities over the sample site following impoundment. In Tunnel Lake, it is likely that our sample site was not an area of sediment deposition prior to impoundment, and that subsequent sediment deposition has been dominated by downstream movement of erosional material derived from the upstream development of the dams at Rocky Island and then Aubrey Lake. Recent studies have indicated that MeHg appears to be stable in sediments and that changes in the ratio of total Hg to MeHg may reflect anthropogenic effects (Benoit et al., 1994; Hultberg et al., 1994). If these results are substantiated, analysis of reservoir sediment cores for both Hg and MeHg could provide considerable insight into the effects of impoundment on MeHg dynamics.

3.2 METHYLMERCURY PRODUCTION IN EXISTING RESERVOIRS

3.2.a) ^{203}Hg methylation - Mississagi River reservoirs

Overall Hg methylation was relatively low, with yields of less than 0.3% of the total ^{203}Hg activity added to the sediment assay. This relatively low Hg methylation activity was likely related to the time of collection (late September - early October), as methylation activity in north temperate waters varies seasonally (from < 0.1% to > 3% of the total activity added to the assay), with maximum methylation activity observed in the late summer (Furutani and Rudd, 1980; Korthals and Winfrey, 1987). The observed Hg methylation in the sediments was apparently dependent upon microbial activity, as the activity of acidified samples was significantly less than the methylation activity of circumneutral sediments and circumneutral sediments with added SRB's. These results were consistent with earlier studies where essentially little or no methylation was observed in autoclaved, acidified or formalin treated samples (Furutani and Rudd, 1980; Korthals and Winfrey, 1987).

Both depth and treatment significantly affected methylation activity, when activity was expressed per gram sediment (Table II). Although methylation activity of littoral samples was significantly greater than that of profundal samples, the 'depth effect' may have been caused by differences in organic content of the sediments. The importance of organic content was supported by regression analysis, in which a significant positive correlation (r^2 =0.44), was observed between the log of methylation activity and organic content. Consequently, depth did not significantly affect methylation, when activity was expressed per unit weight of organic sediment (Table II). The significant correlation between methylation and organic content of the sediment appears to be general, as similar relationships between methylation activity and sediment organic content have been observed for northern Manitoba reservoirs (Jackson, 1988). Methylation activity was also affected by a variety of other factors including clay content, oxygen and sulphide concentrations, and the availability of inorganic Hg (Jackson 1988). Further, as temperature appears to be the major factor controlling the relative rates of Hg methylation and MeHg demethylation in littoral and profundal sediments (Ramal et al. 1993), the effects of drawdown on the thermal budget of the reservoir may also significantly affect net MeHg production. The differences between lakes and reservoirs may be particularly pronounced in reservoirs such as Tunnel Lake, where we observed no indication of thermal stratification. It is likely that much more precise predictions of the methylation capacity of a reservoir could be developed by incorporating these additional factors in the analysis, but development of these relations would require much more extensive sampling and integrative modelling.

As location (reservoir) did not significantly affect methylation activity, the present experiments were unable to distinguish an effect of age or reservoir preparation methods on sediment Hg methylation activity. Similarly, we were unable to detect a significant difference in sediment methylation activity between Aubrey Lake, which was cleared of vegetation before impoundment, and the other reservoirs. However, as sediment Hg methylation activity was positively correlated with organic content of the sediment, it is logical to assume that measures taken to reduce the organic content of sediments in new reservoirs would reduce Hg methylation and subsequent accumulation of MeHg within the aquatic ecosystem. Assessment of the efficacy of pre-impoundment clearing of vegetation, in reducing the organic content of the sediments and subsequent Hg methylation, would thus require an integration of the effects of the reservoir preparation on Hg methylation and MeHg demethylation of sediments and overlying water throughout the whole reservoir.

Although the average Hg methylation activity of sediment samples with added SRB's was approximately twice that of sediments without added SRB's, the response was sufficiently variable that the differences were not statistically significant. The variability in response to added SRB's likely resulted from differences in the 'native' microbial communities among sediments, and in the abilities of the added SRB's to adapt to the different sediments. The apparent tendency for increased methylation activity with the addition of SRB's is consistent with observations that inhibition of sulphate reduction by addition of molybdate also inhibits Hg methylation (Gilmour and Henry, 1991; Gilmour et al., 1992). Sulphate addition may also stimulate Hg methylation in some cases (Gilmour and Henry, 1991; Gilmour et al., 1992), but above an optimal sulphate concentration, the production of sulphide (through sulphate reduction) may inhibit methylation (Winfrey and Rudd, 1990; Gilmour et al., 1992).

3.2.b) Net MeHg flux - Eugenia and Spence Lakes

A positive net flux of MeHg was observed in all samples, with the final concentration of MeHg always greater than the initial and intermediate concentrations. Net MeHg flux did not differ significantly between reservoirs, with average values of 21.0 ± 4.8 ng Hg m^{-2} d^{-1} (mean ± SE; n=5) for Spence Lake and 28.0 ± 5.5 ng Hg m^{-2} d^{-1} (n=6) for Eugenia Lake. For each reservoir, net MeHg flux of the 'replicate' cores varied roughly threefold. Although similar, large variations were also observed in the moisture content (%), fines (% of dry sediment ≤ 0.6 mm), and LOI (% dry wt.) of the top 5 cm of the sediment cores, net flux of MeHg was not significantly correlated with any of the above factors.

The net MeHg flux rates measured for both reservoirs were considerably greater than the annual average value of 6 - 7 ng Hg m^{-2} d^{-1} observed in the ELA wetland pond, Lake 979, prior to impoundment (Sellers et al. 1994), and the value of 2.4 ng Hg m^{-2} d^{-1} estimated for the entire riverine wetland (≈ 10 % wetland) of Lake 979 (St.Louis et al., 1994). However, the net flux rates for Spence and Eugenia Lakes were determined for samples collected in mid-August, and the samples were incubated at 26°C. Net methylation of Hg varies with season and temperature, with peak activities observed during the later part of the midsummer period (Korthals and Winfrey, 1987; Ramal et al., 1993). If the Q_{10} of net MeHg flux is assumed to be 2.0, the average observed net MeHg fluxes of 21 - 28 ng Hg m^{-2} d^{-1} would correspond to values of 7.5 - 8 ng Hg m^{-2} d^{-1}, at a temperature of 10°C. Thus, the measured net MeHg flux rates appear to be generally similar to those measured at the ELA. Unfortunately, comparable data using these methods at other locations are not presently available, and these data are not directly comparable with methylation rates determined using radioisotopic methods for sediments from Mississagi reservoirs.

The roughly threefold variation of net MeHg flux within a set of 'replicate' cores was sufficient that the difference between reservoirs was not significant. If this variation is consistent, it may also be difficult to detect the roughly fourfold variation in net MeHg flux which would be expected (assuming a Q_{10} of ≈ 2) over the ≈ 20°C range of temperature typical of most temperate lakes. Although larger sample sizes may appreciably reduce this variability, it is apparent that future studies must focus on understanding its underlying causes. Future research must also address the procedures for consolidating the 'microscale' measurements obtained using sediment core incubation techniques and the 'macroscale' values obtained by whole lake mass balance techniques (St.Louis et al., 1994).

4. Conclusion

Our reservoir stories thus devolve into a series of post-modern vignettes, rather than a unified tale of epic proportions. In particular, reservoir (watershed) specific differences may supersede general trends, with the difference between headpond and run-of-river reservoirs particularly significant. In general, Hg and organic accumulation rates, rather than concentrations, appear to be sensitive as indicators of impoundment in sediment cores from the four Ontario reservoirs we examined. The combination of the apparent post-impoundment increase in Hg and LOI accumulation rates and the consistent significant positive correlations we observed between sediment Hg with LOI are in accord with earlier studies, which demonstrated that the increase in Hg and organic supply caused by erosion and release from flooded soils is central to post-impoundment changes in the dynamics of Hg in reservoirs. Similarly, significant positive correlations of sediment Hg with concentrations of chlorophyll derivatives and other pigments suggest a general relationship between Hg and reservoir productivity. If recent studies using the ratio of total Hg to MeHg in sediment cores as an index of anthropogenic effects are substantiated, a similar analysis of reservoir sediment cores could provide considerable insight into the effects of impoundment on MeHg dynamics in reservoir and reservoir sediment cores.

Our comparative surveys of Hg methylation in reservoirs were significantly hampered by the high degree of variability in methylation activity among 'replicate' samples. For the Mississagi reservoirs, methylation activity was positively correlated with organic content of the sediment, but we were unable to resolve the effects of reservoir age or preparation methods. Similarly, the large range of variation in net MeHg flux observed among replicate samples may have obscured differences in net MeHg flux in Spence and Eugenia Lakes. Future studies should focus on resolving the underlying causes of this variability and in consolidating the 'microscale' measurements obtained using sediment core incubation techniques and the 'macroscale' values obtained by whole lake mass balance techniques. Our results also suggest that factors other than Hg supply and methylation may be important to the MeHg dynamics in fish after reservoir impoundment.

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TABLE 1: SUMMARY OF RESERVOIRS SAMPLED

	Location	Impoundment Date	Storage Volume ($m^3 \times 10^6$)	Drawdown (m)	Fish Hg[a]
LADY EVELYN LAKE	47°20'N 80°10'W	1916	313	5	*
ROCKY ISLAND LAKE	46°55'N 83°04'W	1949	388	11.6	***
AUBREY LAKE	46°55'N 83°13'W	1969	60.7	3.1	***
TUNNEL LAKE	46°27'N 83°26'W	1949	86.1	5.8	***
EUGENIA LAKE	44°19'N 80°30'W	1915	21.5	4.7	*
SPENCE LAKE (HANNA CHUTE)	45°00'N 79°18'W	1926	0.518	0.4	*****

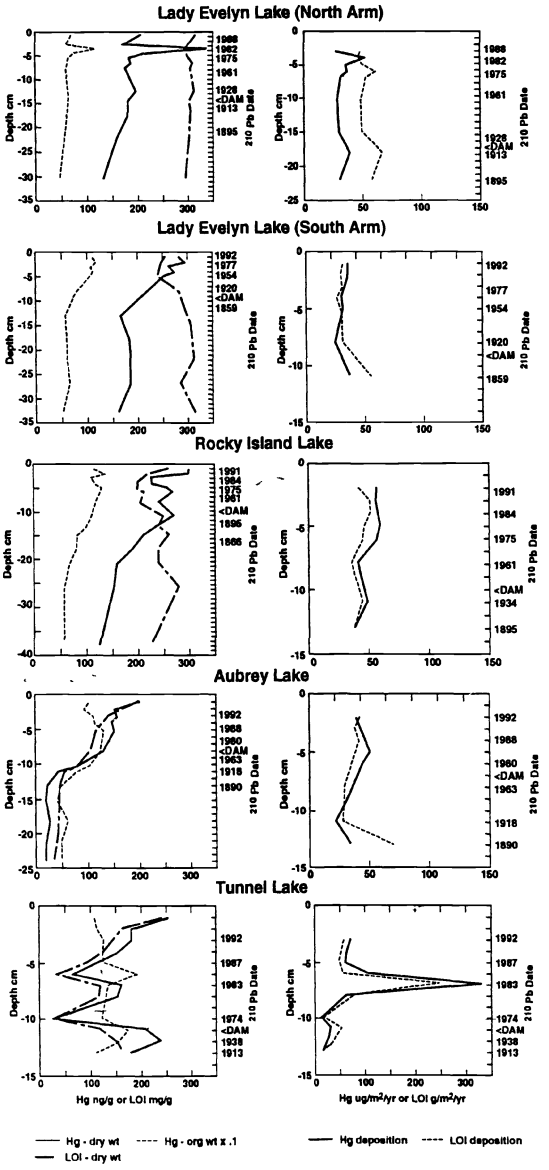
[a] Relative assessment of fish mercury based on OMEE/OMNR (1993) from lowest (*) to highest (*****)

Table 2: Hg methylation activity of sediments from Mississagi Reservoirs

	Acidified Sediment	Circumneutral Sediment	Circumneutral Sediment + SRB*
Rocky Island Lake- profundal	430 24 [a] 2354 131 [b] (3)[c]	13245 9315 71415 35820 (4)	24823 133036 (2)
Rocky Island Lake- littoral	670 352 1807 945 (3)	9409 1952 25112 5145 (5)	32380 6773 86987 18117 (4)
Aubrey Lake- profundal	139 76 914 450 (3)	2507 575 18394 4464 (5)	2672 454 18543 2209 (3)
Aubrey Lake- littoral	147 64 429 248 (3)	22076 3525 61583 14716 (6)	29209 3521 76396 5645 (3)
Tunnel Lake- profundal	51 699 (1)	1180 16164 (2)	3501 47958 (1)

* Sulphate Reducing Bacteria (details given in text)
[a] mean DPM (disintegrations per minute) / g sediment SE (for $n \geq 3$)
[b] mean DPM / g organic sediment SE (for $n \geq 3$)
[c] number of samples

Figure 1. Hg and loss on ignition (LOI) concentrations and accumulation rates in sediment cores from Lady Evelyn (North and South Arms), Rocky Island, Aubrey and Tunnel Lakes.



MERCURY UPTAKE PATTERNS OF BIOTA IN A SEASONALLY ANOXIC NORTHERN CALIFORNIA RESERVOIR

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Abstract. Biotic uptake of mercury (Hg) in Davis Creek Reservoir, California increased dramatically in conjunction with the entrainment of anoxic hypolimnetic water into the mixed layer. This indicated a seasonal pulse increase of bioavailable Hg associated with thermal destratification. The effect was more pronounced in juvenile bass (70-200% seasonal increases in muscle Hg concentration), as compared to adults (15-25% increases), and was most distinct in zooplankton, which spiked to concentrations of 3-6 mg/kg, dry weight, immediately following fall destratification (130-270% seasonal increases over pre-fall levels). In addition to the general buildup of methyl Hg in the hypolimnion under anoxic conditions, a dense layer of photosynthetic anaerobic bacteria just beneath the thermocline is implicated as a potentially important seasonal source of methyl Hg to reservoir fish. Hg increases in juvenile and adult fish correspond to late summer and fall entrainment of upper hypolimnetic water, while zooplankton spike increases may be partially related to ingestion or adsorption of Hg-scavenging manganese oxides, which precipitate following full turnover. A simple and effective, syringe-based cold vapor atomic absorption method for total Hg is also described.

1. Introduction

Seasonal variations in mercury (Hg) dynamics have been described in a number of studies of aquatic systems. Because of the complex biogeochemistry of Hg, a variety of factors have been shown to be associated with spatial and temporal variations in both concentrations and production of aqueous methyl Hg in different systems. Variation in this bioaccumulating Hg species has been linked to pH (Winfrey and Rudd, 1990; Bloom *et al.*, 1991), color/humic substances (Meili and Parkman, 1988; Mierle, 1991), temperature (Parks *et al.*, 1986; Matilainen *et al.*, 1991), particulate matter (Hurley *et al.*, 1991), and algal density (Jackson, 1986; Kaiser *et al.*, 1989). Dissolved oxygen levels and accompanying redox potential have been shown to be among the most important factors influencing both aqueous Hg chemistry and the microorganisms which methylate Hg (Korthals and Winfrey, 1987; Iverfeldt, 1988; Regnell, 1990; Watras *et al.*, 1994). Seasonality in the uptake of Hg by higher aquatic organisms has been associated with corresponding aqueous Hg dynamics in individual water bodies (Jackson, 1988b; Wiener *et al.*, 1990; Bodaly, 1993), as well as with physiological and behavioral patterns in the organisms themselves (Kohler *et al.*, 1986; Bodaly, 1993; Parkman and Meili, 1993).

Davis Creek Reservoir, the site of this study, is characterized by strong thermal stratification between spring and mid-fall, with the seasonal development of anoxic conditions throughout the entire hypolimnion by late August. With the breakdown of stratification in the fall, hypolimnetic water is mixed into the surface layer and aerobic mixing occurs, without ice cover, between December and March. In other research at the site, Gill and Bruland (1992) analyzed reservoir water for organo-Hg compounds; i.e. those containing C-Hg bonds and presumed to be dominated by methyl Hg. This work was done over a two year period during which time the anoxic hypolimnion was found to accumulate organo-Hg at concentrations up to an order of magnitude higher than in the surface waters. During the period of complete aerobic mixing, organo-Hg was low throughout the entire

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water column (<2 ng L^{-1}). In this paper we look at the biotic response to the seasonal pattern of organo-Hg in Davis Creek Reservoir, and link the uptake patterns of total Hg by reservoir zooplankton and fish to annual limnological cycles of thermal stratification and destratification in a system with a seasonally anoxic hypolimnion.

2. Materials and Methods

Davis Creek Reservoir (Figure 1) is located in the historic mercury mining region of the California Coast Range, approximately 70 miles north of San Francisco. The reservoir was impounded in 1984-1986, as a water supply for a large gold mining operation. The full reservoir covers 80 hectares, with ~6,000 acre-feet of capacity and a maximum depth of 25 meters. The inflowing creek has historically been impacted by an abandoned Hg mine, resulting in reservoir sediment Hg concentrations of <1-20 mg kg^{-1}, dry weight. The region is hot and dry in the summer, with nearly all precipitation falling between November and April. Epilimnetic water is utilized for mining process work and summer evaporation is a significant loss mechanism. Total surface drop per year is ~3 m.

Limnological monitoring and Hg research have continued, uninterrupted, since reservoir formation (Axler *et al.*, 1988; Slotton, 1991). Broodstock largemouth bass (*Micropterus salmoides*) were placed into the reservoir in 1985. Bass born in the reservoir have been collected since 1985 by gill net, seine, and angling; aging was by scale analysis. Muscle samples were taken from the dorsal-anterior fillet quadrant. Juvenile bass (0.2 - 5.0 g live weight) were collected by seine. Muscle tissue was carefully dissected from these very small fish to maintain comparability with the larger bass; the entire fillet was utilized. Zooplankton were collected in nocturnal tows of a weighted hoop net with a 200 µm mesh basket, and strained through a 500 µm sieve. This separated out the bulk of entrained phytoplankton. Zooplankton biomass was typically dominated by a single cladoceran species, *Daphnia pulex*. Plankton was dried to constant weight at 55 °C and homogenized with teflon and glass instruments prior to analysis.

Bacteriochlorophyll was quantified by scanning spectrophotometer readings of acetone extracts of seston retained on 1.2 µm pore size GF/C filters. Water was collected from various depths by Van Dorn sampler. Dissolved oxygen and temperature profiles were taken with a YSI meter (model 51B). Relative, cumulative volumetric entrainment of

hypolimnetic water into the mixed layer was estimated using surface elevation and vertical profiles of temperature and oxygen, together with existing depth/volume curves.

Biota Total Hg Methodology

Total Hg was analyzed in biota samples by cold vapor atomic absorption (CVAA) spectrometry, utilizing a modified micro-delivery system based on a syringe gas-injection procedure first described by Stainton (1971). Samples were digested for 90 minutes with 2:1 concentrated sulfuric (H_2SO_4):nitric (HNO_3) acid in borosilicate test tubes, utilizing heat (95 °C water bath) and pressure (tubes capped securely with teflon-lined screw tops). After cooling tubes in an ice water bath, a consistent volume of 6% potassium permanganate ($KMnO_4$) solution was added, sufficient to leave precipitate in all tubes. Tubes were digested at 80-90 °C for an additional 90 minutes at ambient pressure (without caps) and then topped up to the desired dilution with mercury-free (nitrogen purged) water and capped.

In the detection phase, individual disposable plastic syringes were used to draw 2 ml of well-mixed digest out of each tube, followed by 2 ml of acid reductant mixture. The reductant mixture contained 10 ml H_2SO_4, 5 g hydroxylamine sulfate ($(NH_2OH)_2 \cdot H_2SO_4$), 5 g sodium chloride (NaCl) and 2.5 g stannous chloride ($SnCl_2 \cdot 2H_2O$) per 100 ml, promoting both the rapid dissolution of the permanganate precipitate and reduction of digest mercury to the volatile elemental state. A consistent volume of air was carefully drawn into the syringe, which was quickly capped (needle off) and then mixed by touching the tip to a vortex mixer for 10 seconds. After the permanganate precipitate cleared, the capped syringe was again vortex agitated (15 seconds) and the syringe air was injected into a low-volume, long path-length cuvette, which was mounted in the burner compartment of an atomic absorption spectrophotometer, in the beam path of a mercury lamp set at 253.7 nm. Maximum absorbance (peak height) was reached within 2 seconds; this absorbance was recorded, and the cuvette was readily cleared of mercury for the next sample by flushing with a syringe-full of air. Standards and QA/QC samples were digested and in all other ways treated identically to samples. Exact weights of total digests and injection aliquots were determined by sequential weighings of digest tubes to ± 0.001 g.

Advantages of the approach include: (1) relatively low detection limit: <0.01 mg kg^{-1} Hg in samples; (2) excellent reproducibility and recoveries of spikes and references; (3) ability to re-analyze digests, as only a portion is injected; digests are stable for months; and (4) because stannous chloride never touches digestion tubes, the potential for reductant carry-over is not a concern.

3. Results and Discussion

3.1. ZOOPLANKTON

Zooplankton total Hg was measured 7-13 times per year for four years. We hypothesized that these relatively ephemeral organisms might be useful indicators of potential seasonality in Hg bioavailability. Because they are short-lived, there is no ambiguity as to season of uptake, as is typically the case with adult fish. Furthermore, unlike the reservoir fish, zooplankton were collectable in all seasons.

The single most compelling feature of the zooplankton Hg data record is the presence of extreme seasonal spiking in each of the late fall periods of record (Figure 2). During these times, zooplankton Hg concentrations jumped 2-3 times higher than pre-fall levels, to 3-6 mg kg^{-1} Hg (dry weight). Seasonal spiking coincided with the fall turnover event, as

indicated by the cumulative hypolimnetic entrainment curve superimposed in Figure 2. After peaking, zooplankton total Hg subsequently dropped precipitously each winter.

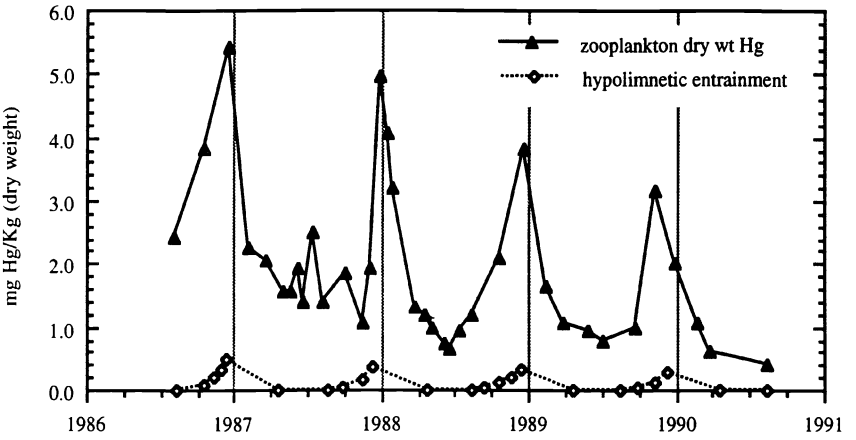

Fig. 2. Zooplankton Hg concentration data record, 1986-1991; with relative, cumulative seasonal entrainment of anoxic hypolimnetic water into the mixed layer superimposed. Peak (100%) entrainment each year has been scaled to 1986 (maximal) hypolimnetic volume, when reservoir was full.

A number of researchers have found anoxic conditions to greatly enhance both Hg methylation (Korthals and Winfrey, 1987; Regnell, 1990; Matilainen *et al.*, 1991) and methyl Hg accumulation in the water (Mason *et al.*, 1993; Watras *et al.*, 1994). Gill and Bruland (1992) demonstrated that the seasonally anoxic hypolimnion of Davis Creek Reservoir was the site of maximal accumulation of dissolved organo-Hg, with concentrations (10-35 ng L^{-1}) an order of magnitude higher than in surface water (1-3 ng L^{-1}). The zooplankton Hg uptake data indicate that this hypolimnetic pool presented a significant pulse of bioavailable Hg to the mixed layer each fall in conjunction with thermal destratification. As zooplankton can accumulate significant proportions of inorganic Hg in addition to organo-Hg (Watras and Bloom, 1992), these total Hg data cannot be attributed solely to uptake of organo-Hg. However, the Gill and Bruland (1992) study found the seasonal accumulations of aqueous Hg in the anoxic hypolimnion to be dominated by dissolved organo-Hg, which accounted for 40-82% of the total (mean = 66%) and 70-92% of the dissolved fraction (mean = 82%).

The annual cycle of zooplankton Hg spike increases and subsequent declines to baseline very closely matches the cycle of Mn precipitation and sedimentation noted at this reservoir. Gill and Bruland (1992) found that annual water column turnover introduced large pulses of both aqueous organo-Hg and dissolved Mn to the mixed layer from the anoxic hypolimnion at turnover. The subsequent cycle of precipitation and sedimentation of Mn was linked to removal of aqueous organo-Hg from the water column, presumably through adsorption onto particulate Mn. The timing of the zooplankton seasonal Hg pattern suggests that the large increases may be partially due to ingestion or adsorption of Mn precipitates by these cladoceran filter feeders.

3.2 YOUNG-OF-YEAR JUVENILE BASS

Seasonality in Hg uptake was also investigated in young-of-year juvenile largemouth bass (Table I, Figure 3). Muscle Hg concentration was utilized in this seasonal work rather than whole body Hg burden due to difficulties in consistently compositing such small individual fish (0.2 - 5.0 g), as well as for comparability with the adult fish and other regional fish data. Unlike zooplankton, which can accumulate significant proportions of inorganic as well as methyl Hg (Watras and Bloom, 1992), fish muscle Hg has repeatedly been demonstrated to consist almost entirely of methyl Hg (Bloom, 1992). In other work, we have found muscle tissue to be the repository of >90% of the total mercury and >95% of the methyl mercury body burden in largemouth bass (Suchanek *et al.*, 1992). Thus, changes in muscle total Hg concentration in rapidly growing juvenile bass provide a good measure of changes in overall methyl Hg uptake and bioavailability.

TABLE I

Juvenile bass total Hg data (wet weight muscle mg Hg kg^{-1} from individual fish)

	Date	n	Mean Hg	Std. Dev.	95% Confidence Interval of Mean
1988	11-Jul	12	0.66	±0.17	0.55 - 0.77
	8-Aug	10	0.74	±0.18	0.61 - 0.87
	10-Sep	23	0.61	±0.15	0.55 - 0.68
	21-Oct	15	1.31	±0.40	1.09 - 1.53
1989	1-Jul	10	0.44	±0.08	0.39 - 0.50
	13-Aug	19	0.65	±0.12	0.59 - 0.71
	26-Sep	19	0.93	±0.22	0.82 - 1.04
1990	29-Jun	23	0.35	±0.12	0.30 - 0.40
	4-Aug	23	0.35	±0.08	0.32 - 0.39
	15-Sep	12	0.82	±0.24	0.66 - 0.97
	24-Oct	10	1.10	±0.16	0.98 - 1.21

Newly hatched juvenile bass taken in early July of 1988 weighed less than 0.5 g and, yet, had accumulated muscle Hg concentrations with a mean of 0.66 mg kg^{-1}, highlighting the overall high level of Hg bioavailability in this young reservoir. Individuals collected in August were approximately double the size of the July set, but muscle Hg concentration remained at a similar level, indicating similar levels of Hg bioavailability throughout the period. Juveniles collected 10-September consisted of larger/older individuals (1.3-4.5 g) than the July-August samples, but had muscle Hg concentrations which were statistically identical to those seen earlier in the summer. However, the October sample set demonstrated a significant departure from the previous uniform trend of muscle Hg concentrations, with concentrations approximately double those found earlier. It is notable that the elevated Hg concentrations in the October 1988 samples varied inversely with size and age, with highest levels in the youngest individuals (Figure 3). These smallest individuals, of a size similar to early season young and almost certainly of a late spawn, were those whose growth and Hg accumulations were

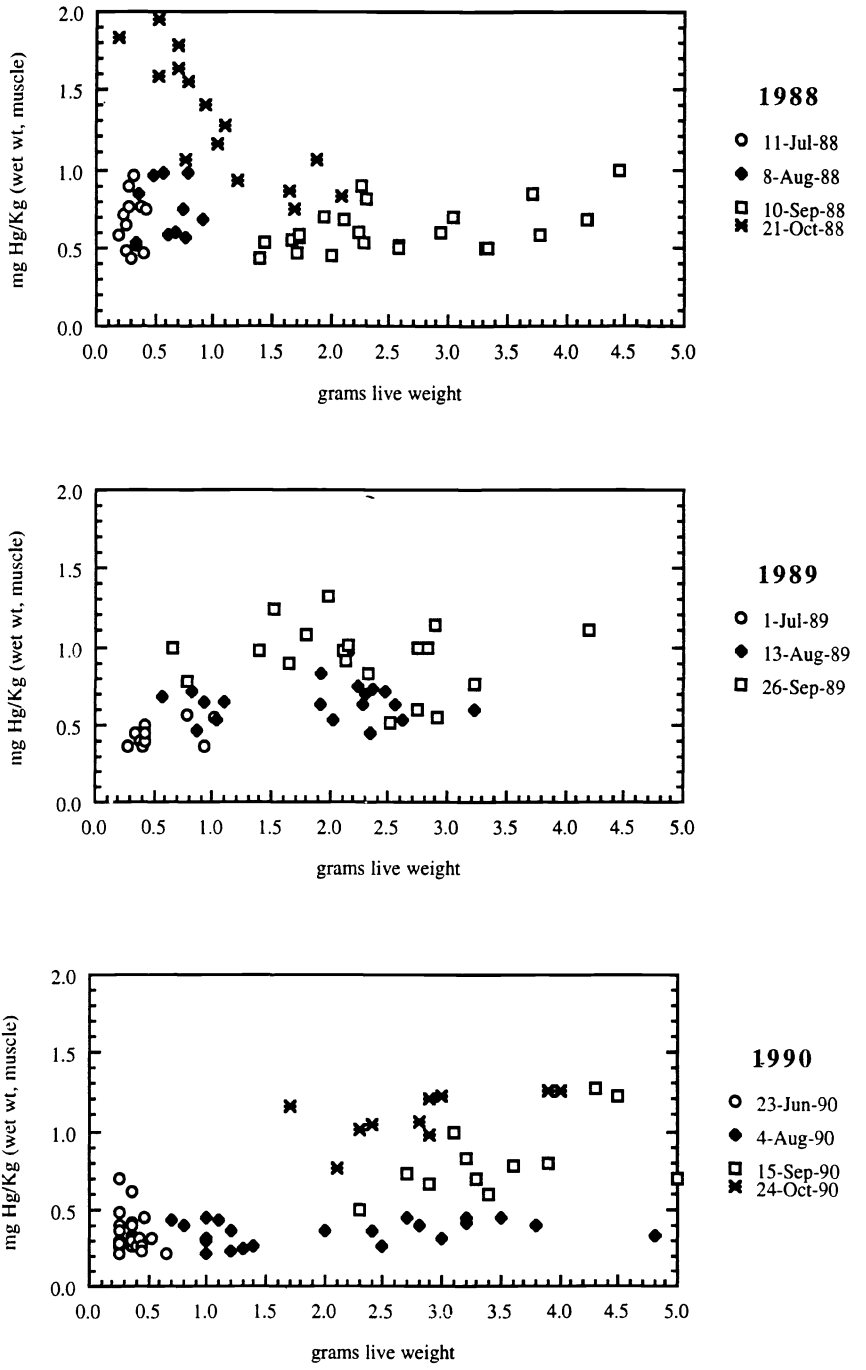

Fig. 3. Young-of-year bass muscle mercury, summer through fall, 1988, 1989, 1990.

proportionately most dominated by the period when anoxic hypolimnetic water was being entrained into surface waters.

A similar pattern was observed in 1989 and 1990. Juvenile bass taken in late September or October of each of the three years of record, and in mid-September of 1990, had significantly elevated Hg concentrations relative to samples taken June through August (Table I). Bass were dormant and unobtainable between mid-fall and spring.

The annual seasonal increases in juvenile bass Hg were noted in September and October, *before* the most significant lowering of the thermocline typically occurred. However, loss of epilimnetic volume due to water usage and evaporation dropped the water surface level by ~0.5 m per month at these times, moving the thermocline a corresponding amount into the upper hypolimnion even when the mixed layer remained a constant depth. In addition, the absolute depth of the mixed layer typically increased somewhat throughout the late summer and early fall due to wind action and lowering temperatures. Together, these two processes resulted in the progressive entrainment of anoxic water from just beneath the thermocline into the mixed layer, from late summer until turnover was complete by late November or early December (Figure 4, also Figure 2). Because the bass were collected prior to turnover (when they became dormant each year), the seasonal increases in muscle Hg corresponded mainly with entrainment of anoxic water from the *upper* hypolimnion.

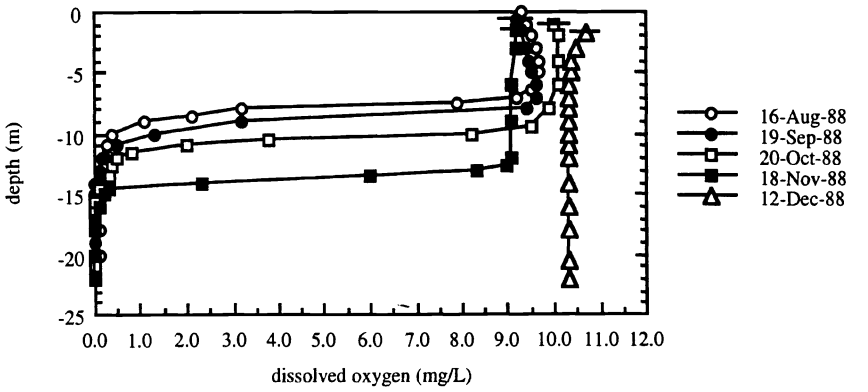

Fig. 4. 1988 profiles of dissolved oxygen throughout period of hypolimnetic entrainment.

The upper hypolimnetic layer, just beneath the thermocline, was of particular interest as this was the location of a dense seasonal lens of photosynthetic anaerobic bacteria (Figure 5). This narrow and well defined layer of purple or green sulfur bacteria was found where light levels were highest in conjunction with anoxia, following the thermocline down from late August through November during each year of our study. While Gill and Bruland (1992) indicated the bottom of Davis Creek Reservoir to be the major source and/or accumulation location of organo-Hg, conclusions from that study are constrained by a coarse sampling interval (2-5 m) which may have missed narrow strata with elevated concentrations (G. Gill, personal communication). An interesting possibility is that the narrow but extremely dense seasonal layer of photosynthetic anaerobes immediately below the thermocline may have been a significant site of Hg methylation and/or accumulation. Indeed, Mason *et al.* (1993) found this to be the case in another system, utilizing fine-resolution (0.1 m) depth profiles of aqueous Hg species and bacteriochlorophyll in an

anoxic estuarine kettle basin. In that study, bacteriochlorophyll and methyl Hg both increased more than 50-fold immediately below the pycnocline in a ~2 m thick lens. Watras *et al.* (1994) and Verta and Matilainen (1994) also describe elevated methyl Hg concentrations associated with layers of similar bacteria. All of these researchers indicate that the photosynthetic anaerobes themselves are almost certainly not the direct sources of elevated methyl Hg, but that co-existing sulfate reducers may be involved. Matilainen (1994) presents experimental evidence for this. At Davis Creek Reservoir, the dense layer of photosynthetic anaerobes developed immediately below the thermocline during the time of year when this stratum was being progressively entrained into the mixed layer where fish were actively growing. The juvenile bass Hg data indicates that this layer may be a seasonally important source of bioavailable Hg to surface waters.

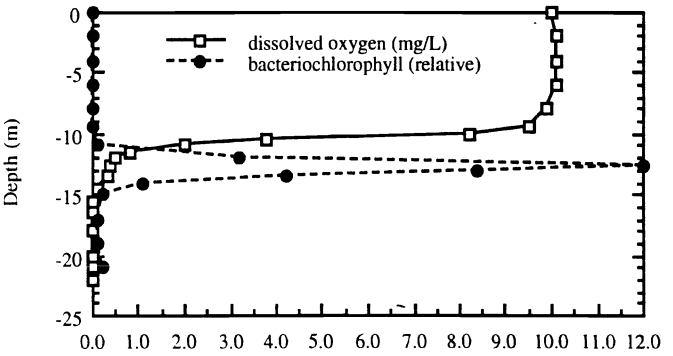

Fig. 5. Distribution of photosynthetic anaerobes in anoxic upper hypolimnion, 20-Oct-88.

3.3 ADULT BASS

Four to 25 bass from the initial 1985 cohort of reservoir-born fish were analyzed for Hg at each of 24 sampling events throughout the 5 years of this study, with average size increasing from 20 g in year 1 to >750 g in year 5. In addition to the overall very high Hg levels (2-4 mg kg^{-1}, wet weight muscle), these data give the indication of a seasonal pattern, though clearly not statistically significant, superimposed on the general decline in muscle Hg concentrations in this cohort of bass as they grew in the newly impounded reservoir (Figure 6). The overall year-to-year declines in mean Hg levels in all the data sets presented throughout this paper can be attributed to declining mercury bioavailability following initial peak levels associated with impoundment and newly flooded soils (Abernathy and Cumbie, 1977; Bodaly *et al.*, 1984; Jackson, 1988a). In each year, bass muscle Hg concentrations declined during thermal stratification between spring and mid summer. The general decline was interrupted in each of the years beginning in the late summer to mid fall, when muscle Hg concentrations typically increased by ~0.5 mg kg^{-1}. This coincided with the juvenile bass seasonal increases. Following turnover, when the bass became dormant, their muscle Hg concentrations remained steady or increased further during the winter, as evidenced by highest annual levels typically occurring in the first spring collection of each year. This was despite the fact that, soon after fall turnover,

aqueous concentrations of organo-Hg have been shown to plummet in this reservoir in conjunction with the precipitation and sedimentation of manganese oxides (Gill and Bruland, 1992). As Hg depuration is relatively minimal in these fish (Slotton, 1991), significant short term decreases in muscle Hg levels could only occur through growth dilution under lower Hg bioavailability. We believe that this process explains the declines noted in bass muscle Hg concentrations during each spring through mid-summer season after initial impoundment. However, with metabolic-based weight loss (as opposed to growth) during November-March dormancy, tissue Hg could become slightly more concentrated, despite lowest aqueous Hg concentrations occurring in that season.

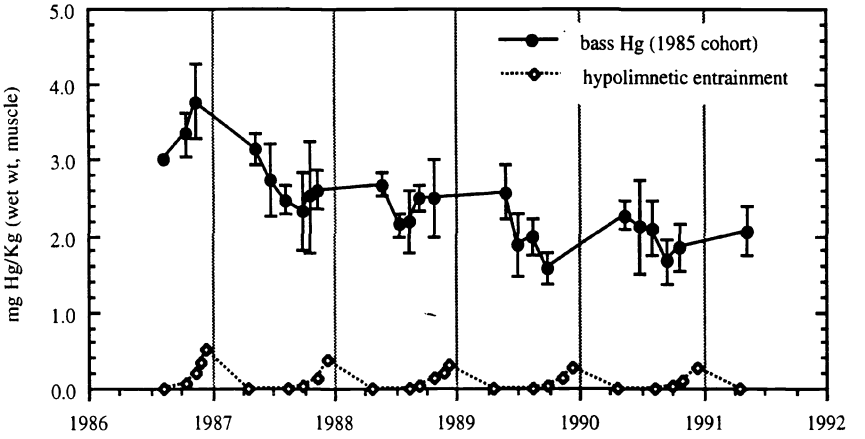

Fig. 6. Bass muscle Hg with 95% confidence intervals, 1986-1991; all plotted points from 1985 cohort. Relative, cumulative seasonal entrainment of anoxic hypolimnetic water into the mixed layer superimposed. Peak (100%) entrainment each year has been scaled to 1986, when full.

4. Conclusions

These biotic data records demonstrate that Hg bioavailability in the surface waters of Davis Creek Reservoir increases in conjunction with the seasonal entrainment of anoxic hypolimnetic water. Zooplankton spike increases coincide with full destratification and may be linked, in part, to ingestion or adsorption of Hg-scavenging manganese oxides, which precipitate following turnover. As the bass become dormant at turnover, destratification-related seasonal increases in bass muscle Hg correspond with the entrainment of anoxic water from the upper hypolimnion, prior to full turnover. Consequently, the dense layer of photosynthetic anaerobic bacteria located just beneath the thermocline is implicated as a potential seasonal source region for methyl Hg, in addition to general hypolimnetic accumulations which peak toward the bottom.

Seasonal response in adult fish Hg concentration is necessarily damped because an uptake time scale of weeks to months represents a relatively small portion of the entire lifetime Hg accumulation, as compared to zooplankton and young-of-year fish. Zooplankton and young-of-year fish are clearly better indicators of seasonal variation in Hg bioavailability than are adult fish.

Acknowledgments

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SEABIRDS AS MONITORS OF MERCURY IN THE MARINE ENVIRONMENT

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Abstract The oceans play a major role in global cycling of mercury and widespread contamination of marine ecosystems has been demonstrated in recent years Monitoring mercury in the marine environment is a priority and biomonitoring has featured prominently in this respect Seabirds, as top predators, present high mercury levels due to food chain amplification and thus will reflect slight variations in environmental mercury and its hazards to humans better than do most invertebrates and cold blood vertebrates There is experimental evidence that levels of mercury in seabirds show a dose-response relationship, so that increased contamination of the environment causes a corresponding increase in the level in birds This coupled with current knowledge on the dynamics of mercury in birds gives a good basis for the use of seabird as monitors of mercury Internal tissues blood eggs feathers and chicks have been used as monitoring units Feathers are the most attractive amongst them They are both chemically and physically stable, accumulate higher mercury levels than other tissues and their sampling is non-destructive However, it is essential to sample a consistent feather area from all birds to minimise the effects of moult and body feathers are the most adequate Feathers from birds in museum collections offer a great potential for the study of synoptic geographical and historical of changes in mercury levels on a global scale with large sample sizes For example, studies with time series of feather samples from seabirds provide evidence of a 3-fold increase of mercury contamination in the marine ecosystem of North-eastern Atlantic over the last 100 years and little increase in mercury contamination in the Southern hemisphere during the same period

1. Introduction

Widespread mercury contamination of marine ecosystems has been demonstrated in recent years (Slemr and Langer, 1992, Thompson et al , 1992a) The oceans play a major role in the global cycle of mercury (Fitzgerald, 1986) and marine fish are the most critical pathway of exposure to mercury in human populations (Clarkson, 1990) Monitoring mercury contamination in the marine environment is thus a priority The use of biomonitors has featured prominently in this respect (Phillips, 1980) In recent years, a considerable effort has been made to obtain a better understanding of the mercury dynamics in seabirds (Braune and Gaskin, 1987, Burger et al , 1992a, Furness et al , 1986, Thompson, 1990) providing a good basis for their use as monitors of geographical, temporal and global patterns of mercury contamination in marine ecosystems

In this paper we review and update the current knowledge of mercury in seabirds and draw attention to aspects to be considered in designing biomonitoring programs for mercury using seabird tissues It is organized in three sections mercury as a marine pollutant, mercury dynamics and variability in seabirds and the use of seabirds as biomonitors

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2. Mercury and the marine environment

EXPOSURE AND TOXICITY. The main concern regarding environmental health risks of mercury is associated with the high consumption of aquatic organisms (particularly fish) with elevated levels of methylmercury (the most toxic form) (Stern, 1993). Methylmercury intoxication is characterized by effects on the central nervous system, especially sensory, visual, and auditory functions and those concerned with co-ordination (WHO, 1990).

There is lack of data on effects of mercury in wildlife. Although seabirds were among the first victims of the Minamata incident in Japan, unfortunately this and similar opportunities have not resulted in comprehensive studies of mercury toxicity (Fimreite, 1979). Mercury levels in tissues of marine vertebrates, especially birds and mammals, are frequently high (Thompson, 1990) and above the thresholds for toxic effects in humans. Despite reproductive impairments under controlled exposure conditions reported in the bird literature (Scheuhammer, 1987) there is little evidence of toxicity at the levels observed in wild populations. Some studies suggest that this results from detoxification mechanisms developed by marine vertebrates (Thompson and Furness, 1989a).

ENVIRONMENTAL CYCLING. Inorganic mercury is efficiently biotransformed into methylmercury in several compartments of the aquatic environment, including sediments (Beijer and Jernelöv, 1979) and the water column (Topping and Davies, 1981). The detection of increased concentrations of methylmercury in oceanic waters below the thermocline (>200 m) indicates *in situ* production of methylmercury in the open ocean (Mason and Fitzgerald, 1990) and therefore higher availability and enhanced bioaccumulation of mercury by organisms in such low oxygen environments. Mercury is also the only metal that is consistently biomagnified through the food chain. This suggests that relatively minor perturbations of key portions of the cycle (e.g. atmospheric deposition and bioaccumulation by fish) could result in major changes in the exposure to, or uptake by, sensitive human or wildlife populations even in remote areas (Lindberg, 1987).

Mercury emissions, both natural and anthropogenic, are dominated by losses of vapor forms to the atmosphere. These forms have a relatively long residence time, conducive to long range transport (Lindqvist, 1991) and this results in truly global dispersion of mercury (Lindberg, 1987). The current anthropogenic emissions of mercury to the atmosphere exceed direct releases to surface waters by more than an order of magnitude (Nriagu and Pacyna, 1988) and are considered to be of the same order of magnitude as atmospheric emissions from natural processes (Lindqvist, 1991). The oceans have a major role in global atmospheric emissions, contributing about 77% of the total present natural emissions (Lindqvist, 1991).

Man-induced mobilization of mercury into the biosphere has increased by two or three times between 1900 and 1970 (Andren and Nriagu, 1979) and atmospheric concentrations over the Atlantic Ocean continued to increase at a rate over 1% per year during the 80s (Slemr and Langer, 1992). Presently, the global atmospheric load of

mercury is considered to be estabilizing (Lindberg, 1987) and the major concerns focus on changes in the general chemistry of the atmosphere (e.g. enrichment in oxidants and acidification) which can somehow enhance mercury deposition and thus have a significant effect on the global cycle.

MONITORING. The human and environmental health risks of mercury coupled with the subtlety of mercury's early toxic effects suggest the need for careful monitoring of key parts of its biogeochemical cycle. Current monitoring covers almost only continental coastal areas but more effort should be directed to the open ocean in the future. Considering the existence of long-range atmospheric transport and deposition of mercury it is expected that potential large-scale and global increases in environmental mercury will be easier to detect in remote oceanic regions than closer to the continents.

Monitoring may rely upon the quantification of mercury in abiotic (air, water, sediment) and biotic (living organisms) compartments of marine ecosystems. Because mercury bioaccumulates in marine organisms (the concentration in the animal body increases to a high dynamic equilibrium or even increases throughout the life of the animal) and it bioamplifies in the food chain (predators accumulate higher tissue concentrations than their food), it is now generally accepted that organisms offer particular advantages to quantify its abundance or bioavailability. Current biomonitoring of pollutants tends to emphasize the use of sedentary invertebrate animals as target species (Phillips, 1980), but in the case of mercury predatory species at the highest trophic levels are particularly advantageous (Furness, 1993). Predatory fish, marine mammals and seabirds are exposed to the highest mercury levels within a particular ecosystem and thus will reflect slight variations in environmental mercury better than do most invertebrates.

3. Mercury in Seabirds

3.1. DYNAMICS: UPTAKE, BODY DISTRIBUTION AND ELIMINATION

The dynamics of mercury in seabirds can be viewed as a several factor model involving ingestion from diet, uptake in the intestine, transport in blood, accumulation in internal tissues (e.g. liver, kidney, muscle) with redistribution to the plumage during feather growth, and elimination in eggs and excreta (Fig. 1).

The bird's plumage contained about 70% of the mercury body burden in adults of some terrestrial and waterfowl species (Honda et al., 1985; 1986a) and 93% of the total burden in adult Bonaparte's gull *Larus philadelphia* after the completion of molt (Braune and Gaskin, 1987) despite plumage forming only 10% of total body weight. The distribution of the remaining mercury burden in body tissues of adult Bonaparte's gull (i.e. excluding feathers) was about 36% in liver, 6% in kidney, 9% in muscle, 1% in brain and 48% in the carcass (Braune and Gaskin, 1987). The plumage is also the major store for mercury in Cory's shearwater *Calonectris diomedea* fledglings, accounting for about 80% of total body burden, followed by the carcass, muscle and liver with about 10,

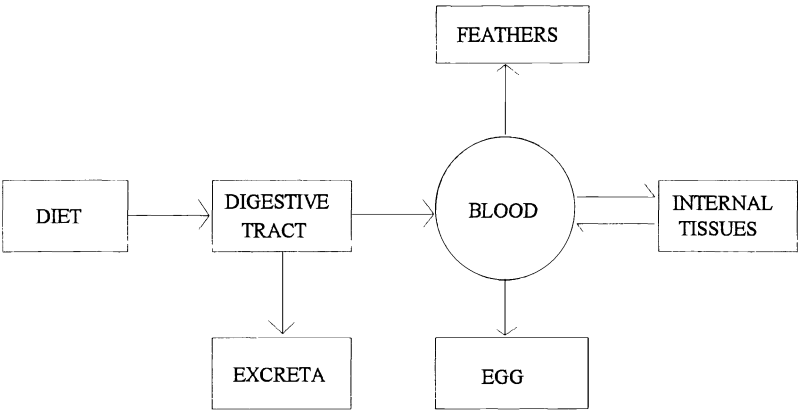

Fig. 1. Simplified model for mercury dynamics in seabirds.

5 and 4% respectively (Monteiro, unpubl. data). The relative mercury burden in the plumage (down) of hatchlings is lower than in adults or fledglings, ranging from 30-38% in eastern great white egret *Egretta alba* (Honda et al., 1985) and common tern *Sterna hirundo* (Becker et al., 1993a). In the latter study, the remaining mercury burden was distributed between the liver (10%) and the carcass (52%).

The plumage of birds is renewed usually every year after breeding. Then, much of the dietary mercury accumulated in soft tissues between molts is mobilized into growing feathers. The mercury concentrations in soft tissues may decrease to less than half as molt proceeds and the 'body pool' of mercury diminishes (Stewart et al., in press) Elimination of mercury via the feathers accounted for over 60% of the total loss from the body during the autumn molt of Bonaparte's gull (Braune and Gaskin, 1987). Additional but minor excretion of mercury also takes place via the feather sheaths (Burger and Gochfeld, 1992). The role of the bird's plumage as major pathway for elimination of mercury has been tested experimentally. About 50% of the intake was shed into the growing feathers of black-headed gull *Larus ridibundus* and Cory's shearwater chicks dosed orally with methylmercury (Lewis and Furness, 1991; Monteiro, unpubl. data). The excretion of mercury via the feces was about 22% of the intake in black-headed gull chicks (Lewis and Furness, 1991).

Egg laying has been postulated (Becker, 1992) to be a significant elimination route for mercury in females (seabird clutches may represent from 15% in single egg clutches to over 50% of female body weight in three egg clutches). Evidence on the quantity eliminated is conflicting and it might be that it is more important in species with higher mercury burdens or laying multi-egg clutches than in species with low mercury burdens or laying a single egg. In some species the amount of mercury transferred to the single egg is small compared to the female's body-burden, and the removal of mercury through the clutch has been thought to be negligible (Honda et al., 1986b). However, recent work has shown that excretion of mercury into the eggs can be fairly substantial in some species with multi-egg clutches (Becker, 1992; Lewis, 1991)

and female herring gulls *Larus argentatus* apparently eliminated nearly 20% more of their body burden than did males (Lewis et al., 1993). This study also found feather mercury levels of female herring gull to be unrelated to levels found in their eggs. This implied that the sources of mercury to eggs and feathers were rather different. An important part of the accumulated body-burden of methylmercury enters the plumage during the autumn molt of the bird and therefore the feather concentration represents mercury intake during the inter-molt period and not only current exposure, whereas egg levels probably indicate mercury ingested one or two weeks prior to egg laying and therefore reflect local contamination at the breeding site (Furness, 1993).

3.2. ACCUMULATION, CHEMICAL FORM AND TOXICITY

Maximum mercury concentrations reported in various seabird tissues are usually below 10-15 μg/g in feathers (fresh weight) and liver (dry weight), and 2 μg/g (dry weight) in eggs; extremely high levels (up to 271 μg/g dw in liver and over 50 μg/g fw in feathers were reported in some procellariiforms from north and south Atlantic remote islands (Muirhead and Furness, 1988; Monteiro et al., submitted). Such species may have high mercury burdens for reasons of natural accumulation or detoxification processes unrelated to pollution, although the contribution of global transport of this metal cannot be ignored. Mercury levels vary enormously both within and between species, and present greater variation than levels of essential metals (Thompson, 1990). Furthermore, the distribution of mercury concentrations within seabird tissue samples tends to be skewed with several high levels, differing markedly from a Gaussian distribution. These findings are consistent with mercury accumulation rather than metabolic regulation (Thompson, 1990).

The form of mercury in seabird tissues has received little attention. Almost all studies deal with total mercury levels (and for simplification total mercury will be designated just as 'mercury' in the following pages). Recent work on the relative proportion of organic and inorganic mercury in liver tissue of seabirds has revealed that the ratio of organic to total mercury varies from 20 to 100% among individuals of south polar skua *Catharacta maccormicki* (Norheim, 1987) and average ratios varied from 3 to 100% in 12 seabird species (Thompson and Furness, 1989a). Both studies found a strong negative correlation between the percentage of organic mercury and the concentration of total mercury. Since most of the mercury in the diet is organic this result suggests the existence of eliminatory mechanisms and detoxifying process in the liver not described yet. In blood, kidney, muscle and egg, mercury accumulates mainly in the organic form (Thompson and Furness, 1989a); in the egg mercury accumulates principally in the white proteins, where is associated with the ovalbumin fraction (Magat and Sell, 1979). Mercury is virtually 100% organic in the feathers where it strongly binds to the disulfide linkages within the keratin molecule (Crewther et al., 1965; Thompson and Furness, 1989b) .

The high levels of mercury found in some seabirds raise questions about its potential toxicity to those species, since they are in the range that would cause toxic effects in terrestrial bird species (Nisbet, 1993) and above the exposure thresholds for initial effects in humans. It is known that the major toxic effect of methylmercury

ingestion in birds is a decreased hatchability due to early embryonic mortality and an increased number of unfertilized eggs (Scheuhammer, 1987). Moreover, mercury and cadmium in kidney tissue have been identified as the cause of lesions in some seabird species (Nicholson and Osborn, 1983). However, recent studies failed to find kidney and liver damage associated with elevated levels of mercury and other heavy metals in Canadian seabirds (Elliot et al., 1992) and have not found effects of mercury on egg-shell quality or hatching success of common terns from an estuary heavily polluted by mercury and other chemicals (Becker et al., 1993b) or in the reproductive performance of great skuas *Catharacta skua* (Thompson et al., 1991).

The absence of any apparent detrimental effects of mercury in seabirds that show high levels, tends to suggest that such levels are natural and the species have evolved to cope with them. Demethylation taking place in target organs (e.g. liver) and co-accumulation of selenium in tissues are protective mechanisms against mercury toxicity in birds and marine mammals (Cuvin-Aralar and Furness, 1991; Pelletier, 1986). Scheuhammer (1987) also suggested that mercury transfer to eggs and the resultant toxic effects may be species-specific. In particular, eggs from fish-eating birds may be more tolerant of mercury pollution than those of non-piscivorous species. For example, in mallard *Anas platyrhynchos* reproductive dysfunctions were seen at levels of 6-9 μg/g of mercury in the egg (Heinz, 1974) whereas levels of 2-16 μg/g found in the eggs of herring gulls had no effect on hatching and fledging (Vermeer and Peakall, 1977).

3.3. CONCENTRATIONS IN TISSUES AND THEIR INTERRELATIONSHIPS

Mercury concentrations (Hg) in seabird tissues may be determined in fresh or dehydrated samples and consequently they were reported in the literature both in fresh weight (Hg_{fw}) and in dry weight (Hg_{dw}) terms. Providing that the fraction of moisture (M, <1) in the samples is known, the inter-conversion of concentrations is possible through the equation: $Hg_{fw}=Hg_{dw}(1-M)$. The use of dry tissue samples for determination of mercury levels is preferable to the use of fresh samples, since it eliminates errors associated with the impossibility of achieving consistency in the wetness of tissues. Most studies report concentrations in soft tissues in a dry weight basis without indication of the moisture fraction, which complicates comparisons with results reported in a fresh weight basis. Typical values of moisture in seabird tissues obtained by dehydration of fresh samples to a constant weight at 50°C were 0.70 in liver and muscle, 0.75 in the kidney and whole egg, and 0.78 in blood (Monteiro, unpubl. data). Consistent dry weights were virtually impossible to achieve in feathers presumably due to immediate reabsorption of moisture in ambient laboratory conditions. Thus, concentrations in feathers are normally reported in fresh weight basis and when reported in dry weight basis probably just mean 'dried at ambient laboratory temperature'.

Mercury concentrations (fresh weight) show important variations between tissues of adult seabirds (Thompson, 1990). Feathers present higher concentrations than internal tissues, with levels varying from below detection limits up to about 50 μg/g. Among internal tissues the highest concentrations tend to occur in liver and, in

descending order, kidney, muscle and eggs. Mercury levels in blood of seabirds remain poorly known but tend to be higher than in eggs (Monteiro, unpubl. data).

Many studies have demonstrated significant positive inter-tissue correlations of mercury levels, either between soft tissues (liver, kidney and muscle) or between feathers and tissues. One goal of the multi-tissue studies is to determine which single tissue would provide the best estimate of levels in other tissues. Liver featured prominently in this respect, as it generally presents strong positive correlations with other soft tissues, especially kidney (Muirhead and Furness, 1988). Feathers and eggs were also included in analysis of tissue intercorrelations as a mean of predicting internal tissue mercury contamination on the basis of easy collectable samples. Mercury levels in feathers were positively correlated with those of the internal tissues in several species, and levels in eggs were also correlated with those of female liver in herring gull (Lewis et al., 1993). Blood samples offer a relevant but unexplored potential in assessing internal mercury burdens of birds.

The inter-tissue correlations led several authors to determine conversion factors ('ratios') relating mercury concentrations in different tissues (Westermark et al., 1975) Indeed, a ratio of '7:3:1' for mercury concentrations (fresh weight) in feathers, liver and muscle has been used to convert mercury concentrations measured in one tissue, to estimate levels in another (Appelquist et al., 1985; Berg et al., 1966). However, the validity of conversion ratios is limited and apparently there are no general ratios suitable for inter-tissue comparisons of mercury concentrations (Thompson et al., 1990). This derives from confounding factors like the predominant form of mercury present in the liver tissue, sampling date relative to the stage of molt sequence and types of feather used for analysis (see below) which seriously affect the ratios' values.

3.4. FACTORS CAUSING VARIABILITY OF MERCURY CONCENTRATIONS

3.4.1. Inter-specific factors

Variations in mercury concentrations between bird species potentially reflect many factors, including feeding and migratory habits, body size, life span, molt strategy and taxonomic influences on physiology (Walsh, 1990).

There is a tendency for mercury concentrations to be highest in species feeding on fish (or on other seabirds) (Braune, 1987). However, when one compares mercury levels among predominantly fish-eating species, levels apparently do not show clear patterns or any evident association with diet composition (Elliot et al., 1992). Particularly high concentrations have been found in some species of procellariiforms (Muirhead and Furness, 1988). Slow molt patterns were indicated as a major reason for the elevated mercury levels in internal tissues and feathers of some large albatrosses. However, small procellariiforms with annual molt cycles also exhibit such enhanced mercury levels and these might be related with particularities of the metal dynamics within this taxonomic group (Monteiro et al., submitted).

3.4.2. INTRA-SPECIFIC FACTORS

The reported variations of mercury concentrations in specific target tissues within bird species potentially reflect the effects of factors like molt, age, sex, season and laying sequence.

MOLT. Mercury concentrations present great variations between and within feather types of individual adult birds. This variability is largely due to molt since levels correlate well with their relative position in a given molt sequence, the first-molted feathers having higher mercury concentrations; as the molt progresses, mercury concentrations decrease as they converge toward a minimum level for each tissue (Furness et al., 1986). This pattern is most strikingly shown by the tendency for a general asymptotic decline of levels along such feather sequences as the primaries, corresponding to the order in which feathers have been renewed. Thus comparisons between studies are greatly complicated unless feathers from a similar position in the molt sequence are analyzed. Body feathers present less variation in mercury concentrations than do flight feathers and allow comparability between different studies (Furness et al., 1986).

AGE. As adult birds can only be aged accurately by means of a unique and durable identification marker, there are relatively few bird populations with a large number of individuals marked in this way and investigations into age-related changes in mercury concentrations in adult seabirds have been few in number and limited to the study of levels in feathers. In all of them (a gull, three species of albatrosses, a skua and a tern), it was unequivocally found that mercury in body feathers did not accumulate with adult age (Burger et al., submitted; Furness et al., 1990; Thompson et al., 1991, 1993b). This finding is a remarkable exception to the general pattern of age/size bioaccumulation of mercury in other marine vertebrates (Thompson, 1990). This might be a consequence of a peculiar mercury dynamic among birds that is based mainly on a balance between the metal dietary intake and the elimination to the plumage during the annual molt. The seasonal lowering of mercury in internal tissues after molt observed in a variety of seabirds (see below) supports this hypothesis.

The few reported results on age-related variation of mercury levels in chick plumage are contradictory. Levels were found to be independent of age in great skua chicks (Thompson et al., 1991), but increased with age of common tern chicks from polluted areas (Becker et al., 1993a). Conversely, mercury concentrations in the plumage of chicks (over a wide range of body size) from several seabird species from the Azores are negatively correlated with their age (Monteiro et al., submitted); levels in breast feathers of nearly fledged common tern and Cory's shearwater chicks were respectively 60 and 80% lower than those in down of hatchlings of the same species (Fig. 2).

The period from hatching to fledging is characterized by a high growth rate and a high rate of protein synthesis and this may lead to differences in the handling of mercury by growing chicks (Jugo, 1977; Lewis, 1991). The decrease of plumage mercury levels with chicks' age might be a natural pattern deriving from the lowering of mercury inputs to plumage due to metal dilution to growing internal tissues. Such 'growth dilution effect' is reflected in important variations of levels between the early down and the final

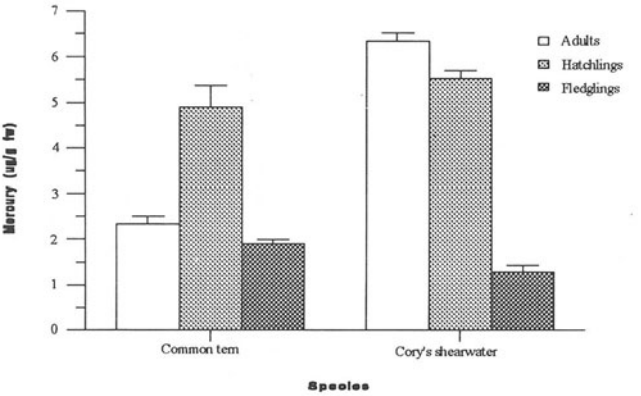

Fig. 2. Variation of mercury levels (mean ±s e , µg/g fresh wt) between breast feathers of adult, down of hatchlings and body feathers of fledglings for Common tern *Sterna hirundo* and Cory's shearwater *Calonectris diomedea* from the Azores

plumage (see Fig 2) and might be masked in most polluted environments by the enhanced introduction of mercury into the young from contaminated food, leading to increases with age

Plumage mercury levels tend to be lower in chicks than in adults and reported adult chick ratios fall between 1 2-5 9 (Furness et al , 1990, Monteiro et al , submitted) Variability of adult chick ratios is partially explained by the influence of chick age in plumage mercury concentrations and whether levels in adult body feathers were compared with levels in down or well-grown feathers of their young Nevertheless, adult young mercury level ratios appear to be taxonomic- and species-specific, for example the adult(body feather) hatchling(down) ratio is about 1 in Cory's shearwater and other procellariiforms, while in larids it varies from about 0 5 in common tern and roseate tern *Sterna dougallii* to over 2 in herring gull (Monteiro, unpubl data)

Mercury concentrations in soft tissues were higher in adults than young common murres *Uria aalge* (Stewart et al , in press) and several species of herons and egrets (Hoffman and Curnow, 1979) This might be a natural pattern, entirely expected due to the longer exposure time available to older birds However, this is contradicted by two field studies with common terns breeding in North-east American coast, mercury levels were found to be identical in liver of adults and chicks (Gochfeld and Burger, 1987) and higher in breast feathers of fledglings than in adults (Burger et al , submitted) Such findings emphasize the need of further study for the elucidation of age-class variations in mercury levels in seabird tissues

Sex Reproductive processes could lead to differences in mercury dynamics between male and female seabirds One might predict mercury levels to fluctuate over the breeding season in females and tend to be higher in males, as egg production offers an additional route by which females may eliminate mercury from the body (see above)

Mercury concentrations in body feathers did not differ between sexes in adult red-billed gull *Larus novaehollandiae* (Furness et al., 1990), great skua (Thompson et al., 1991) and herring gull (Lewis et al., 1993). However, mercury levels were slightly but significantly lower in female than male in body feathers of common murre (Stewart et al., in press), primary 1 of herring gull (Lewis et al., 1993) and in primaries 1 to 5 of Bonaparte's gull (Braune and gaskin, 1987). A study of mercury accumulation in internal tissues of common murres found no sex differences of mercury loads in liver, kidney and muscle (Stewart et al., in press). Also levels in liver and muscle of breeding herring gulls were independent of sex (Lewis et al., 1993) and tissue concentrations of female Bonaparte's gulls were not consistently lower than those of males (Braune and Gaskin, 1987).

Concluding, the current evidence for inter-sex variation of mercury levels in seabird tissues is limited to slight lowering of levels in particular feather types in female of some species. The little or null difference in mercury burdens between male and female seabirds apparently suggests that the clutch is relatively unimportant as a mercury sink; for example, the amount of mercury shed by female herring gulls in their clutch (73 μg) is less than 20% of the amount that they put into feathers during molt (404 μg) (Lewis et al., 1993).

SEASON. Seasonal variation of mercury levels in seabird tissues can be considerable and might derive from two major factors, namely physiological process related to breeding and molt, and seasonal dietary changes. Although there is an extensive literature describing mercury levels in seabirds, few papers examined seasonal variations in metal burdens and concentrations within and between populations. In particular, variation in mercury concentrations in soft tissues has to be considered as they may change in mass and composition throughout the breeding period and mercury excretion occurs into eggs and growing feathers.

Mercury loads and concentrations in tissues are highest before molt and a decline in tissue mercury levels associated with feather growth has been demonstrated in several species. The body burden of mercury (excluding plumage) declined by 60% in adult Bonaparte's gulls during the fall molt (Braune and Gaskin, 1987). The mercury burden in liver and kidney of common murres collected at three stages in the breeding season (April, pre-laying; June, post-laying; November, post-molt) declined about 80% for adults and 60% for juveniles between the beginning of the breeding season and the post-molt period. Mercury concentrations in body feathers of the same common murres exhibited no significant seasonal trend, as would be expected since these are renewed only once per year (Stewart et al., in press).

There is a single reported case of seasonal variation of mercury levels in bird feathers. Mercury concentrations in body feathers of Madeiran storm petrel *Oceanodroma castro* showed important seasonal differences and led to the identification of two seasonally distinct breeding populations of this species in the Azores (Monteiro et al., submitted). Spring breeders have mercury levels about 50% lower than fall breeders. Such striking differences in mercury levels between the two populations may reflect different mercury exposure via diet in the breeding or in the post-breeding grounds,

coupled with higher prey consumption and associated enhanced mercury intake in fall breeders, due to higher energetic expenditure in the colder months.

LAYING SEQUENCE. Recent investigations of intra-clutch variation in mercury concentrations of three charadriiform-species revealed the existence of significant declines in levels with the laying sequence in two species (Becker, 1992). The decrease in mercury levels from the first to the last laid egg almost reached 40% in herring gull and common tern clutches. This indicates that female gulls and terns lower their body burden progressively through deposition of mercury in the eggs.

4. Seabirds as Monitors

4.1. SUITABILITY

Current biomonitoring of aquatic environments tends to emphasize the use of sedentary invertebrate animals as target species. By comparison, birds suffer from several apparent drawbacks. They are mobile, so pollutants will be picked up from a wide area, they are long-lived, so pollutant burdens may be integrated in some complex way over time; and they have more complex physiology, and so may regulate pollutant levels better than invertebrates. Furthermore, birds tend to be more difficult to sample, and killing birds may be unacceptable for conservation or ethical reasons. However, some of these characteristics may at times be advantageous. Integrating pollutant levels over greater areas or time-scales or over food webs, may be useful, provided that species are chosen carefully. Less sampling may be necessary if birds can reflect pollutant levels in the whole ecosystem or over a broad area. In addition, since they are high in the food chains, birds may reflect pollutant hazards to humans better than do most invertebrates.

Seabirds in particular offer a number of advantages as indicators of mercury contamination in the marine environment. They are numerous, colonial, and the ecology of most species is well known. Seabird foraging areas range from restricted to wide according to the species and time relative to the annual cycle, and so seabirds may average out ('integrate') from very localized and short-term to meso-scale and long-term variations of mercury levels in the marine environment.

Mercury concentrations in eggs and body tissues of seabirds have been analyzed frequently since the mid 1960s and there is a growing database of mercury levels in populations from coastal polluted areas and populations remote from sources of localized pollution, particularly in the northern hemisphere.

4.2. DOSE-RESPONSE RELATIONSHIPS

The use of seabirds as mercury monitors depends on the assumption that environmental variations will be reflected in levels of mercury in tissues. This assumption has not, however, received, as much scrunity in seabirds as in the case of other proposed marine

biological indicators. At the very least, tissue concentrations should reflect dietary uptake of mercury.

It is documented for poultry and captive non-seabird species that increased dietary doses of methylmercury are reflected in increased tissue concentrations (Heinz, 1974; March et al., 1983) but this was only recently experimentally tested in a seabird. A study with laboratory reared black-headed gull chicks (Lewis and Furness, 1991) showed that feathers and soft tissues incorporate levels of dietary methylmercury in a dose-dependent fashion and the dose-tissue level relationship observed was linear.

The existing experimental studies with poultry, non-seabirds and seabird chicks allows some analogy with natural rates of mercury uptake by adult seabirds, but for a coherent picture a critical appraisal of multi-tissue (e.g. blood, feather and eggs) dose-responses in free-living adults over low chronic ranges is still needed.

4.3. CHOICE OF SPECIES

The requirements of an ideal seabird monitor of mercury pollution were discussed by Walsh (1990). It should be resident within a restricted radius of its breeding colony throughout the year. Its diet should be well known and should show no systematic variation between sampling locations; species feeding on a few prey species are particularly suitable (but the possibility that seasonal movements of prey species could affect metal levels should be noted). Furthermore, reliability of mercury analyses, and ability to discriminate environmental variation, will be improved if the seabird species, or their prey, tend to accumulate relatively high tissue concentrations. The seabird species should also be relatively common and accessible, and sufficiently widespread to provide good coverage of the proposed region monitored for geographical variation. Most seabirds meet only some of the above criteria. However, for many species, diet, seasonal movements and molt are reasonably well known, so some allowance can be made for influences of these variables.

Since different species tend to feed at varying distances from land, it is possible in theory to select species that will reflect metal levels in either inshore or offshore waters. Inferences about environmental variations in metal levels based on tissue analyses of different species are therefore open to question, though inter-specific comparisons may shed light on relative metal loads in different food chains. Apparent tendencies for particular taxonomic or ecological groups to accumulate high levels of mercury may also recommend suitable indicator species.

Procellariiforms (e.g., albatrosses, shearwaters and petrels) are pelagic and accumulate relatively high levels of mercury in their tissues; therefore, they have improved ability to discriminate environmental variation in contaminant levels of oceanic food chains and are suitable indicators for monitoring mercury in the oceanic environments where they breed and forage. On the other hand, the larids (e.g. terns and gulls) and the alcids (e.g. auks, puffins and murres) are better for monitoring mercury in coastal environments, with the common tern (Becker, 1991) qualifying as one of the most suitable monitors due to its wide distribution in the Northern hemisphere and its relative abundance.

4.4. CHOICE OF MONITORING UNIT

Mercury, like other heavy metals, tends to be held in a few particular tissues at much higher levels than in others (see above). This site-specificity of mercury has an important influence on the choice of tissue for monitoring studies. Tissues that tend to accumulate high concentrations are often considered 'good' indicators of metal uptake from the environment. Tissues tending to have low concentrations could still reflect environmental variations, but analytical difficulties may be encountered. Also, such low concentrations might derive from a saturation of metal-accumulatory ability in the tissue. It is sometimes possible to choose a specific tissue to reflect either long-term or recent exposure.

Mercury levels in tissues of juvenile birds are generally less than found in tissues of adults. It is therefore important to sample either from juveniles or adults but not from a mixture of these classes.

4.4.1. Internal tissues

Most studies of mercury in seabirds have used internal soft tissues and liver in particular. However, soft tissues have a number of drawbacks, including seasonal changes in mass and mobilization to the plumage (see above), which can alter perceived metal concentrations even though the total amount in the body is unchanged. Thus mercury concentrations in soft tissues should always be considered in relation to timing of molt and soft-tissue comparisons between populations of adult seabirds are thus ideally based on samples collected immediately before molt, when mercury concentrations are highest and least variable.

For ethical and practical reasons it is important to develop other sampling methods that avoid the need to kill large numbers of birds in order to provide tissues for analysis.

4.4.2. Blood

Blood samples provide a picture of metal levels that reflect short-term exposure (immediate dietary intake) and physiological factors (such as mobilization of reserves for egg production, or increased blood volume at the start of molt). If birds can be caught safely, sampling blood is comparatively easy and does not require that the bird is killed; but this has not been developed far in studies of mercury contamination.

4.4.3. Eggs

The avian egg has been used extensively to monitor mercury as it has several advantages over internal tissues (for reviews see Lewis et al., 1992 and Furness, 1993). Eggs have a highly consistent composition (unlike other internal tissues) and in some cases have been shown to reflect mercury uptake from local foraging more closely than the tissues from adult birds (Barret et al., 1985). They are produced by a clearly identified segment of the population, adult females, although this can be a disadvantage as it precludes sampling from other members. Sampling eggs takes little time, they are easy to handle and they can be readily sampled from the same location each year. They can be collected with

little interference and their removal places less of a drain on the population than the sampling of adults, especially if only one egg is removed from each clutch. When sampling for monitoring studies, eggs should be taken at the same position in the order of laying from each of the clutches to avoid intra-clutch variance. Water loss during incubation and storage might influence concentrations in the egg contents (Stickel et al., 1973); but this can be circumvented if dry weights were used when presenting contamination levels and therefore would allow standardization of published egg data.

Eggs do have some limitations. Mercury in eggs possibly represents dietary uptake in a short period before the egg is laid and so cannot be used to investigate mercury burdens acquired at other times of the year. Unlike feather samples, egg contents are not available from before about 1980, so that historical changes in mercury levels in marine ecosystems cannot be traced from egg contents.

4.4.4. Feathers

Sampling of feathers is an attractive alternative to collecting internal tissues and eggs. Feathers can be removed from live birds with virtually no effect on the birds sampled, especially if body feathers are taken. Feathers can be stored without being frozen, so the logistics of sampling from remote populations are much simpler than with tissue or egg collections. Museums contain large numbers of study skins of birds with data on the date and place of collection. Thus feathers provide an attractive mean of studying historical changes and synoptic geographical patterns in mercury burdens (Thompson et al., 1992a, 1993b).

Detailed research has been done to assess the use of feathers to monitor levels of mercury pollution. It has been demonstrated experimentally that mercury in feathers is strongly bonded and levels are not affected by storage or by vigorous treatments (Appelquist et al., 1984). It has been shown that heavy metals (e.g. cadmium) may be deposited onto the surface of feathers in quantities that mask patterns due to incorporation of dietary or stored metals into feathers during molt (Hahn, 1991). However, mercury is a special case in that atmospheric deposition (as inorganic mercury) appears to be unimportant (Lewis, 1991) and all of that incorporated into feathers from dietary sources is methylmercury (Thompson and Furness, 1989b). So, problems of contamination due to atmospheric deposition or the application of inorganic mercury to museum skins as a preservative were overcome by determining just the organic fraction.

Feathers may have some disadvantages as monitoring units. Mercury concentrations present great variation among feathers of individual adult birds largely due to molt (see above), but such molt effect can be minimized by pooling several small body feathers from a defined plumage area (Furness et al., 1986).

The use of migratory species as monitors apparently poses problems to the interpretation of mercury levels in feathers as they might reflect both exposures to mercury in breeding and wintering grounds. However, it is thought that mercury intake during the breeding period is largely responsible for mercury concentrations in feathers of seabirds with long breeding seasons like procellariiforms (Monteiro et al., submitted), while mercury intake in wintering grounds may play a greater role in determining levels in feathers and tissues of species with short breeding seasons like terns (Burger et al., 1992a).

4.4.5. Chicks

Many of the limitations in using eggs or adult bird tissues as monitoring units are less of a problem if chicks are sampled. Chick body burdens of mercury reflect the amounts in the food they are fed during their development and are thus attributable to intake from a clearly defined time period and limited parental foraging area. There may be a slight complication in accounting for the dose present in the egg but this is likely to be a negligible proportion of the total burden in well-grown chicks, since egg mass represents only about 2-8% of the body mass of fully grown chicks. Furthermore, the chick may be the stage of development at which toxicological effects are particularly evident.

The existence of important age-related variation of mercury levels in chick tissues (which can be dramatic between different developmental stages) implies the need to control for chicks' age or body size in the design of monitoring studies. Mercury burdens in hatchlings tend to reflect burdens in eggs (Becker et al., 1993a); thus sampling of their plumage (i.e. down) is an interesting alternative to egg collection, very little explored, and sample sizes can be greater with less damage to the population. Mercury levels in pre-fledglings tend to be less variable than in adults: chicks tend to be fed on a selected diet of energy-rich foods; dietary specializations of adults are averaged between two parents for species where both parents fed the young; and metal burden is obtained only from a narrow period of chick growth and from foods near the breeding site. As a result, and because all feather types were grown almost simultaneously, mercury levels in the plumage of pre-fledglings are fairly homogeneous (Lewis, 1991). Thus sampling of their feathers is an interesting alternative to sampling of adult feathers.

4.5. CURRENT EVIDENCE FOR ENVIRONMENTAL CHANGE

4.5.1. GEOGRAPHICAL VARIATIONS

Striking patterns of geographical variation are evident from studies of mercury in common murre eggs. They are a fairly sedentary species and have a narrow food range. Eggs collected from 16 colonies around Great Britain and Ireland in the early 1970s showed a 20-fold variation in the mean mercury concentration with the lowest levels (0.8-1.9 μg/g dw) from north-west Scotland to north-east England but markedly higher levels (1.9-4.9 μg/g dw) at five Irish Sea colonies (Parslow and Jefferies, 1975). This is presumably connected with the slow rate of water exchange in the shallow Irish Sea as well as the larger amounts of industrial waste and effluent it receives.

Geographical variations in mercury levels along the German North Sea coast have also been demonstrated using eggs. Herring gull and common tern eggs from seven regions averaged 0.2-0.5 μg/g fw and 0.3-0.7 μg/g fw respectively, except for pronounced peaks of 1.6 and 4.6 μg/g fw at the Elbe estuary, where there is a particular high industrial discharge (Becker, 1989).

Mercury levels in the Mediterranean, from both natural and manmade sources, are high and this is reflected in birds' eggs and soft tissues. Mercury concentrations in eggs, liver, kidney and muscle of Cory's shearwaters breeding in the Mediterranean were

consistently higher than at Atlantic colonies (Renzoni et al., 1986), despite the fact that both populations winter in the Atlantic (Mougin et al., 1988). Herring gulls in the Mediterranean also have higher mercury levels than found in gulls from the Atlantic or North Sea (Focardi et al., 1988; Lewis et al., 1993).

Studies of baseline levels in body feathers have multiplied in recent years (Burger and Gochfeld, 1991; Burger et al., 1992b; Thompson et al., 1992b; Lock et al., 1992; Monteiro et al., submitted). As consequence, there is a growing database of mercury levels in seabird populations that offers promising perspectives for extensive comparisons of geographical, historical and global patterns of mercury pollution within the marine environment in the near future.

4.5.2. HISTORICAL CHANGES

Studies with time series of feather samples from bird populations have demonstrated increased environmental mercury pollution both locally and at a more global scale. The first studies were carried out in Scandinavia after the discovery that the use of alkylmercury-treated seed was resulting in serious contamination of wildlife and mortality of top predators. Berg et al. (1966) showed that mercury levels in predatory birds, especially fish-eaters, had increased several-fold between the 1950s and 1960s. Many of these early studies analyzed total mercury levels in flight feathers (primaries and tail) and then retrospectively excluded from their data sets individual measurements that appeared to be elevated as a result of plumage contamination with inorganic mercury during storage. Such a procedure carries with it the possibility of generating desired patterns through selection of data, although in this case the changes were dramatic and unambiguous.

Studies of total mercury levels in time series of feathers from murres and black guillemots (Appelquist et al., 1985) showed that mercury levels had increased, especially in populations from the Baltic Sea, between around 1900 and the period 1960-1975. This was attributed to the increased use of mercury seed dressings in Scandinavian countries in the 1960s, because levels in populations of these species from Atlantic areas showed smaller increases over the same period. These authors measured total mercury levels in feathers (the distal part of individual primary five) by neutron activation analysis. Many museum collections are contaminated with inorganic mercury, which was often used as a preservative on nineteenth-century study skins, and so it is preferable to use methods that measure only the organic mercury level (see section 3.4.4).

Analysis of organic mercury levels in body feathers of adult seabirds collected in breeding colonies of the British Isles between 1830 and 1990, revealed a widespread increase (2 to 4 times) in mercury concentrations over the past 100 years. This trend was interpreted as a consequence of airborne pollution related to mesoscale transport and wet deposition of mercury (Thompson et al., 1992a). A similar study with seabirds from the southern hemisphere provided evidence for little increase in mercury contamination during this century (Thompson et al., 1993b). Levels of organic mercury in feathers of seabirds from the German North Sea fluctuated over the last century in relation to major variations in regional riverborne mercury pollution (Thompson et al., 1993a). Levels in body feathers of herring gulls showed low levels in the period 1830-1930 (3.8 μg/g), a pronounced and short-lived peak of levels in the 1940s (12.1 μg/g), a drop in the 1950s

to a level somewhat higher than pre-1940 (6.9 μg/g), followed by an increase from the 1950s to the 1970s (10.1 μg/g) and a decrease in the 1980s (5.4 μg/g). These changes can best be explained by a lack of discharge controls in Germany during the 1939-1945 war, increased industrial production through the 1950s to 1970s and then greater control of pollution discharges in the 1980s, resulting in changes in the amount of mercury entering the North Sea estuaries from the major European rivers.

These long-term historical comparisons of mercury levels using feathers from museum skins are only useful if the observed changes reflect changes in mercury pollution of the ecosystem. This likely to be true in most cases but it does rely upon the assumption that the diet of the bird has remained the same over the time period. If a population changes diet then it is likely that the mercury burdens in the birds will alter because different prey species may contain different mercury levels. In order to interpret long-term changes in mercury levels in bird feathers, it is preferable to select species that have narrow and inflexible diets, rather than generalist feeders, and best to consider trends in a variety of species feeding on different prey within the same environment. A further test of the assumption of no change in diet over time could be made by measuring stable isotope ratios of carbon, nitrogen and possibly other elements (Furness, 1993). The ratios of isotopes change through the food chain, with slight isotope fractioning at each step in the food chain, so that changes in trophic levels are reflected by changes in the ratios of isotopes. This can be used to investigate the feeding relationship of birds, even of extinct ones (Holson and Montevecchi, 1991). Since feathers can be used for analysis of stable isotope ratios as well as for mercury analysis, it would be possible to perform isotope ratio studies on the same museum samples used for mercury determinations.

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COMMON LOONS (*Gavia immer*) NESTING ON LOW pH LAKES IN NORTHERN WISCONSIN HAVE ELEVATED BLOOD MERCURY CONTENT

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Abstract. The Wisconsin Department of Natural Resources conducted a pilot study during the summer of 1991 to determine the extent of mercury (Hg) exposure in common loons (Gavia immer) breeding in Wisconsin. Loons are at risk to elevated Hg exposure in Wisconsin because they often nest on acidified, low alkalinity lakes. Fish from these lakes bioaccumulate MeHg to a greater extent than biota from neutral pH lakes. Using nightlighting techniques, 35 adult loons were captured on 20 northern Wisconsin lakes (pH=5.0-8.7) in 1991. Blood and feather samples were collected for Hg analysis. The mean Hg content of blood cells collected from adult loons on low pH lakes ($pH \leq 6.3$) was significantly greater than the Hg content of adult loons collected on neutral/alkaline pH lakes ($pH \geq 7.0$) ($F=19.87$, $P<0.001$). There was a highly significant negative linear relationship between adult loon blood cell Hg concentrations and lake pH ($r^2=0.38$, $F=15.27$, $P<0.001$); indicating loons nesting on low pH lakes receive greater Hg exposure than loons nesting on neutral pH lakes. The relationship was greater amongst adult males ($r^2=0.56$) than amongst adult females ($r^2=0.36$). Because of this documented exposure, an additional 330 loons were captured 1992-94 on 73 lakes in northern Wisconsin. The Hg exposure of adult and juvenile common loons is being quantified. Individual loons were fitted with unique color-coded leg bands, and the 1992-96 reproductive performance, annual return rates, and nesting behavior of adult loons with the known Hg exposure is currently being assessed.

1. Introduction

Most point sources of mercury (Hg) contamination have been identified and controlled in the United States, however Hg contamination persists. Elevated concentrations of Hg continue to be documented in aquatic biota from remote regions of Scandinavia and North America; the most seriously impacted U.S. and Canadian lakes are found in Minnesota, Michigan, Wisconsin, Florida, Ontario, and Quebec (Swain *et al.*, 1992). Many lakes in these states contain fish with Hg levels that pose health risks for human consumption. A mass balance study of Hg in aquatic systems indicates that significant portion of the Hg found in these fish is of atmospheric and anthropogenic origin (Rada *et al.*, 1989). An analysis of lake sediment cores in Minnesota and Wisconsin indicates that the current rate of Hg deposition is 3 to 4x greater than it was in the 1800s (Swain *et al.*, 1992); important deposition sources are fossil fuel combustion, municipal waste incineration, and industrial processes. Aquatic biota from low pH, low alkalinity lakes receiving increased Hg deposition are more likely to bioaccumulate Hg than biota from neutral/alkaline pH lakes. This is reflected in the strong inverse relationship between the pH and alkalinity of lakes in northern Wisconsin and the Hg content of piscivorous fish (Cope *et al.*, 1990; Lathrop *et al.*, 1989). A complex suite of factors contribute to Hg biomagnification in the food web of low pH lakes. Most important are a net increase in the amount of Hg methylated by sediment bacteria (the form of Hg which is toxic and bioaccumulates) and an increased permeability of fish tissue to MeHg absorption (Winfrey and Rudd, 1990). Because of the highly toxic effects of MeHg, concern has been expressed that piscivorous wildlife inhabiting low pH lakes may be exposed to toxic levels of MeHg in their prey (Wiener, 1987; Scheuhammer, 1991).

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The low pH, low alkalinity lakes of northern Wisconsin are important nesting habitat of the common loon (Gavia immer) (Blair, 1990; WDNR unpubl. data). Loons are top predators on these lakes, consuming primarily 10 to 250 g fish, thus are at risk to increased Hg exposure. There is evidence that increased Hg exposure can reduce common loon reproduction. Impaired common loon productivity was related to the consumption of Hg-contaminated prey in Ontario, Canada (Fimreite, 1974; Barr, 1986). Fimreite (1974) observed that common loon chicks were absent along Hg-contaminated reaches of that river system, while Barr (1986) found that loons which nested on Hg-contaminated English River system lakes had lower nest success than did loons nesting on lakes with low levels of Hg in prey items. Barr (1986) indicated that reductions in egg laying and territorial fidelity were associated with mean prey (10 to 250g fish) Hg concentrations of 0.3 to 0.4 ug/g fresh weight (fw).

There is evidence that Wisconsin loons may consume prey with levels of Hg which could impair reproduction. Loons typically consume fish which weigh 10 to 250 grams (Barr, 1986). At least two fish within this size class were analyzed for Hg by the Wisconsin Department of Natural Resources (WDNR) Fish Contaminant monitoring program on seventy five lakes in northern Wisconsin. Fish from 36% of those surveyed (27 lakes) had Hg concentrations in excess of 0.3 ug/g (fw) (WDNR unpubl. data), the level associated with loon reproductive impairment in Ontario (Barr, 1986). In addition, the total Hg content (fw) of livers of 3 loons collected on low pH lakes (pH <6.3) in northern Wisconsin [31 ug Hg/g (fw), Minonk Lake, Vilas Co; 90 ug Hg/g (fw), North Bass L., Iron Co.; and 33 ug Hg/g (fw), Duck L., Iron Co. (Belant and Anderson, 1990)] all exceeded the mean Hg content of livers from loons collected on the contaminated waters of the English River system in Ontario [total liver Hg = 29.7 ± 12.4 ug Hg/g (fw); Barr 1986].

In 1991, the WDNR Bureau of Research, Sigurd Olson Environmental Institute, and Whitefish Point Bird Observatory undertook a pilot study to investigate whether fish Hg contamination poses a health risk to loons nesting in Wisconsin. Common loon Hg exposure was measured on 20 northern Wisconsin lakes (pH 5.0 to 8.7) by capturing common loons and measuring the Hg content feather and blood samples.

2. Materials and Methods

The Wisconsin LoonWatch volunteer loon monitoring network and the Wisconsin DNR Master Waterbody Database were used to identify 80 study lakes (40 "high Hg", low pH lakes and 40 "low Hg" neutral/alkaline pH lakes) in Ashland, Bayfield, Iron, Vilas, Oneida, and Forest counties in northern Wisconsin. This regions represents the "core" of Wisconsin's breeding loon population estimated at approximately 2900 adults in 1990 (Dunn, 1992). Lakes were selected which had a recent history of resident loons and had a broad range of pH (4.8 to 9.2) and alkalinity (-9 to 950 ueq/L). The study lakes were selected to block for variables such as lake size, presence/absence of islands, and shoreline development.

Study lakes were surveyed by boat 1 to 3 weeks after they were ice-free to determine whether loon breeding pair were in residence (late April to mid May). Study lakes with resident loon pair were then revisited mid June to early July to identify which territorial pair had chicks. During the month of July we captured adults and loon chicks on the study lakes. A 6-member capture

crew used 2 sport boats powered with 6 hp gas motors, spotlights, and tape-recordings of loon calls to lure the loon family to the capture boats. The loons were then netted with a salmon landing net, restrained, and transported to shore. Adult and chick secondary feathers and blood were sampled for Hg analysis. Blood was obtained using 22 gauge needles and 10 cm^3 syringes on the adults, 5 cm^3 syringes with 25 gauge needles for the chicks; 10 cm^3 was drawn from the brachial vein of the adults, 3 cm^3 from the brachial vein of the chicks (>3 weeks old). Blood was placed in orange top vacutainers, allowed to clot, then centrifuged at 4500 rpm for 10 minutes. The serum was separated from the clotted material (red blood cells and fibrin) and both portions were frozen. Captured loons were fitted with USFWS stainless steel or aluminum leg bands and were individually marked with color-coded plastic "wrap-around" leg bands glued with an acetone-based adhesive cement.

Feather and blood samples were analyzed at the Animal Health Diagnostic Laboratory at Michigan State University. Feathers, serum, and clot material (blood cells and fibrin) collected in 1991 were analyzed for trace metal and mineral content using inductively coupled argon plasma (ICP) emission spectroscopy (Jarrell Ash Polyscan 61E ICP and Jarrell Ash Model 955). We chose ICP analysis for screening samples as this study was exploratory and ICP allowed for simultaneous analysis of Hg, calcium (Ca), and selenium (Se) in a cost effective manner. While the ICP mercury detection limits were high (1 ug/g Hg), this level was known to be capable of detecting Hg in adult tissues. Feathers were washed with acetone 3 times, rinsed with doubly distilled water once, and finally rinsed once with acetone. Following washing the feather was cut into several pieces, the basal portion of the shaft below the vein was discarded. Before ICP analysis, approximately 1 g (fw) of feather or serum clot were digested with 2 ml HNO_3 in a 95°C oven overnight. Following digestion, samples were quantitatively transferred to 10 ml class A volumetric flasks containing 100 ug/g yttrium, brought to volume with water, inverted several times, then analyzed.

Chick blood samples collected in 1991 were below ICP detection levels, thus an additional 20 loon chicks were captured on 20 Wisconsin lakes in 1992. The Hg concentrations of chick whole blood samples (1 to 3 cm^3) was determined by cold vapor atomic absorption spectrophotometry (DL=0.01 ug Hg/g; Hazelton Environmental Services, Madison, WI). Whole blood was preserved with 10% formalin (1:20 ratio of formalin to blood) and refrigerated until analyzed.

The pH and acid neutralizing capacity (alkalinity) of water samples from the study lakes were also determined. Water samples were collected in clean polyethylene sample bottles with air displacement caps. Samples were refrigerated until analysis (within 4 days of collection). Alkalinity was determined using the gran titration method.

The SAS General Linear Model (PROC GLM, SAS 1982) was used to determine if the mean tissue levels of Hg differed between male and female adult loons and between adult loons sampled on low vs. neutral/alkaline pH lakes.

3. Results and Discussion

Blood and feather samples were collected from 35 adults and 30 chicks captured on 20 lakes in northern Wisconsin in 1991. The pH and alkalinity of the lakes loons were captured on ranged from 5.0 to 8.7 and -9.4 to 889.4 ueq/L respectively and were highly correlated (r=0.98, Table

I). Loon capture success was excellent (88% for adults, 95% for chicks) and injury was minimal (one adult was treated for a minor foot injury and was released; it was reobserved swimming and foraging normally one month later). In addition, 28 of the 30 captured chicks were reobserved 4 to 5 weeks after capture (93%), indicating that handling mortality was slight or none.

Table I

Water chemistry of Wisconsin lakes where loons were captured 1991.

LAKE	COUNTY	pH	ALKALINITY (ueq/L)
Wharton	Vilas	5.0	-5.4
Nineweb	Vilas	5.1	-9.4
Pincherry	Vilas	5.1	-7.0
Wabasso	Vilas	5.5	5.2
L. Bass	Vilas	5.6	5.4
Lumen	Oneida	6.0	8.9
Sugar Maple	Vilas	6.1	13.9
Imogene	Vilas	6.2	21.7
French	Iron	6.3	34.1
Bills	Vilas	6.4	24.8
Jag Lake	Vilas	6.6	34.5
Washburn	Oneida	6.7	46.6
Indian	Vilas	7.0	98.0
Razorback	Vilas	7.5	329.1
Whitefish	Oneida	7.8	637.7
Trude	Iron	7.8	616.2
Muskellunge	Oneida	8.3	544.0
L. Bearskin	Oneida	8.4	715.6
Catherine	Iron	8.4	820.0
Wilson	Iron	8.7	889.4

The samples of adult feathers and blood cells all had detectable levels of Hg, however serum did not. Hg bonds to sulphur within proteins such as keratin and cell membranes and thus is concentrated in feathers and blood cells (Crewther *et al.*, 1965). All loon chick blood samples were below ICP Hg detection limits. The mean Hg content of blood cells collected from adult loons on low pH lakes ($pH \leq 6.3$) was significantly greater than the clot Hg content of adult loons collected on neutral/alkaline pH lakes ($pH \geq 7.0$) (Table II; $F = 19.87$, $P < 0.001$). The mean male and female serum clot Hg levels were not statistically different (Table II; $F = 2.41$, $P = 0.14$). The linear relationship between adult loon blood cell Hg and lake pH was also highly significant

Table II

Feather and clotted blood cell Hg concentrations [(N) Mean (ug/g fw) ± 1SD] of Wisconsin adult common loons

		LOW pH LAKES (pH<6.3)	NEUTRAL pH LAKES (pH≥7.0)
FEATHERS	Adult males	(5) 15 ± 3	(7) 11 ± 3
	Adult females	(7) 9 ± 3	(4) 7 ± 1
	All adults	(12) 12 ± 4	(11) 9 ± 3
BLOOD CELLS	Adult males	(5) 6 ± 2	(7) 2 ± 1
	Adult females	(7) 4 ± 2	(4) 1 ± 1
	All adults	(12) 5 ± 2	(11) 2 ± 1

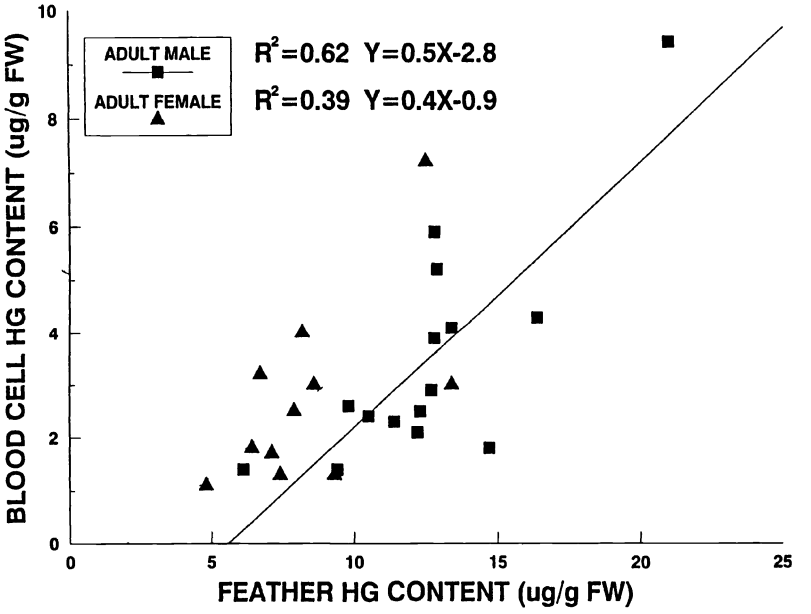


Fig. 1. Wisconsin 1991 adult common loon blood cell Hg content (fw) vs. lake pH

(Figure 1, $r^2=0.38$, $F=15.27$, $P<0.001$); and the relationship was greater amongst adult males ($r^2=0.56$) than amongst adult females ($r^2=0.36$).

Mean feather Hg concentrations were not significantly different between adult loons captured on low vs. neutral pH lakes (Table II; $F=4.02$, $P>0.05$), however males had significantly greater levels than did females (Table II; $F=10.25$, $P<0.01$). The overall linear relationship between adult feather Hg content and lake pH was not significant (Figure 2, $r^2=0.08$; $P>0.05$); however the relationship between adult male feather Hg content and lake pH (Figure 2, $r^2=0.42$; $P<0.05$) was significant.

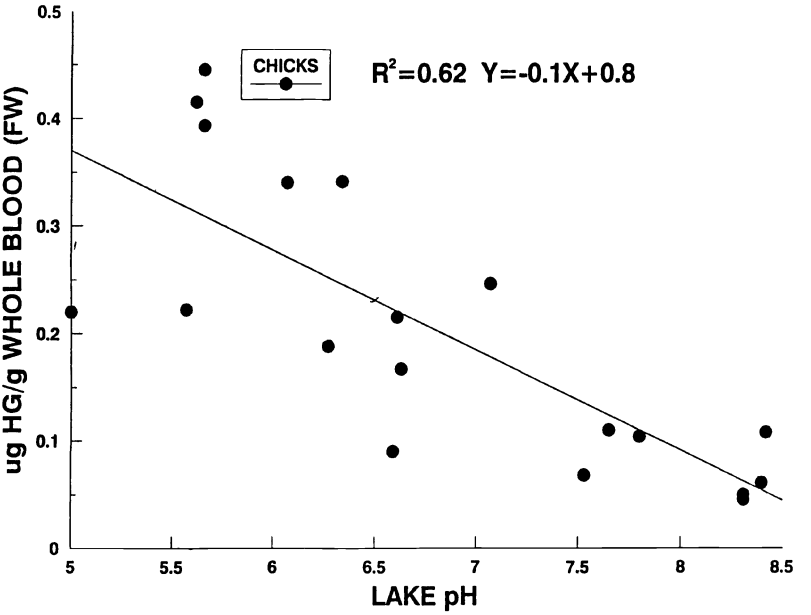
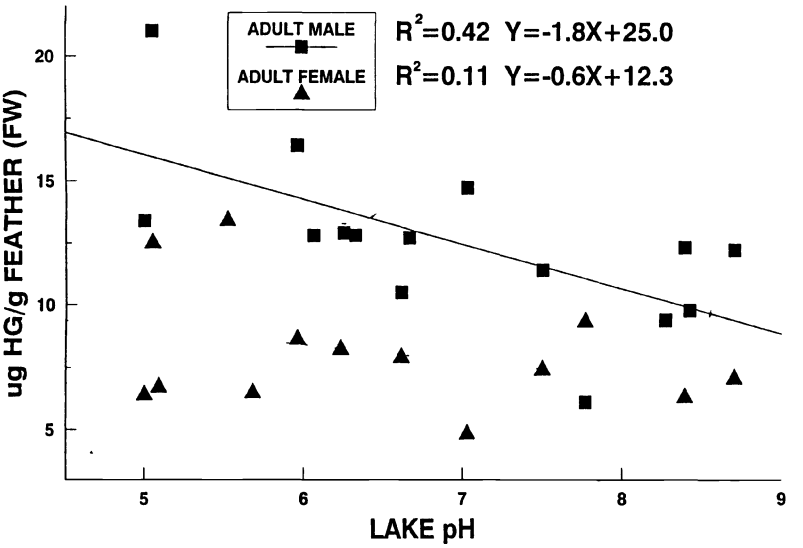


Fig. 2. Wisconsin 1991 adult common loon feather Hg content (fw) vs. lake pH

Feather Hg content represents the body burden of Hg at the time of feather formation; loons molt while on their wintering grounds along the Atlantic coast and Gulf of Mexico (Furness *et al.*, 1986). Therefore, the Hg content of adult feathers collected in the summer represents the loon's Hg burden while it regrew its flight feathers on the wintering grounds, and appears less related to the water chemistry of the lake they nested on. Blood Hg levels more closely reflect the Hg status of loons at the time they are captured. Therefore, the elevated levels of Hg in the blood cells of adult loons nesting on low pH lakes in Wisconsin indicates that they are exposed to greater levels of Hg in their prey than are loon nesting on neutral/alkaline pH lakes. The lesser feather Hg levels in adult females may indicate that they metabolize and/or excrete Hg more efficiently than do males thus have a lower body burden at the time of feather formation. Alternatively,

females are 15 to 20% smaller than males, thus may feed on smaller fish and have lower Hg exposure.

An additional 24 chick common loon blood samples were collected in 1992. All samples tested were above instrument detection levels (DL = 0.01 ug Hg/g). A highly significant linear relationship was found between chick whole blood Hg concentrations (fw) and lake pH (Figure 3, $r^2=0.62$, $P<0.01$). It was anticipated that chick Hg exposure would be most closely associated with the water chemistry of the lake they were captured on because chicks usually receive all their prey from the nest lake while adults may forage on additional lakes.



. Fig 3. Wisconsin 1992 common loon chick whole blood Hg concentrations (fw) vs. lake pH

The linear relationship between 1991 adult common loon blood cell Hg and feather Hg concentrations was significant (Figure 4, $r^2=0.46$, $P<0.05$), with the relationship greater for adult males ($r^2=0.62$) than for adult females ($r^2=0.39$). Though the relationship is statistically significant, the relation is relatively weak for a feather Hg vs. blood Hg comparison. This is not surprising as the loon's winter diet (common loons winter along the U.S. Atlantic and Gulf of Mexico coastline) is obviously different from the diet on the breeding grounds in Wisconsin; size of prey items may also vary. The Hg content of fish (the primary prey item of loons) is known to be species and size specific thus exposure levels likely differ between sites.

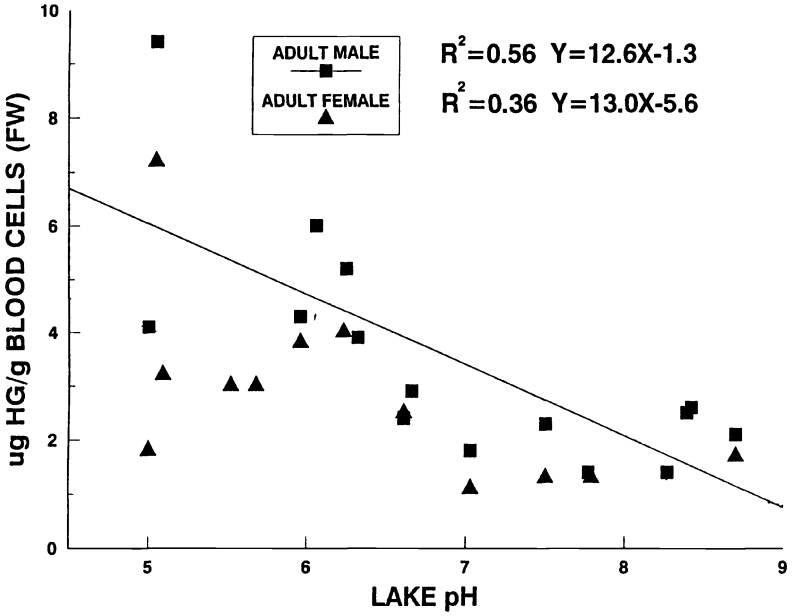


Fig. 4. Wisconsin 1991 adult common loon blood cell Hg content vs. feather Hg content

Serum clot selenium (Se) levels were also greater in adults captured on low pH lakes (Table III; $F=5.18$, $P<0.05$). As Se is known to ameliorate the toxic effects of mercury (Cuvin-Aralar and Furness, 1991) its increased concentration in these samples may indicate that loons possess a mechanism which reduces the toxicity risk. However, the linear relationship between blood cell Hg vs. blood cell Se concentrations (fw) was not significant ($r^2=0.11$, $P>0.05$) and while the blood cell Hg:Se ratio is approximately 1:1 on neutral/alkaline lakes it approaches 2:1 on acidified lakes (Tables I and II).

It has been hypothesized that the availability of nutritionally essential minerals such as calcium (Ca) may be reduced in acidified habitats (Scheuhammer, 1991). The mean serum clot Ca content of adult loons captured on low pH lakes was significantly less (Table III; $F=10.09$, $p<0.005$) than the clot Ca content of adult loons sampled on neutral pH lakes. Male and female Ca levels were similar ($P>0.10$). It has been hypothesized that a scarcity of Ca-rich aquatic invertebrates may occur in acidified habitats and result in reduced avian production (Scheuhammer 1991). The lesser Ca levels in the loon tissue collected from low pH lakes does not necessarily indicate that those loons experience a deficiency, however the fact that there is less Ca in blood cells is of interest.

Table III

Clotted blood cell Se and Ca concentrations [(N) Mean (ug/g fw) ± 1SD] of Wisconsin adult common loons

		LOW pH LAKES (pH<6.3)	NEUTRAL pH LAKES (pH≥7.0)
SELENIUM	Adult males	(7) 3 ± 1	(7) 2 ± 1
	Adult females	(6) 4 ± 2	(4) 2 ± 1
	All adults	(13) 3 ± 2	(11) 2 ± 1
CALCIUM	Adult males	(7) 23 ± 6	(7) 31 ± 9
	Adult females	(6) 16 ± 7	(4) 28 ± 6
	All adults	(13) 20 ± 8	(11) 30 ± 8

4. Conclusion

Adult common loons and chicks captured on Wisconsin lakes with pH ~ 5.3 had elevated Hg concentrations in blood samples. The level of Hg exposure of chicks was more closely related to lake pH than was adult exposure; perhaps reflecting different feeding habits. There is an indication that calcium may also be limited in biota from acidic lakes (loon blood Ca levels were less on acidic lakes); but blood Se levels were elevated, perhaps sparing some of the toxic effects of mercury on low pH lakes. The finding that loons nesting on low pH lakes in Wisconsin have greater Hg exposure justified an expanded investigation into the effect of the Hg exposure on common loon productivity and survival in Wisconsin. WDNR Bureau of Research and Biodiversity, Inc. captured, sampled, and banded an additional 330 adult and chick common loons on 73 Wisconsin lakes 1992-94. Whole blood samples from chicks and adult loons are being analyzed by the US Fish and Wildlife Service and adult feathers are being analyzed at the Animal Health Diagnostic Laboratory at Michigan State University. In addition, the reproductive performance of color-marked loons on the 73 study lakes is being documented 1992-96; field technicians determine annual adult return rates, locate nests, count eggs and chicks, and determine fledging rates. We will also measure whether reduced Ca or increased aluminum concentrations occur in loon tissues on acidified lakes; these compounds may also cause reproductive anomalies in acidified habitats (Scheuhammer, 1991). This data will allow for an assessment of the impact of Hg exposure on common loon nest success in Wisconsin.

ACKNOWLEDGEMENTS

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MERCURY ANOMALIES IN LAKE WATER AND IN COMMERCIALLY HARVESTED FISH, KAMINAK LAKE AREA, DISTRICT OF KEEWATIN, CANADA

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Abstract. Mercury (Hg) was measured in approximately seven hundred samples of surface water collected from Kaminak Lake and nearby small and large lakes in a tundra environment located west of Hudson Bay. Mercury variations were expected to be related to sulphide mineralization, and patterns of Hg enrichment were to be used as pathfinders for locating potentially economic sulphide deposits. Water in the northern part of Kaminak Lake, which is underlain by sedimentary and volcanic bedrock with known potential for sulphide (base metal) mineralization, was consistently enriched in Hg, as were smaller lakes lying along the same bedrock trend. Mercury concentrations in lake trout from a commercial fishery on Kaminak Lake ranged from 0.57 ppm (parts per million = mg/kg or mg/l) to 2.0 ppm Hg (70 samples), exceeding the national consumption guidelines of 0.5 ppm. Subsequently, the Kaminak fishery was abandoned and relocated on nearby Kaminuriak Lake where similar fish species averaged less than 0.5 ppm Hg. High Hg concentrations in fish from this remote, unpopulated region, far from industrial sources of pollution, are related mostly or wholly to local geological phenomena.

1. Introduction

In 1970 and 1971 surface water was collected at over 700 sites and the water column was sampled at several sites in and near Kaminak Lake, located in open tundra about 100 km west of Hudson Bay. Kaminak Lake is a large, shallow, irregular lake with many bays. Its surface is about 53 m above modern sea level; Kaminak and all other lakes sampled were inundated by the sea as a result of glacioisostatic depression from 6000 $\pm$ 500 years ago to as recently as 4000 years ago. Because of oxidation of organics, low productivity, and their young age, lakes generally have less than one metre of modern organic sediment, often overlying several metres of clastic marine sediment. Their waters are highly oxygenated with near neutral pH and very low conductivities (Klassen *et al.*, 1975; Shilts *et al.*, 1976).

2. General geology

The geology of the Kaminak basin is complex, consisting of belts of Archean, sulphide-bearing metavolcanic rocks (Kaminak Group) intruded by igneous rocks of similar age (Davidson, 1971). Set into this crystalline basement are the erosional remnants of a prominent belt of younger (Aphebian) metasedimentary and metavolcanic rocks of the Hurwitz Group. The latter group crops out under and beside the northern part of Kaminak Lake and beneath several of the smaller lakes sampled (Figure 1). The bedrock is overlain by a discontinuous mantle of glacial till and fine-grained marine sediment (Arsenault *et al.*, 1981). A prominent esker forms the northwest shore of Kaminak Lake (Shilts, 1973). The till is dominated compositionally by local material mixed with

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significant amounts of debris glacially eroded from the red volcanic and sedimentary rocks of the late Precambrian Dubawnt Group, which outcrops over 100 km northwest of the study area. There is abundant evidence of temporary occupation of the shores of Kaminak Lake by nomadic Innuit who left significant deposits of caribou bones on the lake bottom, but there is no present population centre closer than 120 km, and the region is 1000's of km from any source of industrial airborne emissions.

3. Sample collection, preparation and analytical methods

The water samples, collected in polypropylene bottles, were acidified upon collection with nitric acid (HNO_3) to a final strength of 0.015 M HNO_3. Filtration was not carried out as the presence of particulate matter in these samples was considered insignificant. Mercury was determined by quartz tube/atomic absorption spectrophotometry (AAS) at 253.7 nm after vaporization to the elemental state by the reducing agent, stannous sulphate ($SnSO_4$). 15 ml of 5% $SnSO_4$ in 1 M sulphuric acid (H_2SO_4) was added to a 100 ml aliquot of the sample and the resulting vapor swept into a heated (90°C) 1 m quartz cell in the light path of the AAS. The lower limit of measurement was 5 ppt (parts per trillion = ng/l); relative standard deviation at 20 ppt was typically 10%.

The results shown here are considered to be potentially low for two reasons. Firstly, the HNO_3 added cannot be assumed to be fully effective in liberating organically bound or complexed Hg to form mercuric ions available for reduction by $SnSO_4$. Secondly, during the interval between collection and analysis Hg could have been lost to varying degrees through adsorption on container (polypropylene) walls and/or reduction to the elemental state by bacterial or chemical action. Nitric acid would have inhibited this loss, but not necessarily prevented it completely. Subsequent research at the Geological Survey of Canada (GSC) showed that addition of 1 ml of 5% potassium permanganate ($KMNO_4$) and 2.5 ml of H_2SO_4 to a 100 ml sample was effective in destroying active reducing bacteria and in oxidizing potential complexing material (Jonasson *et al.*, 1973).

4. Results and discussion

In 1971 a commercial fishery was established at a permanent base camp on the esker at the northwest corner of Kaminak Lake, with the objective of supplying lake trout (*Salvelinus namaycush*) and Lake Whitefish (*Coregonus clupeaformis*) to a processing plant in Rankin Inlet, for eventual sale in southern Canada. Most of the harvesting was carried out near the camp in the northwestern part of the lake, where underlying bedrock is the Hurwitz Group. Because Hg levels in fish were of general concern, Hg was monitored by analyses at the Freshwater Institute in Winnipeg (Sherbin, 1979). Lake trout were found to have Hg concentrations ranging from 0.57 to 2.0 ppm, exceeding the national guidelines of 0.5 ppm. In 1972 the fishery was abandoned and moved to nearby Kaminuriak Lake, where Hg concentrations were acceptable. Reconnaissance Hg data for waters sampled in 1970 indicated that surface waters over Hurwitz Group black slates and volcanic strata and, to a lesser extent, Kaminak Group volcanic strata had relatively high Hg concentrations (Figure 1) (Hornbrook and Jonasson, 1971). Further detailed sampling throughout Kaminak Lake in 1971 confirmed the enrichment of Hg in water in its northern

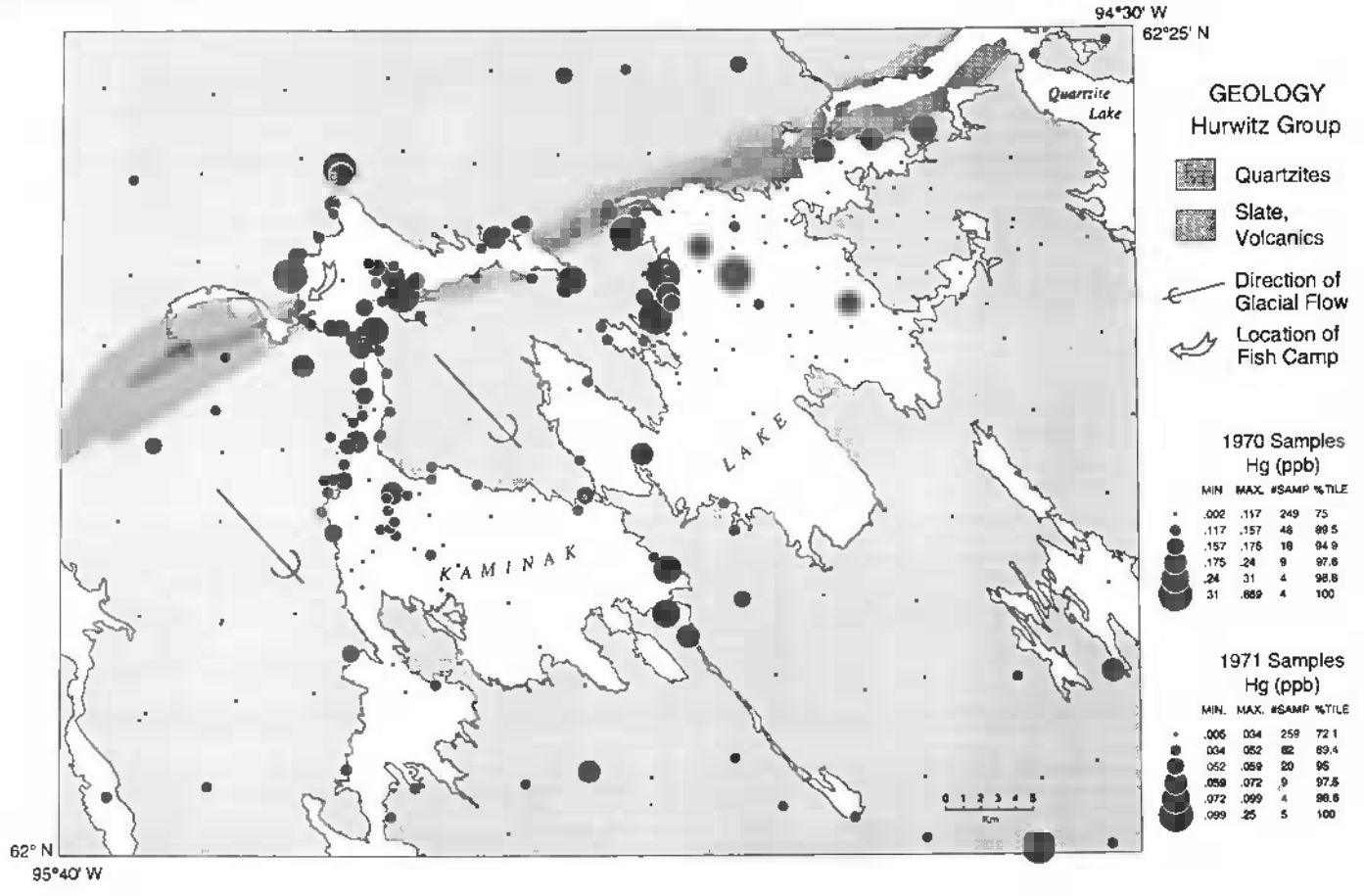

Figure 1: Concentrations of Hg (ppb) in water of Kaminak Lake and nearby lakes

basins (Figure 1) where, coincidentally, most of the fish were harvested. These results were taken to indicate that widely dispersed sulphide minerals in the slate and/or volcanic members of the Hurwitz Group were releasing Hg as part of the ongoing weathering processes affecting these rocks or the glacial sediments derived from them. The fact that Hg was concentrated only in the northern waters of a large, shallow, freely circulating lake suggested that outgassing was a very local and ongoing process. Furthermore, it was and is hard to ignore the relationships between high Hg in the fish and the geographical coincidence of their harvest area with elevated Hg in the water. A similiar relationship between Hg in fish and sulphide-bearing black slates of Aphebian age was postulated by Loukola-Ruskeeniemi (1990) in Finland.

5. Conclusions

(1) The fact that fish from remote lakes near the study area have acceptably low Hg concentrations suggests that their enrichment in Hg in the Kaminak Lake area is related to local natural processes, which ultimately must create bioavailable Hg species.

(2) The correspondence of high Hg concentrations in water only within those parts of Kaminak Lake underlain by Hurwitz slates and/or volcanic rocks suggests that ongoing local geological processes (eg. weathering) are largely responsible for the Hg enrichment in water.

(3) The fact that there are large but coherent variations in Hg concentrations among the hundreds of remote lakes sampled and, indeed, among the hundreds of sites sampled on Kaminak Lake itself, suggests that long distance airborne pollution has a negligible overprint on local naturally generated Hg in this area. Any effects of any airborne sources of Hg are overwhelmed by Hg release from local sources.

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Mercury concentrations in freshwater fishes in New Jersey

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Abstract A statewide screening study found fish Hg concentrations to be correlated with pH, with site-specific factors creating appreciable variation within pH classes High Hg concentrations were found in the Pine Barrens and in some fish from lakes in the rest of the state

1. Introduction and Study Design

The accumulation of mercury (Hg) in fish has important implications for health of humans and fish-eating wildlife. Inputs from point source effluents, non-point source runoff, and from atmospheric deposition may affect a variety of types of waterbodies. Since bioaccumulation is strongly affected by rates of methylation of Hg and by dynamics of methylmercury in waterbodies, the magnitude of bioaccumulation in fish is a function of waterbody characteristics as well as the magnitude of Hg input.

New Jersey is an important region for Hg study because of major industrial production and use in the state, the presence of low pH (4-6) waters with sport fisheries in the Pine Barrens, and the likelihood of atmospheric deposition from local and external sources. In 1992-1993, we made a preliminary assessment of Hg concentrations in fishes from freshwater sites throughout New Jersey, analyzing 313 specimens from 55 sites. The major objectives of the study were to a) determine whether concentrations in fish are of levels which would warrant further study; b) indicate characteristics of sites correlating with Hg bioaccumulation. The study is described in more detail in ANSP (1993).

The target population of waterbodies was defined as: a) sites with public access; b) ponds, lakes and reservoirs greater than 6.1 ha in area; c) freshwater (including tidal) streams and rivers greater than 19.3 km in length. The study design was a stratified random sampling of sites, supplemented by some sites which were nonrandomly selected to sample specific regions or drainages. Strata were defined a priori on the basis of: a) type of waterbody (lotic or lentic); b) geographical region and physiographic province (e.g., Pine Barrens, other Coastal Plain areas, Piedmont-Highlands). Some sites with unusual characteristics (large reservoirs and reaches of the Delaware River) were placed into their own strata. The numbers of sampling sites within strata were allocated with higher sampling intensity in strata expected to have higher bioaccumulation (e.g., Pine Barrens lakes; upland lakes). Within each site, 1 to 11 specimens of 1 to 5 species were analyzed. The target species were largemouth bass and chain pickerel. Other species were analyzed where locally important in the fishery and/or the primary species were not available. Virtually all fish (except crappie) were greater than 24 cm in length.

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2. Methods

Fillets (entire, without skin) of individual fish were ground using a Tissuemizer grinder, digested in concentrated HNO_3 (specific high temperature and pressure program in a microwave oven), and analyzed for total Hg by manual cold vapor atomic absorption spectrophotometry. The mean recovery in 36 spiked samples was 97.25%, the mean %RPD among 36 duplicate sample pairs was 4.65%, and mean recoveries of reference material were 109% (USEPA-2754), 99.4% (NBS-50 albacore tuna) and 99.9% (Can. NRC DORM-1). Detection limits were 0.035-0.036 mg/kg (based on 48 digested blanks).

Water pH was measured at the surface at each sampling site; additional pH data were taken from the United States Geological Survey reports and unpublished sources. Each site was classed by pH group (integral value of pH, except group 8 includes pH ≥ 8) and by pH-waterbody type (pHTYPE), combining the pH group and the waterbody type (L=lake or reservoir; R= river or stream).

For each species, concentrations of Hg ([Hg] hereafter) were standardized for fish total length and compared among classes (pHTYPE or pH group) using analysis of covariance (ANCOVA). Significant [Hg]-length relationships were found for all species except brown and yellow bullheads, black crappie, rainbow trout and northern pike (species with low sample sizes and/or low range of lengths). A single slope was fit to the ln([Hg])-ln(TL) relationship for each species, resulting in different intercepts for each pHTYPE. Length-adjusted comparisons between classes were done using least squares mean [Hg]s, i.e., predicted ln([Hg]) at the mean size of each species, or the predicted [Hg] at sizes corresponding to typical average lengths of age IV or age V fish (Table I). Analyses for largemouth bass were done excluding data from one site (Atlantic City Reservoir, see below) which had very high [Hg].

Fig 1 Average Hg concentration (mg/kg wet weight) adjusted to typical size of age IV fish, for specimens of each species at each site, for different pH groups Points within each pH group are spread around each pH value to separate points Species are brown and yellow bullheads (BB and YB), black crappie (BC), channel and white catfish (CC and WC), chain pickerel (CP), largemouth bass (LMB), and smallmouth bass

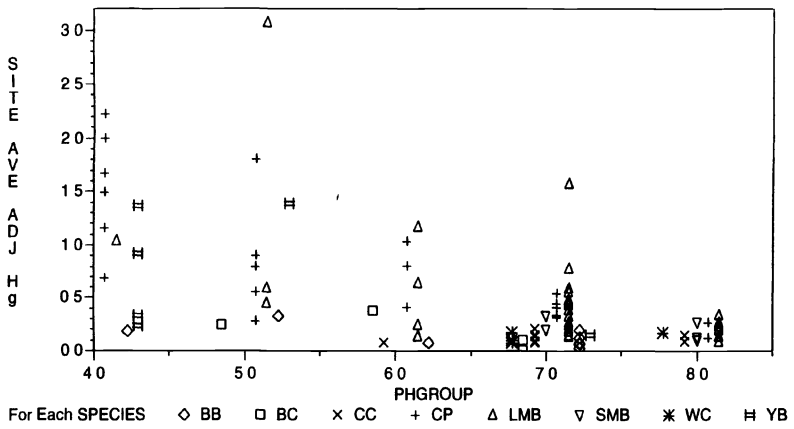
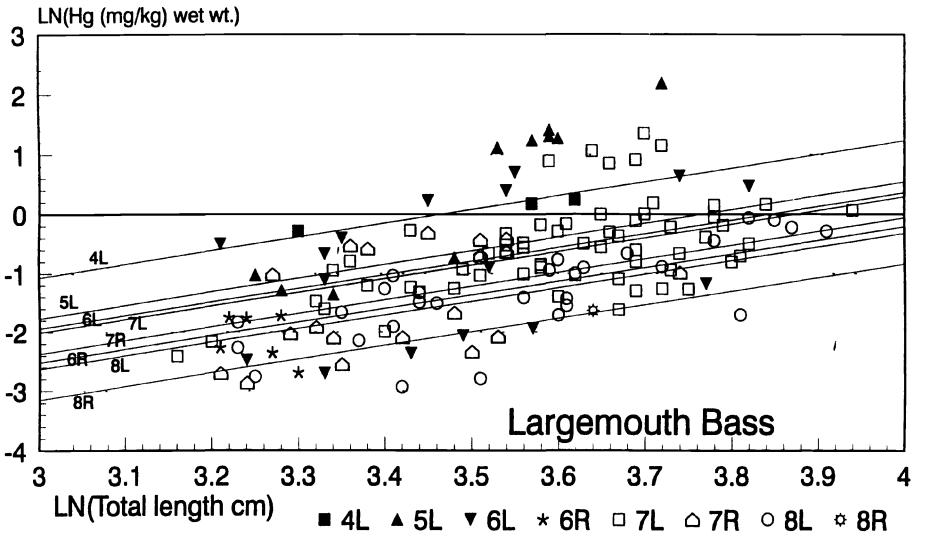


Fig 2 Relationship between ln([Hg]) and ln(total length), classed by pH group and waterbody type Lines show regressions for each pH-waterbody type



3. Results

Concentrations of Hg (as ranges, size-adjusted averages and frequency greater than 0.41, 0.5, 1.0) were highest in lakes and streams in and near the Pine Barrens (e.g., [Hg] up to 2.82 mg/kg in chain pickerel and 1.28 mg/kg in largemouth bass; [Hg] > 0.5 in all pickerel and bass from all Pine Barrens sites), and some lakes in northern New Jersey, including several of the largest lakes. Statistically significant relationships between [Hg] and pH (Fig. 1-3) explain much of the geographical variation in [Hg]. The [Hg]-pH relationship may be due to covariation between pH and factors (e.g. DOC) directly

Fig 3 Relationship between ln([Hg]) and ln(total length), classed by pH group and waterbody type Lines show regressions for each pH-waterbody type

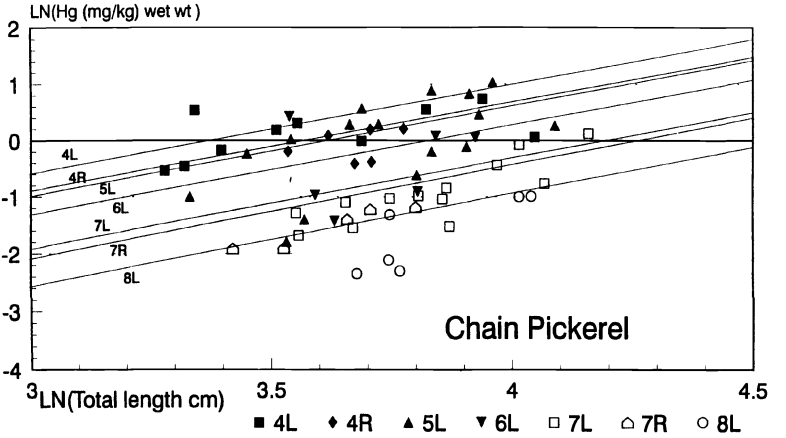


Table I Predicted [Hg] (mg/kg) at total lengths corresponding to typical average lengths of age IV fish

	pHTYPE									
	4L	4R	5L	6L	6R	7L	7R	8L	8R	TL cm
Black crappie	-	-	0 23	0 37	-	0 11	-	-	-	23 2
Brown bullhead	0 18	-	0 32	0 07	-	0 07	0 07	-	-	23 9
Chain pickerel	1 72	1 21	1 17	0 76	-	0 38	0 31	0 18	-	45 5
Channel catfish	-	-	-	-	0 11	0 11	0 11	-	0 11	36 8
Largemouth bass	1 04	-	0 52	0 44	0 25	0 41	0 29	0 22	0 13	32 9
Northern pike	-	-	-	-	-	-	-	0 23	-	64 3
Smallmouth bass	-	-	-	-	-	0 33	0 19	0 13	0 15	28 2
White catfish	-	-	-	-	-	-	0 10	0 10	-	33 6
Yellow bullhead	0 46	-	1 38	-	-	-	0 15	-	-	27 2

controlling [Hg] Variation in [Hg] was relatively high among sites with pH 4-5 (Pine Barrens sites) and pH 5-6 (mainly sites in or near the Pine Barrens with agricultural or residential land uses and relatively large annual variation in pH). [Hg] at 3 sites were much higher than predicted from pH; these include Atlantic City Reservoir (a low pH pond at the edge of the Pine Barrens with probable point source inputs), Manasquan Reservoir (stocked in 1990) and Union Lake (a large, moderately-low pH lake at the edge of the Pine Barrens); maximum [Hg] in these sites were 8.94, 3.87 and 2.02 mg/kg, respectively. Other sites with average [Hg] greater than predicted (from pH and waterbody type) were sites in the industrial Passaic drainage, and several lakes, including a new (1988) reservoir, and a large reservoir with fluctuating water level. Sites with lower [Hg] than predicted were narrow, run-of-river impoundments, tidal sites, and small ponds (especially on the Coastal Plain).

Analysis of an aged subset of chain pickerel indicated that some, but not all, of the [Hg]-pH relationship may be explained by slower growth at lower pH sites. Length-adjustment to sizes typical of age IV fish (Table I) indicate relatively high accumulation in chain pickerel and largemouth bass (pickerel greater than bass at low pH and similar at higher pH) and lower accumulation in white catfish, channel catfish and brown bullhead. [Hg] in yellow bullhead were variable, with relatively high [Hg] at some sites.

Acknowledgements

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MERCURY IN FISH MUSCLE IN ACIDIFIED AND LIMED LAKES

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Abstract. The concentration of Hg in muscle was monitored during 10 to 12 years in different size and age groups of pike (*Esox lucius*) and perch (*Perca fluviatilis*). The study was performed in one reference and five lime treated lakes. Before liming, the highest levels of Hg in fish were measured in a lake with an annual mean pH just above 5.0. Lower levels were obtained both in lakes which were more acidified and in those which were less acidified. After the start of liming, the fastest and largest changes were obtained in the lakes which were moderately acid before liming (mean pH 5.4-5.8). In small perch, the Hg-concentration was markedly reduced in two years and showed an 80 % decrease in ten years. A slower response was registered in the lakes originally having about 0.5 units lower pH. In the most acidified lake (pH 4.9) the concentrations even increased the first years after liming, but decreased again later on. The possible mechanisms involved are discussed.

1. Introduction

Regional lake surveys performed around 1980, showed that the concentration of mercury (Hg) in fish was elevated in numerous forest lakes, even in remote areas in northern Sweden (Björklund *et al.*, 1984). The distribution of Hg in fish was connected to the long-range deposition pattern, as well as to the location of formerly large domestic emission sources. The Hg levels were generally further elevated in the acidified lakes (Lindqvist *et al.*, 1984; Björklund *et al.*, 1984; Lindqvist, 1991). In order to study the possibilities to reduce the Hg-levels, several experimental liming operations were started (Andersson and Kärrhage, 1984; Håkanson *et al.*, 1990; Swedish EPA, 1991). The purpose of this study is to evaluate the effects of liming on the uptake of Hg by fish, in lakes at different phases of acidification.

2. Methods

The studies started in 1977 in four lakes in the Åva area, south of Stockholm and in 1980 in two lakes in the province of Örebro. The lakes are small forest lakes with relatively short turnover times (Table I). Besides pike and perch, sparse populations of roach and cisco were present in some of the lakes. Water sampling was performed 4 to 12 times a year, young perch and pike were generally sampled annually and older individuals every 3 to 4 years.

TABLE I
Hydrological data of the studied lakes

	L.Långsjön	L.Mörtsjön	L.Årsjön	L.Stensjön	L.Rammsjön	L.Ämten
Lake area, ha	10	2	16	41	96	75
Max.depth, m	8.0	4.7	8.4	21.0	17.0	7.5
Mean depth, m	4.0	2.6	3.7	8.7	4.0	2.1
Turnover time, yrs	0.8	0.2	1.4	1.8	1.3	0.7
Catchment, km²	1.7	1.9	1.4	8.2	8.1	7.9
% forested	93	83	94	89	87	70
% wetlands	5	9	5	7	11	29

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pH was determined at the laboratory, mostly within two days after sampling. The fishes were frozen at the day of capture at -20°C. At the laboratory, they were weighed, a piece of dorsal muscle was prepared for freeze drying and bones prepared for age determination. Hg was determined by cold vapor AAS after pressure digestion of the freeze dried sample in conc. HNO_3 (Hatch and Ott, 1968; Uhrberg *et al.*, 1989).

After analysis of generally 20 fishes of each species, the Hg-level was computed for two size-age-groups of pike and four groups of perch. To compensate for difference in growth rate, the Hg-concentration in muscle was normalized by fish weight and age, based on the correlations Hg-weight and age-weight for each case (Andersson *et al.*, 1989). Students-t was used to test the significance of the differences in Hg-concentrations between sampling occasions.

After 1 to 5 years, four of the lakes were limed (limestone, 0 to 0.5 mm), mostly directly into the lakes. All four lakes have been relimed 2 to 3 times during the period. L. Mörtsjön receives water from the limed L. Långsjön, and L. Årsjön is the reference lake.

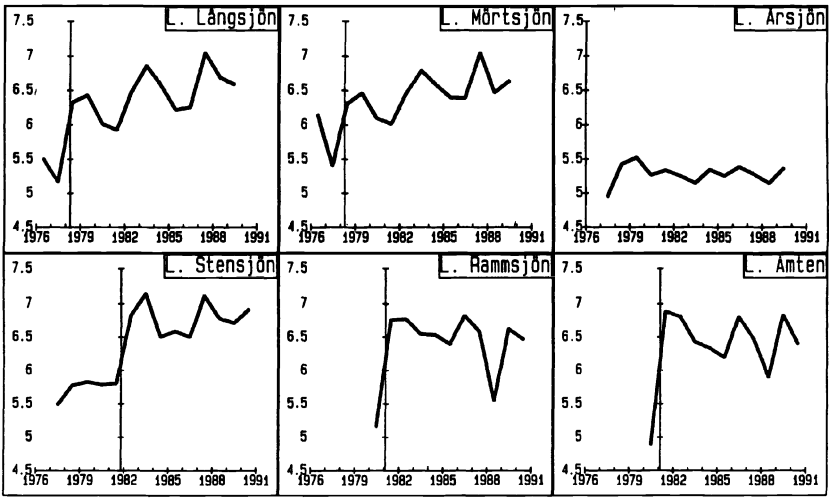

Fig.1. Annual mean pH. The y-axis indicates the start of liming. Lake Årsjön is the unlimed reference lake.

3. Results and Discussion

The variation in Hg-concentration between individuals in a lake at each sampling occasion, was 5 to 50% (rel. sd). Prior to the lime treatments, the highest levels of Hg were found in L. Rammsjön, with an annual mean pH of 5.16, and lower levels were found in the less acid lakes (Figures 1,2), similar to other studies (Björklund and Norling, 1979; Björklund *et al.*, 1984; Lindqvist *et al.*, 1984; Verta *et al.*, 1990). However, the levels were also lower in the most acid lakes, a tendency shown in a few other cases (Verta *et al.*, 1990).

The annual mean pH was generally kept in the range 6.5 to 7.0 during the limed period (Figure 1). As expected, the younger fishes reacted faster to the treatment than the older ones. The trend in Hg-concentrations during the study period is shown in Figure 2. Initially, the fastest decrease in Hg-concentration was noted in the lakes which were less acidified at the beginning of the lime treatment, similar to results from other studies (Håkanson *et al.*, 1990). That is clearly demonstrated by 10 g perch in Lake Stensjön ($p<0.01$-$p<0.05$), and 1 kg pike in lakes Stensjön ($p<0.02$) and Mörtsjön ($p<0.01$).

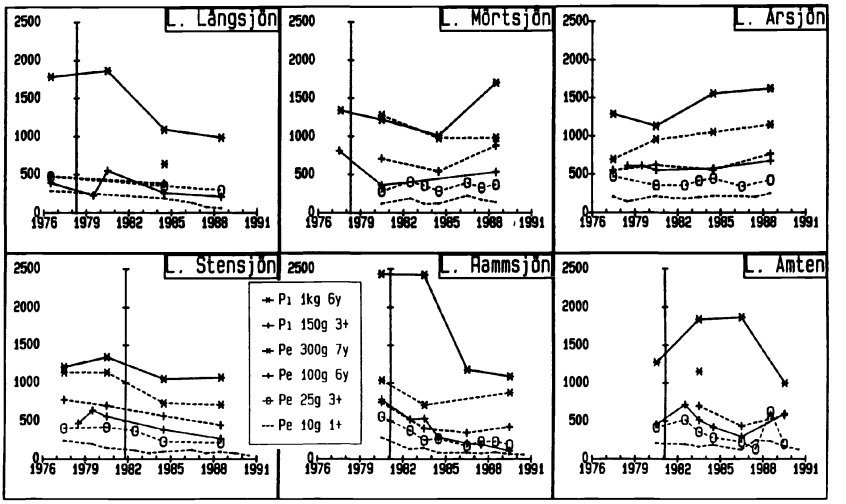

Fig.2. The Hg-concentration (ng/g ww) in muscle of pike (solid lines) and perch (dashed lines), normalized by age and weight. The y-axis indicates the start of liming. Lake Årsjon is the unlimed reference lake.

An initially slow decrease in Hg-concentrations after liming was demonstrated in the moderately acidified lakes Långsjön and Rammsjön, where all the fish groups showed lower levels of Hg after 5-6 years of treatment ($p<0.001$-<0.05). On the contrary, in the most acidified lake (Lake Ämten), an increase was demonstrated during the first years after liming ($p<0.01$-<0.05), remaining until 9 years after the start of the treatment, when a decrease was registered in 1 kg pike ($p<0.01$). Similarly, Hg in pike increased in L. Mörtsjön ($p<0.01$), about 7 years after the beginning of liming in the upstream Lake Långsjön, an effect registered also in other lakes situated downstream from limed lakes (Andersson *et al.*, 1991), as well as in lakes treated with low lime doses in the wetland parts of the catchment (Meili, 1994).

In most earlier studies, a higher concentration of Hg was found in fish in low pH waters. This is why liming has been used as a remedial measure for elevated Hg concentrations in fish. This overall conclusion is supported by this study as well, but only down to a pH of around 5. Below this value, the concentration of Hg in fish is lower. Consequently, after that the acid conditions have caused increased Hg-levels, a further increased acidification seems to result in decreased Hg-levels in fish (outlined in Figure 3).

Many factors promote an initial increase of Hg in fish muscle in the earlier phases of acidification. A change of the food chain structure, e.g. extinction of acid sensitive species, has been shown to influence the Hg-levels in pike and lake trout (Björklund *et al.*, 1984; Cabana *et al.*, 1994). At the last phase of acidification, the decomposition rate is markedly reduced, probably resulting in a larger portion of "inactivated" Hg bound to *Sphagnum*-mosses (Grahn *et al.*, 1976), and to dead organic material. The uptake of Hg in organisms might also be reduced by an increased competition of H^+ ions at cell membranes (Campbell and Stokes, 1985).

Treating such a lake with lime probably causes an initial increase in decomposition of organic matter, causing a release of bound Hg and a stimulated biomethylation of Hg (Wren and Stokes, 1988). As the ecosystem recovers to circum-neutral conditions, the limiting factors for bioaccumulation of Hg increase in importance. If the lake is only moderately

acidified from the beginning, the ameliorating mechanisms favouring Hg-reduction in fish will dominate immediately, resulting in decreased Hg-levels (Figure 3).

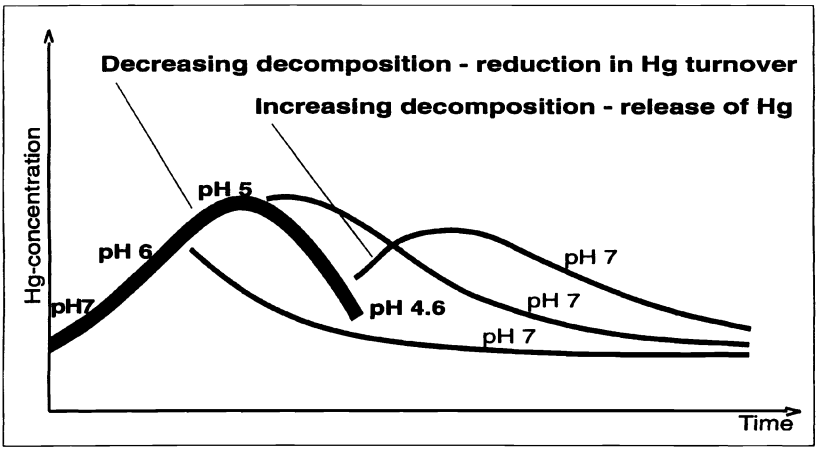

Fig.3. Outline of the general trend of Hg in fish during the acidification process (heavy line) and during lime treatment (fine lines) depending on in what phase of acidification the lake is limed.

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METHYLMERCURY CONCENTRATION IN SHARK MUSCLE BY SPECIES, SIZE AND DISTRIBUTION OF SHARKS IN FLORIDA COASTAL WATERS

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Abstract. The concentrations of methylmercury (MeHg) in 124 samples of muscle taken from nine species of common sharks of varying sizes and locations along the Florida coast were determined. Muscle MeHg levels averaged 0.88 μg/g (wet sample basis) and ranged from 0.06 to 2.87 μg/g, with 33.1% of the samples exceeding the U.S. Food and Drug Administration's 1 μg/g action level. Differences were found in MeHg concentration by species but not by sex. A positive correlation between MeHg levels and shark size was found such that most sharks larger than approximately 200 cm total length contained MeHg concentrations exceeding the 1 μg/g action level. Fetal sharks contained consistently lower MeHg levels than their mothers. Sharks collected off southern regions of the state contained significantly higher MeHg concentrations than those off the northeast coast. The human health concerns for consumers of Florida shark meat are discussed in relation to these findings.

1. Introduction

As apex marine predators, sharks may contain relatively high levels of heavy metals such as mercury (Hg) in their tissues as a result of bioaccumulation up the food web (Forrester *et al.*, 1972; Walker, 1976; Marcovecchio *et al.*, 1991; Leah *et al.*, 1991). Until recently, this has not been a particular concern for human health in the state of Florida due to the relatively low U.S. consumption of shark meat in past decades. Now, however, with greatly increased activity of the commercial shark fishery off Florida (NMFS, 1993) and the resulting higher rate of consumption of shark meat, there is new interest in the Hg content of shark muscle. A 1991 study by the Florida Department of Health and Rehabilitative Services (FDHRS) showed an average methylmercury (MeHg) level of 1.48 μg/g—exceeding the 1 μg/g action level established by the U.S. Food and Drug Administration (FDA)—in a collection of 25 shark meat samples taken from retail markets around the state (FDHRS, 1991). Very little was known about these samples other than the site and date of collection and, in less than half the samples, a market name for the species of shark. To characterize further the Hg levels in Florida sharks, to investigate environmental patterns of Hg in marine fishes and to provide guidance to consumers, we examined MeHg concentrations in Florida coastal sharks in relation to species, size and distribution.

2. Materials and methods

Samples of fresh muscle from 124 sharks of nine species of requiem sharks (family Carcharhinidae) were collected from 1988 to 1992 (Table I). All sharks were caught by

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TABLE I

Average MeHg concentration in Florida shark muscle for nine species in four regions

Region	Blacknose	Blacktip	Bull	Carib. reef	Dusky	Sandbar	Silky	Spinner	Tiger	Totals
		0.34	0.45			0.63		0.09	0.26	0.54
NE		0.40	0.55			0.21		0.00	0.16	0.27
		2	2			21		1	3	29
										3.4
		1.99	1.27			0.86	0.90		0.20	0.93
SE		0.00	0.21			0.22	0.00		0.00	0.39
		1	2			13	1		1	18
										33.3
		2.14	0.97	2.25	1.47	0.73				1.19
Keys		0.40	0.50	0.15	0.13	0.19				0.65
		2	10	2	2	5				21
										38.1
	0.53	1.06	1.11			0.84	0.97	0.75		0.92
SW	0.13	0.08	0.33			0.56	0.57	0.51		0.49
	2	2	15			28	6	3		56
										46.4
	0.53	1.30	1.03	2.25	1.47	0.77	0.96	0.59	0.24	0.88
Totals	0.13	0.83	0.42	0.15	0.13	0.40	0.53	0.53	0.14	0.51
	2	7	29	2	2	67	7	4	4	124
	0.0	*71.4*	*48.3*	*100.0*	*100.0*	*20.9*	*42.9*	*25.0*	*0.0*	*33.1*

In each cell: top number = $\bar{x}$ for MeHg concentration (in μg/g wet weight) of shark muscle tissue samples; middle number = s; bottom number = n. For totals, number in italics = percentage of samples ≥1 μg/g.

Regions: NE = Jacksonville; SE = Cape Canaveral, Port Salerno; Keys = Florida Keys, Ten Thousand Islands; SW = St. Petersburg, Sarasota, Punta Gorda, Ft. Myers.

Shark species: blacknose = *Carcharhinus acronotus*; blacktip = *C. limbatus*; bull = *C. leucas*; Caribbean reef = *C. perezi*; dusky = *C. obscurus*; sandbar = *C. plumbeus*; silky = *C. falciformis*; spinner = *C. brevipinna*; tiger = *Galeocerdo cuvier*.

recreational fishermen or scientific collectors fishing near nine sites in Florida coastal waters of the Atlantic Ocean or Gulf of Mexico (Figure 1). Species, locality, morphometric and other biological data were recorded for each shark. Time of death for the sharks ranged from freshly killed to within 12 hours prior to sample collection. For each shark, a 1 to 1.5 g plug of dorsal white muscle was taken 5 to 10 cm ventral to the base of the first dorsal fin and 2 to 5 cm below the skin from musculature that typically is part of the carcass dressed out for human consumption. Muscle plugs were removed using clean, stainless steel instruments and were placed in sterile polypropylene cryotubes (Nunc). The tubes were immediately sealed, immersed in liquid nitrogen and stored in either liquid nitrogen or a −75°C freezer prior to laboratory analysis.

The frozen tissue samples were overnight-shipped on dry ice from Mote Marine Laboratory (MML) to the FDHRS laboratory in Jacksonville, where they were lyophilized to a constant weight. The lyophilized samples weighing 30 to 600 mg were stored in vacuum-sealed polyethylene bags and delivered at room temperature to the

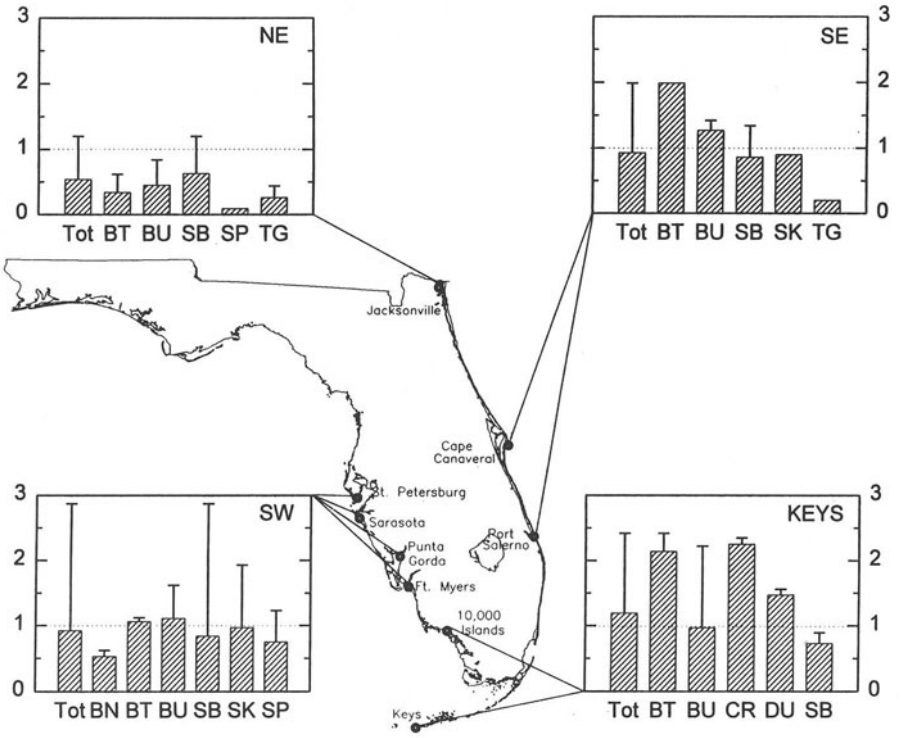

Fig. 1. Methylmercury concentration in Florida shark muscle by region and species. Bars = mean MeHg (μg/g wet weight); lines = maximum MeHg. Dotted lines indicate the 1 μg/g FDA action level. Shark species are as follows. Tot = all species sampled in the region; BN = blacknose; BT = blacktip; BU = bull, CR = Caribbean reef; DU = dusky; SB = sandbar, SK = silky, SP = spinner, TG = tiger

Florida Department of Agriculture and Consumer Services (FDACS) Chemical Residue Lab in Tallahassee for analysis. All samples were identified only by a MML field number with no biological information supplied to either the FDHRS or FDACS labs prior to analysis. Methylmercury concentrations were determined at the FDACS laboratory using a procedure similar to AOAC method 988.11 (AOAC, 1990). To remove lipids, the samples were pre-extracted in polypropylene centrifuge tubes with 25 ml acetone (Optima grade, Fisher Scientific) by vigorous shaking for 15 seconds followed by 5 minutes centrifugation at 3000 rpm and decanting of the supernatant. Acetone pre-extraction was repeated two more times. To remove any other electron-capturing interferences, the samples then were pre-extracted with 20 ml toluene (Optima grade, Fisher Scientific) by vigorous shaking for 30 seconds followed by 5 minutes centrifugation at 3000 rpm and removal of the supernatant. Protein-bound MeHg was hydrolyzed with 10 ml of toluene extracted 1:1 HCl (Trace Metal grade, Fisher Scientific) in HPLC grade water to form methylmercuric chloride and the acid digest was

extracted with 20 ml toluene by gentle shaking for 2 minutes followed by 5 minutes centrifugation at 3000 rpm. Toluene extraction was repeated and the total extract volume was brought to 50 ml with toluene. Na_2SO_4 was added to the toluene extract and the extract was analyzed for methylmercuric chloride with a Hewlett Packard 5890 Gas Chromatograph-Electron Capture Detector (GC-ECD). A 1 μg/g methylmercuric chloride spike solution was made from a stock solution of >99% purity methylmercuric chloride (Johnson Matthey Electronics) and trace metal grade methanol by dilution in HPLC grade water. The recovery surrogate was made from a 1000 μg/g stock solution of ≥97% purity propylmercuric chloride (Phaltz and Bauer) in the same manner as the spike solution.

A standard reference sample, DORM-1 (Canadian National Research Council), consisting of freeze-dried dogfish (shark) tissue with a MeHg concentration of 0.681 to 0.781 μg/g, was analyzed with each set of shark samples. The analytical data of the reference samples indicated that MeHg in freeze-dried shark samples does not degrade over a period of at least 18 months, supporting the integrity of the study material over the time frame of the laboratory analyses (11 to 17 months). Due to the limited amount of material in each sample, the DORM-1 reference material was also used as a spike matrix and its reported mean value (0.731 μg/g) was subtracted from the MeHg concentration of the spiked material. The spike level ranged from 1 to 2 μg/g. Data were reported even if recoveries fell outside the 70 to 120% range. All calculations were based on a calibration curve run at the time of analysis. Results were converted to concentration of methylmercuric chloride in μg/g of muscle wet weight.

The FDACS data were supplied to MML where results were matched with biological information on each shark. Trends in the data were analyzed using the SigmaStat statistical program (Jandel). All data sets were tested for normality and homoscedasticity by Kolmogorov-Smirnov test. For linear regressions, the data were natural log-transformed; if residuals still were not normal or of unequal variance, we used the Spearman rank order correlation test. For nonparametric analysis of variance, we used the Kruskal-Wallis one-way ANOVA on ranks (K-W ANOVA) and Dunn's method for multiple comparison (Sokal and Rohlf, 1981; Dunn, 1964).

3. Results and Discussion

Methylmercury concentrations in the shark samples ranged from 0.06 to 2.87 μg/g wet weight ($\bar{x}$ = 0.88, s = 0.51), with 41 of the 124 samples (33.1%) containing concentrations of 1 μg/g or more (Table I). Mean MeHg concentration by species was lowest in the tiger shark ($\bar{x}$ = 0.24 μg/g; n = 4) and highest in the Caribbean reef shark ($\bar{x}$ = 2.25 μg/g; n = 2). K-W ANOVA detected a significant difference in MeHg among shark species ($p<0.001$) but Dunn's method identified only the Caribbean reef shark as containing concentrations significantly higher than the other eight species. No difference was found in MeHg between the sexes when all species were combined (36 males and 88 females; p = 0.893).

Analysis of the MeHg data by size of shark (Figure 2) revealed a significant positive correlation between MeHg concentration and shark total length when all species were combined ($p<0.001$). In general, MeHg in the muscle exceeded 1 μg/g above a shark size of approximately 200 cm total length. The positive correlation held for the sandbar

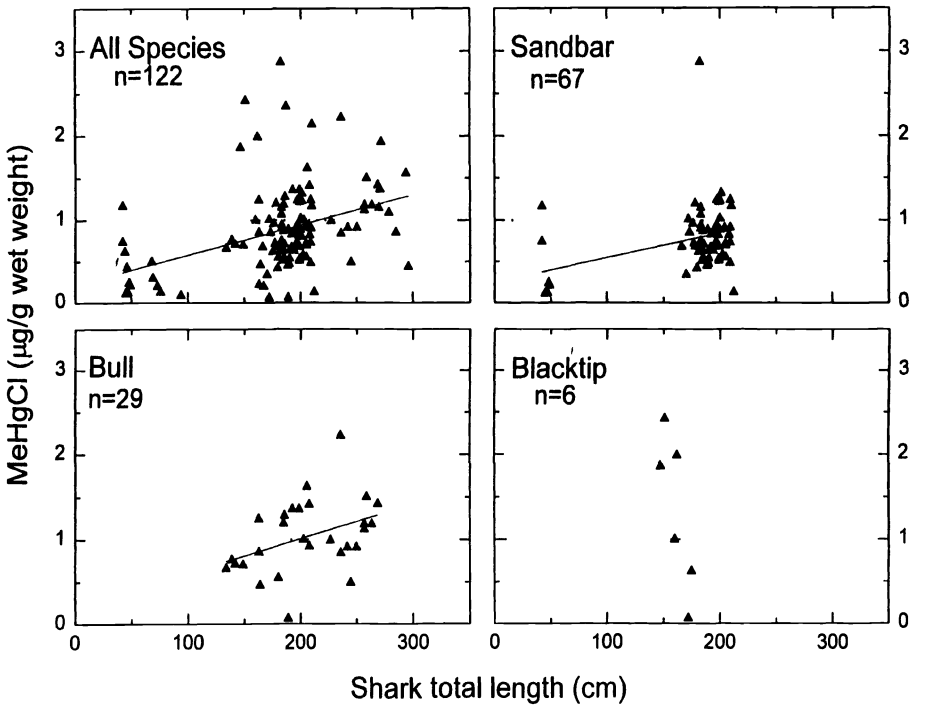

Fig 2 Methylmercury concentration of shark muscle *vs* total length of shark for all species in the study combined and for three species separately Shark length data were not taken for two of the 124 samples in the study and so were excluded Dotted lines indicate the FDA 1 μg/g action level

shark ($p<0.001$; n = 67) and for the bull shark ($p<0.005$; n = 29), which were the two species represented by the largest sample sizes, but did not hold for other species with lower samples sizes over a narrow range of total length, such as the blacktip shark (Figure 2). In all four cases of samples from pregnant female sharks and some of their fetuses, the fetuses contained lower MeHg concentrations than their mothers (Table II).

When the nine collection sites were grouped into four regions (Figure 1 and Table I), MeHg in the sharks was found to vary significantly by location according to K-W ANOVA ($p<0.001$). Regional percentage of shark samples with ≥1 μg/g MeHg ranged from a low of 3.4% in the northeast to a high of 46.4% in the southwest. Dunn's method determined that the northeast sharks contained significantly lower levels of MeHg ($p<0.05$), but the test could not distinguish between the other three regions. Therefore, sharks collected off the southern half of the Florida peninsula from St. Petersburg to Cape Canaveral contained uniformly higher MeHg concentrations than sharks off the northeast coast.

These results indicate relatively high levels of MeHg in the muscle tissue of Florida coastal sharks, with significant differences among species, sizes and distributions of sharks. The positive correlation with size of shark has been documented for other

TABLE II

Methylmercury concentration (μg/g wet weight) in muscle tissue of pregnant sharks and their fetuses

Shark Species	Region	Maternal MeHg	Fetal MeHg
Sandbar	SW	0.85	0.21
			0.24
Sandbar	SW	0.91	0.11
			0.11
			0.12
			0.12
Sandbar	SW	1.26	0.74
			1.17
Tiger	NE	0.44	0.13
			0.20

shark species (Forrester *et al.*, 1972; Walker, 1976; Marcovecchio *et al.*, 1991; Leah *et al.*, 1991) and is most likely related to accumulation of Hg as sharks age and grow, although ontogenetic variations in diet cannot be ruled out. The relatively lower levels of MeHg in northeastern Florida sharks, especially as seen in blacktip, bull, and sandbar sharks, are indicative of environmental and/or stock differences between the northern and southern parts of the state. Further research to increase sample sizes of certain species, size ranges, and locations would help to elucidate these differences and their relationship to the specific migratory habits of Florida coastal sharks.

4. Conclusion

Methylmercury levels in Florida shark species commonly consumed by humans may frequently exceed the FDA action level of 1 μg/g. The human health concerns associated with consumption of shark meat should be weighed in relation to the specifics of the sharks being consumed, *i.e.* the shark species, size (age), and catch location, in addition to an individual's rate of consumption. The two most abundant species in the U.S. east coast commercial shark fishery, the sandbar and blacktip (NMFS, 1993), are of special concern in this regard. Although the mean value of MeHg in the sandbar shark (0.77 μg/g) was below the average for all sharks combined in this study, sandbar tissue samples contained up to 2.87 μg/g MeHg and 20.9% of sandbar samples exceeded the 1 μg/g level. A total of 71.4% of blacktip samples exceeded the 1 μg/g level, although the increase in MeHg levels from sandbar to blacktip ($\bar{x}$ = 1.30 μg/g) was not statistically significant. The MeHg levels of these and other common species such as the bull shark should be monitored in the marketplace and through fishery-independent studies where possible.

Acknowledgments

We thank the FDHRS for freeze-drying of samples, Steve Branstetter for collection of several Keys shark samples, shark tournament directors and anglers for access to sharks, the MML shark collecting crew, and student interns and volunteers for assistance in sample and data collection. This study was supported by grants to REH from the Florida Department of Natural Resources (#C-7521), the Sport Fishing Institute (#SFRP-89-19) and Robert C. Dorion.

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BIOENERGETIC CALCULATION OF MERCURY ACCUMULATION IN FISH

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Abstract. A numerical model was developed for the bioaccumulation of mercury (Hg) in fish. The model is based on the bioenergetic calculation of fish growth, food consumption, respiration, specific dynamic action and waste losses (egestion/excretion) using the program of Hewett and Johnson (1992). Based on the predation and food results obtained, the accumulation of Hg in fish is calculated taking into account the concentrations of methyl mercury (MeHg) in food and water, its intake and accumulation from food and from water, and the removal of Hg from the body. Some species at various levels of food web are considered in the multistep model applications.

The model is used to compute the changes of Hg contents in perch (as prey) and pike (as predator) caused by the release of Hg from the bottom sediments when the Kokemäki River in Western Finland was dredged. The model results were not far from the observed results even though the forcing conditions had been described only roughly.

1. Introduction

Especially in predator fish, much higher concentrations of total mercury (Tot.Hg) are generally found than in the other parts of the aquatic environment. The proportion of methyl mercury (MeHg) also increases at higher levels of the food web (eg. Verta, 1990; Harris, 1991). This variation in MeHg/Tot.Hg-ratios has directed much attention to the problems of the metyhylation/demethylation kinetics *per se* which may not be enough for useful attempts to reach practical solutions.

The accumulation dynamics of Hg and other foreign substances in fish have been known and used in calculations for years (e.g. Norstrom *et al.*, 1976; Elliott, 1976; Kitchell *et al.*, 1974; Borgman and Whittle, 1992). Quite comprehensive overviews have been published about the Hg dynamics and accumulation rates (eg. Huckabee *et al.*, 1979; Harris, 1991). The bioenergetic models for growth dynamics have been established and become easily usable (eg. Bevelhimer *et al.*, 1985; Hewett and Johnson, 1992). Their use is strongly supported by detailed studies of food composition and fish growth (eg. Korhonen and Heikinheimo-Schmid, 1993).

These heterogeneous and non-exchaustive elements can be combined by means of systems analysis into a mathematical model supported by and tested with site-specific data from the application areas. Plans for improved flood protection resulted in observations (Korhonen and Virtanen, 1993; Schultz *et al.*, 1994) and model use (Schultz *et al.*, 1994) at Kokemäki River in Western Finland. The validity of the Hg accumulation model was tested with results observed during past dredging events elsewhere in the river.

The aim of this paper is to present the model and its validity tests in the downstream part of the Kokemäki River. First, the model structure and its parameter values are

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explained. Thereafter the application area and approximations are described, and finally the results are shown and discussed. The justifications of parameter estimates, sensitivity tests and final applications are from the central part of the river. These are explained in another paper by Schultz *et al.* (1994) describing the use and role of the model in practical decision-making and planning.

2. Model Structure and Coefficients

The fish growth (dW/dt) is determined by the bioenergetic balance

$$G = C - (R + S) - (F + U) \quad (1)$$

G = growth rate (g/day)
C = food consumption (g/day)
R = losses by respiration (for body processes and movement, standard metabolism and active metabolism)
S = losses accounted for by specific dynamic action (SDA)
F = egestion (fecal waste losses)
U = excretion (other waste losses)
W = fish weight (g)
t = time (day).

The food consumption C is specified and is futher considered as a sum of several food groups. The metabolic (R, S) and waste (F, U) losses are calculated according to Hewett and Johnson (1992). The final net growth rate G results in changes dW/dt in fish weight W with time t.

The Hg content P in fish is changed respectively

$$dP/dt = Kf + Kw - Lp \quad (2)$$

P = mercury content in fish (mg)
Kf = increase of mercury content from food (mg/day)
Kw= increase of mercury content from water through gills (mg/day)
Lp = decrease of mercury content with losses (mg/day).

$$Kf = Epf * Cpf * C \quad (3)$$

Epf= relative efficiency of mercury intake from food (0 ... 1)
Cpf= methylmercury content of food (mg/kg)
C = food consumed (g/day).

$$Kw = Epw * Cpw * Q \quad (4)$$

Epw= relative efficiency of mercury intake from water (0 ... 1)
Cpw= methylmercury content of water (ng/l)
Q = water flow through gills needed for inhalation (l/day).

$$Q = (R + S)/ (Eox * Cox * Win) \quad (5)$$

R+S= sum of metabolic losses, used for inhalation (g/day)
Eox= efficiency of oxygen intake from water (0 ... 1)
Cox= dissolved oxygen content in water (mg/l)
Win= Winberg's factor for the energy effects of oxygen inhalation (= 3.42 kcal/g = 3.42 g fish/ mg oxygen).

According to Norstrom *et al.* (1976), the mercury losses Lp depend on the fish weight W

$$Lp = Kcl * P * W^r \quad (6)$$

Kcl= relative clearance rate (g^{-r}/day)
P = mercury content in fish (mg)
r = steepness exponent of the weight dependency (−1 ... 0).

The special observations and sensitivity tests in the central part of the river (Schultz *et al.*, 1994) resulted in the numerical values of model coefficients as follows:

Parameter	(Unit)	Perch	Pike
Epf	(-)	0.6	0.6
Epw	(-)	0.12	0.12
Eox	(-)	0.75	0.75
Win	(g/mg)	3.42	3.42
r	(-)	-0.8	-0.58
Kcl	(g^{-x}/day)	0.029	0.029

3. Application area and approximations

The downstream regions of the Kokemäki River within 10 km from the estuary were dredged for flood protection between 1980 and 1987. At these areas the MeHg content is about 0.2 ng/l in water, 0.05 mg/kg in the food of 0 - 3 year old perch and 0.1 mg/kg in the food of older perch. The sediments are mainly clay and silt with Tot.Hg about 2.8 mg/kg at the surface from 0 to 15 cm and 0.06 mg/kg below 15 cm. The drainage area of the river is 26 000 km^2 and the mean flow MQ is 220 m^3/s.

For the validity test, the model is applied to the areas near the estuary for 1970 - 1992. Pike is considered to be the final predator and perch to be its prey, living on heterogenous food. From dredging during the growth season, 1% of sediment Tot.Hg is assumed to be released to water as MeHg. In the two peak flow years 1981 and 1988, when the June - September mean flow was more than twice the average, an additional 0.1 ng/l increase in MeHg in the water is further assumed. Finally, the concentration of MeHg in perch food is assumed to be directly proportional to the concentration of MeHg in water.

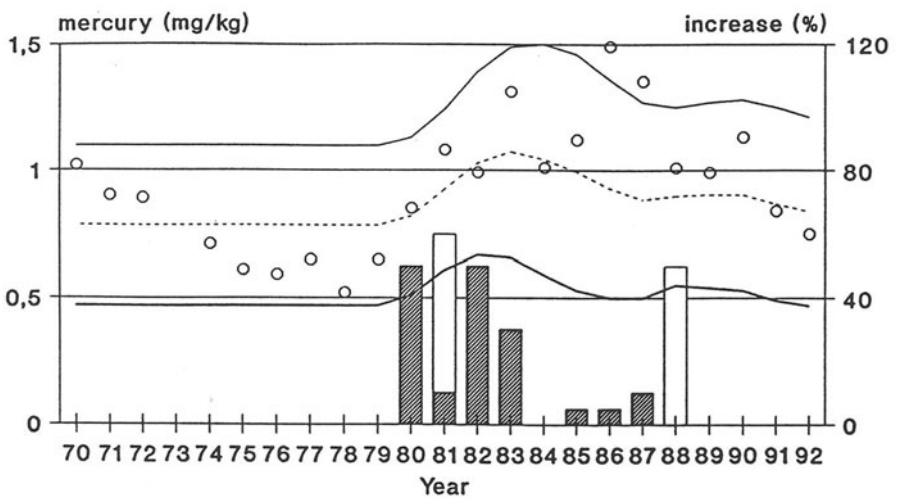

Figure 1. The model results of MeHg in 1 kg male (thin line) and female (thick line) pike and their average (broken line) compared with the observed results (dots, without attention to sex). The relative increases in MeHg in water and food of perch as the results of dredgings (shadowed) and floods (open) are shown by the columns (and the scale on the right axis).

4. Results

The similarity between the observed results and the model results is obvious (Figure 1). Perfect agreement with samples of 2 – 35 fish for 23 years cannot justly be expected, especially when sex distribution of samples is not known. Inaccurate forcing and rough approximations have further smoothed down the model results.

Rapid growth rate of females has decreased their Hg content. Spawning had no effect on Hg concentrations of females since Hg concentration of spawn was supposed to equal that of fish. The high concentrations observed in the begining of seventies are result of high Hg discharges into river (Schultz *et al.*, 1994).

5. Conclusion

Systems analysis is a powerful tool for binding together incomplete data and understanding into most useful practical results and conclusions. In addition, the model helps one to evaluate the relative importance of influencing factors, to distinguish the most important factors from the secondary ones and to direct attention to the most severe gaps in the knowledge. The qualitative agreement between the observed and the model contents of Hg in pike supports the use of model for future predictions and decisions. More accurate quantitative validity tests call for isolated laboratory conditions.

Accumulation of Hg from sediments and from water to the phytoplankton, zooplankton, phytobenthos and zoobenthos is not included in the fish model. These main steps of enrichment can be accessed mainly by laboratory tests.

Under natural conditions, the concentrations of MeHg are controlled by the Tot.Hg concentrations, the season (water temperature) and the trophic level (biological compartment) considered. In the present approach no explicit attention was paid to the methylation and demethylation rates.

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The Methylmercury to Total Mercury Ratio In Selected Marine, Freshwater, and Terrestrial Organisms

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Abstract. Total and methylmercury concentrations were determined in muscle and organ tissue from a wide variety of marine and terrestrial organisms spanning several trophic levels Sediment and water samples from many of the tissue sampling sites were also analyzed to assess the degree of mercury contamination to which the animals were exposed The methylmercury to total mercury ratios were examined to determine whether this ratio is indicative of elevated exposure to organic or inorganic mercury and how it varies relative to tissue type and position in the food chain As an ancillary study, a subset of these tissues was analyzed as 1) wet tissue, and 2) freeze-dried, ball-milled tissue to determine whether the form of sample preparation can adversely affect mercury analysis Results indicate that the methylmercury to total mercury ratios generally approach unity only in muscle tissue of higher food chain carnivorous fish residing in waters that are relatively uncontaminated with respect to inorganic mercury species Herbivorous terrestrial mammals and low food chain marine organisms tend to have very low methylmercury to total mercury ratios Marine animals placed higher on the food chain, such as crabs and lobsters, exhibit somewhat higher methylmercury to total mercury ratios and can exhibit a large variation in this ratio between organ tissue and muscle tissue of the same animal The samples analyzed as both wet and freeze-dried, ball-milled tissue indicate that freeze-drying and ball-milling in no way result in mercury loss or contamination and, in fact, result in better replicate analyses and create a sample sufficiently stable to be archived for several years without refrigeration

1. Introduction

The purpose of this study was to examine the ratio of methylmercury to total mercury in a variety of species, trophic levels, and environments, to determine whether this ratio is affected by the condition of the environment with respect to mercury contamination. The concentrations of methylmercury and total mercury and the resulting ratio of these two compounds were determined for samples of fish muscle and liver (when available), marine invertebrates, and rodents. These samples were collected from a variety of locations, including pristine arctic lakes, marine industrial harbors, offshore marine reference sites, coastal sites ranging from heavily industrialized to pristine, and a shipwreck containing large amounts of mercury released from the cargo. Water and sediment samples were analyzed from theses sites to determine degree of mercury contamination of the sites. The water and sediment data is too voluminous to present in this work but will be summarized where relevent in discussion of the tissue results.

As an ancillary study, total and methylmercury concentrations were measured on a suite of samples using both wet tissue and freeze-dried tissue to examine whether freeze-drying had an effect on the measured concentrations. Freeze-drying is a

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desirable step in sample handling because it results in a long-lasting stable matrix that can be ball-milled into a homogenous sample.

2. Material And Methods

Tissue samples were collected by a variety of means. Arctic fish were collected by hook and line; ground squirrels were trapped. Muscle and liver samples were excised in the field and shipped on ice to the laboratory. Flounder and lobsters were collected by hook and line or by trap. Some of the reference (offshore) samples were purchased from fishermen. All samples from the wreck site were collected by divers, returned to the surface in clean containers, packaged on shipboard and returned on ice to the laboratory. Near-shore mussel samples (east and west coast) were collected with gloved hands, put in clean buckets, and then shucked in a clean air hood at the laboratory. Sediment samples were collected at several of the sites in acid-cleaned glass jars and shipped to the laboratory on ice. Upon arrival at the laboratory, all samples except those to be used for the wet/dry experiment were freeze-dried and ball-milled. The samples were then digested and analyzed for total mercury and methylmercury. To determine total mercury, samples were digested by a strong acid (nitric/sulfuric or nitric/perchloric/hydrofluoric) method. The samples were then analyzed using a cold vapor atomic absorption technique. The typical detection limit for the method was 0.001 μg/g as Hg (1 ppb). For methylmercury analysis, tissue samples were digested with KOH/methanol and then analyzed by the method of Bloom (1989). The typical detection limit is 0.001 μg/g as Hg (1 ppb) for tissue. "Clean" trace metal techniques were used for all phases of this research. National Research Council of Canada certified reference materials for total and methylmercury in tissues (DORM-1, DOLT-1, or TORT-1), matrix spikes, duplicate samples, spiked blanks, and blanks were routinely analyzed to ascertain data quality.

3. Results and Discussion

Because the data are composed of a number of subgroups, results will be discussed as follows: 1) fish and rodents collected at a relatively pristine arctic location, 2) flounder and lobsters collected from inside and outside an industrial harbor on the east coast of the United States, 3) marine invertebrates collected inside and outside the hold of a shipwreck containing large amounts of mercury spilled from the cargo, and 4) mussels collected from sites representative of the east and west coasts of the United States. Group 4 was also used to investigate the effects of freeze-drying samples on the test results.

3.1 ARCTIC FISH AND RODENTS

Samples were collected from or near three lakes in the Alaskan arctic. Muscle and liver tissue from four species of fish were analyzed for total mercury (THg) and

methylmercury (MeHg). The MeHg/THg ratio for all species was 1.00 ± 0.1 for muscle tissue but lower (0.4 to 0.8) for liver tissue (Figure 1). This is common for upper trophic level piscivorous fish (Huckabee et al., 1975). The Hg and MeHg concentrations of the different tissue types of grayling and lake trout are shown in Figure 2; arctic char and whitefish were not included because of the limited number of methylmercury in liver values that resulted from insufficient sample mass. There were two striking differences between the grayling and lake trout. The lake trout had Hg and MeHg concentrations roughly 2-3 times higher than the grayling from the same lake. The trout were generally larger, older fish, and consumed a mixed diet of fish, snails, and insects, whereas the grayling consumed primarily insects based on gut contents (unpublished data). The lake trout also had lower THg and MeHg concentrations in the liver than in the muscle, the reverse was true for the grayling. One would normally expect the proportion of inorganic Hg to be greater in the liver, due to enhanced retention in that organ by metallothionein (Konovolov, 1994). The Hg concentrations in the fish from Feniak Lake were 2-4 times higher than those from Elusive Lake,

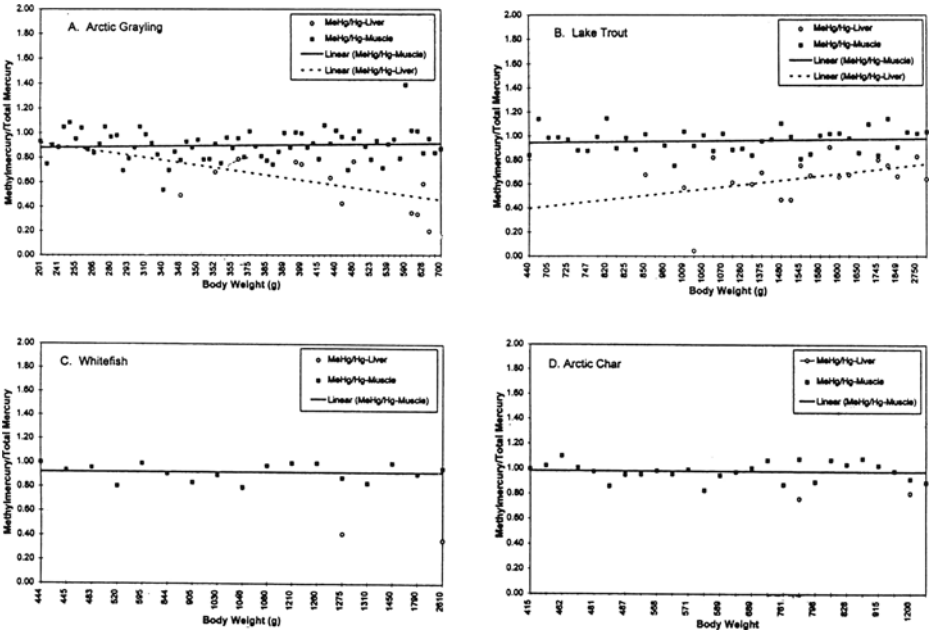

Fig.1. MeHg/THg ratios in arctic fish.

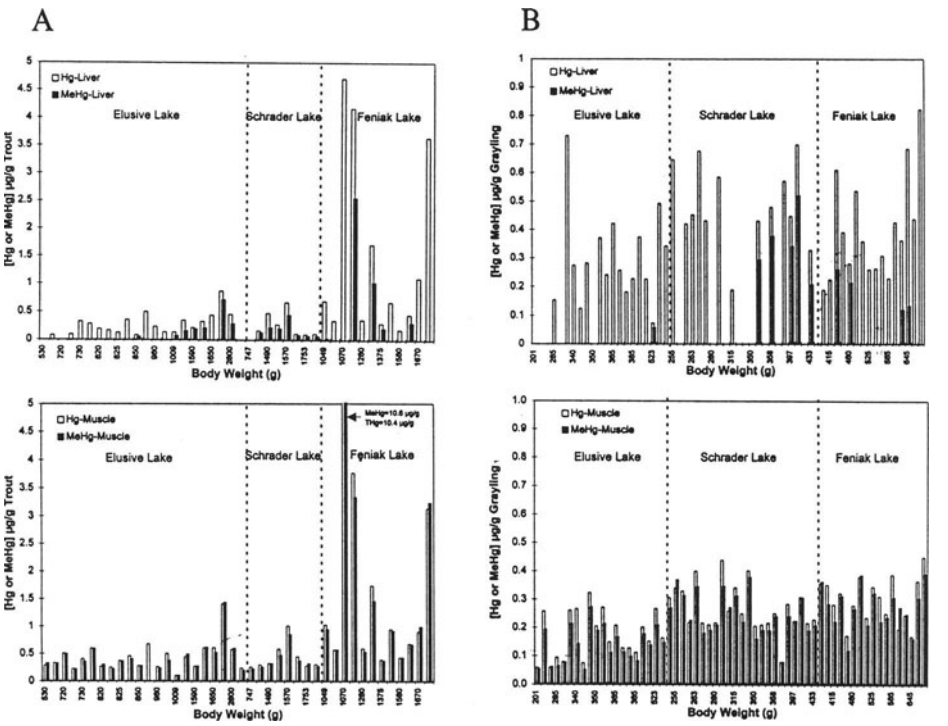

Fig. 2. Mercury speciation in arctic fish by site (A=Trout, B=Grayling)

whereas concentrations in Schrader Lake fish were intermediate between those two lakes, possibly because Feniak Lake had higher Hg concentrations in the sediment. Selenium (Se) levels were also higher in the tissue from Elusive Lake than in that from Feniak Lake. It has been proposed that Se can have a mitigating effect on Hg uptake in fish exposed to Hg-contaminated sediment (Siegel et al, 1991).

Ground squirrel liver tissue from the vicinity of Elusive and Feniak lakes was also analyzed for THg and MeHg (Figure 3). The MeHg concentrations were low (<0.01 to 0.04 µg/g) and consistent between the two lakes. The THg concentrations varied widely between the two lakes, with an average of 0.025 µg/g at Elusive Lake and 0.18 µg/g at Feniak Lake. The elevated THg concentrations at Feniak Lake result in much lower MeHg/THg ratios than at Elusive Lake, and may reflect elevated sediment Hg levels at Feniak Lake resulting from the proximity of Feniak Lake to the mineral-rich deposits of the nearby DeLong Mountains (USGS, 1991).

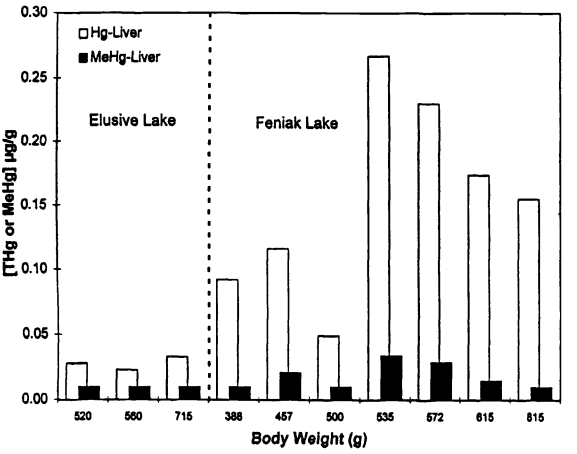

Fig. 3. Mercury speciation in arctic ground squirrels.

3.2 FLOUNDER AND LOBSTER FROM AN INDUSTRIAL PORT

Flounder flesh and liver and lobster claw/tail and hepatopancreas were analyzed from samples collected both in the harbor and from offshore reference sites (Figure 4). The in-harbor lobsters had MeHg/THg ratios of 0.2 to 0.8, with the lowest ratios in juveniles and subadults. This could be because the juveniles and subadults spend more time in burrows and are therefore more exposed to contaminated sediment or because

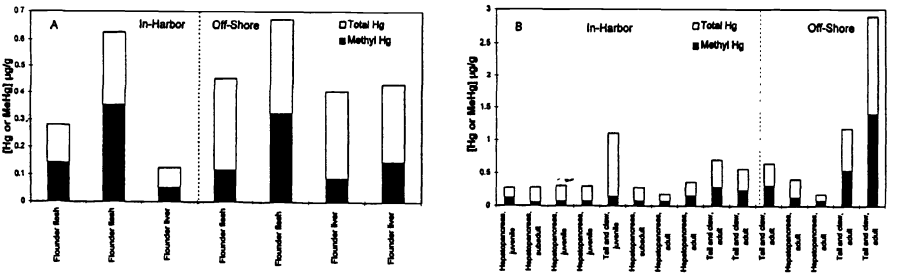

Fig. 4. Mercury speciation in flounder (A) and lobster (B).

the younger animals have not developed the larger MeHg accumulations common to the adults (Wright, 1991). There was no statistically significant difference between the MeHg/THg ratios of in-harbor and offshore adult lobsters. No juvenile lobsters were captured at the offshore reference sites. The flounder tissue results were surprising. The in-harbor flounder had average MeHg/THg ratios approaching unity, whereas the offshore flounder had generally lower ratios (0.25 to 0.9), because the THg concentrations were higher for the offshore fish. However, because sample numbers were limited for this tissue type, perhaps these data should be considered anecdotal.

3.3 INVERTEBRATES FROM A CONTAMINATED SHIPWRECK

Anemones, urchins, starfish, mussels, and crustaceans were collected from both within the Hg- contaminated hold of a sunken vessel and from the uncontaminated seafloor adjacent to the vessel (Figure 5). The vessel is contaminated from spillage of approximately 17,000 pounds of elemental mercury from ceramic ampules after the ship broke up and sank in the 1940's. Contamination is largely confined to the holds. Anemones and starfish were freeze-dried whole, then ball-milled and digested. Mussels and urchins were shucked, and only the soft parts were digested and analyzed. Crustacean flesh and digestive organs were analyzed, as well as several whole small crabs. In anemones, the MeHg concentrations were consistent (<0.01 to 0.04 μg/g) between samples from both inside the hold and on the seafloor, whereas the THg concentrations varied from an average of 0.35 μg/g inside the hold to an average of 0.18 μg/g on the seafloor. As a result, the MeHg/THg ratio varied from an average of 0.05 inside the hold to 0.22 on the seafloor due to the higher THg in organisms inside the hold. A similar trend was seen in the urchins. MeHg concentrations averaged 0.03 μg/g or less, whereas THg ranged from 1 to 223 μg/g in the hold and 0.25 to 6 μg/g on the seafloor. The resulting MeHg/THg ratios varied from 0.0001 to 0.02 inside the hold and 0.003 to 0.07 on the seafloor. In mussels, the MeHg concentration was higher inside the hold (avg. 0.04 μg/g) than on the seafloor (avg. 0.02 μg/g). THg concentrations were also elevated inside the hold (avg. 1.5 μg/g) relative to the seafloor (avg. 0.5 μg/g). The resulting MeHg/THg ratio averaged 0.03 inside the hold versus 0.055 on the seafloor. In starfish, with the exception of a single sample from the hold with highly elevated THg, the THg and MeHg concentrations were not significantly different inside and outside the hold. It is possible that these organisms, which are more mobile than the anemones, urchins, and mussels, had been moving in and out of the hold at will and had therefore been exposed to both environments. The crustaceans showed significant differences in THg and MeHg concentrations and MeHg/THg ratios between tissue types, but lack of data for different tissue types both inside and outside the hold limited the conclusions about these parameters. Whole crustaceans from inside the hold showed the highest THg concentrations (0.3-6.9 μg/g); the single sample collected outside the hold had the lowest concentration. MeHg concentrations for the whole crustaceans were fairly consistent at 0.02 to 0.05 μg/g. The resulting MeHg/THg ratio ranged from 0.003 to 0.125. The highest ratio belongs to the sample collected on the seafloor. All but one of the digestive organ and muscle samples were collected outside the hold. The digestive organs had MeHg/THg ratios of 0.04 to 0.09,

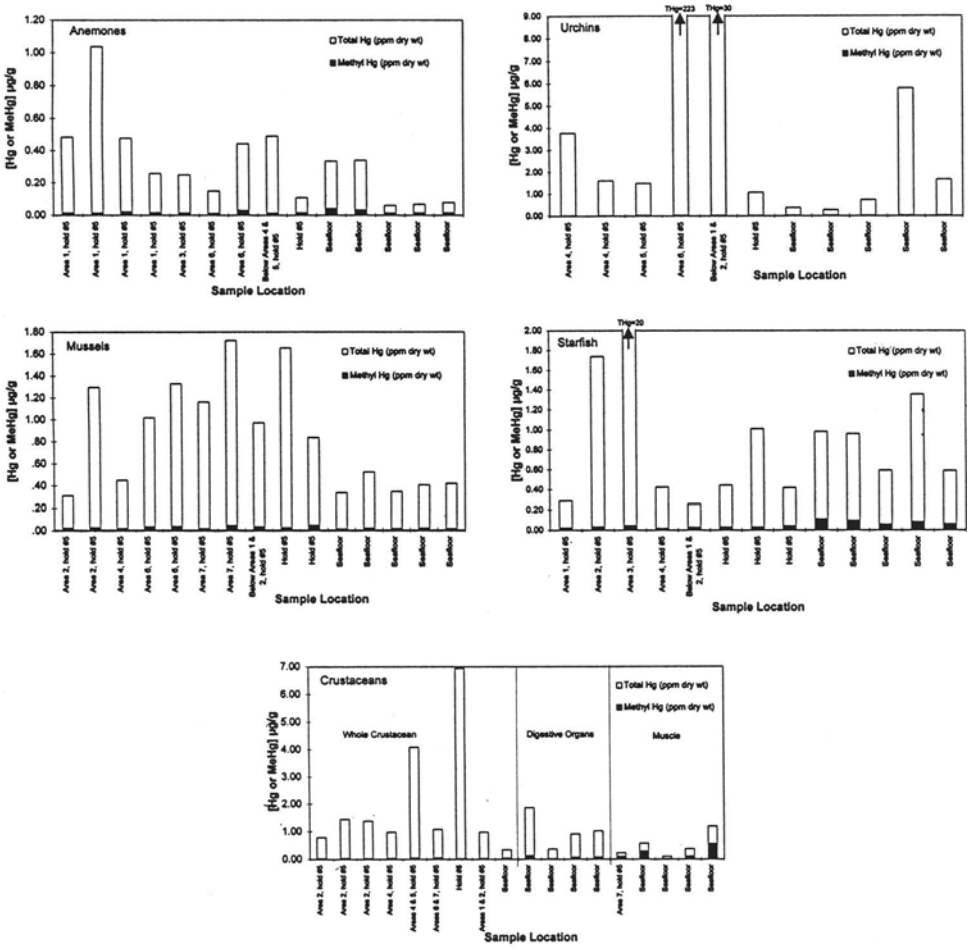

Fig. 5. Mercury speciation in invertebrates from a contaminated wreck

and the muscle samples had MeHg/THg ratios of 0.164 to 1.0, much higher than the digestive organs and whole crustaceans. The single muscle sample collected inside the hold had a MeHg/THg ratio in the middle of the range.

3.4 MUSSELS FROM THE EAST AND WEST COASTS (UNITED STATES)

Shucked mussels from 21 sites along the east and west coasts of the United States were analyzed for THg and MeHg, as well as silver (Ag) and lead (Pb), which can be indicative of pollution from anthropogenic sources (Figure 6). The THg concentrations varied from 0.06 to 0.6 μg/g. The MeHg concentrations varied from 0.02 to 0.2 μg/g.

The MeHg/THg ratios varied from 0.15 to 0.8. When THg and the MeHg/THg ratio are compared with Ag and Pb concentrations, a positive correlation is seen with THg and a negative correlation is seen with MeHg/THg. A subset of 6 of the 21 samples was also analyzed in triplicate as both fresh and freeze-dried tissue. Both THg and MeHg concentrations agreed well between the two sample types (Figure 7). Percentage deviation among the three replicates averaged 2.2% lower for the freeze-dried tissue for both THg and MeHg. This is probably because freeze-dried tissue can be homogenized more effectively by ball-milling than wet tissue can be homogenized by maceration.

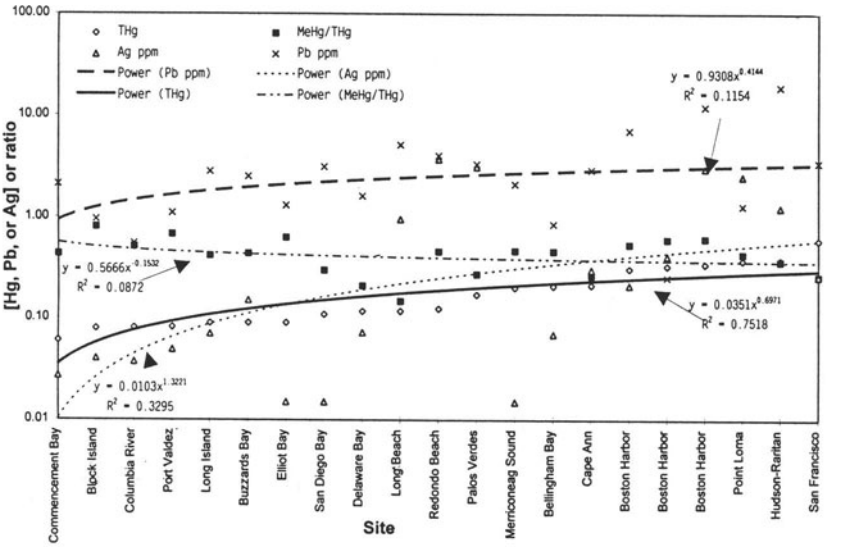

Fig. 6. Contaminant concentrations in mussel samples.

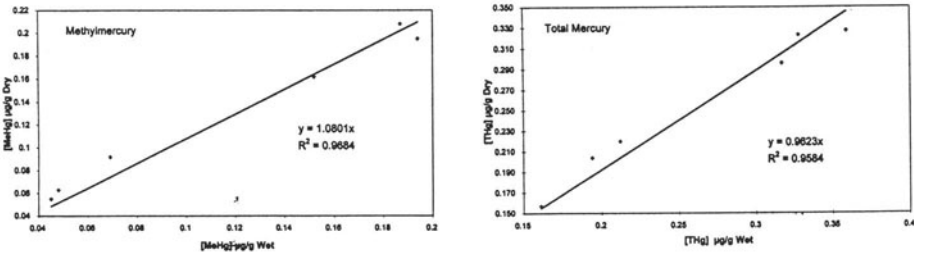

Fig. 7. Comparison of Hg and MeHg analyses in fresh and freeze-dried tissue

4. Conclusions

Results indicate that the MeHg/THg ratio generally approaches unity only in muscle tissue of higher food chain carnivorous fish residing in waters that are relatively uncontaminated with respect to inorganic mercury species. The MeHg/THg ratio in liver tissue of the same fish is generally lower. Herbivorous terrestrial mammals and low food chain marine organisms, such as mussels, urchins, and anemones, tend to have very low MeHg/THg ratios that are apparently influenced by degree of environmental Hg contamination. Marine animals placed higher on the food chain, such as crabs and lobsters, exhibit somewhat higher methylmercury to total mercury ratios and can exhibit a large variation in this ratio between organ tissue and muscle tissue of the same animal. The samples analyzed as both wet and freeze-dried, ball-milled tissue indicate that freeze-drying and ball-milling in no way results in mercury loss or contamination and, in contrast, results in better replicate analyses and creates a sample sufficiently stable to be archived for several years without refrigeration.

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BIOACCUMULATION OF MERCURY AND METHYLMERCURY

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Abstract. The factors controlling the accumulation of mercury in fish are poorly understood. The oft invoked lipid solubility of MMHg is an inadequate explanation because inorganic Hg complexes, which are not bioaccumulated, are as lipid soluble as their MMHg analogs and, unlike other hydrophobic compounds, MMHg in fish resides in protein rather than fat tissue. We show that passive uptake of the lipophilic complexes (primarily $HgCl_2$ and CH_3HgCl) results in high concentrations of both inorganic and MMHg in phytoplankton. However, differences in partitioning within phytoplankton cells between inorganic mercury - which is principally membrane bound - and MMHg - which accumulates in the cytoplasm - lead to a greater assimilation of MMHg during zooplankton grazing. Most of the discrimination between inorganic and MMHg thus occurs during trophic transfer while the major enrichment factor is between water and phytoplankton. As a result, MMHg concentrations in fish are ultimately determined by water chemistry which controls MMHg speciation and uptake at the base of the food chain.

1. Introduction

Mercury (Hg) contamination of fish is a widespread problem with important public health concerns (Weiner and Stokes, 1990; Lindqvist et al. 1991; Fitzgerald and Clarkson, 1990). The increasing concentration of Hg, principally as MMHg, in higher trophic levels of the aquatic food chain contrasts sharply with that of other trace metals whose concentrations remain constant or decrease with increasing levels in the aquatic food web (Bernhard and Andreae, 1984). The "biomagnification" of Hg resembles that of hydrophobic organic trace pollutants rather than that of ionic metals and is generally thought to result from the lipophilic character of MMHg. Few studies have addressed this issue quantitatively, however, and the accepted explanation may be too simplistic. Indeed, the predominance of MMHg in fish muscle rather than fat tissue (Bloom, 1992) indicates that accumulation is not controlled solely by lipid solubility.

This study confirms that neutral complexes of inorganic Hg are as lipid soluble as their MMHg analogs and both Hg and MMHg accumulate in phytoplankton by passive diffusion across the membrane, as found *in vitro* studies (Gutkneckt, 1981; Bienvenue et al., 1984). But, in contrast to MMHg, inorganic Hg is not biomagnified as the trophic transfer from phytoplankton to zooplankton is much more efficient for MMHg. We show that this is due to the greater relative concentration of MMHg in the algal cytoplasm compared to inorganic Hg which is associated with the cellular membranes. Furthermore, a simple model incorporating these factors can account for the general correlations that are observed between Hg in fish and environmental variables, such as the pH of lakes (e.g. Cope et al., 1990; Lindqvist, 1991, Grieb et al., 1990; Haines et al., 1994; Hakanson et al., 1988; Weiner, 1987; Driscoll et al., 1994).

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2. Methods

To ascertain the uptake rate in long-term experiments in which cellular Hg reaches a steady state as it is continuously accumulated and diluted by cell division, cultures of the marine diatom, *Thalassiosira weissflogii*, were exposed to Hg and MMHg at different concentrations and salinities, and were sampled at periods during exponential growth (Mason et al., in prep.). The average concentration per cell was determined from cell counts and total Hg per filter. Hg analyses relied on derivitization and atomic fluorescence quantification techniques (Bloom and Fitzgerald, 1988; Bloom, 1989; Mason et al., 1993). All sample manipulation and degassing was done under clean room conditions. Short-term experiments also involved *T. weissflogii*. As uptake by passive diffusion depends only on the water column speciation, it should not be hindered if the diatoms are stressed i.e. the diatom is acting as an enclosed lipid membrane. This fact allowed us to perform short-term uptake experiments over a much wide variety of pH (range 4 - 8) and chloride concentrations (0.5 M to 10^{-5} M Cl^-). Microscope examination showed that the diatom membrane remained intact under these conditions.

To determine octanol-water partition coefficients (K_{ow}), known volumes of water of varying but known pH and chloride concentration (Cl^- was measured by ion chromatography) containing Hg or MMHg were shaken up with a known volume of octanol. The concentration of Hg or MMHg remaining in the water phase was then determined, allowing the calculation of the overall partition coefficient, D_{ow} (D_{ow} = conc. in octanol/conc. in water). The speciation of the Hg or MMHg in the water was determined using the MINEQL program. Assuming that only neutral complexes partition, it was possible to extract the K_{ow}'s for the various neutral species from the data obtained at different pH and Cl^- concentrations as $D_{ow} = \Sigma\alpha_i.(K_{ow})_i$ where α_i is the proportion of the species i.

To measure trophic transfer of Hg and MMHg between phytoplankton and zooplankton, zooplankton were fed, in 4-5 hour experiments, phytoplankton which had been exposed to either Hg or MMHg in long-term culture. The concentration of Hg and MMHg per cell was determined as well as the cellular fractionation. Cells, broken by sonication, were centrifuged to separate the "membrane" from the "cytoplasm" and the amount of Hg or MMHg in each fraction measured. After zooplankton grazing, fecal pellets, as well as animals, were collected and analyzed, allowing estimation of assimilation from both mass balance considerations and tracer calculations. Assimilation was estimated using the method of Tande and Flagstad (1985), with silicon as the unassimilated tracer i.e.: Assimilation efficiency = $[(Hg/Si)_{food} - (Hg/Si)_{feces}]/(Hg/Si)_{food}$. Mass balance calculations concurred with the results from the ratio method.

3. Results and Discussion

As a simple means to quantify the lipid solubility of mercuric species, we measured the K_{ow}'s of the chloride and hydroxide complexes of inorganic Hg and MMHg (Table 1). As previously reported, $HgCl_2$ and CH_3HgCl are fairly hydrophobic compounds (Faust, 1991; Major et al. 1991). The K_{ow}'s for $HgCl_2$, HgOHCl, and $Hg(OH)_2$ have not been reported before but our values (3.3, 1.2, and 0.05, respectively) are consistent with the range of overall partition coefficients published for inorganic Hg at various OH^- and, usually unreported, Cl^- concentrations (Bienvenue et al., 1984; Halbach, 1985). With these species specific K_{ow}'s, we calculated the overall apparent partition coefficient (D_{ow}) for both MMHg and inorganic Hg in the water in our experiments on the basis of the chemical parameters, chiefly OH^- and Cl^- concentration.

To assess the role of chemical speciation and hydrophobicity in the bioaccumulation of Hg by microorganisms we measured the accumulation of Hg and MMHg by the marine diatom, *Thalassiosira weissflogii*, both in long-term growth experiments and in short-term accumulation experiments. The changes in the accumulation rate with changing Hg and MMHg speciation, for the same total exposure concentration, were best explained by passive diffusion through the membrane rather than by facilitated transport (Mason et al., in prep.). For passive diffusion, the membrane permeability, normalized to surface area, is given by the ratio of the accumulation rate and the exposure concentration (Stein, 1986; Hudson et al., 1994). The resulting slopes of the regressions of uptake rate versus permanent concentration yielded permeabilities that are consistent with each other in the long and short-term experiments (Table 1).

Compound	K_{ow}	Experimental Estimate of P
$HgCl_2$	3.3	7.4*
$Hg(OH)_2$	0.05	0.11
HgOHCl	1.2	--
CH_3HgCl	1.7	7.2
CH_3HgOH	0.07	0.29

*All permeabilities are in units of 10^{-4} cm s^{-1}

TABLE 1: Measured values for the octanol/water partition coefficient (K_{ow}) for Hg and MMHg complexes and estimated permeabilities P (x 10^{-4} cm s^{-1}) for inorganic and MMHg compounds determined experimentally from both long-term and short-term uptake experiments with marine diatoms. The octanol/water partition coefficient of MMHg hydroxide is taken from Faust (1991).

In general, the membrane permeabilities of the four neutral complexes co-varied with their respective K_{ow}'s. The permeabilities for the chloride complexes were smaller than those estimated previously (Gutknecht 1981; Bienvenue et al. 1984) - our calculations assumed the entire membrane was lipid. When corrected for molecular size, our results are comparable with the general correlation between permeability and K_{ow} published by Stein (1986) for organic compounds diffusing through red blood cell membranes (Figure 1). This again is strong evidence that inorganic and MMHg accumulated through passive diffusion of the neutral species in our experiments. While our data confirm that hydrophobic neutral Hg species are the principal Hg compounds accumulating in microorganisms, they do not explain the much greater bioaccumulation of MMHg over inorganic Hg higher in the food chain.

To test if the greater bioaccumulation of MMHg over inorganic Hg is the result of a more efficient trophic transfer, we fed *T. weissflogii* exposed either to CH_3Hg or Hg to marine copepods collected from Massachusetts Bay. The assimilation efficiency (calculated by normalizing the Hg contents of the algae and feces to silica) of MMHg from phytoplankton to zooplankton was four times greater than that of inorganic Hg (62% vs. 15 %) (Figure 2). These results were consistent with the measured distribution of the organic and inorganic Hg between the algal cytoplasm (63% vs. 9%) and membranes (37% vs. 91%) and fit well with the general correlation developed by Reinfelder and Fisher for a suite of elements (Reinfelder and Fisher, 1991). The cellular partitioning and assimilation efficiency of inorganic Hg is similar to that of Ag^+. Both Hg^{2+} and Ag^+ are sequestered in algal membranes, likely through bonding with thiol groups. They are thus poorly assimilated by zooplankters which digest the dissolved cytoplasmic content but simply defecate the membrane material. In this "eat-the-grapes-and-spit-the-skins" model of zooplankton feeding, the efficient assimilation of MMHg, which resembles that of sulfur or phosphorus, is attributable to the high fraction that is sequestered in the algal cytoplasm. The reactivity of MMHg with functional groups in the membrane, particularly thiol groups, is apparently sufficiently lower than that of inorganic Hg to explain the difference. As expected from our laboratory assimilation studies, the ratio of MMHg to inorganic Hg in zooplankton was measured to be four times greater than that in phytoplankton in field experiments at Little Rock Lake, Wisconsin: a factor of 4.5 in one basin and 3.6 in the other, as calculated from their bioconcentration factors (Watras and Bloom, 1992). Others have also noted the greater bioaccumulation of MMHg by zooplankton, which also occurs between zooplankton and planktivorous fish (Boudou and Ribeyre, 1983). Thus, the differential bioaccumulation of organic and inorganic Hg is governed, on the one hand, by the different proportions of each that are present as the neutral hydrophobic complexes and, on the other, by the greater assimilation efficiency of MMHg over inorganic Hg by zooplankton, with further discrimination up the food chain.

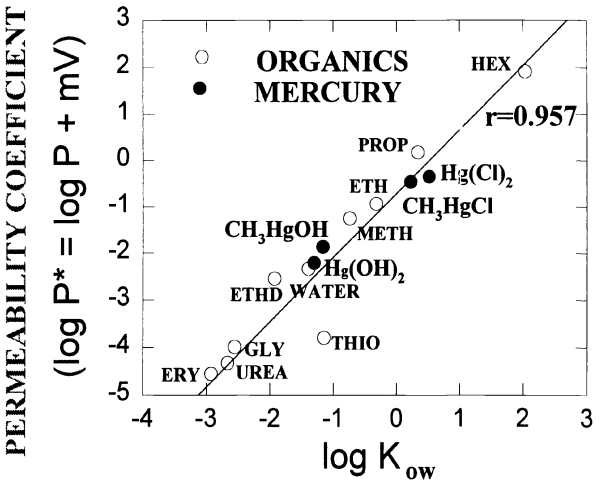

FIGURE 1: Relationship between the relative permeability and the octanol-water partition coefficient (K_{ow}) for Hg species (solid circles) and a variety of organic compounds (open circles). For passive diffusion, the membrane permeability, P is related to the K_{ow} by the following expression: $P = K_{ow}.D_{mem}/l$ where l is the membrane thickness and D_{mem} is the diffusion coefficient of the compound within the membrane. As D_{mem} is a function of molecular size, the general relationship between P and K_{ow} is not linear. By correcting permeabilities for size effects, Stein (1986) derived a relationship between P and K_{ow} that accounts for the decrease in D_{mem} with increasing molecular volume. Based on empirical data for organics diffusing through red blood cell membranes, the size corrected P, P* is given by: $\log P^* = \log P + m.V$ where V is the van der Waals radius ($cm^3\ mol^{-1}$) and m is a proportionality constant with a value of 0.0546 mol cm^{-3}. The corrected permeability data for the organic compounds in Fig. 1 are taken from Stein (1986) while P* for the Hg compounds was calculated using the average values of P from Table 1. Compounds are, in terms of increasing P*: ERY erythritol, UREA, urea, GLY glycerol, THIO thiourea, ETHD ethanediol, WATER, water, METH methanol, ETH ethanol, PROP n-propanol and HEX n-hexanol.

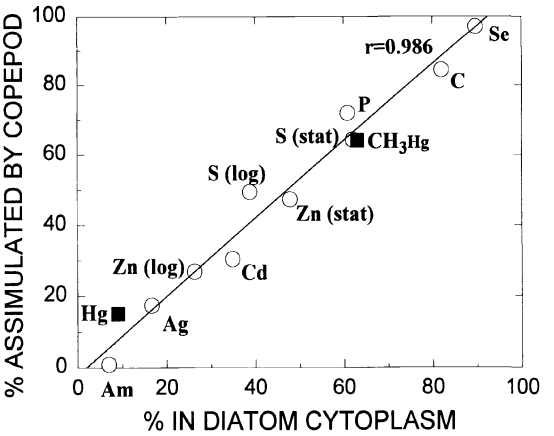

FIGURE 2: Relationship between the amount of MMHg and inorganic Hg assimilated by marine copepods fed diatoms (*Thalassiosira weissflogii*) exposed to Hg and MMHg and the percentage of the Hg found to be associated with the cell cytoplasm. Cell fractionation methods are those of Reinfelder and Fisher (1991). Data from Reinfelder and Fisher (1991) for a number of elements (Am, Ag, Cd, Zn, S, P, Se, C) are also included in the graph. STAT = stationary phase, LOG = log phase.

Because of the greater efficiency in food chain transfer (about a factor of 10 between phytoplankton and planktivorous fish), we can, in a first approximation, consider only MMHg in calculating the relationship between Hg in water and Hg in fish. In seawater, nearly 100% of MMHg is as CH_3HgCl while only 3% of the inorganic Hg is $HgCl_2$. Thus, despite the much lower concentration of MMHg compared to inorganic Hg in seawater (0.05 or less versus 1 pM; Mason and Fitzgerald, 1993), its overall bioaccumulation by planktivorous fish is expected to be at least 16 times greater (0.05 x 33 x 10). In lakes, the relative bioaccumulation depends on the lake chemistry which governs the speciation of Hg^{2+} and CH_3Hg^+. Typically, the percent of MMHg in CH_3HgCl is 0.5 to 1.5 times the percent inorganic Hg in $HgCl_2$ (Mason et al., in prep.). Nevertheless, MMHg still predominates in fish since the ratio of MMHg to inorganic Hg is substantially higher for lakes - around 0.5 (e.g. 0.5 pM MMHg and 1 pM inorganic Hg for Little Rock Lake, Wisconsin; Watras, 1990). Thus, we expect at least 70% of the Hg in freshwater planktivorous fish to be MMHg (0.5 x 0.5 x 10), but not in algae or zooplankton. Note that while most of the discrimination between inorganic and organic Hg occurs during trophic transfer, the major enrichment factor is between the water and phytoplankton (ca $10^{5.5}$ between water and phytoplankton and $10^{6.5}$ between water and fish).

We can estimate the coefficient of proportionality between the phytoplankton and lakewater from our laboratory data taking into account the average size of the algae and their growth rate. If uptake by phytoplankton is limited by the rate of diffusion through the cell membrane, then the average uptake rate measured in the laboratory experiments with *T. weissflogii* (surface area 400 μm^2) of D_{ow} x 6.01 amol/cell/hr/nM exposure (Mason et al., in prep.) must be normalized to the surface area of typical lake phytoplankton (80 μm^2) (i.e. D_{ow} x 1.20 amol/cell/hr/nM exposure). For an average freshwater MMHg concentration of 0.5 pM, the steady state phytoplankton concentration, assuming a growth rate of one division per day (μ=0.7 day^{-1}) (Hudson et al., 1994) and a specific gravity for cells of 1 g mL^{-1} (or 65 pg/cell), is 4.3 x 10^{-2}.D_{ow} (μg/g). The concentration in perch should then be proportional to that of the phytoplankton with a bioconcentration factor that reflects the average increase in concentration in the food chain - a factor of 10 (Watras and Bloom, 1992; Lindqvist et al., 1991). Thus, the MMHg concentration in perch is 0.43.D_{ow} (μg/g).

For the range of D_{ow} values for lakes in Wisconsin, the Adirondacks and in Russia (Watras, 1990; Driscoll et al., 1994; Haines et al., 1994) - from 0.07 for high pH (>7), low chloride lakes to 1.6 for low pH (<5), higher chloride lakes - we estimate a range in fish concentration from 0.03 (0.07 x 0.43) to 0.73 (1.7 x 0.43) μg/g. These values are similar to those measured in perch from these lakes - range from 0.05 to 0.8 μg/g - and, as discussed in detail elsewhere (Mason et al., in prep.), there is a overall correlation between fish concentration and D_{ow} for the combined dataset. Hence, we suggest that much of the observed variability in Hg accumulation in fish in these lakes can be accounted for by variations in the overall lipid solubility of MMHg as determined by the chloride concentration and pH of the ambient waters.

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IMPACTS OF MERCURY CONTAMINATION IN THE SOUTHEASTERN UNITED STATES

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Abstract. Mercury (Hg) contamination from a variety of point and non-point sources, including atmospheric inputs, is currently considered to be the most serious environmental threat to the well being of fish and wildlife resources in the southeastern United States. Fish consumption advisories have been issued in all ten states comprising the U.S. Fish and Wildlife Service's Southeast Region. Both freshwater and marine species have been affected with levels ranging as high as 7.0 ppm in some individuals. Many other species, including various species of reptiles, birds and mammals (including humans) are also contaminated. Impacts noted range from reproductive impairment to mortality.

1. Introduction

Although early investigations (Ogden *et al*, 1973; USFWS, unpubl. data) found elevated levels of mercury (Hg) in some piscine and avian species in Florida, intensive study of Hg contamination did not begin in the southeastern U.S. until 1989 when an endangered female Florida panther (*Felis concolor coryi*) was found dead in Everglades National Park. Tissue analyses revealed that the only contaminant present in relatively high levels was Hg (110 mg/kg [ppm] fresh weight in liver tissue). Consequently, Hg toxicosis was assigned as the cause of death (Roelke, 1990). This single event was the impetus for further studies investigating the sources and impacts of Hg contamination in the U.S. Fish and Wildlife Service's Southeast Region (Region) since 1989. The purpose of this paper is to present a brief synthesis of many of these.

2. Results and Discussion

The Region, comprised of ten southeastern states (Alabama, Arkansas, Florida, Georgia, Kentucky, Louisiana, Mississippi, North Carolina, South Carolina and Tennessee), the Commonwealth of Puerto Rico and the U.S. Virgin Islands, also contains more than 100 National Wildlife Refuges (NWR). Fish consumption advisories, issued when mean Hg concentrations exceed the Food and Drug Administration (FDA) limit of 1.0 ppm (0.5 ppm in Florida), have been issued in all ten states.

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Mercury sources within the Region are many and varied. A chlor-alkali facility was a major contributor in Alabama where sediment concentrations in excess of 7,500 ppm have been found (EAES&T, 1992). Concentrations in chain pickerel (*Esox niger*) from the area ranged from 0.52 to 3.5 ppm, and both frogs (*Rana* sp.) and snakes (*Agkistrodon piscivorus*) contained levels up to 1.6 ppm. Current studies are addressing the impact of Hg contamination on the health and reproduction of a neotropical migrant, the prothonotary warbler (*Prothonotaria citrea*). Mercury has been detected in nestlings and eggs, but histological examination and hormone assays are not yet complete.

Mercury-charged manometers used to measure pressure and delivery from natural gas wells are a major source of contamination in northeast Louisiana. Soil concentrations up to 141,000 ppm have been measured (Louisiana Department of Environmental Quality, unpubl. data) on Upper Ouachita NWR. Mercury levels in largemouth bass (*Micropterus salmoides*) collected in 1992 ranged from 0.52 to 4.04 ppm. Bass from 12 lakes, some of which are within the area of the gas field, were collected in 1993. Concentrations ranged from below detection limits (0.001 ppm) to 1.53 ppm. Other species also have been contaminated. Concentrations in liver tissue of great blue herons (*Ardea herodias*) and raccoons (*Procyon lotor*) from Upper Ouachita NWR ranged from 2.8 to 109.6 ppm and from 2.2 to 26.5 ppm, respectively. In addition, there has been one confirmed case of Hg toxicosis in a human male living near Monroe, Louisiana (Cormier, 1994).

In Tennessee, maximum Hg concentrations result from previous operations of the nuclear facility at Oak Ridge. Sediments in wetland areas adjacent to East Fork Poplar Creek contain more than 1,100 ppm Hg. Concentrations as high as 6.0, 33.2, 3.5 and 7.9 ppm were found in crayfish, earthworms, wrens and shrews, respectively. Stonerollers (*Campostoma anomalum*), a minnow common to the midwestern U.S., contained as much as 6.4 ppm Hg and concentrations in redbreast sunfish (*Lepomis auritus*) ranged from 0.2 to 1.9 ppm. A "no consumption" advisory has been issued.

Pharmaceutical company effluents have enriched sediments in localized areas of Puerto Rico to concentrations of 88 ppm. Mean Hg levels in tilapia (*Tilapia* sp.; =0.16 ppm) and tarpon (*Megalops atlantica*; =0.11 ppm) were well below FDA limits. However, levels of this magnitude could pose a threat to sensitive species of fish-eating birds (Eisler, 1987) and could have been a contributing factor in a major pelican die-off which occurred prior to plant shut-down.

Except for the lower reaches of the Ouachita and Saline Rivers in southeastern Arkansas, atmospheric deposition may be the major source of contamination in the other areas of the region. At Felsenthal NWR (Arkansas), in the Ouachita River basin immediately north of the Louisiana state line, concentrations are much higher than one would expect from atmospheric deposition alone. Abandoned cinnabar mines northwest of the refuge were suspected as the major source; however, it has been shown that Hg levels in fish living in these abandoned mine pits are below FDA limits. Mercury concentrations >3.0 ppm (geometric mean=0.65 ppm) have been found in fillets of bass and other top predators inhabiting the contaminated area (Giese, 1994). Muscle and liver tissue from a river otter (*Lutra canadensis*) collected adjacent to the refuge contained 5.3 and 19.1 ppm Hg, respectively. The Department of Health analyzed sera from 236 persons who admitted consuming more than 2 meals of fish per month from restricted

waters. Of these, 36 individuals had concentrations >20 ppb. However, no clinical signs of toxicosis were observed (Giese, 1994).

In North Carolina, the major area of known Hg contamination is the Lumber River basin. Of 32 stations sampled by the Department of Environmental Health and Natural Resources, fish at 19 stations contained Hg levels exceeding the FDA limit (Hale, 1994). Mean concentrations in muscle and liver tissues from raccoons (n=6) collected on the Alligator River NWR in the northeastern corner of the state were 0.28 (range=0.18-0.61) and 1.77 (range=1.03-3.40) ppm, respectively. In addition, blood and hair of 78 persons living near Lake Waccamaw were analyzed in 1993. The three highest levels noted were 141, 78 and 29 μg/L (ppb). None of those persons tested exhibited any clinical signs of Hg toxicosis.

The South Carolina Department of Health and Environmental Control issued consumption advisories for 13 Lowcountry rivers and the Intercoastal Waterway in March 1994. This action resulted from an extensive sampling program conducted during the previous year. Mercury concentrations in largemouth bass and bowfin (*Amia calva*) were generally greater than those in other species, ranging from <0.25 ppm (both bass and bowfin) in the Santee River to 7.0 ppm in a bowfin from the Little Pee Dee River.

Mercury contamination in Georgia has only been reported in the Okefenokee Swamp and two of the rivers draining it; the Suwannee and the St. Marys. Consumption advisories have been issued for both rivers, but, as yet, mean levels in fish from the swamp are still below the FDA limit. Raccoons (n=5) from Okefenokee had levels of Hg greater than those from North Carolina. Mean concentrations were 0.47 (range=0.23-0.80) and 2.26 (range=1.08-3.81) ppm in muscle and liver, respectively.

Although 75% of largemouth bass sampled in Mississippi contained Hg concentrations >0.5 ppm, only a few exceeded the FDA limit (Folmar, 1994). Consequently, there are currently no state-issued consumption advisories in effect in Mississippi. However, only limited consumption of bass from Tallahatchie and Dahomey NWRs is recommended by the Service.

A fish consumption advisory was issued by Kentucky in November 1993 for the Western Kentucky Wildlife Management Area (WMA) where Hg levels in largemouth bass were as high as 1.29 ppm. The WMA was formerly a U.S. Department of Defense ordnance facility; the probable source of contamination.

Florida presents a special case. Due to the presence of the Florida panther, and the research conducted to determine impacts of Hg contamination on this endangered species, much more is known regarding the source and impacts of Hg in this state than perhaps any other in the Region. Although atmospheric deposition appears to be the major source of Hg, much of this deposition may be from local sources. A recent study (KBN, 1992) indicated that as much as 61% of total Hg emissions in the state were from anthropogenic sources; and that almost one-third of these emissions were derived from incineration of municipal solid wastes and medical wastes. These emissions appear to have a direct impact on nearby areas (Delfino *et al.*, 1993).

Roelke *et al.* (1991) found that reproductive success of the Florida panther, measured in terms of the number of offspring surviving to age 6 months, was significantly correlated with Hg levels in the blood of lactating females. They also found that the major source of Hg for panthers was the raccoon. Maximum mean Hg levels in raccoon muscle

and liver tissues sampled during 1984-1991 (1.80 and 24.0 ppm, respectively) were from animals ($n=5$) collected in Shark Slough, Everglades National Park, adjacent to the territory of the female which died of Hg toxicosis (Roelke *et al.*, 1991). Analyses conducted since 1991 have shown even greater levels of Hg (7.17 and 39.3 ppm in muscle and liver, respectively) in raccoons from south Florida. These levels are greater than any found in the literature. The mean concentration in alligator (*Alligator mississippiensis*) muscle from Shark Slough animals ($n=5$) was slightly less at 3.57 ppm.

Extensive fish sampling throughout the state has shown that the greatest contaminant loads (>3.0 ppm) are in the Everglades area. Most of this area is covered by a no consumption advisory. Marine species also are contaminated. Spotted seatrout (*Cynoscion nebulosus*) from various coastal NWRs have Hg levels in excess of 1.4 ppm. Behavioral and reproductive impacts of Hg on wading birds are currently under study.

3. Conclusions

Mercury contamination in the Southeastern U.S. is a major problem. It is likely that many areas yet to be investigated are also contaminated. Additionally, the potential for unreported human health problems should be investigated. Although a satisfactory solution to problems stemming from area sources may be elusive, it is imperative that point sources be identified and regulated.

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MERCURY IN FISH IN THE SMALLWOOD RESERVOIR, LABRADOR, TWENTY ONE YEARS AFTER IMPOUNDMENT

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The elevated mercury (Hg) levels in fish flesh found after impoundment of a reservoir, are predicted to decline as the reservoir ages The length of time required for a return to background levels is dependent on among other things, the trophic status of the fish Predictions for omnivorous species range between 15 and 20 years while for piscivorous species they vary from 20 to 30 years Fish in the Smallwood Reservoir, Labrador, Canada, were sampled 6 years after impoundment when hg levels were found to be elevated in most species Selected of the sites were re-sampled after 16 years and again after 21 years Mercury in the flesh of omnivorous species such as lake whitefish (*Coregonus clupeaformis*) had returned to background levels after 16 years as predicted However, hg in the flesh of piscivores such as northern pike (*Esox lucius*) and lake trout (*Salvelinus namaycush*) remained elevated even 21 years after impoundment While the levels in lake trout have declined somewhat in that time, there is no evidence of decline in the northern pike either within the reservoir or at downstream stations Models predicting decline in hg levels in piscivorous fish in reservoirs must be re-evaluated in light of this extended data set

1. Introduction

The accumulation of mercury (Hg) in the flesh of fish found in recently impounded reservoirs has been known for twenty years (Smith *et al*, 1974). Because of the health risks to human consumers of these fish, it is important to determine how long after impoundment this will continue to occur. Fish from reservoirs in insular Newfoundland can return to background levels after 7 to 12 years (Scruton *et al.*, 1994). Theoretical models developed by Messier *et al.* (1985) predict returns at 20 years for lake whitefish and 30 years for northern pike. Data collected 16 years after impoundment of the Smallwood Reservoir showed that the Hg levels in flesh of non-piscivores was similar to background while piscivores were still elevated above unimpounded lakes although concentrations in all species except northern pike had declined from the levels observed after 6 years.

The Smallwood Reservoir and sites downstream from the impoundment were revisited in 1992 and the fish from these sites were analyzed to determine Hg levels 21 years after impoundment. Results of this study for three characteristic species (*Esox lucius,* northern pike; *Salvelinus namaycush,* lake trout; *Coregonus clupeaformis*, lake whitefish) are presented here.

2. Materials and Methods

The Smallwood Reservoir in western Labrador, was initially flooded in 1971. It covers an area of 6650 km^2 (Bruce and Spencer, 1979) and traverses a number of geological bedrock types (Scruton, 1984). In 1992, fish were sampled from two sites in the reservoir (Sandgirt and Lobstick) and two sites downstream in the Churchill River (Winokapau Lake and Gull Lake) at locations sampled in 1977 and 1987 (Fig. 1).

The fish were taken in gill nets, sized (fork length), weighed and a sample of dorsal flesh frozen pending analysis. Samples were analyzed for Hg using cold vapor atomic

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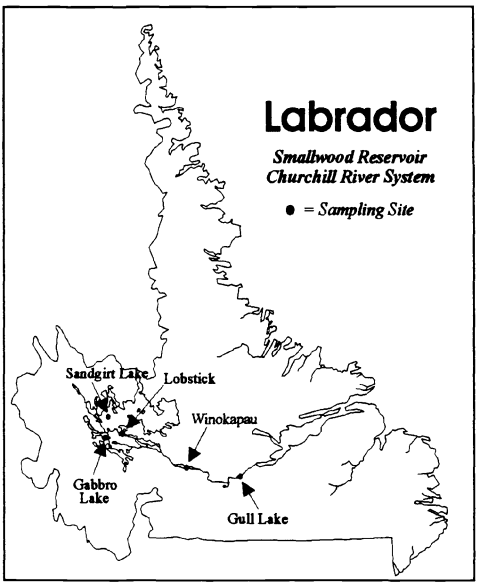

Fig. 1. Map of the Smallwood Reservoir, Labrador showing sites sampled in 1992.

absorbtion (Envir. Can, 1979; Uthe *et al.*, 1970).

Hg concentrations (in μg/g wet weight) in fish from the study sites were compared to those from previous years (1977 and 1987) and to background levels obtained from a survey of fish in 95 unimpounded lakes with minimal anthropogenic influence scattered throughout Labrador (Scruton, 1984). This latter study was selected as a control because it included samples from all of the geological types covered by the Smallwood Reservoir.

The data were log transformed to remove heteroscedasticity. Significant differences in Hg-weight relationships from background and between years were tested using regression analysis. Typically these types of comparison have been made using a standard length fish (e.g. Brouard *et al.* 1990). However, this approach is only valid if the slopes of both the control and the impounded site relationships are the same. If the slopes differ significantly then not only will information be lost using only a single point comparison but also, incorrect conclusions can be drawn particularly concerning larger, older fish. Other problems with the use of standard size in this context have been raised recently by Somers and Jackson (1993).

3. Results and Discussion

Preliminary analyses indicated that there was no significant difference among sites either in the reservoir or downstream for any of the species examined. Therefore, for each species, data from all sites were pooled for analysis. This means that while in some species, Hg levels are elevated above background down stream of the reservoir, there is no evidence of a gradient with distance from the reservoir as was seen in 1977 and 1987 (Brouard *et al.*, 1990).

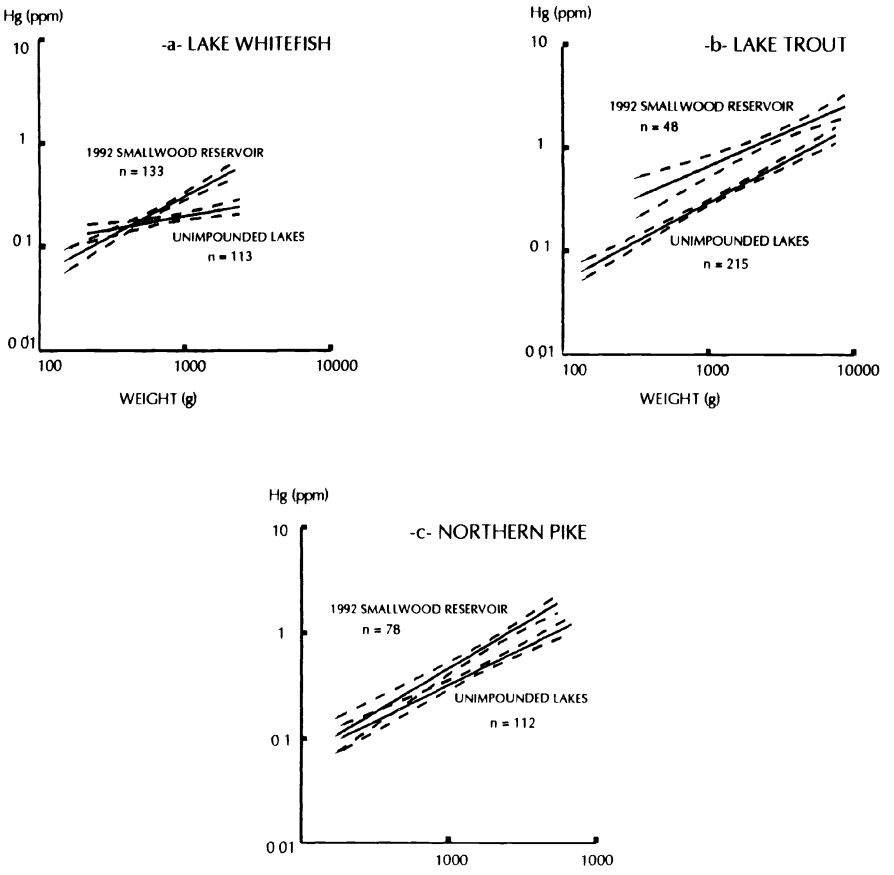

Figure 2 Predicted changes in Hg concentration (µg/g) as a function of weight (g) for lake whitefish (a), lake trout (b) and northern pike (c) in unimpounded lakes and in the Smallwood Reservoir system in 1992 Dashed lines indicate the 95% confidence intervals

Data from unimpounded lakes of Labrador indicate that even without human influence, Hg concentration increases with body size. In non-piscivores, concentrations are still very low (e.g. 0.05 - 0.45 µg/g for lake whitefish) but in lake trout and northern pike, the concentration of Hg exceeds the 0.5 ppm Canadian Regulatory limit in many of the larger fish. This is particularly true for lakes in western Labrador. Here again, comparisons solely among fish of a standard size may not adequately reflect the situation.

Sixteen years after impoundment, the Hg concentration of a standard length lake whitefish from the reservoir was not different from background levels (Brouard *et al.*, 1990). However, regression analysis comparing 1992 to the unimpounded lakes (Fig. 1. a) shows a significant difference in slopes ($P \leq 0.001$) between the two relationships, indicating that the larger older fish may still be carrying high body burdens.

Hg levels in lake trout were still significantly elevated ($P \leq 0.001$) over background in 1992 (Fig. 1. b) although they had declined slightly from 1987. The slopes of the two relationships are not significantly different (Fig. 2. b). This means that even the youngest lake trout in the reservoir still have elevated body burdens of Hg.

Even after 21 years, northern pike is not showing any significant decline in Hg levels. There is no significant difference between pike sampled in 1987 and in 1992 and they are still significantly higher ($P \leq 0.001$) than background levels (Fig. 1. c).

4. Conclusions

Hg levels of lake whitefish from the Smallwood Reservoir have returned to normal with the exception of some of the largest fish that have slightly elevated Hg concentrations as compared to background populations. This supports the predictions of Messier *et al.* (1985) of a twenty year return to normal.

Piscivorous fish such as lake trout and northern pike continue to contain more hg than fish from unimpounded sites. Levels in lake trout have begun to decline for fish of all sizes while northern pike show no indication of a return to background.

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MERCURY IN ZOOPLANKTON OF NORTHERN WISCONSIN LAKES: TAXONOMIC AND SITE-SPECIFIC TRENDS

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Abstract. Mercury content and speciation were determined in freshwater zooplankton from twelve northern Wisconsin (USA) lakes that spanned gradients of dissolved organic carbon (DOC, 1.6 to 20.9 mg/L) and pH (4.6 to 7.2). MeHg in crustacean taxa ranged from 1 to 479 ng/g dry weight, and from 2 to 45 ng/g in the invertebrate predators. Total Hg in the predators ranged from 20 to 153 ng/g. Although the highest MeHg values were found in the herbivores from high DOC lakes (and the experimentally acidified basin of Little Rock Lake), we observed considerable variation in the relationship between MeHg content of zooplankton and lakewater DOC. Bioconcentration factors (BCF) for both MeHg (3.5 to 7.1 log units) and Hg (3.7 to 5.4 log units) decreased with increasing lake DOC, while pH effects were not as apparent. Bioconcentration of MeHg was higher than Hg indicating that MeHg increases while non-methyl Hg declines in progressively higher trophic levels. Biomagnification factors (BMF) for Hg and MeHg were low relative to BCF. The BMF for crustaceans averaged 0.4 log units for MeHg and -0.5 log units for Hg, indicating that MeHg increased 2.5-fold from seston to crustacean herbivores, while non-MeHg concentrations declined. Unlike BCF, BMF were not related to DOC or pH. In contrast to studies of vertebrate predators, both BCF and BMF in the invertebrate predator *Chaoborus* , were lower than those in presumed prey. These observations point toward several complexities in the transport of Hg species in the lower levels of aquatic foodwebs.

1. Introduction

The high concentrations of mercury (Hg) in fish inhabiting remote lakes with low ambient Hg concentrations has led to increasing interest in the biomagnification of this element in the lower food web. Analytical refinements, which now make it possible to determine both total-Hg and monomethyl-Hg (MeHg) in small quantities (<1mg) of dried animal tissues, allow us to look more closely at the distribution of Hg species in trophic levels below fish (Watras and Bloom, 1992). This provides a means to track the trophic transfer of MeHg from primary producers through successive levels of consumer organisms, and to more fully evaluate the relative importance of uptake pathways at different trophic positions. It also permits us to examine the influence of food web structure and water quality as factors affecting the bioaccumulation of Hg. By careful sampling and taxonomic sorting, estimates of body burdens in small numbers of zooplankton of different taxa are possible. These data are of great potential utility as they represent the intermediate levels of the pelagic food web.

During a study of seven northern Wisconsin seepage lakes, five of which are covered in the present study, Watras *et al.* (1994) reported Hg bioconcentration factors for seston and age-1 yellow perch decreased with increasing pH, while MeHg bioconcentration factors decreased with increasing dissolved organic carbon (DOC). In a simplified foodchain for Little Rock Lake, Watras and Bloom (1992) showed that bioconcentration factors of MeHg

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increased roughly three-fold per trophic level from phytoplankton to fish. In contrast, non-methyl Hg became less concentrated at higher trophic levels.

Current studies are exploring the dependence of Hg concentrations, methylation, and biomagnification, on the site-specific characteristics of the diverse lakes in northern Wisconsin. The objective of the present study was to collect and analyze Hg in the dominant zooplankton taxa from a subset of these lakes. The purpose was to investigate mercury concentrations, bioaccumulation in zooplankton of different trophic levels, and to examine the relative effects of DOC and pH.

2. Materials and Methods

Twelve lakes in northcentral Wisconsin (46°N 89°W) were sampled during the ice-free period of 1993. These lakes were chosen because they span wide gradients of DOC (from 1.6 to 20.9 mgC/L) and pH (from 4.6 to 7.2). Methods for water collection and anlysis were similar to those of Watras *et al.* (1994). Water samples were taken from 2 m in each lake within one week of zooplankton sampling. Briefly, we determined Hg and MeHg in unfiltered and filtered (0.4 μm) water samples and calculated the particulate fraction by difference. Analytical methods followed Bloom and Fitzgerald (1988) and Bloom (1989).

Sampling of zooplankton was conducted during the late afternoon and evening to insure collection of *Chaoborus* specimens. Samples were collected by vertical hauls of a non-metallic net (20 cm diameter, 153 μm mesh) at a station representing the maximum depth of the lake. Clean technique was followed during all phases of sample collection, handling and analysis. Samples were sorted and processed within 12 hours, usually within 4 hours, of collection.

Sorting the individuals of various taxa was conducted in a laminar-flow hood inside the clean laboratory, using acid-cleaned Pasteur pipets and Teflon™ petri dishes. Sorted samples were rinsed several times by successive pipetting with low mercury (< 0.3 ng/L) water. Once the dominant herbivorous and predaceous taxa had been isolated, replicate subsamples were transferred into 3-mL Teflon™ vials for Hg and MeHg analysis. Depending on sample taxon, we collected from 1 to 25 individuals per vial to assure sufficient material for these analyses (>0.1 mg). A drop of rinse water was also collected for mercury analysis, and was then used as a procedural blank. Vials were then double bagged and frozen until analyses could be undertaken. Replicate samples for dry weight determinations were collected into pre-tared Aluminum boats, dried overnight at 65°C, and weighed to the nearest 0.1 μg on a Cahn C-31 Electrobalance.

Prior to analysis samples were digested overnight at 65°C. Digestor was added to thawed samples, which were recapped, and sealed in temperature-resistant plastic bags. For the Hg analysis, 200 μL of HNO_3/H_2SO_4 (5/2 v/v) was added to each vial; for the MeHg analysis, 200 μL of KOH/Methnol (1/4 w/v) served as the digestor. Samples for Hg determinations were analyzed following the protocol of Bloom and Fitzgerald (1988). Determination of MeHg followed aqueous phase ethylation, carbotrap collection, separation by isothermal gas chromatography and cold-vapor atomic fluorescence detection (modified from Bloom, 1989). The pH of the MeHg digestates was adjusted in the sparging vessel

with 100 μL of an acetate buffer (2M sodium acetate in 2M acetic acid) prior to the addition of ethylating agent.

During both Hg and MeHg analyses, detector response was measured with a HP3396 Series II integrator; peak areas were used in all calculations. Coefficients of variation on replicated standards averaged 11% during Hg (1 ng) and 6% during MeHg (0.1 ng) analyses. Detection limits (3xSD of Reagent Blanks) ranged from 4 to 9 pg for Hg and from 0.6 to 5 pg for MeHg. Procedural blanks were always below the limit of detection. Reagent blanks, which contributed from 14 to 25 pg during Hg analyses, and from 3 to 4 pg during MeHg analyses, were subtracted from the appropriate samples.

Bioconcentration factors (BCF) for zooplankton were calculated using the ratio of the zooplankton Hg concentration (Hg_Z, ng/gdw) and the dissolved Hg concentration (Hg_D,ng/mL) for each sample. BCF for the seston, or particulate pool, was similarly calculated by first correcting the particulate pool (Hg_P, ng/L) to a dry weight basis using the SPM (mg/L), correcting units, then dividing by Hg_D (ng/L). While most of the SPM in these lakes is biogenic, detritus is included in the estimation of SPM and therefore the BCF for seston. In this respect the BCF for seston is analogous to K_d, the particle/water partition coefficient. Biomagnification factors (BMF) for the crustacean zooplankton were calculated as the quotient of the zooplankton concentration, Hg_Z (ng/g), and the particulate concentration expressed on a dry weight basis (i.e. Hg_P, ng/g). This calculation yielded an apparent BMF, as we assumed that bulk SPM collected at a depth of 2 m was representative of the food selected by herbivorous zooplankton. Apparent BMF for *Chaoborus* used the mean concentration for crustacean taxa collected in each lake from which *Chaoborus* samples were collected. BCF and BMF are expressed in $\log_{10}$ units.

3. Results and Discussion

Whole water Hg concentrations ranged from 0.43 to 4.79 ng/L Hg, and from 0.04 to 2.20 ng/L MeHg in the lakes sampled for zooplankton. Dissolved Hg concentrations in these lakes ranged from 0.27 to 4.50 ng/L Hg, and from 0.03 to 1.95 ng/L MeHg. Concentrations of particulate Hg ranged from 0.06 to 1.27 ng/L for Hg, and from 0.02 to 0.19 for MeHg. Total suspended matter (SPM) ranged from 0.90 to 6.0 mg/L. BCFs for the seston were between 4.24 and 6.07 for Hg, and between 4.58 and 6.78 for MeHg. Both Hg and MeHg BCF for seston decreased with increasing lake DOC (Figure 1a), while the relationship was not as pronounced with lake pH (Figure 1b).

Methyl Hg concentrations in herbivorous taxa ranged from 1 to 479 ng/g dry weight. Taxa represented in these samples included *Holopedium gibberum* (40-419 ng/g), *Diaptomus oregonensis* and *D. minutus* (22-66 ng/g), *Daphnia pulex*, *D. galeata mendotae*, and *D. ambigua* (1-211 ng/g), and one sample of *Bosmina longirostris* (479 ng/g). The MeHg concentration in one sample of the predator Hydracarina was 251 ng/g. Methyl Hg concentrations in *Mesocyclops edax* , an omnivore, ranged from 24 to 30 ng/g. An overview of zooplankton food selectivity and dietary plasticity can be found in Sprules and Bowerman (1988). Methodological problems confounded the results for total Hg in the crustaceans and mites; these ranged from 2 to 165 ng/g, and were generally lower than the MeHg estimates in replicated samples. We have since determined that the digestion protocol used for total Hg may not completely recover the entire MeHg fraction during

total Hg analyses. The total-Hg data for crustaceans and mites presented here should be therefore viewed with caution. Samples of *Chaoborus* larvae apparently did not suffer from this incomplete digestion.

There are few previous studies of total and methyl Hg concentrations in zooplankton with the taxonomic resolution provided here. Watras and Bloom (1992) presented data for the cladocerans *Holopedium* and *Daphnia* collected from the two basins of Little Rock Lake during October 1989. Little Rock Lake was divided into two basins in 1984, one of which was experimentally acidified from 1985-1991 (Watras and Frost, 1989). MeHg burdens (pg/individual) of the current dataset, 0.9 and 2.38 ± 0.51 for reference and treatment basins agree with the previously reported values of 0.86 ± 0.49 and 3.2 ± 0.49 (Watras and Bloom 1992).

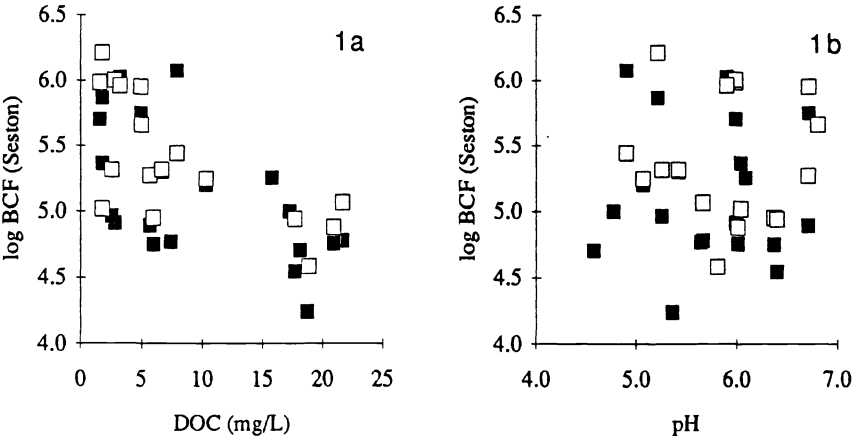

Fig. 1. Bioconcentration of Hg (closed) and MeHg (open) in seston.

The dominant predator collected from these lakes was the larval dipteran *Chaoborus punctipennis* , with occasional samples of *C. americanus* . MeHg concentration in these samples ranged from 2 to 45 ng/g dry weight (mean=13, SD=11, n=13), while estimates of Hg ranged from 20 to 153 ng/g (mean=57, SD=32, n=21). In samples collected in a given lake and analyzed for both Hg and MeHg (n=11), MeHg ranged from 7 to 29% of the Hg. Hg concentrations in these predators, on a dry weight basis, were therefore generally lower than those found in the herbivorous taxa.

An important consideration in viewing these data is the constraints one operates under when collecting samples for these analyses. Individuals of a given taxon are separated from the bulk sample and subsampled for separate Hg, MeHg, and dry mass determinations. These variables are not, therefore, estimated on the same sample. Furthermore, because of the requirements of subsample size and the difficulty of initial sorting, true sample replication is not very practical. In several instances, however, we collected and analyzed replicates for the MeHg and Hg analyses. Replicated samples for MeHg (n=5) averaged 17% and ranged from 0 to 40% difference, while those for Hg (n=3) averaged 24% and ranged from 10 to 38% difference.

Bioconcentration factors for zooplankton ranged from 3.68 to 5.43 for Hg, and from 4.04 to 7.10 for MeHg. It is interesting to note that the predatory mites, Hydracarina, sampled

from Little Rock Lake (reference basin) showed the highest bioconcentration of both Hg (5.4) and MeHg (7.10). In contrast, bioconcentration of both Hg and MeHg by the predatory *Chaoborus spp.* was generally lower than that of the other taxa (Figure 2).

Bioconcentration of Hg in zooplankton, while showing considerable scatter, tended to decrease with increasing lake DOC (Figure 2a). This trend was more pronounced for MeHg than for Hg. The lakes sampled separated naturally into two groups: one with lakes <10 mg/L, and one with the lakes >15 mg/L DOC. Examination of the data for *Chaoborus spp.* , which had a large enough number of samples for such analysis, revealed that samples from lakes <10 mg/L DOC had higher bioconcentration of both Hg and MeHg (Wilcoxon Signed Ranks Tests significant at p=0.0001 and 0.005 respectively). Bioconcentration of MeHg showed a weak negative correlation with lake pH, but there was no relationship between bioconcentration of Hg and pH (Figure 2b).

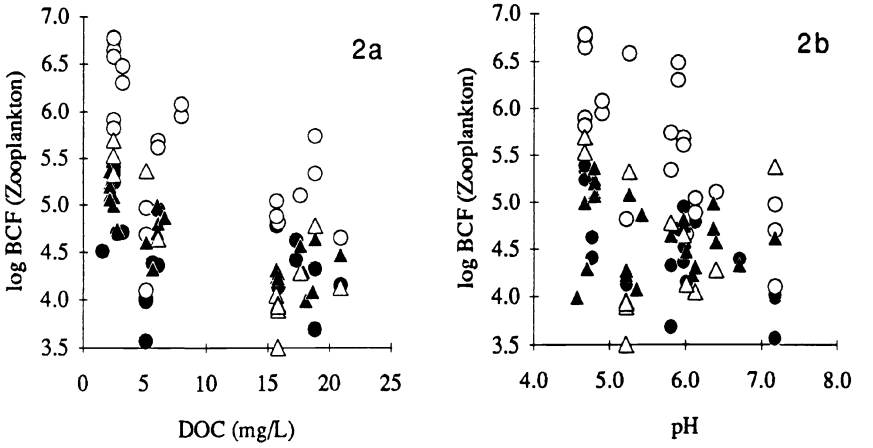

Fig. 2. Bioconcentration of Hg (closed) and MeHg (open) in individual zooplankton species. Circles show data for crustaceans, triangles show *Chaoborus* .

The decreasing BCF with increasing DOC suggests that bioavailability of Hg and MeHg is lower at higher DOC. This could be explained by DOC complexing the Hg, such that DOC and the biota essentially compete for Hg. Further, the scatter of BCF at each DOC value suggests that dissolved Hg concentrations may not necessarily by themselves be strong predictors of zooplankton Hg and MeHg concentrations. The scatter of BCF at any concentration of DOC may reflect a combination of species-specific effects such as age, growth rate, trophic position, and seasonal trends in diet, Hg_Z, and $MeHg_Z$.

Biomagnification factors for the crustacean taxa ranged from -1.45 to -0.02 for Hg, and from -0.29 to 1.17 for MeHg. Typically, only the MeHg factors for the crustaceans were greater than zero, indicating biomagnification relative to the seston. The negative BMF for total Hg, and the positive BMF for MeHg support the hypothesis of Watras and Bloom (1992) that non-methyl Hg becomes more dilute and MeHg more concentrated as Hg is moved up the lower food web. There was no trend in BMF for the crustacean taxa with either DOC (Figure 3a) or pH (Figure 3b).

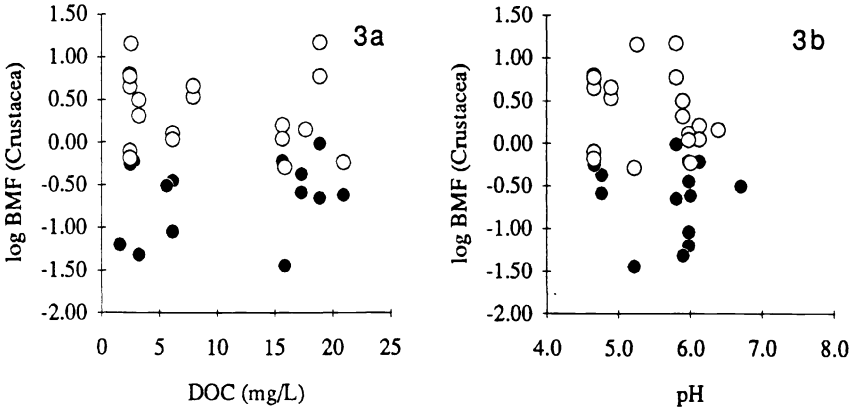

Fig. 3. Biomagnification of Hg (closed) and MeHg (open) in individual crustacean species.

BMF for *Chaoborus* showed strikingly different patterns (Figure 4). Unlike results for the crustacean taxa, the *Chaoborus* BMF for Hg is generally higher than the MeHg factor. Moreover, most BMF are negative for *Chaoborus* , indicating a lack of biomagnification of either Hg or MeHg.

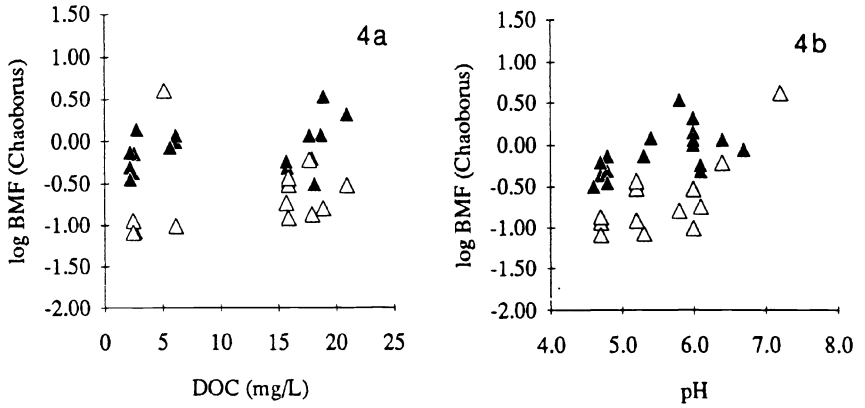

Fig. 4. Biomagnification of Hg (closed) and MeHg (open) in *Chaoborus spp* .

The reason for negative BMF values in *Chaoborus* is unclear. It may partly reflect our assumptions about the trophic structure of these lakes. Our approach throughout this study was to survey Hg concentrations in the dominant predaceous and herbivorous invertebrate taxa in each of the lakes. We have assumed that *Chaoborus* feed on the same zooplankton that we selected from bulk samples, and that they are exposed to the average Hg and MeHg concentrations in these prey. In reality, *Chaoborus* may select prey with much lower Hg concentations thereby biasing our estimates. However, even if we assume

that *Chaoborus* feed on bulk seston , like their presumed prey, the BMF for Hg and MeHg would be lower than those calculated for crustacean zooplankton. Given this observation and the fact that Hg is bioaccumulated to a higher degree than MeHg in *Chaoborus*, we hypothesize that different factors regulate bioaccumulation in these invertebrate predators.

While the lower concentrations in invertebrate predators seem the contradict current notions of biomagnification, previous workers have noticed similar phenomena. Parkman and Meili (1993), for example, observed Hg concentrations in profundal predaceous chironomids were lower than profundal detritivorous chironomids. Immature *Chaoborus* in the plankton may have very different physiologies than adult crustaceans. *Chaoborus* are relatively long lived, and undergo dramatic ontogenetic changes in diet and vertical migration behavior (Moore, 1988). The Hg content of individuals, on a dry weight basis, integrates exposure and depuration during these changes. Dry weight-based concentrations may not fully reveal underlying mechanisms involved in bioaccumulation. Meili (1991) suggests normalizing Hg concentrations to nitrogen (N) content, which implies association with proteins as a mechanism of bioaccumulation. We do not have information on the N content of *Chaoborus* in our samples, but feel that such mechanistic approaches to the unexpected results for Chaoborus would be fruitful in future studies.

Much of the previous work on bioaccumulation in freshwater food webs has prudently proceeded under simple notions of the transfer of materials between successive trophic levels (Meili, 1991; Watras and Bloom 1992). The concept of primary producers (phytoplankton), primary consumers (zooplankton), secondary consumers (planktivorous fish) and top predators (piscivorous fish) related in a linear model of the food web may be misleading. For instance, many phytoplankton groups, including those dominant in these lakes (eg. the cryptomonads, chlamydomonads) are known to be facultative mixotrophs (see Sandgren 1988 for reviews). Such trophic plasiticity may affect Hg_P, and confound efforts to examine biomagnification.

The assumption of biomagnification, as calculated here, is that the SPM *en toto* (and that sampled at 2 m) is the food ingested by the primary consumers. This is likely not the case. It is likely, however, that the small herbivores are feeding on small particles such as bacteria and picoplankton (*sensu* Burns 1968). These food groups may have quite different Hg concentrations and dynamics than the larger phytoplankton species, which may be selected by the larger herbivores. In a study of a small Finish lake, Rask *et al.* (1994) found total Hg concentrations were generally lower in copepods (20 to 250 ng/g) than in cladocerans (120 to 600 ng/g). They hypothesized that this was due to differences in food selectivity of these groups of herbivores. Our results for MeHg support this hypothesis. Certainly the differences in metabolic rates, feeding ecologies, and the quality of available food to planktonic herbivores complicates considering them as a trophic "guild" in the strict sense. As we become more precise with our analytical work, we must remain aware of such complexities in the lower food web.

4. Conclusions

Surveys of twelve lakes have advanced our knowledge of Hg concentrations in dominant zooplankton species, and has demonstrated the significance of taxonomic and site-specific differences. Bioconcentration of Hg in zooplankton decreased with increasing lake DOC, while pH did not have a strong effect. Biococentration of MeHg was higher than total

mercury, supporting the hypothesis that methyl Hg progressively accumulates in progressively higher trophic levels of food webs while non-methyl Hg declines. Biomagnification in crustacean zooplankton was several orders of magnitude lower than bioconcentration. BMF for MeHg in these taxa generally were positive while BMF for Hg were negative, further evidence that MeHg is the form of Hg accumulated. Taxonomic differences may reflect different feeding selectivities missed with the use of bulk seston in our calculations of biomagnification.

We were surprised to find that Hg concentrations in the invertebrate predator *Chaoborus* were lower on a dry weight basis than those of the crustacean taxa, the presumed prey. Calculation of BMF using the crustaceans sampled shows the intriguing pattern that accumulation of Hg is higher than MeHg in this invertebrate predaotr. These results suggest different mechanisms govern Hg bioaccumulation in *Chaoborus*. We feel that dietary plasticity, ontogenetic changes in physiology, feeding and migration are issues deserving further study.

Acknowledgements

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PART Xa

AQUATIC CYCLING OF MERCURY IN BIOTA AND SEDIMENTS

PROSPECTS FOR MODELING THE BEHAVIOR AND FATE OF MERCURY, GLOBALLY AND IN AQUATIC SYSTEMS

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Abstract. The phenomena of cold condensation and fractionation of chemical contaminants on a global scale are discussed. The net result of these phenomena is that concentrations of certain atmospherically transported contaminants are higher than expected in the condensed, i.e. non gaseous media of water, soils, sediments and biota as a result of the temperature dependence of partitioning and transport phenomena. It is argued that the phenomena are best investigated by a combination of monitoring and modeling. This approach is illustrated in the form of a nine meridional segment model for hexachlorocyclohexane. It is suggested that this approach should be applied to Hg, but this is not presently possible because of the lack of data on Hg species properties and conversion rates. Available data have been used to test the hypothesis that lower temperatures cause enhanced partitioning from the atmosphere to a lake ecosystem at low temperatures by compiling a three species model of an atmosphere-water-sediment-fish system at 25 °C and 0 °C. Preliminary results show that the effect of this drop in temperature is to cause increases in concentrations throughout the aquatic ecosystem of factors of three to four, other factors being equal. Thus it is likely that a comprehensive global model will show that Hg is subject to the global fractionation phenomenon. It is recommended that attempts be made to develop such a model.

1. Introduction

There has been a growing realization that certain organic chemicals have reached unusually high concentrations in polar regions. A review of monitoring data and consideration of the environmental and physical chemistry of these compounds has led to the suggestion that some form of global fractionation or distillation may be occurring in which chemicals of different properties migrate to the colder polar regions with different behavior patterns (Wania and Mackay, 1993a). The phenomenon was first suggested by Rappe in 1971 (Rappe, 1974).

The purpose of this paper is to discuss if Hg is subject to the same phenomenon. Ottar (1979) noted that "the worldwide distribution of Hg must be governed by much the same wind and temperature changes as affect the long term and long range dispersion of the chlorinated hydrocarbons". Subsequently, he pointed out, that these chemicals, "which after initial deposition can be re-emitted to the atmosphere by sublimation, must be subject to a systematic long term transfer from warmer to colder regions" (Ottar, 1981). This process was simultaneously suggested by Lantzy and Mackenzie (1979) who noted it "could result in selective enrichment of atmophile metals in atmospheric particulates at high latitude relative to these particulates at mid and low latitudes".

In broad terms, it is believed that, with respect to their volatility and thus global fractionation behavior, persistent organic chemicals may fall into four classes as dictated by their subcooled liquid vapor pressures P_L Pa.

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(1) **Low volatility**. Chemicals of low vapor pressure (log P_L at 25 °C < -4) are mainly aerosol-associated in the atmosphere and are deposited by wet and dry deposition fairly close to sources, i.e. within 1000 km. Strong latitudinal gradients in concentrations are expected. Examples are heavy (i.e. with high chlorine number) polychlorinated biphenyls (PCBs) and high molecular weight polycyclic aromatic hydrocarbons such as benzo-a-pyrene (BaP).

(2) **Intermediate volatility**. These substances tend to change from the gas phase to the aerosol phase within the global environmental temperature range (approx. -40 °C to +40 °C). They may thus be transported many thousands of kilometers and tend to "condense" out of the atmosphere when some critical temperature is reached. Latitudinal concentrations in the atmosphere will drop with increasing latitude but the rate of drop is variable with volatility. Within this class we distinguish further:

(2a) **Relatively low volatility**: These chemicals with subcooled liquid vapor pressures in range -2 > log P_L > -4 will start to condense before they reach polar latitudes. Maximum concentrations in condensed media are likely to be found in the temperate and boreal regions, and will decrease towards the pole. Examples are the intermediate PCBs, highly chlorinated bornanes (CHBs) and the DDT-related chemicals.

(2b) **Relatively high volatility**: These chemicals with subcooled liquid vapor pressures in range 0 > log P_L > -2 will only condense at temperatures well below 0 °C and thus at high, i.e. polar, latitudes. Examples are the HCHs, HCB, and the lighter PCBs and CHBs.

(3) **High volatility**. These chemicals with high vapor pressures (log P_L > 0) exist in the atmosphere primarily in the gas phase at all environmental temperatures. They are globally transported by air advection and atmospheric concentrations tend to be similar with latitude. Examples are persistent volatile organic chemicals, such as the chlorofluorocarbons.

2. Atmosphere to Condensed Media Partitioning and Transport

It is useful at this stage to digress to examine some physical/chemical and environmental aspects of this issue. For simplicity we lump into one category all condensed media, i.e. soil, water, ice, sediment, fish, mammals, and vegetation. For a chemical there exists a mean condensed (i.e. non atmospheric) phase to air equilibrium partition coefficient K_{CA} which will have a temperature dependence dictated by the enthalpy of phase change which is approximately the enthalpy of vaporization from liquid to gaseous state. Applying the Clausius-Clapeyron or Van't Hoff relationship suggests that

$$\ln (C_C / C_A) = \ln K_{CA} = A + \Delta H / RT$$

Typically ΔH is 50 kJ/mol, thus decreasing temperature from 25 °C to 0 °C will increase K_{CA} by a factor of approximately six.

If the concentration of a chemical was constant throughout the global atmosphere and condensed media were in equilibrium with this atmosphere we expect to observe high concentrations in cold regions, indeed the relationship will be

$$C_C = K_{CA} \cdot C_A = C_A \cdot e^{(A+\Delta H/RT)}$$

This temperature dependence of partitioning is a fundamental factor contributing to the global fractionation of atmospherically distributed chemicals. In addition, at low temperature there is increased partitioning to aerosols which are subject to wet and dry deposition, thus transport from atmosphere to the condensed ecosystems may be faster. There are several other factors.

(1) The reduction in air-water partition coefficient K_{AW} causes not only a change in air-water equilibrium but also a change in the diffusional resistance between air and water. The conventional two resistance model is

$$1/k_{OL} = 1/k_L + 1/(k_G \cdot K_{AW})$$

where k_{OL} is the overall mass transfer coefficient (MTC), k_L and k_G are the water and air side MTCs and K_{AW} is the air-water partition coefficient. When K_{AW} falls, the gas phase diffusion resistance ($1/k_G K_{AW}$) rises thus transfer rates between air and water are reduced, thus any contaminant in water will be retained longer.

(2) At low temperatures degrading reactions are probably slower, thus the persistence of organic chemicals is increased. This is of course not applicable to Hg, however temperature will affect the rates of methylation and demethylation reactions.

(3) Finally, the presence of snow and ice undoubtedly modifies the fate of these chemicals considerably, causing them to be deposited faster and retained longer in condensed form.

There are thus several complementary and competing factors which are difficult to uncouple. Their net effect on contaminant levels is difficult to deduce, but the general conclusion for several presistent organic chemicals is that there is preferential migration from atmosphere to condensed media at low temperatures, thus we should expect concentrations in these media to be higher then expected from simple consideration of atmospheric dispersion. There is, we conclude, a need to model such phenomena to estimate the magnitude of these effects and the interaction.

Figure 1 is an attempt to depict these phenomena in graphical form. It is a plot of percent sorption of some organochlorinated chemicals to aerosols (and thus indirectly to other condensed media) as a function of temperature using the relationship of Mackay *et al.* (1986), sub-cooled liquid vapor pressures calculated from literature data (Wania *et al.* 1994) and the volume fraction of aerosols in air listed in Table III.

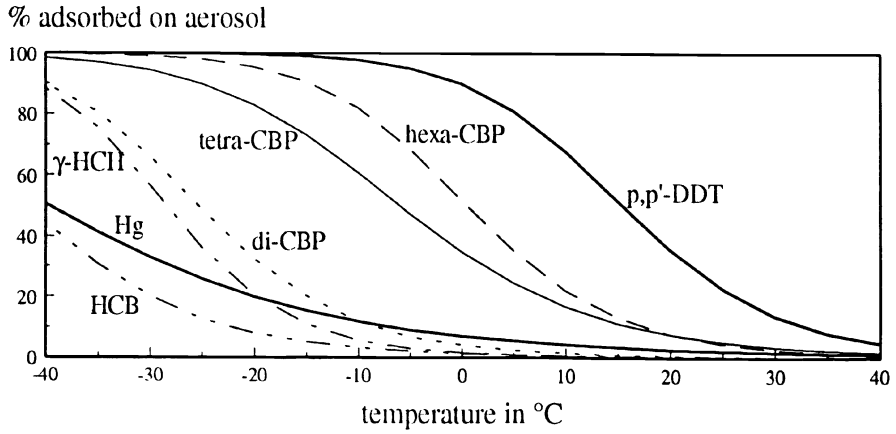

Fig 1: vapor/particle-partitioning of several organochlorine chemicals and total Hg as a function of temperature.

A substance such as HCB is generally gaseous and condenses onto aerosols only at very low ambient temperatures. BaP, on the other hand, is always "involatile". The PCBs extend over the entire range. The chemicals which display the greatest tendency for global fractionation are those which lie on the left of the diagram, have high K_{CA} values (because of hydrophobicity and low vapor pressures) and are persistent.

We thus suggest that to determine how Hg fits into this picture it is necessary to pursue two complementary courses of action (i) measure Hg levels in the atmosphere and in condensed media over a range of latitudes and (ii) model Hg behavior using our best estimates for chemodynamic processes, then compare the findings. This paper is an attempt to start this global modeling process for Hg.

Accordingly we first describe briefly an existing model of organic chemical fate to give an impression of what can be done. In doing so we use the fugacity approach because it simplifies the algebra. This approach has been described in previous publications (Mackay, 1991; Wania and Mackay, 1993b, 1994). Second, we discuss how such a model can be applied to Hg, including its speciation. Finally we give illustrative calculations of the atmosphere-to-aquatic ecosystem partitioning of Hg as a function of temperature and discuss the results in terms of the likely identification of a global fractionation effect.

3. A Global Distribution Model for Persistent Organic Chemicals

To understand and quantify the global dispersion and accumulation processes of persistent organic chemicals subject to the "cold condensation" phenomenon, we have developed a meridional multi-compartmental non-steady state mass balance model based on the fugacity approach. A detailed description of the model structure is given elsewhere (Wania and Mackay, 1993b, 1994). The global environment is divided into nine climatic zones, each of which is represented by six well-mixed and thus homogeneous environmental compartments: air, fresh water, fresh water sediments, ocean water, cultivated soil and uncultivated soil. The model is one-dimensional in the atmosphere because it averages environmental parameters and chemical concentrations zonally and vertically. The 54 compartments are connected by a number of diffusive and advective transport processes with particular emphasis on the exchange processes between the atmosphere and the Earth's surface. Meridional transport occurs in the atmosphere and the surface ocean. The climatic zones vary in their environmental characteristics such as dimensions, soil properties, and most importantly temperature. Some environmental properties such as temperature and meridional atmospheric exchange coefficients are modeled to fluctuate seasonally.

Physical-chemical properties of the modeled chemical have to be supplied together with their temperature dependence as well as estimates of climate- and medium-specific first order degradation rate constants. A scenario of chemical discharge, specifying time, magnitude and location, i.e. compartment and climatic zone, of all chemical releases into the global environment for example over a 30 year period is then used to calculate concentrations, amounts, degradation rates and transport fluxes as a function of latitude and time.

The model synthesizes information on a multitude of processes in a comprehensive manner and thus helps to identify the major factors controlling the global dispersion

behavior of chemicals. Illustrative calculations with this model showed the crucial role of temperature and its influence on the partitioning behavior of organic chemicals (Wania and Mackay, 1994). They also revealed how the global distribution behavior of chemicals depends on their volatility. The more volatile chemicals such as light PCBs, HCB and the HCHs are transported more readily to higher latitudes, while the less volatile chemicals such as DDT tend to condense and remain in mid latitudes (Wania and Mackay, 1994).

In a first attempt to simulate the long term fate of a persistent organic chemical on a global scale, we estimated an emission scenario for the hexachlorocyclohexanes (α- and γ-HCH) for the time period from 1945 to the present based on limited information available in the literature and calculated rates, distributions and concentrations as a function of time. Figure 2 shows the global compartmental distribution of α-HCH calculated for summer 1985. The model results suggest that the bulk of the α-HCH emitted into the environment still resides in the soils which received this pesticide during application. The other major global reservoir is the world oceans holding about 20 percent of the total global inventory of the α-HCH. The major processes controlling the global mass balance are degradation in the cultivated soils, leaching into fresh water, evaporation from soils and receiving waters and atmosphere-ocean exchange. There is a net poleward transport of this chemical in atmosphere and oceans. The calculated concentrations are somewhat higher than observations but overall agreement is satisfactory.

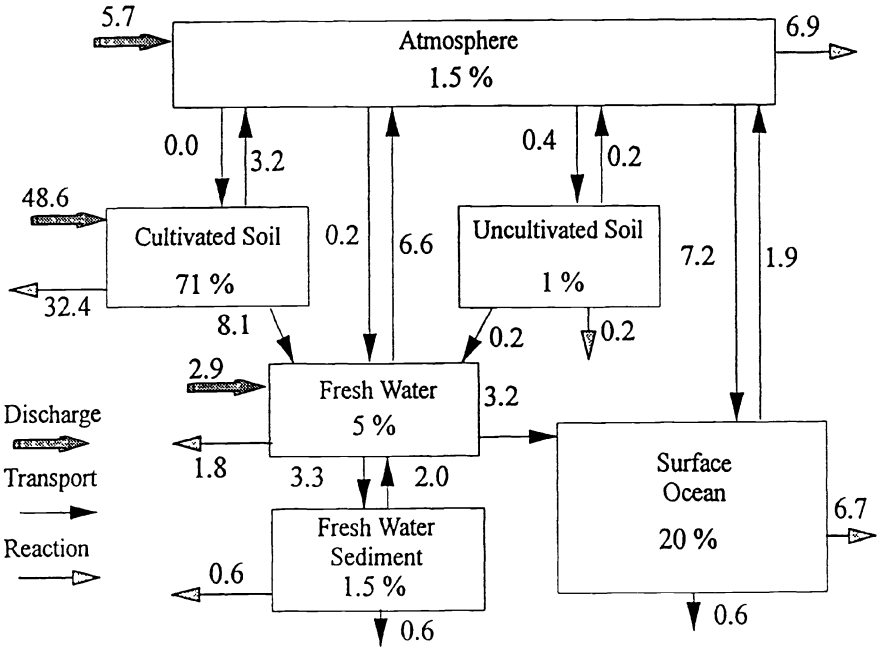

Fig. 2: Global mass balance for α-HCH in units of kt/a calculated for summer 1985 by the global distribution model

4. Modeling Mercury

In principle, modeling Hg involves (i) identification of all major species, (ii) determination of their partitioning properties between all media including temperature dependence and (iii) determination of all inter-species conversion rates. A set of differential mass balance equations can then be set up for each of the S species in P phases, i.e. there are S·P equations. This approach currently poses problems largely because of uncertainties about the inter-species rate expressions. The application of fugacity-type models to such systems has been discussed by Diamond and Mackay (1992) who showed that a tractable approach is to define the proportions of each species in each medium, thus avoiding the need to deduce interspecies rates. The preferred approach is that of "aquivalence" rather than fugacity since some species may be non-volatile.

For the present purposes three groups of Hg species were selected: elemental, inorganic (e.g. various Hg ion species) and organic (e.g. MeHg species). From a review of the literature (Iverfeldt and Lindqvist, 1984; Lindqvist *et al.*, 1984; Schroeder *et al.*, 1991; Concord Scientific, 1981) average group partition coefficients with respect to water at 25 °C in Table I were selected, as were the enthalpies of phase change which enable these partition coefficients to be deduced at any desired temperature. The proportions of each species in four media were selected as shown in Table II. These proportions were assumed to be independent of temperature. This may not be true as methylation is retarded at lower temperatures. It should be noted that the proportions in a bulk medium such as air including aerosols differ from those in the individual gas and aerosol phases.

TABLE I

Dimensionless partition coefficients K and enthalpies of phase change ΔH in J/mol for the three mercury species used in model calculations

	Elemental Hg		**Inorganic Hg**		**Organic Hg**	
	K	ΔH	K	ΔH	K	ΔH
air/water	0.32	20 000	0.000001	30 000	0.30	30 000
aerosol/water	1 000 000	-5000	10 000 000	-5000	3 000 000	-5000
sediment solids/water	20 000	-5000	100 000	-5000	5000	-5000
suspended solids/water	30 000	-5000	200 000	-5000	10 000	-5000
fish/water	1	0	1000	0	5 000 000	0

TABLE II

Concentration fractions of the three Hg species used in model calculations

	Elemental Hg	**Inorganic Hg**	**Organic Hg**
Input Values			
air (vapor phase)	0.9998	0.0001	0.0001
water (disolved phase)	0.020	0.900	0.080
sediment (solid phase)	0.010	0.980	0.010
fish (bulk fish)	0.020	0.020	0.960
Calculated Values			
aerosols	0.003	0.997	0.000
suspended solids	0.003	0.992	0.004
sediment pore water	0.041	0.797	0.163
Bulk Phases			
air	0.980	0.020	0.000
water	0.014	0.933	0.053
sediment	0.010	0.980	0.010

These data were used to generate Z-values for all species in all media and an overall Z value applicable to total Hg. This enabled all species and overall D-values to be calculated and a single mass balance equation can be written for total Hg in each medium. It is noted that the Z-values for fish are not equilibrium values; they represent observed concentration ratios. For a detailed introduction into fugacity modeling and the the concept of Z- and D-values refer to Mackay (1991).

5. A Model of Mercury Fate in Lakes

The QWASI model for modeling the fate of organic chemicals in a lake, which is described in more detail elsewhere (Mackay *et al.*, 1983; Mackay, 1989), was modified for a speciated chemical such as Hg. The model consists of a well-mixed water compartment with suspended solids in equilibrium underlain by a sediment compartment consisting of sediment solids and pore water. No soil or terrestrial media such as vegetation are included. Rates of various transfer processes between sediment, water, and the overlying air compartment (which is not part of the mass balance, but has a fixed, user-specified concentration,) are calculated for a steady-state situation. The input of enthalpies of phase change for all partition equilibia in the model makes it possible to calculate chemical behavior at different ambient temperatures. This modified model was used to illustrate - on a simpler level than the global distribution model mentioned above - the impact of temperature on mercury behavior in the environment. Environmental parameters describing a generic lake with typical characteristics of a small temperate lake were used in these calculations (Table III).

TABLE III
Environmental parameters used in model calculations for Hg with QWASI model

lake surface area	1 km^2	air side MTC over water	1 m/h
water depth	10 m	water side MTC	0.01 m/h
sediment depth	3 cm	dry deposition velocity	7.2 m/h
aerosols in air	$2 \cdot 10^{-11}$ m^3/m^3	sediment-water exchange MTC	0.0004 m/h
suspended solids in water	$3 \cdot 10^{-6}$ m^3/m^3	particle deposition rate	$1.2 \cdot 10^{-8}$ m/h
pore water in sediment	0.85 m^3/m^3	sediment resuspension rate	$3.9 \cdot 10^{-9}$ m/h
hydraulic residence time	1.72 a	sediment burial rate	$2.0 \cdot 10^{-9}$ m/h
rain rate	0.8 m/a	scavenging ratio	200000

Calculations were performed at 25 °C and 0 °C assuming that input of Hg to the lake occurs only from the atmosphere. The atmospheric concentration of total Hg was assumed to be 1 ng/m^3. Essentially the model is assessing how this lake will respond if it is exposed to the same atmosphere, but at different temperatures. It could be viewed as the same lake at different latitudes. The steady-state mass balance for the three Hg species as calculated by the model is shown in Figure 3. Table IV lists the calculated concentrations. A comparison with Hg concentrations and fluxes measured in a small temperate lake (Fitzgerald *et al.*, 1991) indicate that the calculated behavior is reasonably close to the real environmental conditions.

The calculations suggest that low temperatures drive Hg from the atmosphere into the water and the sediment. The annual net depositional flux of Hg from the atmosphere to the lake increases more than 3-fold from 3 to 10 g between 25 °C and 0 °C, although the total atmospheric concentration is the same in both cases. The fraction of total Hg in air, which is adsorbed to aerosols increases from 2 to 6.8 % at the lower temperature.

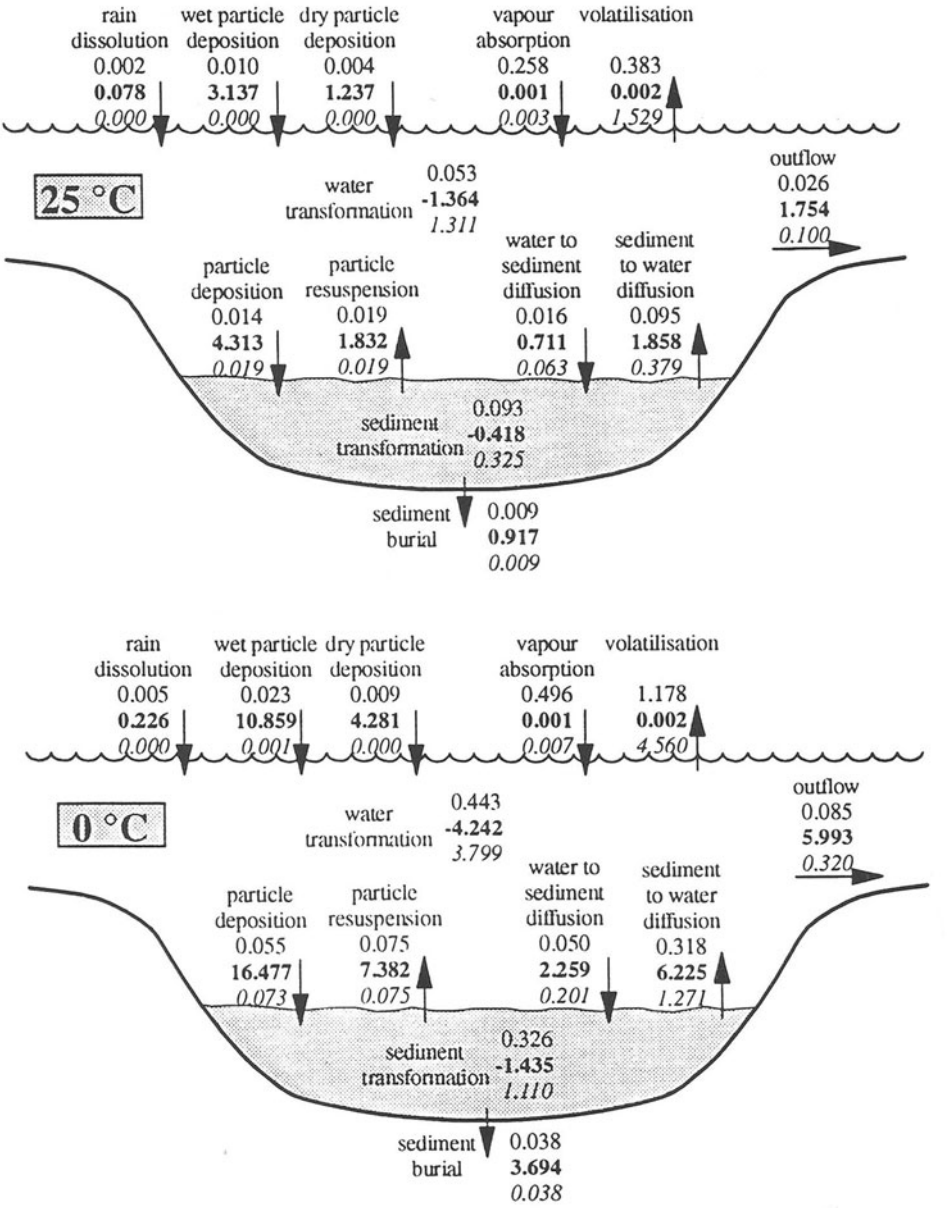

Fig 3. Fluxes of the three species of Hg in units of g/a calculated with the QWASI model for a generic temperate lake at 25 °C and 0 °C exposed to a constant air concentration of 1 ng total Hg / m^3. The upper numbers (in normal print) stand for elemental Hg, the middle numbers (in bold print) for inorganic Hg and the bottom numbers (in italic print) for organic Hg.

This increased vapor-to-particle partitioning is responsible for increased wet and dry particle deposition at lower temperatures. As a consequence of this enhanced deposition, all other processes such as outflow, interspecies conversion, and those across the water-sediment interphase, increase accordingly. The steady-state concentrations increase 4-fold in sediment and 3-fold in fish (Table IV).

Table IV
Concentrations calculated by the QWASI model for the three Hg species at 25 °C and 0 °C

	aerosols in ng/g solids		**water** in pg/L		**sediment** in ng/g solids		**fish** in ng/g wet weight	
	25 °C	*0 °C*	*25 °C*	*0 °C*	*25 °C*	*0 °C*	*25 °C*	*0 °C*
Elemental Hg	1.17	2.79	4.92	15.88	0.30	1.20	0.00	0.00
Inorganic Hg	377.1	1305	324.7	1100	29.13	117.4	0.20	0.64
Methyl Hg	0.04	0.13	18.58	59.37	0.30	1.20	90.2	286.5
Total Hg	378.3	1308	348.2	1185	29.73	119.8	90.4	287.2

Mercury thus shows a "cold condensation" behavior quite comparable to that displayed by relatively volatile persistent organic compounds such as HCB or the HCHs (class (2b)). The vapor-particle partitioning as a function of temperature is very similar to that displayed by these chemicals. The fraction of total Hg in air adsorbed on aerosols as a function of temperature in the range between -40 °C and +40 °C as calculated by the model is depicted in Figure 1. While almost entirely in the gas phase at typical temperate temperatures, Hg increasingly "condenses" onto aerosols at lower temperatures and half of it is sorbed at about -40 °C. The curve for Hg lies just between the lines for HCB and γ-HCH, two chemicals which have been identified as prime candidates for preferential accumulation in polar latitudes according to the global fractionation hypothesis.

In the case of Hg there is a distinct trend for atmospheric concentrations to decrease with increasing latitude between temperate and arctic regions (Schroeder *et al.*, 1994). The factor by which the concentration falls is of the order of three, which is similar to the factor by which the cold condensation effect enhances concentrations in condensed phases in the model calculations. The net result is that we may expect to find mercury concentrations in condensed phases which are relatively constant with latitude despite the remoteness of colder regions from sources. It should be noted, however that latitudinal concentration profiles, particularly in biota will be influenced by additional temperature effects on methylation and demethylation reactions as well as uptake and depuration kinetics.

In this connection it is noteworthy that Steinnes and Andersson (1991) concluded from the distribution of Hg in Norwegian mosses and soils that "the airborne supply of Hg to the terrestrial environment in remote areas under cold climates may be considerably higher than anticipated before" and attributed this to enhanced dry deposition.

6. Conclusions

Mercury is unique among metals because of its volatility and thus its susceptibility to long range atmospheric transport on a global scale. In this respect it is similar to

persistent organic chemicals for which not only global contamination has been observed, but a global fractionation effect is increasingly accepted. Such effects are best investigated by a combination of monitoring and modeling. The modeling approach has been illustrated for an organic chemical. It is suggested that this approach be applied to mercury. At present data available are inadequate to accomplish this task. As a step in this direction we have used available data and treated a much simpler system of an atmosphere-aquatic ecosystem at two temperatures and with three Hg species. From this study we conclude that there is a strong temperature dependence of atmosphere-to-aquatic ecosystem partitioning, and probably also of atmosphere-to-terrestrial ecosystem partitioning. This will cause enhanced concentrations in condensed media such as soils, water, sediments, and biota at low temperatures. Not only are the partition coefficients affected by temperature but the fluxes from air are also increased. It is hoped that this study will encourage further monitoring and modeling of the global behavior of this fascinating and important element.

Acknowledgments

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IMPACTS OF MERCURY ON BENTHIC INVERTEBRATE POPULATIONS AND COMMUNITIES WITHIN THE AQUATIC ECOSYSTEM OF CLEAR LAKE, CALIFORNIA

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Abstract Benthic invertebrates from Clear Lake, site of an inactive mercury (Hg) mine, were analyzed for population and community level parameters in response to a significant point source of sediment-associated Hg Using multiple regression, at least one taxon (*Placobdella* leeches) showed a significant decline and another taxon (*Procladius* midges) showed a significant increase in response to increasing sediment Hg Responses of invertebrates to sediment Hg levels are complex, likely due to partial confounding between sediment Hg (especially methyl Hg), grain size and depth Stepwise multiple regression analyses indicate that individual taxa often responded significantly to several environmental factors *Chironomus* populations declined with increasing grain size, depth and total Hg, *Procladius* declined with increasing depth, but increased with increasing sediment grain size and Hg levels, *Chaoborus* declined with increasing depth, oligochaetes increased with increasing TOC, and *Placobdella* leeches declined with both increasing depth and sediment Hg levels Additional multi-variate routines were used to demonstrate more complex relationships than are typically elucidated by standard multiple regression statistics The complex results presented here may indicate that there are significant population effects above some threshold of sediment Hg concentrations Community level parameters (diversity and evenness) declined with increasing sediment Hg levels, but with considerable variation at low Hg levels Simple regression yielded a negative relationship between diversity and evenness versus sediment total Hg that was nearly significant, and one with sediment methyl Hg that was not close to significance Multiple regression indicated that depth was more important than sediment Hg in describing the variation in diversity

1. Introduction

Mercury (Hg) is one of the best known heavy metal pollutants. In marine or aquatic habitats it is most closely bound to sediments or particulate material in the water column (Luoma, 1989; Gill and Bruland, 1990; Suchanek *et al.*, 1993). Since Hg is highly insoluble, water does not hold a significant proportion of the Hg pool but it can act as an important transport medium for particulate-bound Hg. Therefore, most significant environmental impacts associated with Hg can be ultimately traced to the sediment-bound pool, especially for benthic invertebrates, which are food sources of higher trophic level taxa.

While considerable information exists on Hg (primarily as total Hg) levels and effects in many invertebrates, fishes, mammals and birds (see review by Eisler, 1987), very little work has been published on resulting population or community level effects. Many forms of pollution are known to induce population declines and community level changes, mostly as declines in numerical abundance, species richness or diversity parameters (Moore *et al.*, 1979; Winner *et al.*, 1980; Bazzanti and Seminara, 1987; Suchanek, 1993, 1994). Moore *et al.* (1979) showed decreased benthic invertebrate population and diversity levels with distance from a mine that was a point source for several heavy metals, although they point out that this decline may have been due to other environmental factors as well. Winner *et al.* (1980) found similar negative impacts on stream invertebrates in relation to heavy metal pollution.

Here we describe the results of a study on benthic invertebrate population and community responses to Hg at Clear Lake, California. Mining operations from ca. 1872-1957 at the Sulphur Bank Mercury Mine at Clear Lake deposited an estimated 100 metric tons of Hg into the aquatic ecosystem of the lake. Inorganic Hg contamination in surficial sediments at the mine face has been measured as high as 250 μg/g, although results from different studies show considerable scatter in highest values. In the vicinity of the mine Suchanek *et al.* (1993, in prep a, in prep b, unpublished data) found sediment total Hg of 183 μg/g, meHg (meHg) of 15.9 μg/kg, chironomid body burden up to 27.69 μg/g, and

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oligochaete body burden up to 41.67 μg/g. All of these values declined linearly or exponentially with distance from the mine, falling nearly below detection in sediment and to less than 0.5 μg/g in invertebrates at a distance of ca. 30 km from the mine. The present study assesses the potential influence of mercury contamination from the mine and other physical factors upon individual benthic invertebrate populations and the diversity of the benthic invertebrate community at Clear Lake.

2. Materials and Methods

Clear Lake (39°00'N; 122°45'W), located in the coast range, is the largest natural lake entirely within the borders of California. It is also shallow (mean depth *ca.* 10m), polymictic, highly eutrophic and experiences frequent noxious blue-green cyanobacteria blooms during late summer/fall and sometimes late spring (Richerson *et al.*, 1994).

Quantitative invertebrate samples for population and community analyses were collected from 36 muddy lake bottom sites in Clear Lake using a 6 inch Ekman dredge (volume = 3540 cm^3) during September 1992. Sampling sites were arranged along transects within each arm such that the greatest number of sites was in the region of the steepest gradient of sediment Hg concentrations (Figure 1). Each community sample consisted of two Ekman grabs, yielding a volume of 7080 cm^3 for each sample. Invertebrates were sieved using a 0.5 mm sieve bucket, fixed in 5% formalin and preserved in 70% ethanol. Wet weights were measured using an Ohaus Analytical Balance (detection limit = 0.0001g) after extraneous surface moisture was removed by blotting dry for 1 minute.

A summary of the analytical techniques for sediment Hg, Total Organic Carbon (TOC) and grain size are provided here, but are described more fully in Suchanek *et al.* (in prep a). Sediment total Hg levels were analyzed for 36 stations (see Figure 1) using standard cold vapor atomic absorption. MeHg levels were analyzed at 24 stations using aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection, as developed by Bloom and Porcella (1989). All meHg analyses were performed by Brooks Rand, Ltd., Seattle, WA, utilizing ultra-clean methodology. TOC was analyzed in lake sediments by modified EPA SW-846 Method 9060A utilizing a TOC analyzer. Grain size was determined with EPA method D 422-63, which utilizes sieving for grain sizes above 75 μm and an air dispersion sedimentation sorting process, with detection by hydrometer, for smaller grain size fractions.

Data (both numerical abundance and weights) were analyzed with ANOVA, curve fitting routines and multiple regression analyses using the statistical visualization program JMP version 3.0 for Macintosh (SAS Institute, Inc.). Stepwise multiple regression analyses were then performed on numerical abundance data for each species fitted to a Poisson distribution using the S-PLUS program for DOS-Windows (version 3.1) by StatSci, Inc. Because the relationships between independent variables were complex, local (smoothing) regression models in the LOESS routine of S-PLUS were also used to produce "*conditioning plots*" to evaluate the behavior of meHg on individual taxa as a function of the most statistically significant variables in the analysis. Invertebrate biomass was used to calculate Shannon-Wiener (ln) diversity, Simpson diversity and Evenness.

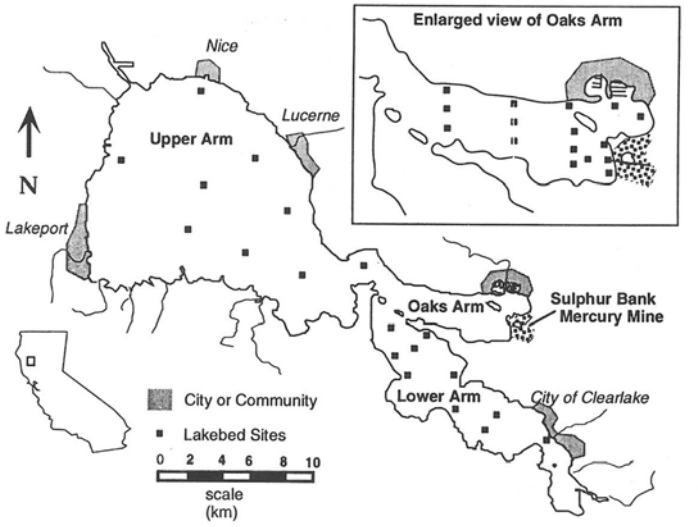

Fig. 1. Location map for study sites near the Sulphur Bank Mercury Mine at Clear Lake, California.

3. Results and Discussion

Profundal sediments within Clear Lake are composed primarily of soft flocculent muds with predominantly clay-sized particles (Suchanek *et al.* 1993) and do not support a rich infauna. Sediment total Hg levels range from 0.27 μg/g (in the Lower Arm ca. 22.4 km from the mine) to 183 μg/g (about 0.88 km from the mine) and meHg levels range from 0.18 μg/kg (22.4 km from the mine) to 15.9 μg/kg (1.1 km from the mine) (Suchanek *et al.*, in prep a).

The five most abundant taxa found within profundal sediments of Clear Lake during this study and analyzed for population estimates and community diversity indices are provided in Table I.

Population-Level Responses:

The five taxa of profundal invertebrates were highly variable (spanning over two orders of magnitude) in their numerical abundance and biomass among the 36 stations analyzed from Clear Lake. However, numerical abundance was usually tightly correlated with biomass (R^2 for *Chironomus* = 0.748, *Procladius* = 0.844, *Chaoborus* = 0.803, pooled oligochaetes = 0.683, *Placobdella* = 0.581). Most taxa usually occurred in relatively low numbers (i.e. less than ca. 20 per sample), except oligochaetes, which sometimes reached nearly 400 individuals per sample. Because numerical abundance and biomass were correlated, and because numerical counts were more easily fitted to a Poisson distribution, most analyses evaluating population responses to environmental variables were performed on numerical abundance values.

Benthic invertebrate populations, as measured by numerical abundance and biomass, are plotted as a function of sediment total Hg levels (Figure 2) and meHg levels (Figure 3). Initial viewing of these plots indicates that *Chironomus* appear to decline exponentially with increasing sediment Hg (especially total Hg), whereas *Procladius* appear to increase in response to sediment Hg levels (Figures 2A,B; 3A,B). The phantom midge, *Chaoborus*, also appeared to decline exponentially or linearly as a function of sediment Hg levels (Figures 2C, 3C). The taxon with the greatest biomass and highest numerical abundance was oligochaetes. Several oligochaete genera exist within the sediments of Clear Lake, but all were pooled in this study. There was no clear relationship between sediment Hg levels and oligochaete populations (Figures 2D, 3D). On the other hand, *Placobdella* leeches exhibited an exponential decline with increasing sediment Hg levels (Figure 2E, 3E).

Although there appear to be striking declines in the populations of several taxa as a function of sediment Hg levels, other environmental factors complicate the picture. Stepwise multiple regression models were used to determine the relative significance of depth, grain size, TOC, meHg and total Hg on numerical abundance and biomass for each taxon (*Chironomus*, *Procladius*, *Chaoborus*, oligochaetes and *Placobdella*).

Results from these analyses indicate that Clear Lake benthic invertebrate populations are responding to a variety of environmental variables, with the most influential factors being depth, grain size and meHg. One major difficulty that arose in analyzing the responses of these taxa to environmental variables was the fact that sediment Hg concentrations are partially confounded with grain size ($P < 0.001$, $R^2 = 0.274$). Further complicating the analysis is the fact that meHg is even more strongly confounded with total Hg ($P < 0.001$, $R^2 = 0.387$). This created some problems in establishing a basis for causality, but despite these difficulties, some clear trends emerged from further analyses.

Table II provides a summary of the Poisson fitted regression analyses. It should be noted that the results reported in this table reflect significance values from a conservatively approximated F-test (S-PLUS routine). First, Poisson regression analyses were performed for each taxon against meHg and total Hg. These individual regression results indicate that only the positive relationship of the midge *Procladius* and the negative relationship of the leech *Placobdella* were statistically significant.

Next, stepwise multiple Poisson regression analyses were used to select variables influencing abundances (and biomass) based on depth, grain size, TOC and meHg considered together. Then this same procedure was followed using the same independent variables and total Hg. MeHg and total Hg were not run together because of their strong correlation.

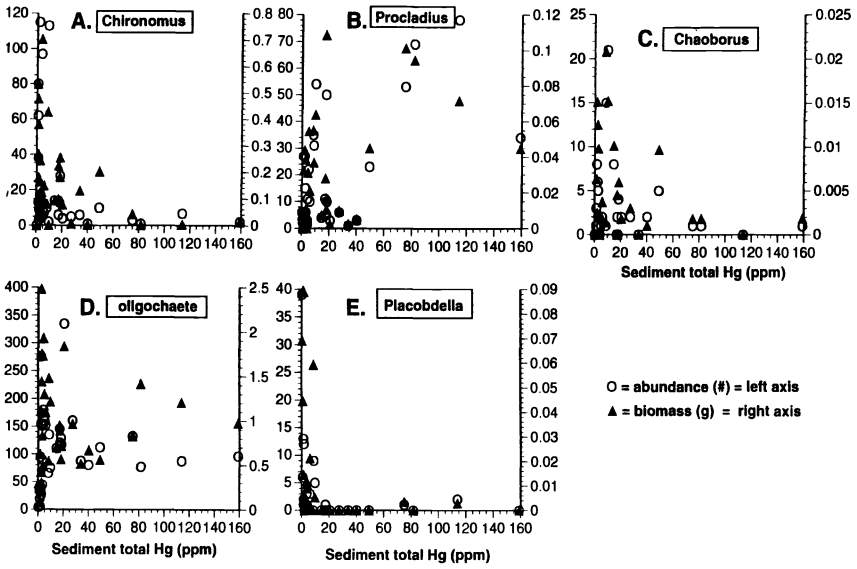

Fig. 2. Benthic invertebrate abundance and biomass as a function of sediment total Hg. A= Chironomus, B= Procladius, C= Chaoborus, D= Oligochaetes, E= Placobdella

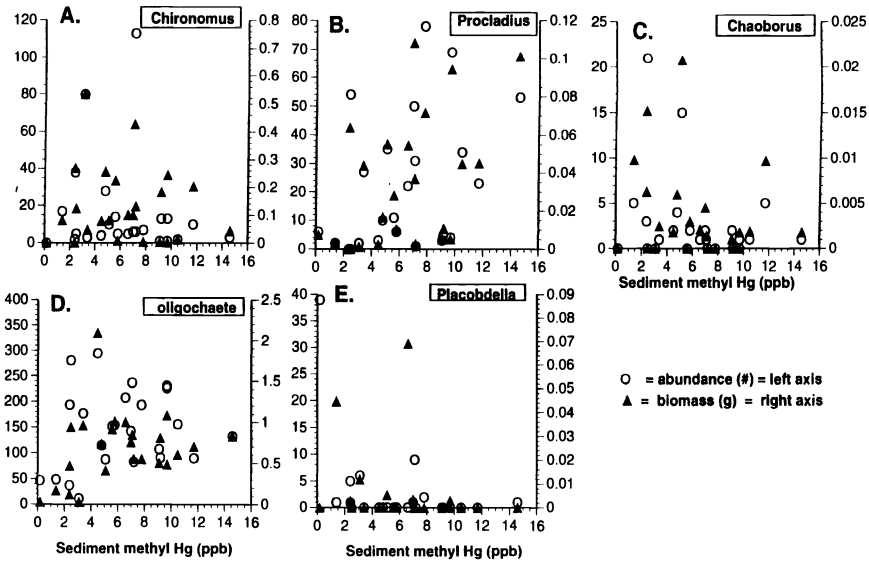

Fig. 3. Benthic invertebrate abundance and biomass as a function of sediment meHg. A= Chironomus, B= Procladius, C= Chaoborus, D= Oligochaetes, E= Placobdella

With respect to results for multiple Poisson regressions using meHg, as above, only *Procladius* (+) and leeches (-) exhibited statistically significant relationships with meHg, but depth had a more significant influence on *Procladius* and apparently a less less significant influence on leeches than did meHg. In this analysis, *Chironomus* also showed a significant negative relationship to grain size, whereas oligochaetes were positively related to total organic carbon and *Chaoborus* was negatively related to depth.

However, when this multiple regression model was fitted using total Hg instead of meHg, several additional significant variables were observed. *Chironomus* as well as leech populations showed statistically significant negative relationships with total Hg. Furthermore, both oligochaetes and *Procladius* varied positively with increasing total Hg, but in each case, other variables (such as grain size for *Procladius* and total organic carbon for oligochaetes) exhibited stronger significance levels. Leeches varied positively with increasing grain size, but very negatively with depth and total Hg. *Chaoborus* again showed a significantly negative response to depth, but no other variables.

In summary, leeches exhibit the strongest and most consistent statistically significant negative response to both total Hg and meHg, although depth and grain size likely play a major role in their distributions as well. *Chironomus*, while exhibiting no significant results with individual regression analyses, consistently varies negatively with grain size, but also reponds negatively to increasing depth and total Hg. Analyses on *Procladius* yield somewhat mixed results: this species varies positively with increasing meHg and total Hg, but also shows significant influence from depth and grain size. *Chaoborus* exhibits a statistically significant relationship only with depth.

TABLE II

SUMMARY OF POISSON FITTED REGRESSION ANALYSES

Individual Regressions	Chironomus	Procladius	Chaoborus	oligochaetes	leeches
methyl Hg	ns	¥ (+)	ns	ns	* (-)
total Hg	ns	** (+)	ns	ns	ns
Multiple Regression Analyses using meHg					
depth	ns	*** (-)	* (-)	ns	* (-)
grain size	*(-)	ns	ns	ns	ns
total organic carbon	ns	ns	ns	* (+)	ns
methyl Hg	ns	* (+)	ns	ns	*** (-)
Multiple Regression Analyses using total Hg					
depth	* (-)	ns	* (-)	ns	*** (-)
grain size	* (-)	*** (+)	ns	ns	*** (+)
total organic carbon	ns	ns	ns	** (+)	ns
total Hg	* (-)	¥ (+)	ns	¥ (+)	** (-)

ns = P > 0.1; ¥ = 0.1 > P > 0.05, * = P < 0.05, ** = P < 0.01, *** = P < 0.001
(-) = negative relationship, (+) = positive relationship

For *Chironomus* the most important factor influencing variability in Clear Lake was sediment grain size, with population levels declining as grain size increased. *Procladius* populations, on the other hand, declined dramatically with increasing depth ($P < 0.001$), but increased with increasing meHg ($P < 0.05$). *Chaoborus* showed a significant negative relationship with depth ($P < 0.05$), whereas oligochaetes responded positively to TOC ($P < 0.05$). *Placobdella* leeches exhibited the strongest negative response to increasing sediment meHg ($P < 0.001$) and a less significant ($P < 0.05$) negative response to depth.

It is interesting to note that these results indicate the two taxa exhibiting the strongest statistically significant population responses to sediment Hg levels, either total Hg or meHg, were the chironomid *Procladius* and the leech *Placobdella*, both of which are predators on benthic organisms (see Table I). The other predator, *Chaoborus*, while exhibiting no significance using multiple regression models, still exhibited notable declines with increasing sediment total Hg (see Figure 2C). Populations of the two detritivores studied, *Chironomus* and oligochaetes, did not show any statistically verifiable relationship to sediment Hg levels, even though visually the *Chironomus* plot exhibited a population decline with sediment total Hg levels greater than ca. 40-50 μg/g (see Figure 2A). This apparent decline of *Chironomus* with increasing Hg levels is most likely due to the partial confounding of Hg and grain size; this relationship is verified by the results of multiple regression analyses given in Table II.

These statistical results are curious in that visually there are decreases in the population levels of three of the five taxa as a function of increasing sediment Hg levels (see Figure 2A, 2C, 2E). This might indicate a threshold effect with a sharp decline in population levels after a given level of sediment Hg, which would not be detectable under the multiple regression models used. For *Chironomus* it is clear from the regression analysis that grain size (rather than sediment Hg concentration) is a strong determinant of population levels. But for species like *Chaoborus* and *Placobdella*, which do not show such strong relationships to grain size, there may be threshold effects; as with *Chiromomus, Chaoborus* populations may be limited above ca. 40-50 μg/g sediment Hg, and *Placobdella* populations may be limited above ca. 10 μg/g sediment Hg.

A "threshold effect" might be realized if there were some type of physiological impairment that occurs at high Hg levels. In fact, Swedish lakes with more toxic sediments produce chironomids with deformed mouth parts (Weiderholm, 1984) and oligochaetes that were smaller and sexually immature (Weiderholm and Dave, 1989). Warwick (1991) similarly found deformities in *Procladius* ligulae and antennae at sites highly contaminated with Hg.

Because of the confounding between sediment meHg, sediment total Hg and depth, there are complexities that were not detected using these multiple regression models. Therefore, one additional routine was employed in order to further evaluate the more subtle behavior of these populations in relation to Hg under varying conditions of the other most significant environmental variables. Those most influential environmental variables detected during the multiple regression analyses (above) were input into the LOESS (local regression model) routine of S-PLUS to produce "conditioning plots". This produced a series of 6 X 6 (= 36 for a two factor display) additional regression plots yielding population responses for each taxon in response to meHg under varying conditions of those most significant variables. As above, count values were fit directly using local smoothing algorithms. Figure 4 provides a heuristic diagram summarizing the output from these series of plots. In these diagrams the actual plots have been eliminated; only the trends are presented. Each quadrant represents a summary of the most significant trends from a series of 3 X 3 (= 9) plots.

Conditioning plots in Figure 4 indicate that the relationships examined and described under the assumptions of the multiple regression model above are more complex than might be expected. For instance, for *Chironomus* (Figure 4A), the population response to meHg

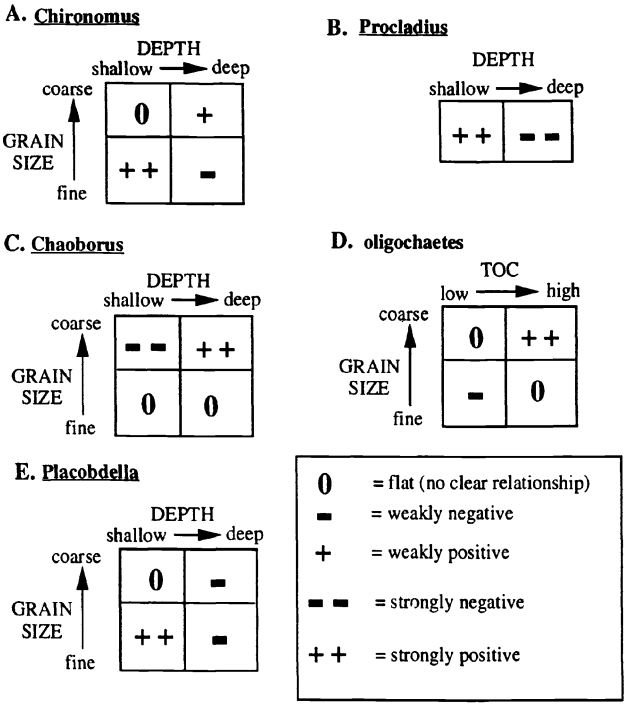

Fig. 4. Conditioning plots showing the relationship between changing population levels and sediment meHg concentrations as a function of the most significant independent variables as determined by stepwise multiple regression analysis.

under conditions of low grain size and shallow depth is strongly positive, but at deep depths, it becomes weakly negative. Furthermore, under the same deep depth regime, the relationship changes sign again with an increase in grain size. Similarly, there is a dramatic switch in the population response of *Procladius* to meHg under changing depth regimes. This indicates that the results obtained by fitting prescribed regression models to these types of data may not reveal more subtle and complex relationships within the system.

There are likely to be additive and multiplicative factors responsible for the distributions of these benthic invertebrate populations. Standard multiple regression statistics yield an overall appreciation of the gross level population responses that are strongly influenced by specific environmental variables. However, given the types of coconfounding present in these data, it is quite possible that several variables act in concert to influence the abundance and distribution of these populations, but the specific contributions from specific environmental variables cannot be clearly delineated. Sediment Hg appears to have some significant influence on these benthic invertebrate populations, especially for the leech *Placobdella* at deep depths. Whether other, more subtle, interactions involving Hg are present will be evaluated during an ongoing seasonal investigation at Clear Lake during 1994-1995.

Community-Level Responses:

Shannon-Wiener and Simpson diversity indices and Pielou's Evenness index each exhibited a decline in community diversity as a function of increasing sediment Hg concentrations, for both total Hg and meHg. Figure 5 shows that there is a tighter relationship between

Shannon-Wiener diversity and sediment total Hg than with sediment meHg. Although Simpson's index (not shown) is not as sensitive (i.e.- gives relatively less weight) to the presence of rarer species, both indices show virtually identical results. In either case, the regression lines plotted in Figure 5 represent a decline in diversity and evenness as a function of increasing Hg, which proved to be close to statistical significance at P = 0.1103. However, diversity showed greater significance with depth than either total Hg or meHg. These results are compatible with those of Moore *et al.* (1979) who found increasing species richness and diversity with distance from a mine (but indicated that other factors may be responsible for this trend) and Warwick (1991) who found reduced species richness at sites highly contaminated with Hg. It is unclear what influence a more in-depth and precise taxonomic identification of oligochaetes would have on these results.

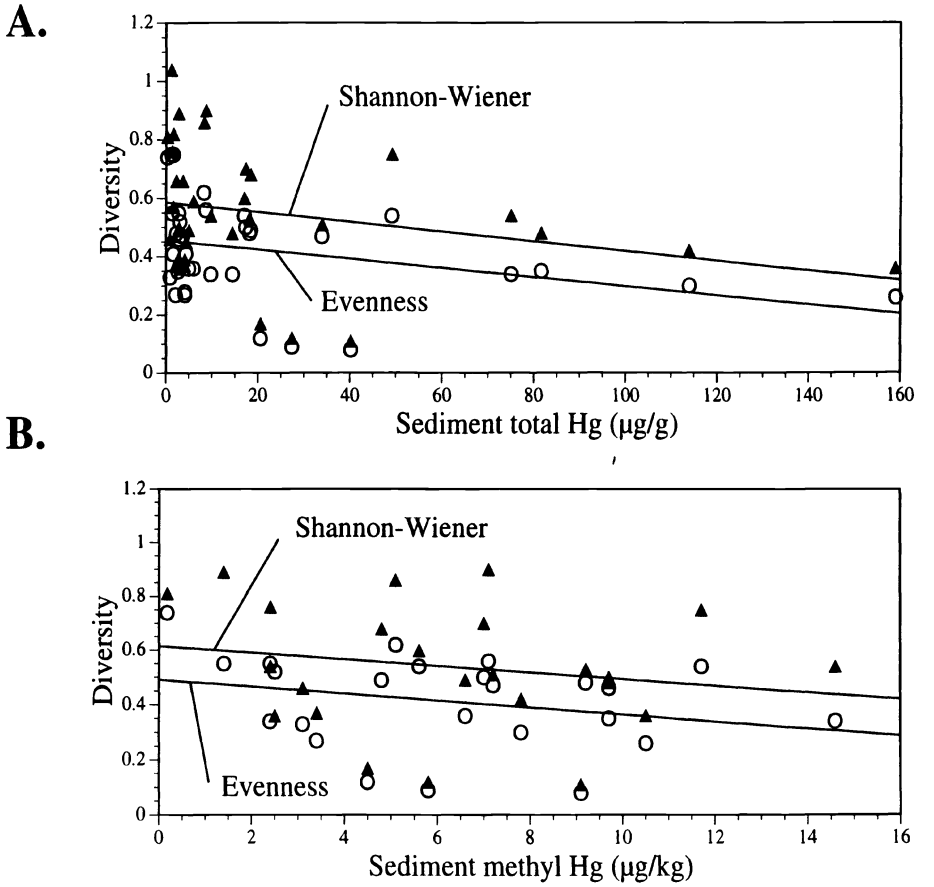

Fig. 5. Shannon-Wiener diversity and Evenness as a function of A= total sediment Hg concentrations, B= sediment meHg concentrations. Solid triangles = Shannon-Wiener; Open circles = Evenness

4. Conclusions

Populations of benthic invertebrates at Clear Lake showed complex relationships to sediment Hg levels and several environmental parameters including depth, grain size and TOC. Standard multiple regression statistics using Poisson fitted models indicated that each of the five taxa analyzed were responding most significantly to a unique combination of natural environmental variables and sediment Hg levels. While plots of population parameters versus sediment Hg levels yield visual relationships, multiple regression analyses produced statistically verifiable relationships to sediment Hg in only a few taxa.

Populations of the leech *Placobdella* yielded the most significant negative relationship to increasing sediment Hg (especially at deep depths), whereas the midge *Procladius* appears to have a positive relationship to increasing sediment Hg levels (especially at shallow depths). This positive relationship may indicate a species-specific resistance to Hg and/or be related to reduced competition from another chironomid midge (*Chironomus*) in regions of high sediment Hg. *Procladius*, *Chaoborus* and *Placobdella* all had significant relationships to depth, *Chironomus* responded most significantly to grain size and oligochaetes most significantly to TOC (and not depth), but each responded differently to sediment Hg levels at varying depth regimes.

Community level parameters (diversity and evenness) declined with increasing sediment Hg levels with considerable variation at low Hg levels. Simple and multiple regression analysis yielded a relationship between diversity/evenness that was nearly significant for sediment total Hg, but not close to significance for sediment meHg.

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DIFFERENT FACTORS RELATED TO MERCURY CONCENTRATION IN SEDIMENTS AND ZOOPLANKTON OF 73 CANADIAN LAKES

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Abstract: Surficial sediments were sampled with a light-weight gravity corer at 175 sites in 73 Ontario and Québec lakes and zooplankton was collected with a 225 µm mesh size net in 24 lakes. Hg concentrations in surficial sediments (0-2 cm) ranged from 3 to 267 ng g^{-1} dry weight with a mean of 80 ng g^{-1} dry weight for all sites. A regression model including organic content of sediments and the ratio of the catchment area / lake surface explained 60% of the variation in sediments Hg concentrations. Hg in zooplankton ranged from about 25 to 377 ng g^{-1} dw with a mean of 108 ng g^{-1} dw and was weakly correlated with catchment area, primary productivity and TOC. Our data indicate that an important fraction of Hg originates from the catchments, but do not show a clear west-east regional gradient for Hg concentrations in surficial sediments or in zooplankton.

1. Introduction

During the past few decades, attention paid to mercury (Hg) pollution and its effects on human health, due to the consumption of contaminated food, has been extended from locally polluted areas to regions remote from anthropogenic sources of contamination. Canada, Scandinavia and theUnited States are particularly affected with Hg concentrations in fish of many natural and artificial aquatic environments often exceeding public health guidelines (0.5-1.0 mg kg^{-1}) (Håkanson *et al.*, 1988; McMurtry *et al* , 1989; Meili, 1991a; Lathrop *et al.*, 1991). The magnitude of the problem in remote lakes is illustrated by the fact that in Sweden, over 10 000 natural lakes are presently estimated to bear predatory fish having Hg concentrations greater than 1 mg kg^{-1} weight weight (ww) for a body weight of 1 kg. Furthermore, the "Sport Fishing Guide" of Ontario and the "Guide de consommation du poisson de pêche sportive en eau douce" of Québec propose limited consumption of certain species of fish for 30 to 40% of the studied lakes (all remote from industrial centres). Although opinions regarding the reasons for the widespread Hg contamination of lakes vary considerably, long distance atmospheric transport is suggested as the primary source of Hg to remote regions (Björklund *et al.*, 1984; Swain *et al.*, 1992; Lucotte *et al.*, 1994). Having an estimated residence time of one year (Lindqvist and Rodhe, 1985; Nater and Grigal, 1992), atmospheric Hg is deposited via wet and dry precipitation, and enters lakes either directly or from the catchment area and will

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eventually accumulate in sediments. As Hg is weakly susceptible to diagenetic remobilization (Wren *et al.*, 1991; Louchouarn *et al.*, 1993), the observed increase of Hg concentration near the surface of sediment profiles is interpreted as reflecting an increase of atmospheric deposition (Evans, 1986; Swain *et al.*, 1992; Lucotte *et al.*, 1994). Therefore, time-averaged patterns of Hg deposition provided by lake sediments reflect the contamination exposure of the aquatic ecosystem. As surficial sediments (0-5 cm) contain 90 to 95% of all Hg present in a lacustrine ecosystem (Verta, 1984), a transfer of sedimentary Hg to the food chain could lead to high Hg levels in predatory fish. This study was undertaken to evaluate the level of Hg burden in sediments from Ontario-Québec lakes and to examine factors contributing to Hg levels in zooplankton, since they represent a major source of food for small fish, these organisms are an important link in freshwater food webs.

2. Materials and methods

2.1. DESCRIPTION OF THE STUDY AREA

The lakes cover a large geographic range across north-eastern Ontario and south-western Québec, are generally remote, and exhibit considerable variability with respect to catchment geology (Figure 1). The catchments of the lakes in the region of Algonquin Provincial Park in the Minden-Bancroft-Peterborough area, and the ones in Réserve Faunique Mastigouche north of Montréal , consist primarily of continental shield rocks, largely granites and gneisses. The Bancroft area has some sulphide deposits. Paleozoic sedimentary and meta-sedimentary rocks make up the catchments of most of the lakes in the Eastern Townships of Québec, south and east of Montréal. Additional information describing the study areas can be found in Rowan (1991).

2.2. SAMPLE COLLECTION

Sediment sampling was conducted during the summers of 1990 and 1991 at 175 sites in 73 Ontario and Québec lakes, using a light-weight gravity corer (15 cm in diameter)(Table I). The overlying water of the core was removed with a 60 ml plastic syringe without disturbing the surface layer (0-2 cm), which was thean carefully siphoned into a syringe and redistributed in prewashed polypropylene vials. Relative water content (% ww) was determined by drying overnight at 60 ^{o}C, and relative organic content (% dry weight) (dw) was obtained by ashing dry sediments at 550 ^{o} C.

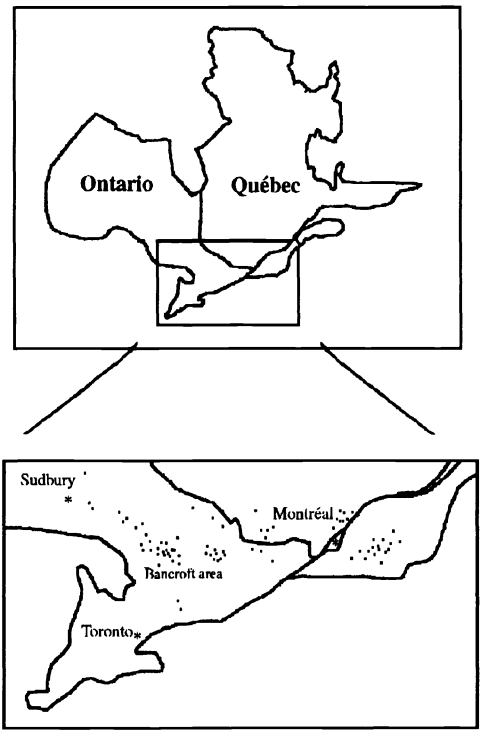

Figure 1: Map of Ontario and Québec showing the study area of the 73 lakes

Both Eh and pH of the sediments were measured using a Hach Eh/pH meter. Zooplankton were collected by horizontal and vertical tows with a 225 μm mesh size net, and were immediately frozen on dry ice in prewashed polypropylene vials. Although the samples collected with the net were dominated by zooplankton , they may also have contained phytoplankton or small fragments of debris such as leaves or bark., since no on-site sorting was conducted.. Catchment area and lake surface were determined from maps. Additional data on lake morphometry (mean depth, maximum depth) and physico-chemical variables (alkalinity, SO_4 and chlorophyll *a* concentrations, TOC, and colour of the water column) were obtained from the data inventory of the Ontario Ministry of Natural Resources (MNR) and the Ontario Acid Sensitivity database (MOE) (Neary *et al.*, 1990).

2.3. SAMPLE ANALYSIS

For Hg analyses, all samples (sediments and zooplankton) were freeze-dried for 3 days prior to acid digestion. All labware was acid washed in 10% HNO_3 and triple-rinced with double-distilled water. Digestions were conducted in a polypropylene-lined, laminar flow hood. For fine-grained sediments and zooplankton, 0.25 to 1 g aliquot were placed in Teflon digestion tubes with 8 ml of dilute aqua regia (3 H_2O: 3HCl: 1 HNO_3). The tubes were heated for 3 hours at 80^0 C within an aluminium heating block, left overnight, and then brought up to a final volume of 25 ml with double-distilled water in polyethylene volumetric flasks. For coarse-grained sediments, 2 g of sample were used.. The references materials, Buffalo River sediment (NBS SRM 2704) and DORM-1 (NRCC) for zooplankton, were treated identically to the other fine-grained samples, as were all blanks and standards. Hg was analyzed using the hydride generation and amalgam technique by cold vapour atomic absorption spectrometry on a Perkin Elmer 5100 equipped with an autosampler. Hg concentrations are expressed as ng g^{-1} dw. The detection limit was 0.1 ng g^{-1}. To normalize the data and reduce the heteroscedasticity, all data were log transformed (except pH, latitude and longitude).

TABLE I

Summary of Hg concentrations and watershed characteristics of the studied lakes (N=number of lakes or sites sampled, SD=standard deviation, Min=minimum, Max=maximum).

Variables	N	Mean	SD	Min	Max
Lake morphometry and location					
lake surface (km^2)	73	8.1	15.3	0.05	104.4
watershed area (km^2)	73	78.8	198.7	0.2	1300.0
ratio watershed area/lake area	73	10.2	10.4	0.6	51.9
maximum depth (m)	67	23.9	293.3	1.9	83.7
mean depth (m)	67	9.47	7.1	2.3	40.2
latitude north (degree, minute)	56	45 07 N	01 50	44 12	48 07
longitude west (degree, minute)	56	76 41 W	05 20	70 52	80 17
Lake water chemistry					
chlorophyll *a*	167	5.9	8.8	0.7	64.0
conductivity ($\mu S\ cm^{-1}$)	31	60.7	55.6	16.0	220.0
alkalinity ($mg\ L^{-1}$)	25	17.5	25.8	0.43	11.7
pH	73	7.1	0.84	4.2	8.6
colour (Hazen units)	29	18.6	16.22	2.5	81.7
TOC ($mg\ L^{-1}$)	29	2.6	3.5	0.73	20.0
Hg in zooplankton ($ng\ g^{-1}$ dw)	24	107.6	76.2	25.5	376.9
Sediment characteristics					
water content (% ww)	172	78.72	20.8	22.2	99.3
organic matter (% dw)	157	20.1	14.1	0.6	63.8
Eh	126	-105.8	129.4	-401.1	455.9
pH	140	6.5	0.6	4.0	7.9
Hg ($ng\ g^{-1}$ dw)	172	79.6	57.2	3.3	267.1

3. Results and discussion

3.1 GENERAL SEDIMENTS CHARACTERISTICS

The water content of our sediment samples varied between 22.2 and 99.3% of water with a mean of 78.7%. The mean volatile organic matter content of dried sediments ranged from 0.6 to 63.8% and exceeded 45% in 8 lakes (Table I).

3.2. MERCURY IN SEDIMENTS

Hg concentrations in surficial sediments (0-2 cm) ranged from 3.3 to 267.1 ng g^{-1} dw (n=172) with a mean of 79.6 ng g^{-1} dw for all sites. This concentration goes up to a mean of 95.6 ng g^{-1} dw (n=73), if we consider only the deepest area of the lakes. Andren and Nriagu (1979) suggest 330 ng g^{-1} dw as a global average for Hg concentration in the upper layers of fresh water sediments. In an extensive survey of the Great Lakes, Thomas and Jacket (1976) reported a Hg mean concentration of 347 ng g^{-1} dw (minimum = 4, maximum = 9500, some areas were contaminated) in the upper 3 cm. These values are high compared to the ones reported by Björklund *et al.* (1984) where surficial (0-3 cm) sediment concentrations in southern Sweden ranged from 150 to 500 ng g^{-1} dw (mean=294) and from 50 to 250 ng g^{-1} dw in the northern part of Sweden (mean=101). The global Hg value suggested by Andren and Nriagu (1979) might have been overestimated, since in recent years, improvement of instrumentation, better control of reagents and the development of ultraclean protocols, have aided in reducing the risk of contamination, and hence resultes in data lower than previously reported (Tremblay *et al.*, 1993a). Our surficial concentrations are similar to the range of values found in the remote regions of northern Sweden, as well as the majority of studies in remote areas cited in Table II.

Hg levels in the lake sediments of our study were significantly correlated with both the organic matter content (r=0.73) (Figure 2) and the water content (r=0.60) in the sediments, the water depth at the sample location (r=0.32), and with the drainage ratio (catchment area / lake area) (r=0.25), but only two variables, explaining 59% of the variations, were retained following a stepwise regression model. The regression model includes the organic matter content and the drainage ratio. The latter explains only 7% of the variations.

Our regression model is the following:

$$\text{Log Hgsed} = 0.877 + 0.644 * \text{Log organic matter} + 0.235 * \text{Log drainage ratio}$$
$$R^2=0.59;\ n=157,\ p < 0.001$$

No correlations were found between Hg levels in sediments and pH, Eh, TOC, colour or alkalinity of the water column. The co-variation of Hg with organic matter content is expected, as Hg is firmly bound to organic matter in the water column, as well in the sediments (Wren *et al.*, 1991; Arakel and Hongjun, 1992; Louchouarn *et al.*, 1993; Lucotte *et al.*, 1994). It has been shown that fine organic particles have a high affinity

TABLE II

Data from literature on Hg concentration in lacustrine sediments (ng g^{-1} dw, mean (±standard deviation or range); #S=number of sites or #L=number of lakes sampled; r=correlation coefficient; S or P =surficial sediments or coresprofiles; * some sites or lakes are contaminated).

References	Hg	Correlated variables	# S or L	r	S or P	Region
Sørensen *et al.*, 1990	174 (±109)	dissolved Hg water color water TOC	77 L	r= 0.35 r= 0.43 r= 0.39	surficial (0-6cm)	Minnesota, USA
Lucotte *et al.* ,1994	40-250	% organic matter	10 L	r=0.93	profiles	Québec, Canada
Evans, 1986	200-580	ratio wtshed/larea	14 L		profiles	Ontario, Canada
Wiener *et al.*, 1990	10-160	% organic matter	21 S 2 L	r=0.98	surficial (0-5cm)	Wisconsin, USA
Rada *et al.*, 1989	90-240		11 L		surficial (0-6cm)	Wisconsin, USA
Stokes *et al.*, 1981	30-150				surficial	Ontario, Canada
Johnson, 1987	10-190		14 L		profiles	Ontario, Canada
Wren *et al.*, 1983	10-300	% organic carbon % S	14 S	r=0.46 r=0.90	surficial	Ontario, Canada
Sloterdijk, 1991	133 (0.5-1400)	% organic carbon clay	98 S	r=0.38 r=0.39	surficial (0-4 cm)	Québec, Canada*
Thomas and Jaquet, 1976	347 (4-9500)	%organic carbon Clays Fe_2O_3	405 S 31 S 163 S	r=0.60 r=0.41 r=0.38	surficial (0-3cm)	Great lakes,Canada *
Johansson, 1985	100-400	% organic matter water pH	196 L	r=0.37 r=-0.40	surficial (0-1 cm)	Sweden
Håkanson *et al.*, 1988	587 (±1117)	pH color	177 L	r=0.21 r=-0.23	surficial (0-1 cm)	Sweden
Björklund *et al.*, 1984	50-250	% organic matter	62 L		surf. and prof.	Sweden
Verta *et al.*, 1986	150 (50-290)		36 L		surficial	Finland

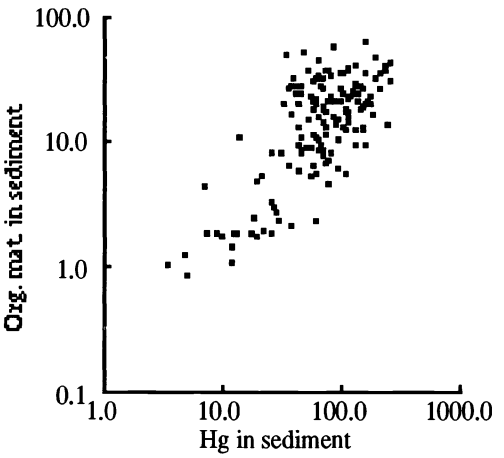

Figure 2: Relationship of organic matter (Log Org. Mat. sediment, %) with Hg concentration (Log Hg sediment, ng g^{-1} dw) in surficial sediments (0-2 cm) (r=0,73, n=172).

for metals (Dillon and Evans, 1982; Evans, 1986), therefore the correlation between the concentration of Hg in sediments and water depth or water content of the sediments may be owing to the fact that a larger fraction of fine organic particles settles in the deep lakes, where erosion and wave action are reduced, and where the water residence time is longer. Other factors that could cause the observed variation in metal content are local differences in supply from the lake catchment as, shown by the relationship with the drainage ratio, and the differences in the accumulation rate of sediments in the different lakes (Rowan *et al.*, 1992; Blais and Kalff, 1993). It has been clearly demonstrated that the rate of Hg accumulation in sediments is influenced by the size and the type of the catchment (Suns and Hutchin, 1990; Mierle and Ingram, 1991; Swain *et al.*, 1992, St.Louis *et al.*, 1994). Our results confirm these studies as they indicate that an important fraction of sediment Hg originates from the catchment.

3.3. MERCURY IN ZOOPLANKTON

Hg in zooplankton ranged from about 25.5 to 376.9 ng g^{-1} dw, with an average of 107.6 ng g^{-1} dw. These values are similar to few studies listed in Table III, where the Hg concentrations vary between 75 and 550 ng g^{-1} dw. Hg in zooplankton was poorly correlated with the catchment area ($r=-0.20$, $p<0.1$), with the primary production as determined by the concentration of chlorophyll *a* ($r=0.24$, $p<0.1$), and with the TOC ($r=0.17$, $p<0.1$). No correlation was found between Hg levels in sediments and Hg levels in zooplankton. This lack of relationship indicates that the transfer of Hg from lacustrine sediments to the food chain is either more likely due to benthic organisms, as proposed by

Tremblay *et al.* (1993b), or that the statistical relationship between the environmental exposure and the accumulation in biota may be weakened by a wide range of processes (e.g. uptake, excretion, growth dilution...) controlling the transfer of contaminants to biota.

TABLE III

Data from literature on Hg concentration in zooplankton (ng g^{-1} dw, mean (±standard deviation or range); #L=number of lakes sampled; r=correlation coefficient.

References	Hg	Correlated variables	# L	r	Region
Sørensen *et al.*, 1990	87.9 (±48.8)	Log Hg in water	53	r= 0.45	Minnesota, USA
		water TOC		r= 0.49	
		water pH		r=-0.42	
		Catchment area		r=-0.36	
Meili, 1991a	80-500	water pH	60	r=0.57	Sweden
		water color	55	r=0.52	
Surma-Aho *et al.*, 1986	220 (110-550)		2		Finland
Watras and Bloom, 1992	75(49-89)		2		Wisconsin, USA
Plourde *et al.*, 1994	172-460		4		Québec, Canada

In contrast to Sørensen *et al.* (1990) and Meili (1991b), we did not observe any significant relationship between zooplankton Hg levels and water pH. This might be caused by the small range of pH found in our lakes (7.1±0.82, Table I).

Hg concentrations in zooplankton have previously been shown to be correlated with catchment area, TOC or colour (Table III), variables that often indicate an influence of terrigenous organic matter. Since organic matter transported from catchments to lakes is an important carrier of Hg (Iverfeldt and Johansson, 1988; Mierle and Ingram, 1991), terrigenous run-off may be an important source of Hg for zooplankton, especially since humic matter can serve as a food source for bacteria, fungi and, possibly zooplankton (Tranvik, 1989; Hessen *et al.*, 1990). This detrital terrigenous organic matter is characterized by a lower nutritive value. Therefore, in order to satisfy their food needs, zooplankton must ingest a large volume, thus potentially exposing themselves to a greater quantity of Hg (Meili 1991a).

Widespread anthropogenic Hg distribution is of special interest for Québec and Ontario where sport fishing is an important industry. Hg concentrations in fish can be estimated from our data using a mean of 5 for the ratio of zooplankton Hg concentration (dw) to that of 1 kg pike (ww) (Meili, 1991b). Estimated Hg levels in 1 kg pike for the lakes sampled range from 0.13 to 1.9 mg kg^{-1} ww, and exceed 0.5 mg kg^{-1} ww in half of the lakes, indicating a problem similar to Sweden. In contrast to Håkanson *et al.* (1988) in Sweden and Lathrop *et al.* (1991) in Southern Ontario who found a regional Hg pattern,

our dataset does not suggest a regional gradient for Hg concentrations in surficial sediments or in zooplankton, for the 700 km west-east transect. These results concur with previous observations by Lucotte *et al.* (1994) over the boreal forest domain, along a 10^{o} latitudinal gradient from Montréal to James Bay in Northern Québec.

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RELATIONS BETWEEN ORGANIC CARBON AND METHYLMERCURY IN HUMIC RICH SURFACE WATERS FROM SVARTBERGET CATCHMENT IN NORTHERN SWEDEN

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Abstract. Monthly sampling of a mire outlet and two tributaries, one of them originating in the mire, on the Svartberget catchment in northern Sweden was performed during one year. The concentration of total organic carbon (TOC) in the three waters was fairly high (10-40 mg/l). Methylmercury (MeHg) was analysed in the original water sample (MeHg-whl) and in the humic fraction (MeHg-hum). The MeHg-hum increased with increasing concentration of humic substances (HS; measured as absorbance at 254 nm) in the water. A seasonal variation of the MeHg-hum/TOC ratio was superimposed on a negative relationship to the water flow, which indicates that the methylation is a slow process which results in a rapid drainage of the storage during periods of high flow. A minimum of the MeHg-whl/TOC ratio observed during the spring flood was followed by a slow increase during the rest of the year.

1. Introduction

Most of the mercury (Hg) originating from atmospheric deposition is immobilized as organic complexes in soils. A minor fraction of the Hg is transported from the soils to surface waters, a redistribution which is closely related to the transport of dissolved organic matter (Iverfeldt and Johansson, 1988; Aastrup *et al.*, 1991; Mierle and Ingram, 1991). Also methylated Hg forms (MeHg) are released from soils and transported by dissolved organic matter (Lee and Hultberg, 1990). The transport of Hg and MeHg seems to be correlated not only with the concentration of total organic carbon (TOC) but also to the concentration of dissolved humic matter (Lee and Hultberg, 1990; Meili *et al*, 1991; Mierle and Ingram, 1991). However, it is not yet clearly found how large a fraction of the MeHg is directly associated to the humic fraction.

The aim of this study was to investigate the relation between Hg, MeHg and organic matter in a small catchment in northern Sweden during one year. The study was focussed on the occurrence of MeHg in the humic and non-humic fractions of the water in an attempt to elucidate seasonal variations.

2. Experimental

The study was performed on the Svartberget Catchment (50 ha; Figure 1) in northern Sweden. The catchment is forested with mature spruce and pine on podzol soils. The sampling was conducted in two tributaries (Kallkällbäcken and Västrabäcken; sites K and V, respectively) and the mire outlet (site M) from which Kallkällbäcken originates. The area is thoroughly described elsewhere (Bishop, 1991; Lee *et al.*, 1994). The amount and chemical composition of water entering Kallkällbäcken from the subcatchment below the mire was calculated from the difference in concentration at sites

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A and E. This assumes that elements were not lost, nor gained from the stream channel or atmosphere.

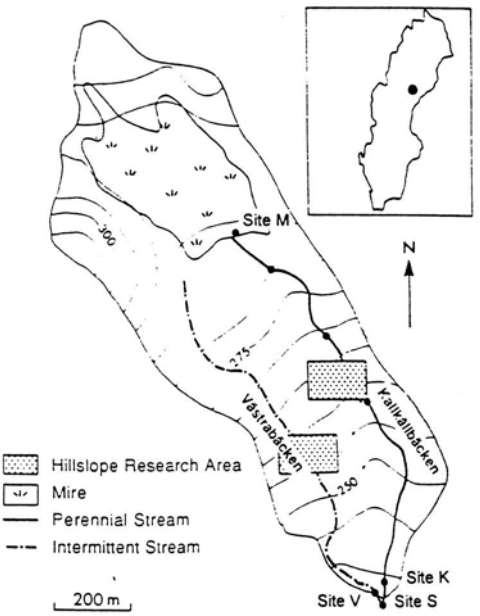

Figure 1. The Svartberget catchment

Weekly sampling of stream water and mire water was performed during the period January 1 to December 31, 1993. All samples were analysed for TOC (Shimadzu TOC-5000 with catalytic combustion) and absorbance at 254 nm (Beckman DU-8 spectrophotometer) as well as pH and the major dissolved anions and cations.

Monthly water samples were collected during the same period for analysis of total concentration of MeHg (MeHg-whl) and MeHg in the humic fraction (MeHg-hum) as well as of the total concentration of Hg (Hg-tot). Vessels in contact with MeHg or Hg were made of borosilicate glass, pyrex glass or teflon. Polyethylene bottles were used in the fractionation of the organic material. Glass ware, teflon and silicone rubber tubes were leached in 2-4% HCl. These items as well as the plastic ware were acid-washed (20%HNO_3 + 1% HCl) for at least 24 hours and thorougly rinsed with Milli-Q-water prior to use.

The humic fraction of the organic matter was isolated on a weak anion-exchange resin, diethylaminoethyl-Sephadex-A25 (Pharmacia Fine Chemicals) in a batch procedure (Pettersson *et al* ,1993). The resin was pretreated with HCl (suprapur) and rinsed with Milli-Q-water. After a contact time of 20 minutes the supernatant, containing the non-humic fraction, was decanted and collected.

Analysis of MeHg was conducted on the original water sample (MeHg-whl) and on the non-humic fraction. The concentration of MeHg-hum was assessed as the difference between these analyses. The MeHg was determined using a GC-CVAFS technique with

aqueous phase ethylation and using a distillation preseparation step (Bloom, 1989; Horvat *et al.*, 1988).

Analysis of Hg-tot was performed after an oxidative treatment with BrCl prior to reduction by $SnCl_2$ (Bloom and Crecelius, 1983). The Hg was preconcentrated on a gold trap and analysed by a double amalgamation helium dc-plasma atomic emission method (Iverfeldt and Lindqvist, 1982; Iverfeldt, 1984).

Samples were taken more frequently during the spring flood (April 24-29) and a rain storm during the summer (July 23-28). Those samples were analysed following the same scheme as for the monthly samples.

3. Results

The seasonal variation in water flow, pH and TOC in the mire outlet, Kallkällbäcken and Västrabäcken is shown in Figure 2. The flow pattern (Figure 2a) was almost identical for the three waters, although the runoff in Västrabäcken was only 18% of the flow in Kallkällbäcken. In both tributaries pH was relatively high (5.5-6.0) during the period of low flow in the winter (Figure 2b). The spring flood resulted in a decrease of the pH (to 4.0 and 4.5 in Kallkällbäcken and Västrabäcken, respectively), after which it increased slowly during summer and autumn. The pH of the mire was 0.3-1 pH unit lower than the pH in Kallkällbäcken during the whole year except for the spring flood when the difference was less than 0.3 pH units.

The mire outlet and Kallkällbäcken below the mire had a fairly high TOC (20-40 mg/l), while Västrabäcken had a lower TOC (8-25 mg/l) during the period studied (Figure 2c). During the spring flood the TOC exhibited different patterns in the mire and the two tributaries. The TOC was fairly constant in the mire from January until the spring flood when a rapid decrease occurred, due to dilution with melted snow which comprised 60% of runoff (Bishop *et al.*, 1994). Generally, increased water flow tends to lead to an increase of TOC during the snow-free period (Bishop *et al* , 1990). This was observed also during the spring flood in Kallkällbäcken and Västrabäcken. The increase was, however, less pronounced in Kallkällbäcken. The diluted mire water interfered with the raised TOC level caused by discharge from the soil to Kallkällbäcken, which neutralized the expected increase (Bishop *et al.*, 1994). The increased TOC during summer and autumn coincided often with rain periods, leading to discharge of organic matter from the soil.

The content of humic substances (HS) in the water can be estimated from absorbance determinations at 254 nm. Thus, the ratio absorbance/TOC gives a measure of the fraction of the TOC which consists of HS. A comparison of the three waters studied (Figure 3a) showed that the mire and Kallkällbäcken contains a larger fraction of humic matter than Västrabäcken during the whole year, except for the month before the spring flood when both creeks had a larger fraction of HS than the mire.

The concentration of MeHg-whl varied with high values during the winter that dropped sharply during spring flood after which the concentration increased during the summer period. This increase, however, was interrupted during periods of high flow. The overall pattern was similar; the concentration of MeHg at the three sampling points differed, especially during periods of low flow (Figure 3b; Lee *et al.*, 1994).

The seasonal variation and negative relation to flow observed for MeHg-whl was not

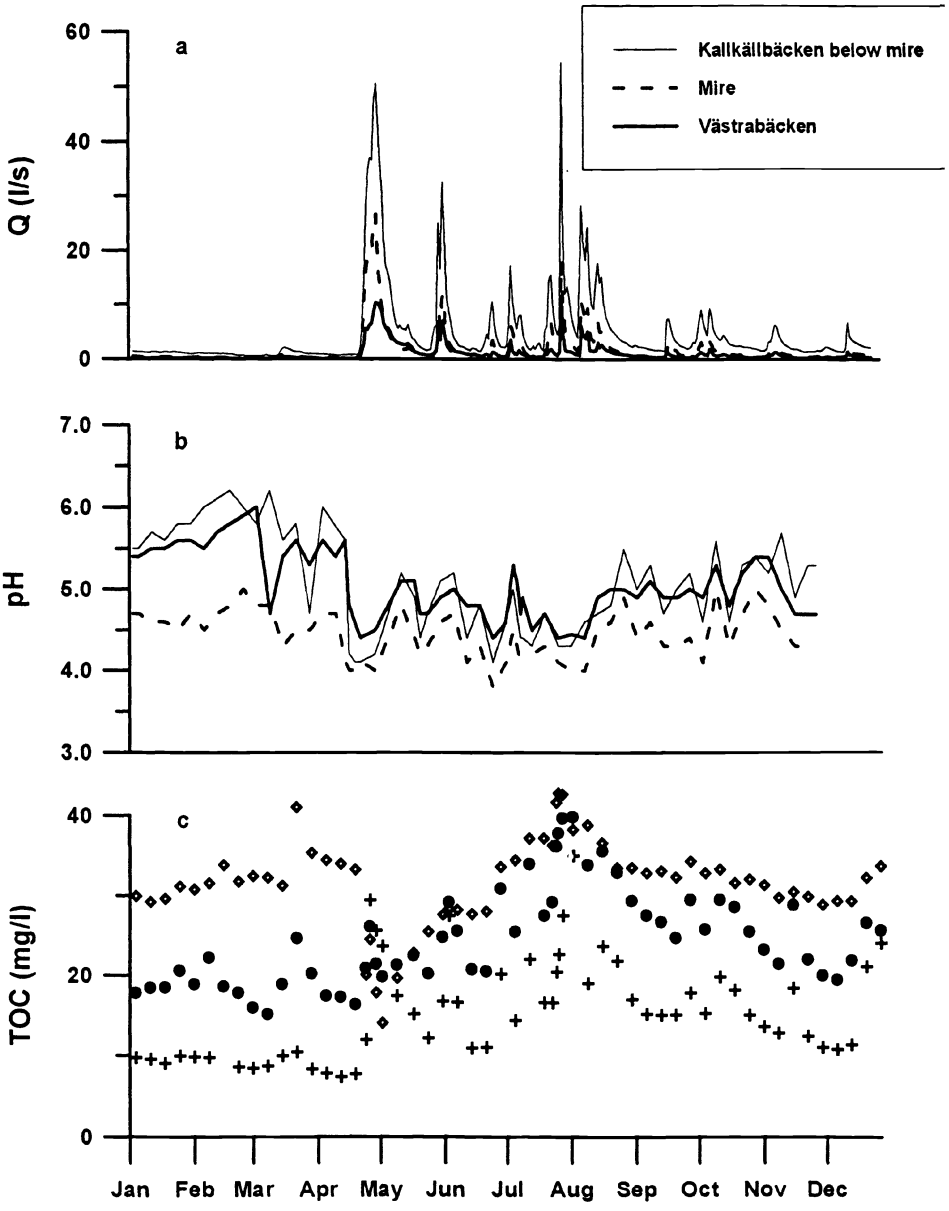

Figure 2. Seasonal variation of a) Flow (Q); b) pH and c) TOC in the Mire (◊), Kallkällbäcken (•) and Västrabäcken (+).

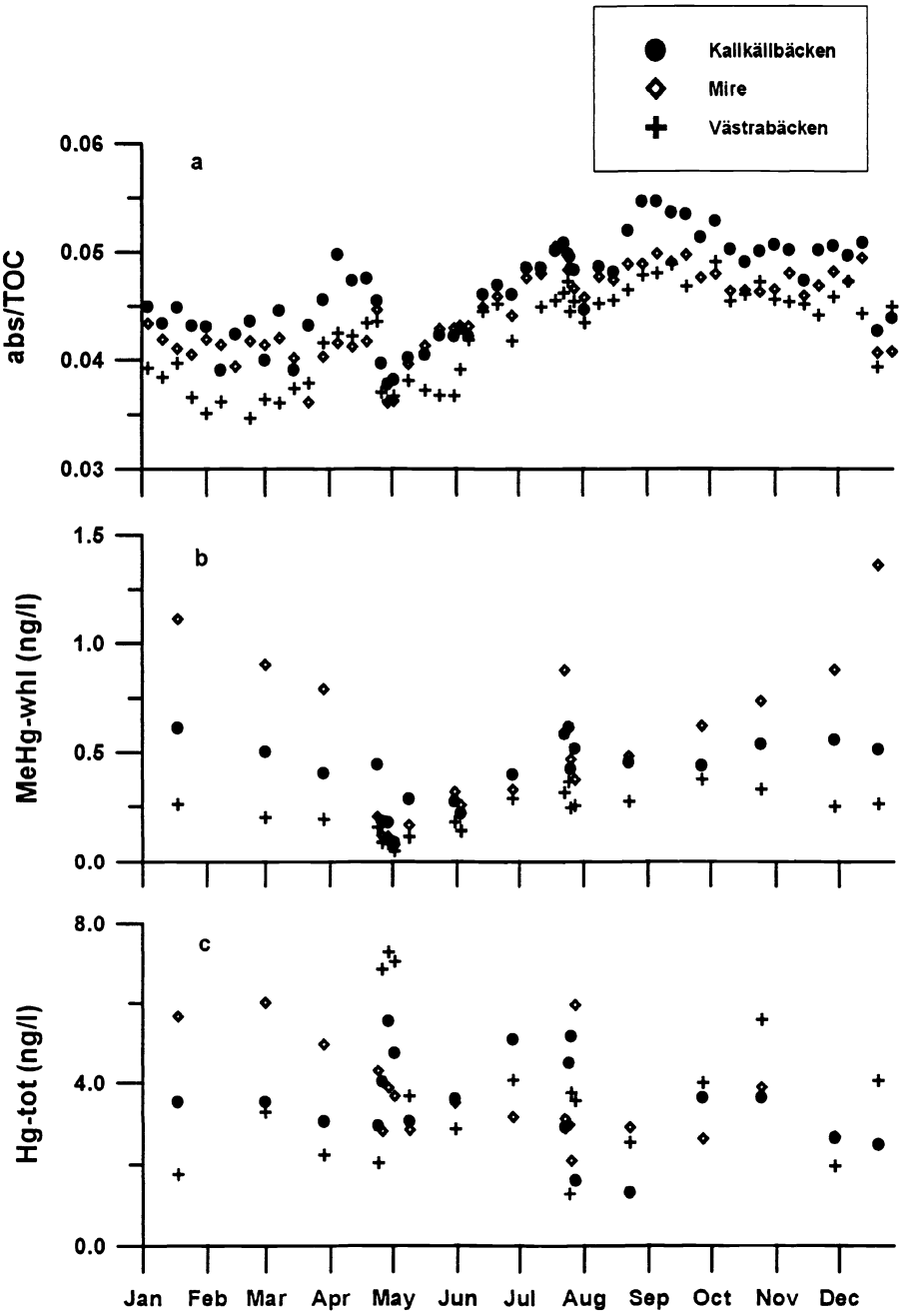

Figure 3. Seasonal variation in a) humic fraction of TOC; b) MeHg-whl and c) Hg-tot in in the Mire (◊), Kallkällbäcken (•) and Västrabäcken (+) .

seen for Hg-tot (Figure 3c). There was an increase of Hg-tot during spring flood. The concentration of Hg-tot in Västrabäcken was at times higher than in the other sites, whereas Västrabäcken usually had the lowest MeHg. The extremely high levels in Västrabäcken indicate that there was a large amount of Hg stored in the soil which was released by the spring flood.

4. Discussion

Since Hg forms strong complexes with organic material (see e.g. Mantoura *et al.*, 1978), Hg is expected to correlate with the TOC. Methylmercury also has the tendency to be associated with organic material. Earlier studies (Lee and Hultberg, 1990; Lee and Iverfeldt, 1991) have shown that the concentration of MeHg-whl increases with increasing concentration of humic substances. However, in this study, also MeHg-hum varied with the concentration of HS in all three waters (Figure 4). Moreover, the MeHg-hum/MeHg-whl ratio tends to approach unity with increasing concentration of HS (Figure 5). Thus, the more HS that are present, the larger is the fraction of MeHg which is bound to humic matter. High values of the MeHg-whl/TOC ratio (>0.014) were obtained for samples collected during January and February (Figure 4). The MeHg-whl/TOC ratio reached a high level in the mire and Kallkällbäcken also during the first day of both the spring flood and the rain epsiode in July. This suggests that there is fraction of easily mobilized MeHg which can be rapidly discharged during the initital phase of an episode and is the main source during periods of low flow.

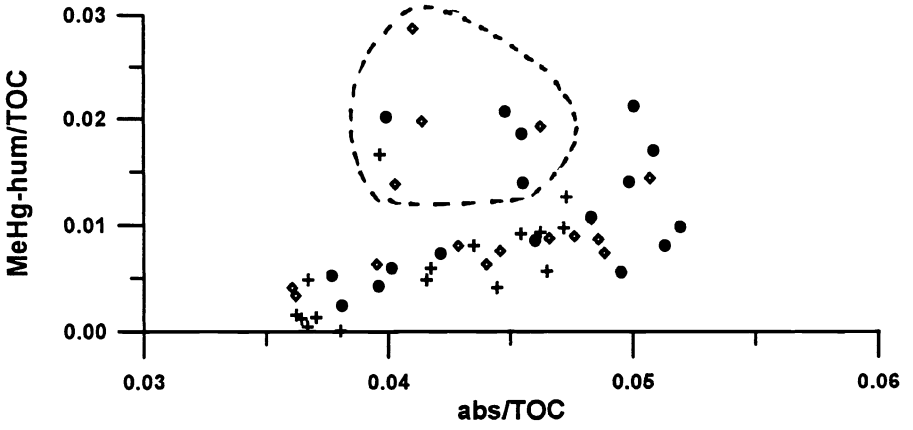

Figure 4. MeHg-hum/TOC *vs* absorbance/TOC (at 254 nm) in the Mire (◊), Kallkällbäcken (•) and Västrabäcken (+). Data from January and February as well as the first day of the spring flood and the rain episode are within the dotted line.

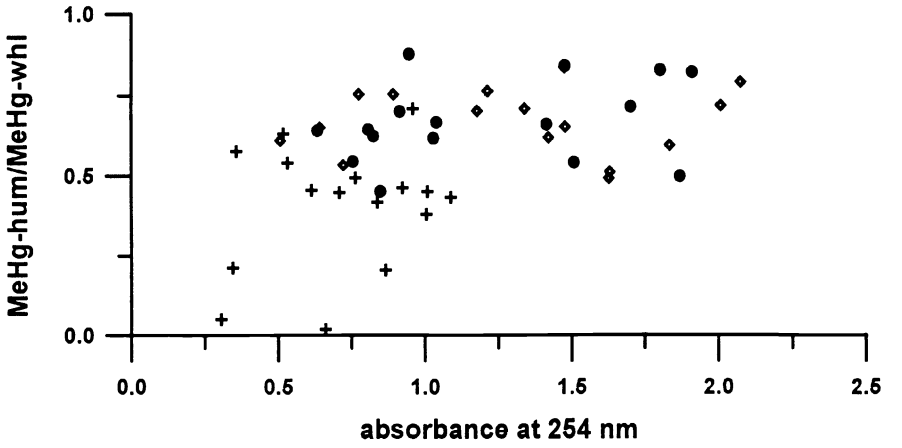

Figure 5. The ratio MeHg-hum/MeHg-whl *vs* absorbance at 254 nm in the Mire (◊), Kallkällbäcken (•) and Västrabäcken (+).

Calculations of the ratio MeHg-whl/TOC were made monthly for the whole year and for two episodes, the spring flood and the heavy rains in July. The MeHg-whl/TOC ratio showed the same pattern in both the mire and the creeks over the year (Figure 6). The values of the ratio were quite similar on each occasion at the different locations, in contrast to the relatively large variation in the concentration of MeHg-whl. Starting on a high level in January, the ratio decreased throughout April. After reaching a minimum during the spring flood, the ratio slowly increased during summer and autumn. The trend was interrupted during periods of high flow. These results clearly show that there was a negative correlation between the MeHg-whl/TOC ratio and flow. Thus, the formation of MeHg available for output seems to be a relatively slow process which results in a rapid drainage of the storage during periods of high discharge. Total organic carbon, by contrast, increases in concentration with flow.

The very low level of the MeHg-whl/Hg-tot ratio during the spring flood suggests that the biological or chemical processes involved in the methylation of Hg are seasonal dependent, which is in agreement with a study of Korthals and Winfrey (1987). Consequently, there is no (or insignificant) methylation during the winter period. The high level of the MeHg-whl/Hg-tot ratio in the discharge in July might be a result of a recent transformation of Hg to MeHg. Analyses of soil water and water centrifugated from moss samples in the stream banks resulted in MeHg/TOC ratios similar to those of the creeks, which indicates that the pool of MeHg might be found in the living stream bank mosses (Bishop *et al.*, 1994).

The yearly output of Hg-tot and MeHg in the humic and non-humic fraction was calculated for the different subcatchments. The total output summarized in Table I (Lee *et al.*,1994) is well in agreement with the yearly output from other catchments in

Sweden (Lee and Hultberg, 1990). The ratio between MeHg-hum and MeHg-whl shows that a larger fraction of the MeHg was bound to the humic fraction in the mire outlet and in Kallkällbäcken below the mire than in Västrabäcken, which is in accordance with the higher concentration of humic substances in the mire and Kallkällbäcken .

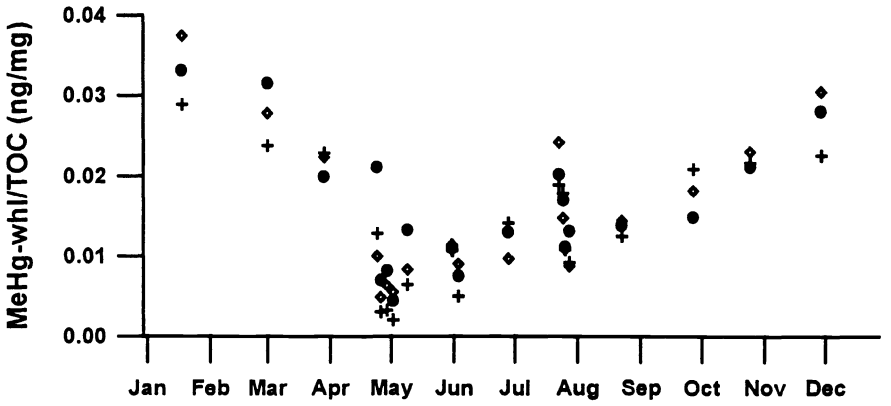

Figure 6. Seasonal variation in the MeHg-whl/TOC ratio in the Mire (◊), Kallkällbäcken (•) and Västrabäcken (+).

TABLE I
Yearly output of Hg and MeHg from the subcatchments

Subcatchment	Hg-tot mg/km^{2}yr	MeHg-whl mg/km^{2}yr	MeHg-hum/MeHg-whl
Mire	1520	170	0.61
Kallkällbäcken below the mire	1220	110	0.65
Västrabäcken	1810	80	0.44

5. Conclusions

MeHg analyses of humic rich surface water showed that the fraction of MeHg-hum increased with increased concentration of humic matter in the water. The seasonal variation of the MeHg-whl/TOC ratio was superimposed on a negative correlation with

the water flow. The minimum of the MeHg-whl/TOC ratio observed during the spring flood was followed by a slow increase during spring and summer. A possible source for the MeHg bound to organic matter seems to be the stream bank mosses.

Further investigations are needed to obtain more details about the sources of MeHg. The results of these examinations would hopefully contribute to the development of a model which can describe the patterns of MeHg output that vary with both season and flow rate. The key feature of that model should be the relationship between MeHg and TOC.

Acknowledgements

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Mercury Accumulation Trends in Florida Everglades and Savannas Marsh Flooded Soils

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Abstract. Global and regional increases in atmospheric mercury (Hg) concentrations have previously been identified as the cause of increased mercury accumulation rates in north temperate lakes in Sweden, Wisconsin, and Minnesota Atmospheric deposition can often account for elevated Hg concentrations in fish from these systems Mercury levels in sportfish collected from some areas of the Florida Everglades and Savannas Marsh exceed limits that are acceptable for human consumption Forty five soil cores and soil grab samples were retrieved from the Everglades and Savannas Marsh wetlands Eighteen sediment cores were dated radiochemically with ^{210}Pb and ^{137}Cs using γ-ray spectroscopy to determine modern and historic mercury accumulation rates for these subtropical wetland systems Recent ("post-1985") Hg accumulation rates averaged 53 $\mu g\ m^{-2}\ y^{-1}$ (23 to 141, n=18) corresponding to an average rate increase of 4 9 times (1 6 to 19 1) over those observed around the turn of the century This accumulation seems to result more from either global or regional atmospheric deposition rather than from lateral transport via overlying surface water The trends for mercury accumulation match those reported for lakes in Sweden and the northern United States, even though these systems are distinctly different in their climate, vegetational composition, and location We provide the first data on accumulation of mercury in subtropical wetland systems, and demonstrate the feasibility of radiochemical dating of wetland sediment

1. Introduction

Mercury concentrations exceeding 1 5 mg kg^{-1} (wet mass) were discovered in some sportfish retrieved from the Florida Everglades and Savannas Marsh during a 1989 statewide survey (Ware et al., 1990) Fish consumption advisories were issued for this subtropical wetland, exemplifying the concerns of human health from dietary Hg uptake Further, the ecological impact of Hg biomagnification was identified after the death of an endangered Florida panther was attributed to acute Hg toxicosis (Roelke et al., 1991) Our study examines soil Hg stratigraphy to understand changes in Hg accumulation that have occurred throughout the Everglades since the mid-1800's

Approximately 95% of atmospheric Hg occurs as gaseous elemental Hg with an atmospheric residence time of 0 7 to 2 0 years (Nater and Grigal, 1992) The remaining atmospheric Hg reserve is primarily in particulate form, which can readily be deposited as dryfall or scavenged during rain episodes (Fitzgerald et al., 1991) Anthropogenic emissions of elemental Hg enter the global cycle and may be distributed far from their source, and particle-bound Hg emissions may establish regional concentration gradients in nearby soil (Nater and Grigal, 1992) Recent increases of Hg accumulation, reported for north temperate lake systems in Sweden, Wisconsin, and Minnesota, have been attributed to increased atmospheric fallout (Meger, 1986, Lindqvist et al., 1991, Swain et al., 1992) Mercury may be delivered to aquatic systems in industrial, urban, and agricultural runoff from point and non-point source discharges (Mitra, 1986), and

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alteration of the hydrodynamics of aquatic systems may facilitate the release and transport of historically accumulated Hg through oxidation and deep cracking of sedimentary materials (Lodenius, 1990).

In contrast to the previously described north temperate lakes, the Everglades and Savannas are dynamic subtropical wetland systems, subject to hydrologic variability, fire, and human related activities. The Everglades has been altered hydrologically during the past century to establish agricultural lands, to enhance stormwater storage and water supply capability, and to accommodate encroaching urban development (Blake, 1980; SFWMD, 1992). The hydrodynamics of the Savannas Marsh have been influenced by adjacent recreation and sand mining activities, roadway construction, and surface runoff inputs from urban development (Jurgens, 1981).

The Everglades wetland (5600 km^2) is divided into four major hydrologic units: three Water Conservation Areas (WCAs) and Everglades National Park (ENP) (Figure 1). The Everglades is generally considered oligotrophic, based on dominant plant communities and ambient nutrient concentrations, and is characterized by peat soils to the north and marl deposits to the south. Sawgrass (Cladium jamaicense) marshes dominate large expanses of this system. During the 20th century, regions south of Lake Okeechobee were drained for agriculture, and canal systems were constructed to control water movement, and to divert water to coastal urban centers (Blake, 1980). Presently, some areas of the remaining Everglades are subject to prolonged dry periods and other locations experience extended periods of inundation (SFWMD, 1992).

The Savannas Marsh (SAV) is a dynamic, linear wetland system (20 km x 2 km) just west of the Indian River Ridge in St. Lucie and Martin counties (Figure 1). It is a strip of marshland, ponds, lakes, and islands, perched about 4 m above mean sea level, and characterized by rich inundated muck soils overlying relict sand dune on a hardpan (Jurgens, 1981). Hydrologic alteration of the marsh began in the 1940's, with the construction of the Savannas Recreation Area, and has become more extensive since the 1960's through residential development that occupies approximately 50% of the watershed.

Our field study of Everglades and Savannas Marsh soils was initiated in 1992 to identify the spatial distribution of Hg and temporal changes in Hg accumulation. The study arose from concern that regional anthropogenic activities were causing elevated Hg concentrations in fish. Spatial and temporal changes in accumulated Hg may identify 1) historic, pre-development Hg accumulation, 2) chronological changes in Hg accumulation, and 3) regional gradients of Hg accumulation in recent soils.

2. Materials and Methods

Sampling sites encompassed diverse conditions of hydroperiod, soil type, and human impact. Sites in the Water Conservation Areas (WCAs) and Everglades National Park (ENP) were accessed by airboat or pontoon-equipped helicopter and those in the Savannas (SAV) were accessed by canoe. Soil cores (10 cm i.d.) were collected, using PVC push corers, from 43 locations in the Everglades (January to July, 1992) and 2 locations in the Savannas Marsh (January 1992). Coring sites in the Everglades were generally inundated by 20 to 40 cm of water, while those in the Savannas were under 100 to 140 cm of water. Cores were extruded and sectioned into two centimeter intervals, and then stored frozen in sealed plastic bags.

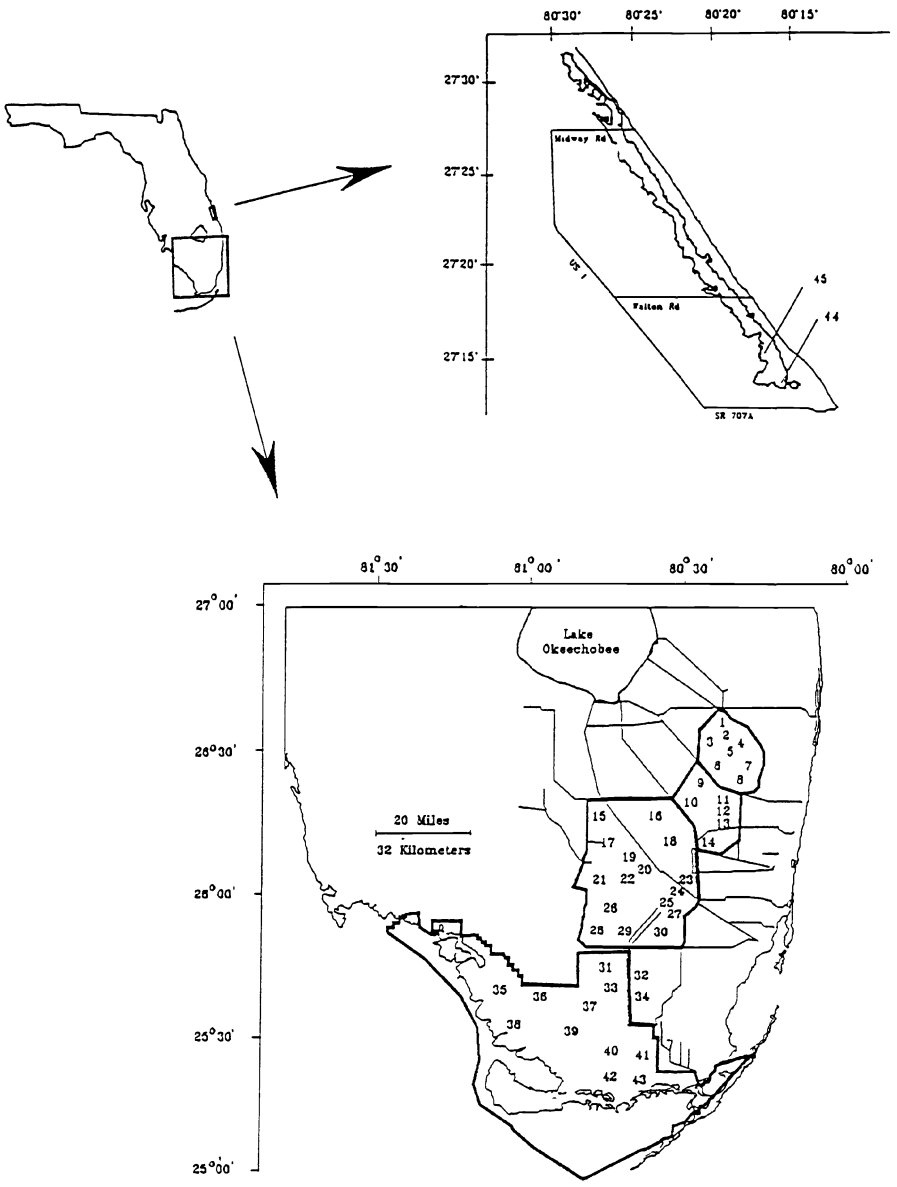

Fig 1. Sampling locations in the Florida Everglades (bottom map) and Savannas State Reserve (upper right map). Everglades samples were retrieved from the four hydrologic basins, Water Conservation Area 1 (WCA1)(sites 1-8), WCA2 (sites 9-14), WCA3 (sites 15-30), Everglades National Park (ENP)(sites 31-43). Two Savannas (SAV) cores were retrieved (sites 44 and 45).

Percent solids ($g_{dry}\ g_{wet}^{-1}$) and bulk density ($g_{dry}\ cm^{-3}$) were determined using 10 to 20 cm^3 of well-mixed, wet soil Measured volumes of wet sample were weighed in tared aluminum dishes, dried at 104°C for 24 hours, cooled, and then reweighed

Total Hg was determined by cold vapor atomic absorption spectrophotometry after digestion of wet samples (2 g) for two hours at 95°C under acidic, oxidizing conditions (USEPA, 1986) Mercury was reduced by stannous chloride addition (0 35 M, 10 mL min^{-1}) using a Perkin Elmer MHS-10 cold vapor generator (Perkin Elmer Corp , Norwalk, CT) and was quantified using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer (detection limit = 10 ng g^{-1})

Activities of ^{210}Pb and ^{137}Cs were measured by direct γ-assay using intrinsic germanium well-detectors (Princeton Gamma Tech)(Gottgens, 1992) Samples for isotope analysis were dried at 95°C for 24 hours, pulverized by mortar and pestle, weighed, and placed in small low-density polypropylene tubes (capacity 4 mL) The volumes of the samples and standards (Department of Energy, New Brunswick Laboratories U-Th standards) were matched to ensure the same counting efficiencies for both Counting times varied from 7 to 26 hours depending on sample weight Standards were run to track efficiency (counts γ^{-1}) and to calculate a ^{226}Ra conversion factor (pCi counts^{-1} s^{-1}) Sample spectra were analyzed for activity in the 46 5 keV (^{210}Pb) and 662 keV (^{137}Cs) peaks Activities at 295 keV (^{214}Pb), 352 keV (^{214}Pb), and 609 keV (^{214}Bi), representing uranium series peaks, were used to compute supported levels of ^{210}Pb

To calculate age/depth relationships in soil cores, the activity of unsupported ^{210}Pb was estimated by determining total and supported ^{210}Pb activity The age of a soil layer is calculated from its activity of unsupported ^{210}Pb Because the half-life of ^{210}Pb is only 22 3 years, this dating technique is restricted to about a 150-year time span Calculation of ^{210}Pb dates followed the constant rate of supply (CRS) model (Appleby and Oldfield, 1983)

Uncertainty analysis was based on the random variation of counting errors associated with radioactive decay and the impact of that uncertainty on the CRS dating model This unavoidable source of uncertainty is often a predominant source of imprecision Because the recorded counts in nuclear counting experiments follow a Poisson distribution, the predicted standard deviations were estimated as the square root of the mean number of counts Counting errors in the calculation of net isotope-activities were propagated using first-order analysis Monte Carlo simulation (Palisade Corp , 1990) was used to estimate error associated with the calculation of age and soil accumulation rate following the CRS model The probability density function for simulated ^{210}Pb activities was approximated by a normal distribution with the mean equal to the measured activity and a range equal to the counting error

3. Results and Discussion

3 1 SEDIMENT GEOCHRONOLOGY

Results of paleolimnological analyses may be presented in units of concentration or as rates of accumulation Concentration, expressed as a relative measure of sediment composition (e g mg g^{-1}), is the conventional way of expressing sediment stratigraphy (Griffiths and Edmondson, 1975) Such data, however, are vulnerable to variations in sedimentation of other components in the profile These variations may result in dilution

of the target analyte This problem can be eliminated by calculating accumulation rates Such rates are normalized to time, thus avoiding the problem of covariance among different sedimentary components

The eighteen dated cores from the Everglades and Savannas Marsh showed an average ^{210}Pb residual of 15 5 pCi cm^{2} (sd=3 5) The range of residuals corresponded to ^{210}Pb atmospheric fallout rates between 0 33 and 0 67 pCi cm^{2} y^{1} This range was well within the normal range of ^{210}Pb fallout rates of 0 2 to 0 9 pCi cm^{2} y^{1} (Appleby and Oldfield, 1983) Additional support for age/depth relationships may come from matching peak ^{137}Cs activity in the profile with a ^{210}Pb-determined age of 1963 (Rood, 1993) These peaks (or the onset of ^{137}Cs activity in the absence of a distinct peak) occurred in the profiles (n=18) at an average ^{210}Pb-determined age of 1962, although the range of age values was considerable (1942 to 1978) This may suggest some post-depositional mobility of ^{137}Cs up or down in the core

Uncertainty in the CRS dating model associated with the statistical fluctuations of nuclear decay were examined using Monte Carlo simulations (Palisade Corp , 1990) Dating uncertainty increased with age of the sediment because counting error increases with the lower ^{210}Pb activity in deeper core sections Ninety-five percent confidence intervals ranged from ±1 year in soils deposited 10 years before present, ±3 years at 30 years, ±5 years at 60 years, ±10 years at 120 years before present These ranges corresponded with error estimates reported by Binford (1990) for Florida lake cores analyzed with alpha spectrometry Large dating errors in the bottom sections of the cores made ^{210}Pb dates unreliable for sediments older than 120 years A more thorough presentation of error associated with sediment core dating will be published at a later time

3 2 SEDIMENT MERCURY GEOCHRONOLOGY

Mercury accumulation rates were calculated as the product of the sediment accumulation rate and Hg concentration at each depth interval of a soil profile Rate profiles were averaged, by hydrologic region, to show large-scale geochronology (Figure 2) "Range bars" show the maximum and minimum rates measured among combined cores Mercury accumulation rates increased gradually between 1900 and 1940, with more pronounced mid-century increases Twelve of the eighteen cores showed subsequent rate increases during the 1970's and 1980's Some sites showed increased Hg accumulation rates during the last two decades despite constant soil accumulation rate profiles or uniform Hg concentration profiles This decoupling of Hg concentration and Hg accumulation rate illustrates the inherent flaw associated with inferring Hg deposition using concentration profiles alone

Recent Hg accumulation rates averaged 53 µg m^{2} y^{1} (23-141, n=18) This was 4 9 (1 6-19 1) times higher than accumulation rates around the turn of the century Post-1985 Hg accumulation rates of Savannas cores were 3 4 times higher than their corresponding "ca 1900" rates In the Everglades, temporal changes in average Hg accumulation rates progressed geographically from 5 9 and 4 0 times increases in ENP and WCA3 (post-1985/1900), respectively, to 8 7 and 7 8 times increases in WCA2 and WCA1 (Table I) More pronounced rate increase in the north Everglades regions (WCA1, WCA2) compared to southern regions (WCA3, ENP) suggests at least three possible explanations 1) some northern source of Hg in overland sheetflow, 2) non-uniform atmospheric deposition of Hg with more deposition in the northern Everglades, or, 3)

non-uniform, post-depositional mobility of Hg among soil types with Hg retention decreasing spatially from WCA1 south to ENP.

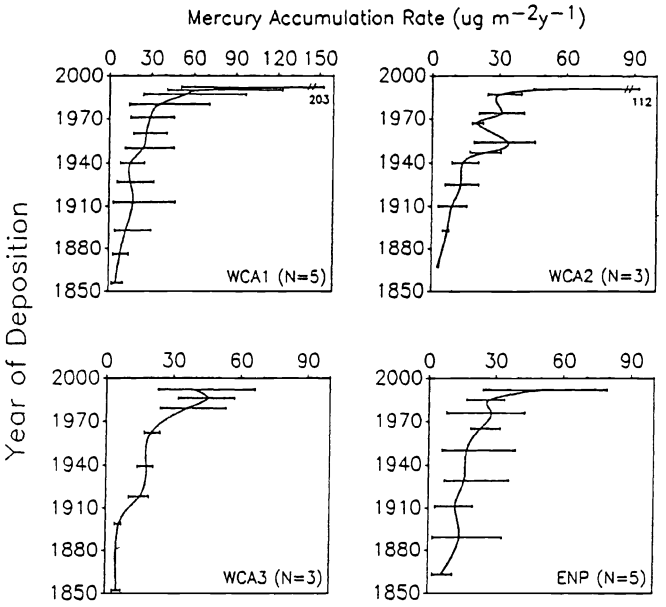

Fig. 2. Mercury accumulation rates (μg m^{-2} y^{-1}) over time, determined using ^{210}Pb and ^{137}Cs dating of sediment cores, for Water Conservation Areas 1-2-3, Everglades National Park, and Savannas State Reserve. Bars show the maximum and minimum rates measured among the cores. Number of cores per area (N) indicated.

Agricultural activities to the south of Lake Okeechobee have resulted in increased erosion and soil oxidation (Blake, 1980). These processes can facilitate the transport of applied and naturally-occurring Hg (Lodenius, 1990) from agricultural land to surrounding areas. However, the most dramatic Hg accumulation rate increases for Everglades soil cores occurred in the center of WCA1 in an area believed to be least impacted by agricultural runoff (Richardson et al., 1990).

A 1990 Hg emissions survey identified four primary anthropogenic sources (KBN Engineering, 1992): municipal solid waste (MSW) combustion (14.6% of total Florida mercury emission), medical waste incineration (14.0%), paint application (11.1%), and the electrical utilities industry (10.7%). Natural processes contributed 38.9% of Hg emissions in Florida and the remaining 10.7% resulted from other human activities. Presently, there is little information regarding long term atmospheric deposition of Hg in Florida.

Mercury does not migrate readily in organic soil or sediment (Engstrom et al., 1994; Winfrey and Rudd, 1990; Gobiel and Cossa, 1993). Although mineral soils may release Hg more readily than organic-rich soils under conditions of high salinity and low pH, it remains unclear whether this mechanism is significant under typical environmental conditions found in the Everglades. Although, it is plausible that Hg retention by Everglades marl may be less than retention by organic soils, organic-rich cores from WCA3 yielded the lowest Hg accumulation rate increases in the four hydrologic units of the Everglades.

Eight cores showed distinct increases in surface (0 to 4 cm) Hg concentrations, five cores showed no change and three cores showed distinct concentration decreases near the surface. There is no recurrent trend in Hg concentration profiles to suggest post-depositional migration of Hg in our wetland cores. This finding matches previous core incubation (Engstrom et al., 1994), porewater enrichment (Gobiel and Cossa, 1993), and methylation/mass balance (Winfrey and Rudd, 1990) studies that suggest that apparent Hg concentration profiles primarily reflect temporal changes in Hg input. For our Everglades cores, Hg concentration profiles were influenced by changing rates of soil accretion. Temporal changes in Hg accumulation rate best describe changes in Hg input and are not likely confounded by post-depositional migration in the core profile.

3.3 SPATIAL DISTRIBUTION OF MERCURY IN THE EVERGLADES

Mercury concentrations in surface soils were highest in WCA1 and WCA2 (Table I). All WCA1 sites yielded Hg concentrations exceeding 100 (110-410) ng g^{-1}. Four of the six sites in WCA2 exceeded 100 (110-390) ng g^{-1}, while five of fifteen sites in WCA3 exceeded 100 (110-330) ng g^{-1}. One of twelve ENP cores exceeded 100 ng g^{-1} with a concentration of 140 ng g^{-1}. Forty-one percent of surface Hg concentrations for Everglades sampling sites exceeded 100 ng g^{-1}, 16% exceeded 200 ng g^{-1} and 9% exceeded 300 ng g^{-1}. Historic ("1900") Hg concentrations exceeded 100 ng g^{-1} at only 11% of all Everglades sites (3 WCA1 sites, 2 WCA3 sites).

Organic-rich soils from the Water Conservation Areas exhibited higher overall Hg concentrations than the mineral sediment from southeastern Everglades National Park. Low Hg concentrations in some organic soil occurred in locations that were dry during our sampling period, and that experience frequent and extended dry periods (SFWMD, 1992). For example, the drier sites in northern WCA3 and northeast ENP, have an average surface Hg concentration of 70 ng g^{-1} (20-100, n=9). Mercury losses by leaching

Table 1 Mercury paleostratigraphy of Florida Everglades and Savannas Marsh soil cores (data represent combined averages for cores within a given hydrologic basin, data in parentheses indicate the range of values identified for the cores considered)

	WCA1	WCA2	WCA3	ENP	SAV
Sediment Geochronology					
--Unsupported ^{210}Pb Activity					
--Cumulative Residuals (pCi cm^{-2})	14.4	12.2	17.2	18.0	15.0
--Surface Activity (pCi g^{-1})	10.4	9.3	12.5	9.2	15.6
--^{210}Pb Fallout Rate (pCi cm^{-2} y^{-1})	0.45	0.38	0.54	0.56	0.47
--Sedimentation Rate (g cm^{-2} y^{-1})					
--Historic ("ca 1900")	0.018	0.021	0.016	0.033	0.027
--Recent (post-1985)	0.047	0.042	0.069	0.060	0.027
Sediment Mercury Geochronology					
--Mercury Accumulation Rate (µg m^{-2} y^{-1})					
--Historic ("ca. 1900")	14 (5-29)	8 (4-12)	10 (7-11)	14 (2-28)	10 (10)
--Recent (post-1985)	79 (45-141)	59 (35-95)	39 (28-55)	40 (23-57)	34 (31-37)
--Ratio (post-1985 rate/"ca. 1900" rate)	7.8	8.7	4.0	5.9	3.4
Sediment Mercury Abundance					
--Mercury Concentration (ng g^{-1})					
--Historic ("ca 1900")	81 (41-135)	47 (36-73)	55 (10-101)	44 (16-89)	42 (27-64)
--Recent (post-1985)	243 (45-479)	155 (64-390)	99 (10-329)	67 (20-140)	98 (57-120)
--Enrichment Factor (EF)	2.7	2.7	0.9	0.8	1.5

resulting from repeated drying and flooding may have occurred at these sites average (Lodenius, 1990) Mercury concentrations in pre-development ("ca 1900") soils were highest in WCA1, with maximum concentrations not exceeding 140 ng g^{-1} Overall, surface Hg concentrations exceeded deep soil concentrations in 86% of the sampling sites

While changes in Hg concentration profiles cannot clearly define temporal changes in Hg accumulation, they can characterize potential bioavailability Enrichment factors (EF) have been used by others to relate present metal concentrations to historic background concentrations (Meger, 1986, Engstrom et al., 1994) An enrichment factor is calculated as the change in metal concentration divided by the background level

$$\text{Enrichment Factor (EF)} = ([Hg]_{recent} - [Hg]_{background})/[Hg]_{background}$$

The average enrichment factor for all Everglades and Savannas sites was 1 4 (-0 8 to 9 6, n=45) The average EF for the Everglades and Savannas falls within the ranges identified in previous lake studies Minnesota lakes yielded EFs of 0 8-4 5 (n=8) while EFs for lakes in Wisconsin ranged 0 8-2 8 (Engstrom et al., 1994) Variability in our wetland cores likely results from spatial variation of soil and habitat types, hydrologic variability, and the large number of cores taken (n=45) The similarity among EF's for these wetlands and the previously reported lakes suggest similar trends of Hg accumulation in these systems and/or similar physicochemical processes affecting Hg in both lake sediment and wetland soil The EF can characterize temporal changes in Hg abundance at the soil-water interface, where it is most available for biotransformation Although most sedimentary Hg is rendered unavailable because of strong associations with organic matter and sulfide complexes (Lindberg and Harriss, 1974), the 140% increase in average

soil Hg concentrations in the past 100 years may indicate a corresponding increase in bioavailable Hg in Everglades soils since the turn of the century.

4. Summary and Conclusions

Mercury concentrations in Everglades surface soil averaged 120 (20-410) ng g^{-1} for 45 coring sites. This averaged 2.4 (140%) times higher than for corresponding deep soil concentrations with the largest increases measured in WCA1 and WCA2. Increased Hg bioavailability via soil-to-water mass transfer mechanisms has likely resulted from Hg enrichment at the soil surface in the Everglades and Savannas Marsh wetlands since the turn of the century.

Mercury accumulation rate profiles were examined, rather than concentration profiles, to avoid the confounding influence of in-situ Hg dilution from changing soil accumulation that may occur over time. Post-1985 Hg accumulation rates averaged 53 (23-141) μg m^{-2} y^{-1} corresponding to a rate increase of 4.9 times (1.6-19.1, n=18) since the turn of the century. Since around 1900, Hg accumulation rates increased most in WCA1 and WCA2 cores (7.8 and 8.7 times higher, respectively) and increased least in Savannas Marsh cores (3.4).

Rates increased starting about 1940, due perhaps to mid-century alteration of the hydrologic structure of the Everglades, increased regional agricultural, urban development, and atmospheric input. As of this writing, there is insufficient information regarding regional inputs to quantify any direct causal relationship between Hg accumulation rate increases and regional human activities. Our findings are similar to trends reported for lakes in Minnesota, Wisconsin, and Sweden. This agreement is significant, perhaps indicating a generalized process that leads to similar accumulation rates over widely varying geographic regions. This research provides the first data on Hg accumulation in subtropical wetland systems and supports the feasibility of radiochemical dating of wetland soil cores. Current research is considering micro- and meso-scale heterogeneity of Hg accumulation, and atmospheric Hg deposition patterns, while future studies will be need to determine point and non-point Hg emissions from regional anthropogenic activities.

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ULTRA TRACE LEVEL MERCURY IN THE EVERGLADES ECOSYSTEM, A MULTI-MEDIA CANAL PILOT STUDY

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Abstract. The Florida Everglades ecosystem is composed of the largest deposit (9600 km^2) of near neutral peat in the world extending south of Lake Okeechobee to Florida Bay The federal Central and South Florida Flood Control Project (C&SF) has sectioned the historic Everglades with a system of canals and levees to control water for urban and agricultural development, resulting in pronounced hydrologic modifications to the natural system As a part of a comprehensive ecological risk assessment of mercury (Hg) contamination in the Everglades ecosystem, a pilot study of canals was initiated in September 1993 to determine the extent and magnitude of total (HgT) and methylmercury (MeHg) in water, sediment and fish A probability-based random sampling grid was used to obtain consistent estimates of Hg contamination over this large geographic area Two hundred canal sampling locations were selected as probability samples by associating grid points on the sampling frame with specific canal sections for independent sampling cycles Of this number 50 locations were randomly selected for sampling in this pilot study The selected canal points were sampled from north to south during a six day period. Cumulative distributions with 95% confidence intervals were calculated and used to determine a canal system median concentration for selected water, sediment and fish constituents The percent exceedance of each median, by hydrologic subarea, was determined to demonstrate the existence and direction of spatial gradients in the system North to south (high to low) gradients were apparent for total phosphorus (TP), sulfate (SO_4), dissolved organic carbon (DOC), conductance, HgT and MeHg in water However, the gradients were reversed from south to north for HgT in sediments and fish (Gambusia sp) The greatest Hg concentrations in Gambusia sp occurred in the same canals where largemouth bass had previously been found to be most contaminated

1. Introduction

Since the initial detection of elevated levels of mercury (Hg) in freshwater fish in 1989 (Ware, et al., 1990), it has become increasingly apparent that South Florida has an extensive Hg contamination problem. The State of Florida has issued human health fish consumption advisories due to Hg contamination that either bans or restricts the consumption of largemouth bass and other freshwater species from over two million acres encompassing the Everglades and Big Cypress National Preserve. The maximum concentrations found in largemouth bass (4.4 mg/kg) and bowfin (over 7 mg/kg) collected from the Everglades are the highest concentrations found in Florida to date. Mercury contamination has also been found at levels of concern in largemouth bass throughout Florida's surface waters (Lange *et al.*, 1993). Mercury accumulation through the food web may reduce the breeding success of wading birds (Frederick and Spalding, 1994) and the viability of the endangered Florida panther (Roelke *et al.*, 1991).

The sources, distribution, magnitude, transport, transformations and pathways of Hg through the Everglades ecosystem are poorly known. Among the possible Hg sources in south Florida are natural mineral and peat deposits (Rood *et al.*, this volume) atmospheric deposition from global, regional and local (e.g., fossil-fuel fired electrical

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generating plants, garbage incinerators, medical laboratories, paint and agricultural operations) sources. Although there are multiple interactions among these sources and several possible pathways for Hg transport and bioaccumulation through the Everglades ecosystem, none of these individual sources appear to adequately explain the vast area apparently contaminated.

The purpose of this paper is to summarize the preliminary results of a pilot study of the Everglades canals using an Environmental Monitoring and Assessment Program (EMAP) probabilistic sampling design (USEPA, 1993). This comprehensive ecosystem monitoring effort is organized under the ecological risk assessment framework (USEPA, 1992) and focuses on a conceptual model of the biogeochemical cycling of Hg in the Everglades ecosystem (Stober *et al.*, 1992). The ecological risk assessment framework includes relevant assessment questions to be answered, problem formulation, analyses, risk characterization and ecosystem monitoring. The latter component is essential in risk management as a means to track the effectiveness of strategies employed over time through adaptive management.

This study is designed to answer policy-relevant questions that focus on the extent, magnitude, trends, and associations of Hg with other environmental parameters, as well as to provide information for the initial phase of the ecological risk assessment process. These activities are a part of a larger, interagency effort to study Hg contamination in the Everglades. The canal pilot study provides initial information on the spatial extent and magnitude of Hg contamination in the canal system.

2. Study Area

The Everglades ecosystem contains the largest deposit of near neutral peat (pH 5.8 to 7.6) in the world. This system encompasses 9600 km^2 in a region about 60 km wide by 160 km long and extends south of Lake Okeechobee to Florida Bay (Figure 1). The federal Central and Southern Florida Flood Control Project (C&SF), which spans decades of operation, has sectioned the historic Everglades into the Everglades Agricultural Area (EAA), five Water Conservation Areas (WCA's) including Loxahatchee National Wildlife Refuge (WCA-1), Everglades National Park (ENP), and other areas drained for urban and agricultural development, resulting in systemic modifications to the natural "sheet flow" hydrology of the Everglades.

Inorganic Hg has been sequestered in peat deposited throughout the geologic time of accumulation. Pristine Everglades wetland soils are not highly reduced (anaerobic), albeit flooded much of the year (Bachoon and Jones, 1992). The marsh is extremely nutrient limited although portions of the Everglades wetlands are eutrophic due to excess nutrient enrichment from agricultural drainage (Belanger *et al.*, 1989; Davis, 1994). Consequences of this enrichment include imbalances in native marsh flora and fauna, such as changes to periphyton and macrophyte communities and anaerobic conditions which may significantly facilitate the microbial transformation of inorganic Hg to its toxic form via methylation. The extensive system of deep canals with low oxygen content in the Everglades ecosystem may provide a prime environment in which Hg is methylated and then transported through the system.

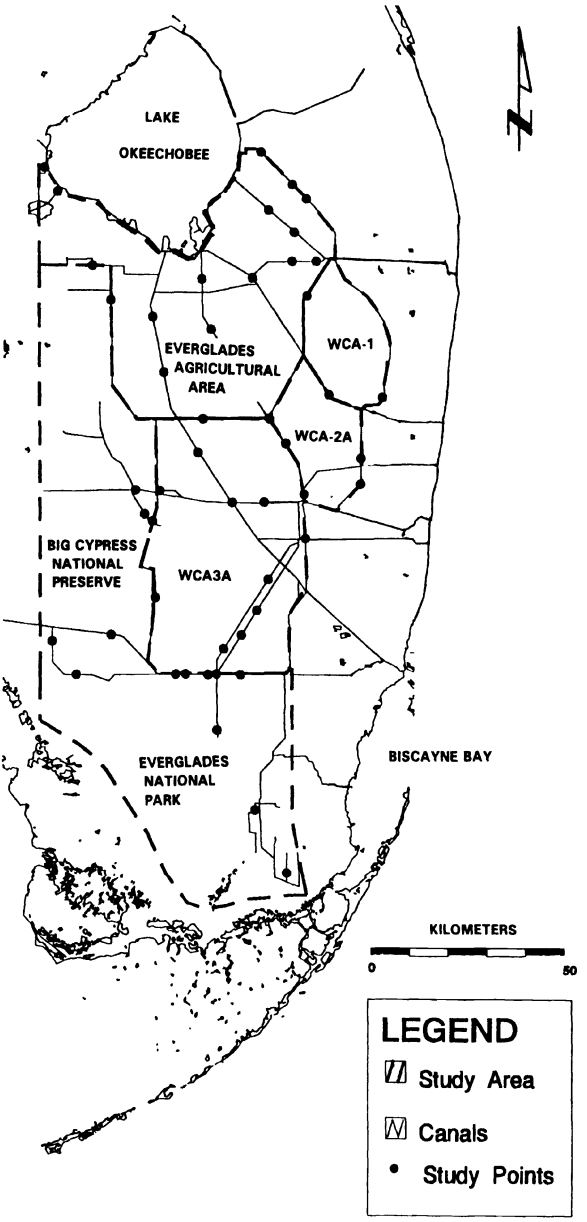

Fig. 1. The Everglades ecosystem study area and canal sampling stations for the September 1993 sampling event.

3. Materials and Methods

3.1. STATISTICAL SAMPLING DESIGN

The large geographic area apparently contaminated with Hg poses special sampling considerations that are not normally encountered in traditional assessments. A probability-based sampling strategy, which can be directly integrated into an assessment, is being used. The sampling design is derived from the approach developed by USEPA EMAP (Messer *et al.*, 1991, Overton *et al.*, 1992, Stevens, in press, Larsen *et al.*, in press). Probability samples ensure that every element in the resource has a chance of being included in the sample, that this chance is known (i.e., its inclusion probability), and that the sample will provide consistent, unbiased estimates of the population characteristics (i.e., mercury contamination).

The sampling grid for South Florida represents a 7x7 fold enhancement over the EMAP base grid. This density results in points distributed across the entire study area. The interpoint distance with the enhanced grid density is about 4 km with a hexagon area of about 13 km^2 around each grid point. The inclusion probabilities and weighing factors were uniform for each of the grid points. Each grid point represents a probability sample such that statistical estimates of the proportion of resources or geographic area with various attributes in each medium can be provided with known confidence.

Fifty sampling locations in the canals for each of four sampling cycles were selected as probability samples by associating EMAP grid points on the sampling frame with specific canal sections. Canal segments in each of the hexagons were identified, measured for length, assigned a cycle, and clustered into 20 groups containing approximately the same total length of canal/groups. The segments for each cycle were then randomly ordered within hexagon and cluster, and placed end-to-end in this random order. The inclusion probability for each canal segment was computed as the proportion of the canal length within the hexagon to the total length of canals. Aggregation of the canal segments into clusters with similar latitude and longitude was done to preserve the spatial distribution of canals. A systematic sample selection procedure with a random start was used to select 50 sites for sampling cycle 1 (Figure 1) and repeated to select 50 different canal stations for each of cycles 2-4. The inclusion probability is uniform within each cycle.

Selection of the canal locations as probability samples implies that the population estimates of Hg contamination and water quality within defined concentration ranges can be provided with known confidence intervals. Successive sampling cycles will be repeated each year during both wet and dry seasons. Repeat sampling of the same stations does not begin until cycle 5, which will occur during the third year of study.

3.2. FIELD SAMPLING

Sixty percent of the 50 canal sampling stations were accessed by helicopter and the remainder by boat. All stations were located with GPS equipment (corrected accuracy ± 25m). A synoptic sample over the entire ecosystem proceeding from north to south was completed in a six day period from September 13 to 18, 1993. Weather conditions were similar throughout this entire period.

A clean sampling protocol was used to eliminate contamination of water samples in the field. A "clean hands"/"dirty hands" procedure was used with "clean hands" wearing shoulder length polyethylene gloves (Polyethylene PPE glove) handling a two liter Teflon® (FEP) bottle for ultra trace level Hg sampling, submersing each bottle under the water surface (no filter employed), removing the lid, filling the bottle, replacing and tightening the lid underwater and replacing in a zip-lock polyethylene bag from which the bottle was drawn. The "dirty hands" wearing vinyl cuff length gloves assisted in opening and closing the zip-lock bag, labeling, record keeping and placement of the bagged sample in a second bag in a plastic ice chest/cooler. All field samples were kept in a cooler used exclusively for low level Hg samples until returned to the laboratory. The samples were acidified with 1 ml of trace metal grade HCl per 100 ml of sample in a "Hg-free" clean laboratory upon return to Florida International University (FIU). Daily water field blanks were taken into the field with each field crew and analyzed for ultra trace level total Hg before and after transport to the field.

In addition water samples were collected for the analysis of sulfate (SO_4), total phosphorus (TP), dissolved organic carbon (DOC), and turbidity. Daily calibrated in-situ water quality meters were used to measure water temperature, dissolved oxygen, pH, conductivity and depth on the surface and bottom at each canal station.

A stainless steel petite ponar dredge, previously cleaned and sealed in plastic, was used to obtain canal sediment samples. A sample was used only when the dredge was retrieved full with no apparent disturbance to the surface of the sediment. The sample was placed in a clean glass pan and mixed thoroughly with a plastic spoon. Large pieces of plant material, mollusc shells and other debris were separated from the fine sediment and discarded. Three 120 ml plastic cups were filled approximately 75% full at each station and sealed in zip-lock plastic bags and placed on ice. The dredge was thoroughly rinsed in canal water between stations.

Mosquitofish (Gambusia sp.) were collected from the canal at each station with a dipnet. An effort was made to collect twenty individuals at each station, which were handled with vinyl gloves, placed in a whirlpak bag, labeled and stored on ice in a cooler.

3.3. ANALYTICAL PROCEDURES

Jones *et al.*, (this volume) presents a full description of the analytical methodology used in this study for ultra trace level mercury determinations using cold vapor atomic fluorescence spectrometry.

To meet QA/QC requirements and to support the FIU analytical capability, split samples were analyzed by EPA Region IV, Environmental Services Division (ESD) in Athens, GA and Battelle Marine Science Laboratory in Sequim, WA which was also responsible for MeHg analysis. The former two laboratories used the above described methods while the latter laboratory used the methodology developed by Bloom and Fitzgerald (1988) and Bloom (1989).

Unfiltered water samples were used for the determination of total organic carbon (TOC) and total phosphorus (TP). TOC was measured by acidifying to pH < 2 with 3 N HCl, purging the sample with CO_2-free air, and analyzing for total carbon using a hot platinum catalyst direct injection analyser. TP was determined using a dry ashing and

acid hydrolysis technique (Solorzano and Sharp, 1980). Turbidity was determined by nephelometry using formizan calibration standards.

4. Results and Discussion

Preliminary analysis of the cycle 1 canal pilot sampling data was made using statistical programs to develop a cross-correlation matrix of all 21 variables. Cumulative distributions (CD) with upper and lower 95% confidence limits were then developed using the probability sample of stations, for the entire canal system and each variable. Example CD's are shown for total phosphorus (TP) and MeHg in water and HgT in fish for the Everglades canal system (Figure 2a, b, and c, respectively). TP and MeHg values in water ranged from 2.95 to 302.3 μg/L and from 0.11 to 1.4 ng/L, respectively. HgT in fish ranged from 7.97 to 405.1 ng/g. The data were then divided by hydrologic subarea into Everglades Agricultural Area (EAA), Water Conservation Areas (WCA's), Everglades National Park (ENP) and Big Cypress National Preserve (BICY). The respective number of stations in each subarea were: EAA - 20, WCA's - 14, ENP - 8, and BICY - 8.

CD's for water TP and MeHg and fish HgT in each of the four hydrologic subareas are presented in Figure 3a, b and c, respectively. It is apparent that the distributions change between subareas. The shape of the CD's and the magnitude of the concentrations by subarea suggest possible sources and sinks, as indicated by the concentrations of both TP and MeHg in water.

A subset of variables are shown to demonstrate the existence of spatial gradients and possible associations with Hg (Table I). These variables included total phosphorus, sulfate, dissolved organic carbon, surface conductivity, bottom dissolved oxygen (DO) HgT, and MeHg in water, and HgT in sediment and fish tissue (Gambusia sp). A median (50%) concentration for each canal system variable was determined from each canal system cumulative distribution. Presence or absence of a gradient was determined by calculation of a percent exceedance from the median. Selection of the system median does not imply the establishment of an optimum system concentration. This can only occur following the acquisition of additional data.

The percent exceedance (Table I) of this median system concentration for each variable by hydrologic subarea indicates the existence and direction of spatial gradients in the system. North to south (high to low) gradients are apparent with TP, SO_4, DOC, conductance, HgT and MeHg in water. However, the gradients are reversed from south to north for HgT in sediments and Gambusia sp. The highest concentrations found in Gambusia sp. occur in the same canal reaches in which the highest bass concentrations were found (Lange, personal communication). Dissolved oxygen was generally low (median = 1.28 mg/L) in bottom waters throughout the canal system.

HgT in water ranged from 0.27 to 15.5 ng/L with a canal system median of 1.74 ng/L. These samples were unscreened and occasionally suspended particles were obviously included, possibly resulting in higher total mercury values. These samples were taken during the wet season when water movement, particle suspension and transport was expected.

The median concentration for MeHg in water was 0.39 ng/L with a range from 0.11 to 1.4 ng/L. Most studies as reviewed by Weiner and Spry (1994) found that freshwater

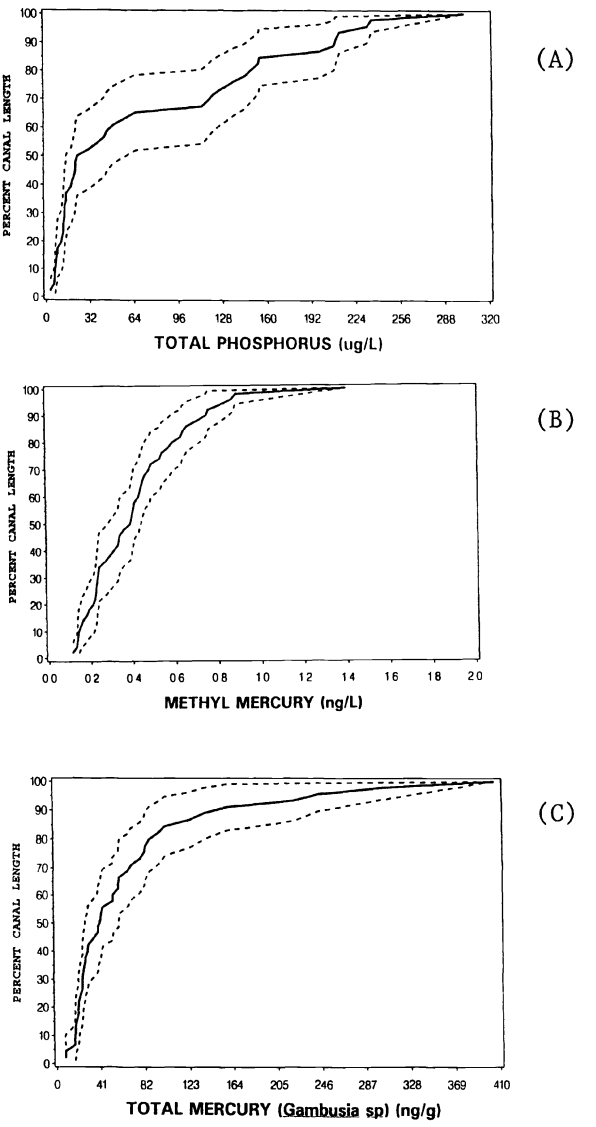

Fig. 2. Cumulative distributions for total phosphorus (A) and methlymercury (B) in water and total mercury in Gambusia sp. (C) with 95% confidence intervals showing percent length of canal in the Everglades ecosystem.

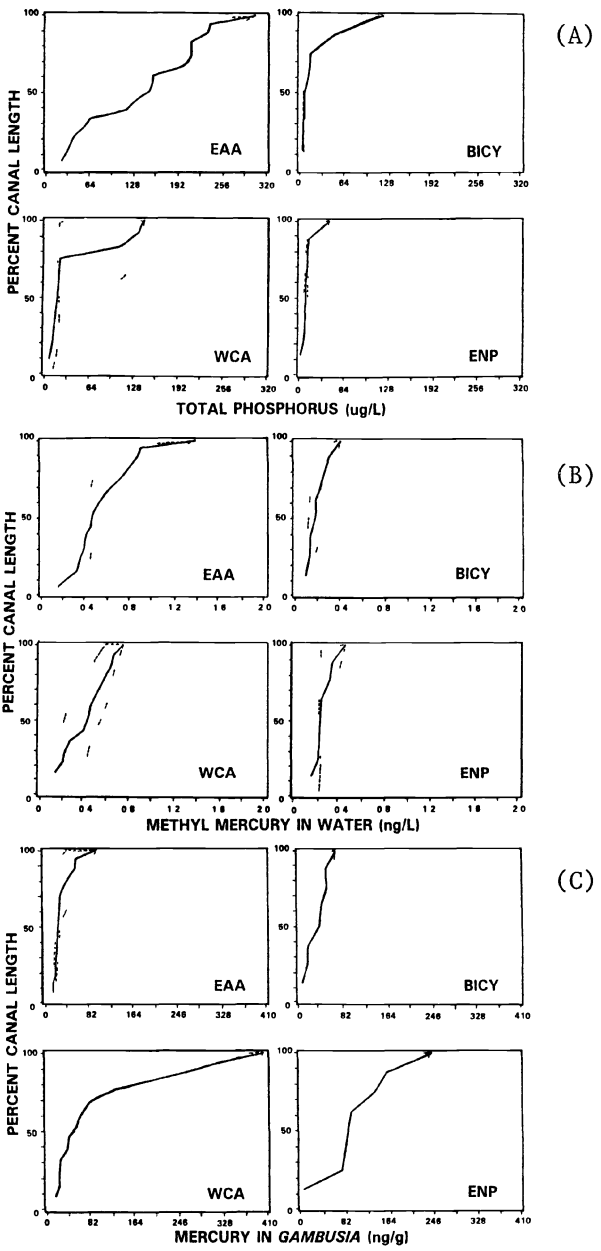

Fig 3 Cumulative distributions for total phosphorus (A) and methylmercury (B) in water and total mercury in Gambusia sp (C) with 95% confidence intervals showing percent length of canal by hydrologic subarea in the Everglades ecosystem

TABLE I

System sample size, parameter, and canal median, minimum and maximum concentrations in water, sediment and fish with percent exceedance of canal median concentration by hydrologic subarea. (EAA = Everglades Agricultural Area; WCA = Water Conservation Areas; ENP = Everglades National Park; BICY = Big Cypress National Preserve)

SYSTEM					SUBAREA PERCENT EXCEEDANCE			
N	PARAMETER	CANAL MEDIAN	MIN	MAX	EAA	WCA	ENP	BICY
			WATER					
46	TP	23.0 µg/L	2.95	302.3	100	25	12.5	25
50	SO_4	10.5 mg/L	5.00	170.0	85	43	25	12.5
46	DOC	23.0 mg/L	6.80	60.1	72	67	25	0
49	S-COND	652. µmhos	168.	1954.	65	72	25	0
44	BOT-DO	1.28 mg/L	0.03	4.83	53	36	50	75
50	HgT	1.74 ng/L	0.27	15.5	80	50	12.5	12.5
50	MeHg	0.39 ng/L	0.11	1.4	70	64	12.5	12.5
			SEDIMENT					
50	HgT	67.0 µg/kg	6.4	460.0	40	43	63	75
			GAMBUSIA					
45	HgT	41.0 ng/g	7.97	405.1	25	62	87.5	50

systems have MeHg concentrations at less than 5% of total mercury, while the Everglades samples approached 10% for this initial sampling. St. Louis *et al.*, (in press) reported somewhat higher concentrations of MeHg in surface waters draining wetland areas in Canada.

If these gradients continue to hold with subsequent sampling events, additional studies will be implemented to develop explanations for the reversal in the Hg gradients in sediment and fish as compared to water. Several possibilities exist: 1) the highest sediment and fish concentrations exist generally south of the major diversion canals in the system, possibly resulting in a low flow deposition zone for Hg transported from upstream to the southern canal system, 2) higher nutrient enrichment in the north may mobilize Hg resulting in long term transport and accumulation in the south, 3) the sulfate gradient suggests that sulfate maybe reduced to sulfide in the ENP and BICY canals implicating the sulfur cycle in the speciation and availability of mercury, 4) the lower DOC downstream suggests the carbon cycle maybe a factor in the speciation and availability of MeHg, 5) an aquatic biomass gradient (e.g., algal productivity or the structure of the aquatic community) from north to south could explain more efficient bioaccumulation in the southern canals than is apparent in northern canals and/or 6) the southern part of the canal system may have been impacted more by wet/dry deposition over an extended period of time from local air pollution sources located east in the urban area.

Specific process studies at strategic locations identified by the canal system monitoring data are planned to determine net methylation in canal water and sediments, the dynamics of particles in methylation and transport of MeHg, and the abiotic reactions of organic and inorganic Hg in association with high concentrations of dissolved organic material.

5. Conclusions

Application of the EMAP probability sampling design across the entire Everglades ecosystem clearly demonstrates that this approach provides important regional insight which complements and provides critical perspective for small-scale site-specific studies. This monitoring approach has already provided a new and improved understanding of the system and can be expected to produce additional data with known uncertainty as temporal and seasonal patterns are defined. Increased understanding of the interactions between the canal and marsh systems will be realized as the probability sampling strategy is extended to the greater marsh areas of the Everglades beginning in early 1995. The monitoring data will also be used to further define spatial and temporal gradients and to design and locate specific process studies needed to provide the information required to develop biogeochemical Hg cycling models for the canal and marsh systems which can be applied in a ecological risk assessment for the Everglades ecosystem.

Acknowledgments

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Division, R-EMAP, Athens, GA.; USEPA Office of Research and Development, EMAP; US Department of the Interior, National Biological Survey, South Florida/Caribbean Field Unit, US National Park Service, Everglades National Park and Big Cypress National Preserve; US Fish and Wildlife Service, Loxahatchee National Wildlife Refuge; Southeast Environmental Research Program at Florida International University; and Battelle Marine Sciences Laboratory, Sequim, WA. State agencies participating in the overall study are the Florida Department of Environmental Protection, South Florida Water Management District and the Florida Game and Freshwater Fish Commission. FTN Associates Ltd, Little Rock, Arkansas assisted in development of the study plan.

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TEMPERATURE, pH AND PHOTOPERIOD EFFECTS ON MERCURY BIOACCUMULATION BY NYMPHS OF THE BURROWING MAYFLY *Hexagenia rigida*

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Abstract: Accumulation of $HgCl_2$ and CH_3HgCl by *Hexagenia rigida* nymphs from contaminated sediment and water column was investigated experimentally, taking into account 3 abiotic factors (temperature, pH and photoperiod). When the contamination of the experimental units was based on sediment compartment, Hg concentrations at the whole organism level revealed very high bioaccumulation differences between the two chemical forms of Hg (ratio close to 20 in favour of MeHg). When Hg compounds were added to the water column, the highest Hg accumulation rates were observed for MeHg, but with a small difference between the 2 compounds (ratio close to 2.0-3.0). These bioaccumulation processes were very dependent on the 3 abiotic factors taken into account, especially temperature and water column pH.

1. Introduction

Among aquatic species, burrowing organisms are particularly exposed to Hg contamination from the sediment compartment, via substrate ingestion and/or metal transfers from the porewater, and from the water column, via permanent currents within the burrows, for respiratory and/or trophic purposes.

Two laboratory experiments were designed in order to quantify the actions and interactions of three abiotic factors - temperature, pH and photoperiod - on inorganic mercury ($HgCl_2$) and methylmercury (CH_3HgCl) bioaccumulation by nymphs of the burrowing mayfly *Hexagenia rigida* (Mc Dunnough - Ephemeroptera). The two contamination sources (sediment and water column) were studied separately, during 15 days' exposure.

The purpose of this paper is to present a synthesis of the comparative analysis of Hg bioaccumulation at the whole organism and gill levels and to assess the relative preponderance of the uptake routes, in relation to the different ecotoxicological conditions studied.

2. Materials and Methods

The experimental unit (EU, 12x12x30 cm) consisted of a three-compartment microcosm: natural sediment (homogeneous silt from the Garonne river - natural Hg level = 97 ± 5 (SD) $\mu g\ Hg.kg^{-1}$ (ww) - 5 cm deep), 2.9 L of dechlorinated tap water and 4 nymphs (151.6 ± 7.6 mg/EU). Mass culture of *Hexagenia* was initiated in the laboratory from eggs collected in the field each summer (Freshwater Institute, Winnipeg, Canada) (Friesen, 1982 ; Saouter et al., 1991).

Contamination of the water column was based on twice daily additions of identical amounts of mercury in the EUs: 2x5 ml of aqueous solutions of $HgCl_2$ or CH_3HgCl (Merck - 0.8 mg $Hg.L^{-1}$). Evolution of Hg concentrations in the dissolved and particulate phases was analyzed during the 15 days' exposure, for each experimental condition, jointly with turbidity measurements.

Contamination of the sediment compartment was based on additions of CH_3HgCl or $HgCl_2$ using aqueous solutions (500 mg $Hg.L^{-1}$), in order to obtain a final concentration of 5 mg $Hg.kg^{-1}$ (ww) for the inorganic compound and 0.5 mg $Hg.kg^{-1}$ for MeHg.

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For each contamination source, a complete experimental design was drawn up, including the combinations of the different levels for the three abiotic factors selected: 10, 18 and 26°C for the temperature; 6, 12 and 18h of light per day for the photoperiod; 5.0 and 7.5 for the water column pH. Two replicates were set up for each condition giving to 80 EUs per experiment (including controls).

Total Hg determination in the biological samples was carried out by cold vapour atomic absorption spectrometry (Varian AA 475 - detection limit = 5 ng Hg), after a digestion step (pure HNO_3, 95°C in a pressurized medium, during 3 h). Bioaccumulation in the nymphs was analyzed at whole organism level (concentrations $\mu g\ Hg.kg^{-1}$ ww, and burdens, ng Hg) and at the gills level (burdens and relative burdens, %). Natural levels of total Hg in the nymphs were $124 \pm 18\ \mu g\ Hg.kg^{-1}$ (ww; whole organism) and 1.5 ± 0.3 ng Hg (gills); these values were systematically deducted.

The data were analysed using multiple linear regression (Tomassone, 1993). An alpha risk equal to 0.01 was adopted for the statistical significance of the effects observed. F values were calculated with reference to the inter-replicate variance.

3. Results and Discussion

Figure 1 shows the results obtained at the whole organism level. In our experimental conditions, the two Hg compounds were more accumulated when introduced in the water column, according to the differences between the order of magnitude in initial Hg concentrations in the sediment and water compartments - respectively $mg\ Hg.kg^{-1}$ and $\mu g\ Hg.L^{-1}$ -, in relation to the metal partitioning and bioavailability. However, greatest concentrations of Hg were observed in the nymphs when EUs were contaminated with the organic form, but the differences are strongly linked to the contamination source: a factor close to 20 between the two mercury compounds for the sediment source, if the difference between the initial Hg concentrations is taken into account, and a factor close to 2.5 for the water column source.

Analysis of Hg bioaccumulation at the gills level clearly showed that metal burdens in this organ were small when contamination of the EUs occured via the sediment source (relative average burdens < 6%) (Odin et al., 1994b). In contrast, contamination via the water column gave rise to an important accumulation in this organ: relative burdens were close to 40 to 50% after $HgCl_2$ exposure and 30 to 40% after CH_3HgCl exposure (Odin et al., 1994a). These differences between the two contamination sources could be directly linked to the uptake routes: direct uptake from the water is predominant when EUs are contaminated via the water column, whereas the trophic route is predominant when Hg is added to the sediment. These results are in agreement with data obtained previously under similar exposure conditions, at the gut level: an important accumulation of Hg was measured in the digestive tract when nymphs were exposed to contaminated sediment (43% and 25% of the metal bioaccumulated in the nymphs were located in the gut after contamination by inorganic Hg and CH_3HgCl respectively). A reverse trend was observed when Hg compounds were initially introduced in the water column, average relative burdens being close to 8 and 20% respectively (Saouter et al., 1991, 1992). The structural and functional properties of the biological barriers at the interface between the nymphs and their surrounding medium play an important role at this level: for example, the gut wall is relatively impermeable to inorganic Hg, but is characterized by a great capacity of fixation during the contamination phase; MeHg, on the other hand has a very high capacity to cross the gut barrier and to be transferred to the other tissues via the haemolymph (Boudou et al., 1991).

Impacts of the three abiotic factors studied are very important on Hg bioaccumulation by *H. rigida* nymphs, with strong interactions, especially between temperature and pH, and marked differences between the two contamination sources.

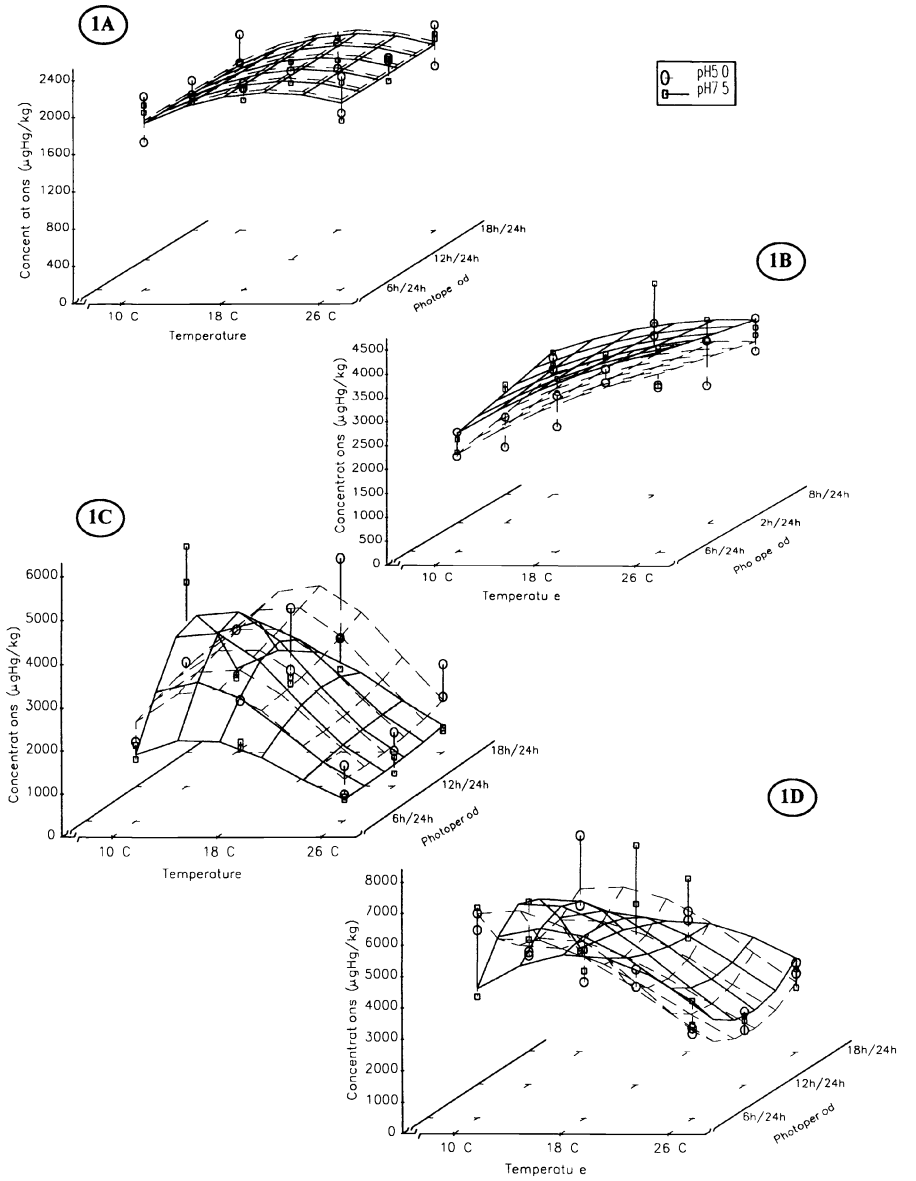

Fig. 1: Total Hg concentrations in *Hexagenia rigida* nymphs (whole organism), as a function of the initial contamination source (1A and 1B: sediment source; 1C and 1D: water source), Hg chemical form initially added (1A and 1C: $HgCl_2$; 1B and 1D: CH_3HgCl), temperature, photoperiod and water column pH. Symbols: average values/EU; 2 replicates/condition. Plans on the 3D plots correspond to the multilinear regression models.

An increase in temperature gave rise to an increase in Hg quantities bioaccumulated at the whole organism level, when nymphs were contaminated via the

sediment compartment (Figures 1A and 1B). An inverse trend was observed after 15 days exposure via the water column source (Figures 1C and 1D). Nymph activity was directly affected by this factor. It increased with the temperature, thus contributing to an increase in the amounts of sediment ingested and in the amounts of metal bioaccumulated from the sediment. However, it also led to an increase in bioturbation (average turbidity values in the water column: 5 NTU at 10°C and around 60 at 26°C), which modified metal partitioning in the water column considerably, leading to a marked decrease in bioavailability. If the differences between Hg concentrations in the dissolved phase (50-85% at 10°C and 20% at 26°C) are taken into account, in order to simulate identical exposure conditions via the direct route, corrected bioaccumulation values revealed an important increase when the temperature moved from 10 to 26°C (data not shown).

The pH factor did not influence to any great extent Hg concentrations in *H. rigida* nymphs contaminated via the sediment source (Figures 1A and 1B). However, when exposure was via the water column, there were important and similar effects at whole organism and gills levels, but with complex interactions with the other two controlled factors. So, when EUs were contaminated by $HgCl_2$, acidification gave rise to a global increase in Hg concentrations. For the organic form, this trend was inversed when temperature was in the range of 18 to 26°C; between 10 and 18°C, effects also varied in relation to the photoperiod. Acidification of the water column involved a modification in the chemistry of the overlying water and in the partitioning of Hg, which may explain several differences observed according to the initial contamination source (Gilmour and Henry, 1991); for example, a decrease in pH gave rise to an increase in metal concentrations in the dissolved phase (data not shown), as the metal is more bioavailable at the gill interface (Odin et al., 1994b).

The third factor, photoperiod, played a small but significant role in Hg transfers via the sediment source. When Hg compounds were added to the water column, its effects on bioaccumulation appeared to be more important but also more complex, due to the interactions with the other factors considered and to the non-linear trends among the three modalities of the photoperiod. Burrowing organisms are characterized by a negative phototropism; they are protected by the substrate from light rays, which minimize the direct influence of the daily period of light. For example, turbidity measurements in the water column were not significantly affected by the 3 photoperiod durations studied. Further experiments are currently being set up in order to analyze the direct and indirect effects of this factor.

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UPTAKE OF AQUEOUS METHYLMERCURY BY LARVAL *CHAOBORUS AMERICANUS*

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Abstract. The uptake of monomethylmercury (mmHg) from water by larval *Chaoborus americanus* was studied. When exposed to aqueous mmHg for 6 days, the pattern of uptake was sigmoidal. The concentration of mmHg in the exposure water, however, was subject to demethylation and volatilization and therefore decreased over time. A model of passive diffusive uptake underestimated the uptake constant while a bioenergetics-based uptake model provided a reasonable estimate. The data suggest that uptake is not merely a passive diffusive process but may be coupled with oxygen uptake.

1. Introduction

Invertebrate predators may have profound implications for the bioaccumulation and transfer of contaminants within aquatic food webs (Rasmussen *et al.*, 1990). To date, few studies have been published that examine the dynamics of contaminants, particularly mercury (Hg) and monomethylmercury (mmHg), in invertebrate predators. This study addresses the uptake of mmHg from water by the predacious aquatic insect larva, *Chaoborus americanus*, and compares the uptake rate to that predicted by models of passive diffusive and bioenergetics-based uptake.

2. Methods

2.1 UPTAKE EXPERIMENTS

Seven groups of early-fourth-instar *C. americanus* (average 10 animals group^{-1}) were placed into beakers containing 1 l of soft, low-DOC (<0.4 mg C l^{-1}, approx. 5 mg Ca l^{-1}) water and maintained at 20°C. DOC had been removed from the water by circulation through a 0.5 µm carbon filter and a UV sterilization unit for a period of 24 hours. Methylmercuric chloride, as $CH_3{}^{203}HgCl$ (Amersham, Oakville ON; specific activity = 49.15 mCi g^{-1}), was added to the beakers in the following concentrations: 3 beakers of 2.2 ng mmHg ml^{-1}, 3 beakers of 4.2 ng mmHg ml^{-1}, and 1 control beaker of 0 ng mmHg ml^{-1}. These concentrations were selected because at lower mmHg exposures uptake was not detectable for several days. The activity of each group of animals was measured after 4, 8, 24, 48, 96, and 144 hours of exposure using a sodium iodide crystal gamma counter (average detection limit = 0.7 ng Hg, counting efficiency = 15%). The animals were dried and weighed at the end of the experiment. The exposure water was sampled at 24 hour intervals and analyzed for total Hg after digestion with BES (20% HNO_3, 2%HCl, 0.05% $K_2Cr_2O_7$) using $SnCl_2$ reduction and Atomic Absorption Spectrophotometry. The experiment was performed twice and the data pooled for statistical analysis. Uptake of mmHg from food was not considered in these experiments.

An aqueous mass balance experiment was performed to determine the extent of demethylation and loss of mercury to volatilization during the uptake experiment. A beaker containing 1 l of low-DOC water with a mmHg concentration of 4.4 ng ml^{-1} was fitted with a plexiglass cover containing two 4 mm

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holes and placed in a water bath at 20°C. Air was drawn through a teflon tube placed into one of the holes at a rate of 240 ml min^{-1} by a vacuum pump and was bubbled through an air sampler containing 10 ml of BES to trap any Hg present in the airflow. The second hole functioned as an air inlet. The BES in the sampler was collected, replaced, and analyzed for total Hg after 24, 48, 72, and 96 hours of incubation. Water from the beaker was collected at the same time as the air samples and was analyzed for both total and inorganic ($SnCl_2$-reducible) Hg.

2.2 MODELLING

Passive diffusion model

This model assumes that the uptake of mmHg from the water source is a simple diffusive process dependent upon surface characteristics alone. It is defined as:

$$R = \frac{([mmHg]_{ext}-[mmHg]_{int}) * A}{r}$$

where R is the net uptake rate (ngHg $animal^{-1}$ $hour^{-1}$), $[mmHg]_{ext}$ is the external mmHg concentration (ng ml^{-1}), $[mmHg]_{int}$ is the internal mmHg concentration (0 ng $animal^{-1}$ at time 0), A is the area over which diffusion occurs (2.72 x 10^{-10} m^2, based on an average dry weight of 0.903 mg and the unpublished morphological relationships of N. Yan and V. Visman), and r is the diffusion resistance (0.2 to 13.8 hour m^{-1}, based on Mierle, 1985 and assuming an unstirred layer thickness ranging from 20 to 200 μm). Correction factors were applied for consistency of units.

Bioenergetics model

This model assumes that the uptake of mmHg is coupled with metabolic rate. As metabolic rate increases, so should the uptake of mmHg due to increased flushing of respiratory surfaces. The mathematical description for gross uptake from water is defined as follows:

$$R = \frac{[mmHg]_{ext}}{[O_2]_{ext}} * M * \frac{DmmHg}{DO_2(1-([O_2]_{int}/[O_2]_{ext}))}$$

where $[O_2]_{ext}$ is the external oxygen concentration (assumed saturation), $[O_2]_{int}$ is the internal oxygen concentration (assumed to be zero in a respiring animal), $DmmHg/DO_2$ is the diffusivity ratio (assumed to be 0.26 based on Rodgers and Beamish, 1981), W is the weight of the animal (0.903 mg), and M is the metabolic rate (nl O_2 μg^{-1} $hour^{-1}$ = 0.78*W(ng dry weight)$^{-0.33}$, Yan *et al.*, 1991; Cressa and Lewis, 1986). While the diffusivity ratio has been shown to be sensitive to water hardness, the soft-water value of 0.82 (Rodgers and Beamish, 1983) is not used in these simulations because the fish used in the determination of the diffusivity ratio are likely to have been subjected to stressful conditions.

Calculation of uptake rate constants

The uptake rate constant, k (ml $animal^{-1}$ $hour^{-1}$), was calculated algebraically for both of the models and compared to the empirical value obtained from the uptake experiment. Once the experimental uptake curves were defined mathematically, k was calculated directly using the equation $k = R/[mmHg]_{ext}$. In all cases, k was calculated for time 0 before there was any buildup of mmHg in the animal and before depuration could occur. In addition, the precise mmHg concentration in the water was known only at time 0.

3. Results and Discussion

The uptake of mmHg by *C. americanus* during the uptake experiment exhibited a distinct sigmoidal increase (Figure 1A) and therefore a logistic function was used to describe the data. The logistic function is considered to be merely descriptive and does not infer specific uptake mechanisms. With an initial exposure concentration of 4.2 ng mmHg ml^{-1}, the uptake curve plateaus at 44.8 ngHg $animal^{-1}$ (Figure 1A). At an exposure concentration of 2.2 ng mmHg ml^{-1}, the plateau is at 22.2 ng mmHg $animal^{-1}$. The concentration of total Hg in the water decreased rapidly after 24 hours (Figure 1B). This decrease could be attributed to neither losses from uptake by *Chaoborus* nor adsorption to the beaker walls. The aqueous mass balance experiment provides insight with respect to the fate of Hg in the exposure medium. After 48 hours of incubation, significant demethylation occurred as the proportion of inorganic Hg increased linearly to 14% at 96 hours. In addition, 21% of the initial amount of Hg added to the beaker was lost to volatilization. The beakers in the uptake experiment were uncovered, and therefore likely to lose even more Hg to volatilization.

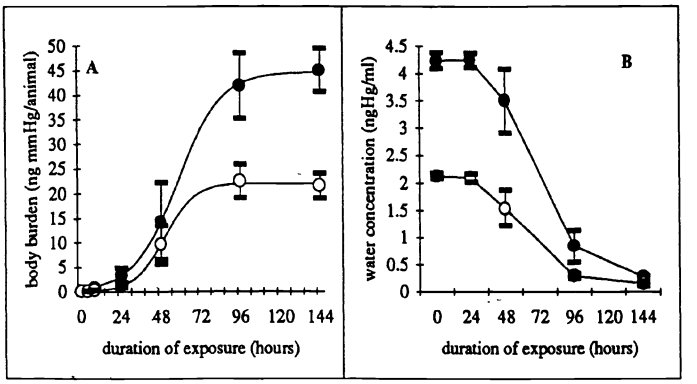

Fig. 1. Results of uptake experiments. A. Increase in mmHg body burden upon exposure to mmHg in water. B. Total Hg concentrations in the water. Open circles represent initial mmHg concentrations of 2.2 ng mmHg ml^{-1}; closed circles 4.2 ng mmHg ml^{-1}. Vertical bars indicate one standard deviation above and below the mean.

The sigmoidal pattern of uptake exhibited in the uptake experiment has previously been observed in other animals (Brisbin *et al.*, 1990). The cause of such a pattern, however, has yet to be determined and therefore only uptake at time 0 is considered for modelling purposes. Because the exposure concentrations used in these experiments were unnaturally high, it is possible that the animals entered a sub-lethal pathological state in which some morphological or physiological barrier to uptake had disintegrated, thereby permitting an increase in mmHg uptake. Alternatively, the animals may have been accumulating inorganic Hg in addition to mmHg. If inorganic Hg is accumulated faster than mmHg, an increase in uptake rate as inorganic Hg becomes more available would be observed. It has also been reported by Rodgers and Beamish (1983) that the efficiency of mmHg uptake relative to O_2 uptake by fish increases in the presence of inorganic Hg. As inorganic Hg becomes more available due to demethylation, we may therefore observe an increase in uptake rate. It would be interesting to model

the change in uptake rate as a function of Hg speciation in the water, but unfortunately such data are not available for time>0. This exercise would prove particularly interesting because mmHg has been shown to accumulate much faster than inorganic Hg in two other aquatic invertebrates, *Daphnia magna* and *Hyallela azteca* (Lloyd, 1979; Trudel, 1980), but the possibility of one form of Hg facilitating the uptake of another form has not been explored in invertebrates.

The experimentally-determined value of k was 0.0042 ml animal^{-1} hour^{-1} for the 2.2 ng mmHg ml^{-1} treatment and 0.0097 ml animal^{-1} hour^{-1} for the 4.4 ng mmHg ml^{-1} treatment. These values do not differ significantly from each other because of overlapping estimate ranges based upon the confidence limits of the function parameters. The mean value of k is therefore considered to be 0.007 ml animal^{-1} hour^{-1}. Because uptake is proportional to the exposure concentration, this value of k may be used to predict uptake at ambient mmHg levels. Further experiments focussing upon the initial uptake period have been performed to refine the estimate of k, and will be published at a later date.

The passive diffusion model predicts that k will lie between 1.3 x 10^{-6} and 1.5 x 10^{-6} ml^{-1} animal^{-1} hour^{-1}. This represents an underestimation by a factor of about 4700-5400. Bioenergetics, however, predicts k to be 0.0017 ml animal^{-1} hour^{-1}, which does not differ significantly from the experimentally determined value. If we do not assume that $[O_2]_{int}=0$, then the predicted value of k increases and deviates from the average experimentally-determined value. While uptake may indeed be a passive diffusive process, the rate appears to be linked with oxygen uptake. This is particularly interesting because unlike fish, for whom bioenergetics modelling of contaminant uptake has been reasonably successful, *Chaoborus* lack specialized respiratory structures with a large surface area (Säether, 1972).

4. Conclusions

The pattern of mmHg uptake from water by *Chaoborus americanus* appears to be sigmoidal over a 144 hour period. The uptake rate constant, k, is in the order of 0.007 ml animal^{-1} hour^{-1}. A model of simple passive diffusion underestimates k by a factor of 5400, while bioenergetics provides a reasonable estimate of k. Uptake appears to be not merely a process of simple passive diffusion but may be coupled with oxygen uptake.

Acknowledgements

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THE INFLUENCE OF TROPHIC LEVEL AS MEASURED BY $\delta^{15}N$ ON MERCURY CONCENTRATIONS IN FRESHWATER ORGANISMS

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Abstract. The relationship between mercury (Hg) concentrations in freshwater biota and trophic position, as defined by stable nitrogen isotope ratios ($\delta^{15}N$), was examined in 6 lakes in northwestern Ontario. The heavier isotope of nitrogen (^{15}N) increases an average of 3 parts per thousand (‰) from prey to predator and is used as a measure of an organism's trophic position. Dorsal muscle from lake trout, burbot, walleye, northern pike, white sucker, lake cisco, lake whitefish, and yellow perch was analyzed for Hg and $\delta^{15}N$ using flameless atomic absorption and mass spectrometry respectively. Within each lake, log Hg was significantly related to $\delta^{15}N$ (r^2 ranged from 0.47 to 0.91, $P < 0.01$). For four species, yellow perch, northern pike, lake cisco, and lake trout, log Hg was positively related to $\delta^{15}N$ (r^2 ranged from 0.37 to 0.47, $P \leq 0.09$) across all lakes. We also used $\delta^{15}N$ measurements (assuming a 3‰ shift between an organism and its diet) and the developed within-lake regression equations to calculate a prey Hg for each individual fish. These food Hg values were then used to predict predator Hg using Norstrom *et al*'s bioenergetics model. Predicted results were strongly correlated to measured Hg concentrations ($r = 0.91$, $P < 0.001$), indicating that $\delta^{15}N$ has potential to be used in modeling.

1. Introduction

The highest concentrations of mercury (Hg) are commonly found in those fishes occupying the top trophic level (e.g., Verta, 1990; Bodaly *et al.*, 1993). Food chain length, and individual growth rates and age result in among- and within-lake variability in Hg levels in these top predators. Elevated concentrations of Hg have been found in old slow-growing fishes (e.g., Bache *et al.*, 1971) and in top predators from lakes with the longest food chains (Cabana *et al.*, 1994; Futter, 1994).

Trophic classifications for the above studies have been estimated using inferred feeding behaviour, or stomach content analyses. However, fishes are opportunistic feeders whose diets (and trophic levels) often change as they grow, and can vary significantly among individuals of the same species (Trippel and Beamish, 1993). Stable isotope ratios of nitrogen ($^{15}N/^{14}N$; $\delta^{15}N$) provide an alternative to conventional methods for determining an organism's trophic status (e.g., Hesslein *et al.*, 1991). The heavier isotope of nitrogen increases an average of 3 parts per thousand (‰) from prey to predator (see review by Peterson and Fry, 1987) due to the preferential excretion of the lighter isotope through metabolic processes (Gaebler *et al.*, 1966). $\delta^{15}N$ integrates a signal from an organism's diet over the time period of tissue turnover (months or years, Hesslein *et al.*, 1993) and can therefore be used as a continuous measure of trophic behaviour.

In this study, we examined the relationship between trophic position, as determined by $\delta^{15}N$, and Hg concentrations in fishes from six lakes of the Northwestern Ontario Lake Size Series (NOLSS; Fee and Hecky, 1992). These lakes range in surface area from 0.88 to 347 km^2. The Hg and $\delta^{15}N$ data used in this study are a subset of the data published in Bodaly *et al.* (1993) and Fudge *et al.* (1994). Further, we investigated the

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potential for $\delta^{15}N$ to be used in conjunction with Norstrom *et al.'s* (1976) bioenergetics model to predict Hg in fishes. Results indicated that $\delta^{15}N$ is a powerful tool for predicting Hg in fishes from various trophic positions within a food web. Its usefulness for among-lake studies requires further investigation.

2. Methods

The characteristics of the NOLSS lakes and their fish assemblages are described by Fee and Hecky (1992) and Fudge *et al.* (1994) respectively. Northern pike (*Esox lucius*), walleye (*Stizostedion vitreum*), lake trout (*Salvelinus namaycush*), burbot (*Lota lota*), lake whitefish (*Coregonus clupeaformis*), lake cisco (*Coregonus artedii*), white sucker (*Catostomus commersoni*) and yellow perch (*Perca flavescens*) were collected between 1987 and 1989 (Bodaly *et al.*, 1993). Age, weight, length and stomach content data for these fishes are given in Fudge *et al.* (1994).

Dorsal muscle was analyzed for Hg using flameless atomic absorption as described in Hendzel and Jamieson (1976). $\delta^{15}N$ was measured on dried dorsal muscle following methods given in Hesslein *et al.* (1989).

The portion of Norstrom *et al.*'s (1976) model describing both the uptake of Hg from food and its depuration was programmed in STELLA (High Performance Systems) which is a package for numerical modeling. Since this was a general test of the approach, the parameter values used were those specified by Norstrom *et al.* for yellow perch, even though they are species (and perhaps location) specific. The definitions of weight at age and the growth rate, as required for the model, were made by assuming a linear growth rate for the fish. This was calculated for each individual fish as weight/(age-1). This approximation gave the best estimate of weight from age because of the lower absolute weight gain in very young fish. Yellow perch from NOLSS lakes were not included in the modeling because age data were not available. The level of Hg in the food was selected as the concentration one trophic level (3 ‰) below that of each fish for which the Hg was simulated. We used the developed within-lake regression equations between log Hg and $\delta^{15}N$ to calculate prey Hg concentrations.

Statistical analyses was conducted using log-transformed Hg data. Least squares linear regression and Pearson's product moment correlation analyses were used to examine relationships within lakes and species.

3. Results and Discussion

Results of Hg and $\delta^{15}N$ analyses for each species from the NOLSS lakes are shown in Table I. All Hg concentrations were calculated on a wet weight basis. Within any of the lakes, individuals of one species had $\delta^{15}N$ values covering 2 ‰ or less.

$\delta^{15}N$ was not significantly correlated with fish weight, length or age for lake trout, walleye or burbot ($P > 0.2$). $\delta^{15}N$ was significantly correlated to age for lake cisco ($P = 0.001$, $r = 0.608$), length and age for lake whitefish ($P = 0.024$ and 0.035, $r = -0.568$ and -0.528), and length and weight for northern pike ($P = 0.008$ and 0.010, $r =$

0.600 and 0.592), white sucker (P = 0.027 and 0.002, r = - 0.353 and - 0.475), and yellow perch (P = 0.033 and 0.018, r = 0.552 and 0.599). These relationships indicate that these species change their trophic behaviour as they grow. The negative correlations found for lake whitefish and white sucker cannot be explained at present.

For all sites but Orange Lake, mean $\delta^{15}N$ in fish muscle tended to be higher in smaller lakes. Stomach content data for the fishes in this study are very limited (Fudge *et al.*, 1994). For this reason, it is difficult to determine if changes in the trophic behaviour of fishes among lakes are causing this trend. For species such as white sucker, a shift in trophic position does not seem likely. It is possible that differences in basal $\delta^{15}N$ exist among these lakes, as found in Estep and Vigg (1985) and Kling *et al.* (1992). This may result in among-lake differences in fish $\delta^{15}N$ that are not due solely to trophic positioning. Bodaly *et al.* (1993) found increasing Hg in fishes with decreasing lake size. This relationship was attributed to higher Hg methylation rates in smaller lakes due to their higher epilimnetic temperatures. Among-lake differences in basal $\delta^{15}N$ may be due to variations in epilimnetic temperatures, nutrient availability or species composition. At present, the possible covariance between lake size and $\delta^{15}N$ in fishes requires further investigation.

TABLE I

Mean Hg (ug g^{-1} wet weight) and $\delta^{15}N$ (± SD) for species collected from NOLSS (lakes are arranged from largest to smallest surface area).

		Trout	Sydney	Musclow	Linge	Orange	Green
White	$\delta^{15}N$	6.9±0.6	6.8±0.5	7.2±0.4	7.6±0.6	6.1	9.5±0.7
Sucker	Hg	0.14±0.08	0.12±0.06	0.10±0.03	0.16±0.08	0.17	0.06±0.03
	n	10	7	4	8	2	8
Cisco	$\delta^{15}N$	5.5±0.3	7.8±0.3	8.8±0.2	8.6±0.3	7.5±0.6	11.1
	Hg	0.03±0.01	0.15±0.03	0.16±0.03	0.13±0.04	0.22±0.07	NA
	n	3	4	4	8	7	2
Lake	$\delta^{15}N$	7.6±0.7	8.1±0.1	9.3	9.5±0.6	-	-
Whitefish	Hg	0.13±0.06	0.17±0.05	0.04	0.21±0.10	-	-
	n	6	4	2	4	-	-
Yellow	$\delta^{15}N$	-	7.0±1.2	7.3±0.8	-	7.0±0.3	-
Perch	Hg	-	0.08±0.04	0.06±0.02	-	0.11±0.05	-
	n	-	8	4	-	3	-
Northern	$\delta^{15}N$	9.2±1.3	8.8	10.2±0.3	10.5	9.7±0.2	11.9
Pike	Hg	0.30±0.09	0.34	0.44±0.26	0.92	0.99±0.37	1.14±0.29
	n	3	1	4	2	4	4
Walleye	$\delta^{15}N$	9.5±0.5	9.3±0.3	10.5±0.5	10.6±0.6	9.6±0.5	-
	Hg	0.52±0.17	0.37±0.33	0.43±0.21	0.89±0.22	1.22±0.45	-
	n	6	7	8	8	8	-
Lake Trout	$\delta^{15}N$	10.2	10.4±0.5	-	11.3	-	-
	Hg	0.35	0.45±0.15	-	0.58	-	-
	n	2	4	-	1	-	-
Burbot	$\delta^{15}N$	9.8±0.3	9.9±0.4	-	-	-	-
	Hg	NA	0.41±0.23	-	-	-	-
	n	6	4	-	-	-	-

Within all six lakes, significant relationships between log Hg and $\delta^{15}N$ in fish muscle

were found (Table II). Examination of the data for each species across all lakes revealed significant relationships between log Hg and $\delta^{15}N$ for yellow perch, northern pike, lake cisco and white sucker, and a positive but not significant relationship between these variables for lake trout. The regression equations (± SE, ANOVA) are as follows:

Yellow Perch: log Hg (ug g^{-1}) = - 2.16 (± 0.32) + 0.15 (± 0.04) $\delta^{15}N$; r^2 = 0.45, n = 15, P = 0.006.
Northern Pike: log Hg (ug g^{-1}) = - 1.80 (± 0.50) + 0.16 (± 0.05) $\delta^{15}N$; r^2 = 0.39, n = 18, P = 0.006.
Lake Cisco: log Hg (ug g^{-1}) = - 2.08 (± 0.32) + 0.15 (± 0.04) $\delta^{15}N$; r^2 = 0.37, n = 26, P = 0.001
White Sucker: log Hg (ug g^{-1}) = - 0.24 (± 0.25) - 0.09 (± 0.03) $\delta^{15}N$; r^2 = 0.19, n = 39, P = 0.005
Lake Trout: log Hg (ug g^{-1}) = - 2.04 (± 0.79) + 0.16 (± 0.08) $\delta^{15}N$; r^2 = 0.47, n = 7, P = 0.09

There were no significant relationships between log Hg and $\delta^{15}N$ for lake whitefish (r^2 = 0.006, P = 0.93), walleye (r^2 = 0.007, P = 0.12) and burbot (r^2 = 0.015, P = 0.88).

TABLE II

Regressions between log mercury (ug g^{-1} wet weight) and $\delta^{15}N$ (‰) through the food webs of the NOLSS lakes (ANOVA, $P < 0.01$).

Lake	n	Slope (± SE)	Intercept (± SE)	r^2
Trout	30	0.21 ± 0.03	- 2.46 ± 0.27	0.58
Sydney	39	0.17 ± 0.02	- 2.17 ± 0.23	0.51
Musclow	26	0.21 ± 0.04	- 2.68 ± 0.41	0.47
Linge	31	0.23 ± 0.04	- 2.68 ± 0.37	0.53
Orange	24	0.29 ± 0.03	- 2.82 ± 0.25	0.81
Green	12	0.48 ± 0.05	- 5.76 ± 0.50	0.91

The concentrations of Hg in fishes that were predicted using Norstrom *et al.*'s model are compared to measured values for all species from all lakes in Figure 1. A strong correlation between predicted and measured Hg was found (r = 0.91, $P < 0.001$) indicating that $\delta^{15}N$ has potential for modeling Hg in fishes. We have combined the effects of trophic structure and growth in our predictions of Hg, but we have not formally integrated the two processes in a unified model. We have not allowed for any change in prey Hg which may result from either a choice of food at a higher trophic level or from older individuals as food from the same trophic level. In spite of the approximations, the results are quire good. A more challenging test of this approach will come with data from lakes which are less similar physically, chemically, and in fish population characteristics than the NOLSS lakes.

4. Conclusion

There are a number of factors which contribute to Hg concentrations in fishes such as relative availability of methylmercury in the ecosystem, and individual growth rate, age, and trophic position. $\delta^{15}N$ is useful as a measure of a fish's relative trophic position

because stomach content data are often limited or unavailable, and do not reveal seasonal variations in diet. In this study, $\delta^{15}N$ identified the relative trophic position of individual fishes and was significantly related to Hg levels within each food web for all six lakes. From the results of the modeling, it also appears that $\delta^{15}N$ can be used to determine prey Hg and therefore predict Hg in fishes. However, the possible effect of lake size on nitrogen cycling and basal $\delta^{15}N$ needs to be investigated before $\delta^{15}N$ can be applied across systems to predict Hg levels in fishes.

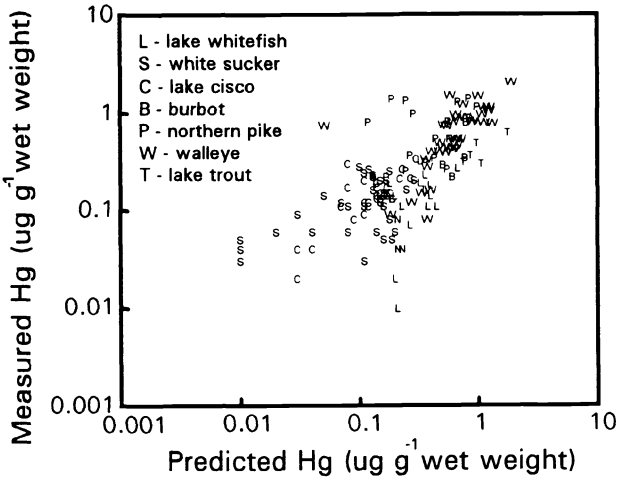

Fig. 1. Predicted versus measured Hg in all species from the NOLSS lakes.

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PRELIMINARY RESULTS ON THE ROLE OF RIVERS IN TOTAL Hg CONCENTRATIONS IN MARINE SEDIMENTS AND BENTHIC ORGANISMS OF A COASTAL AREA OF ITALY

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Abstract. The paper reports the results of mercury (Hg) concentrations in the <20 μm grain-size fraction of shallow sediments of the northern Tyrrhenian sea, collected near the mouths of rivers flowing down from the Monte Amiata area (central Italy), which is characterized by cinnabar mineralization which was developped as mercury mine in the past A few species of benthic marine organisms collected in the sediment sampling area were also analyzed From the results, it emerged that the rivers contribute to the Hg concentration in the marine sediments which already contain high natural Hg background levels The benthic organisms, which reflect sediment contamination, showed high Hg concentrations as well

1. Introduction

From preliminary results it was hypothesized that the Albegna river, which drains the Monte Amiata area, rich in deposits of cinnabar (HgS) and known for the past Hg mining activity, was responsible for the Hg enrichment of the marine sediments of part of the northern Tyrrhenian sea (Barghigiani *et al.*, 1986) and consequently of high Hg levels in some benthic and nonbenthic organisms of this area (Barghigiani *et al.*, 1986 , 1991).

In this work we extended the investigation to the influence of two more rivers flow into this marine area, the Fiora, which also drains Monte Amiata, and the Ombrone, as well as to the Hg content in other benthic species characteristic of the area, since Hg levels in benthic organisms reflect those in sediments (Hornung *et al.*, 1984).

The high Hg concentrations encountered in the marine organisms of the Tyrrhenian sea (UNEP/FAO/WHO, 1987) and concern for possible risks stemming from the frequent use of marine organisms for human consumption have attracted the interest of the scientific community to this problem.

The Hg in the sediments was determined in the <20 μm grain-size fraction, the fraction considered most suitable for monitoring metals in sediment samples from coastal and estuarine areas (Ackerman *et al.*, 1983).

2. Materials and Methods

2.1. STUDY AREA AND SAMPLE COLLECTION

The sediments were collected with a gravity corer, or a Shipek grab where the Livorno

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harbor master office did not authorize use of core samplers, at the stations shown in Figure 1 during a survey conducted in April 1993 with the oceanographic ship *Urania* of the Italian National Research Council.

The marine organisms were collected earlier, from early 1989 to mid-1990, in the same area shown in Figure 1.

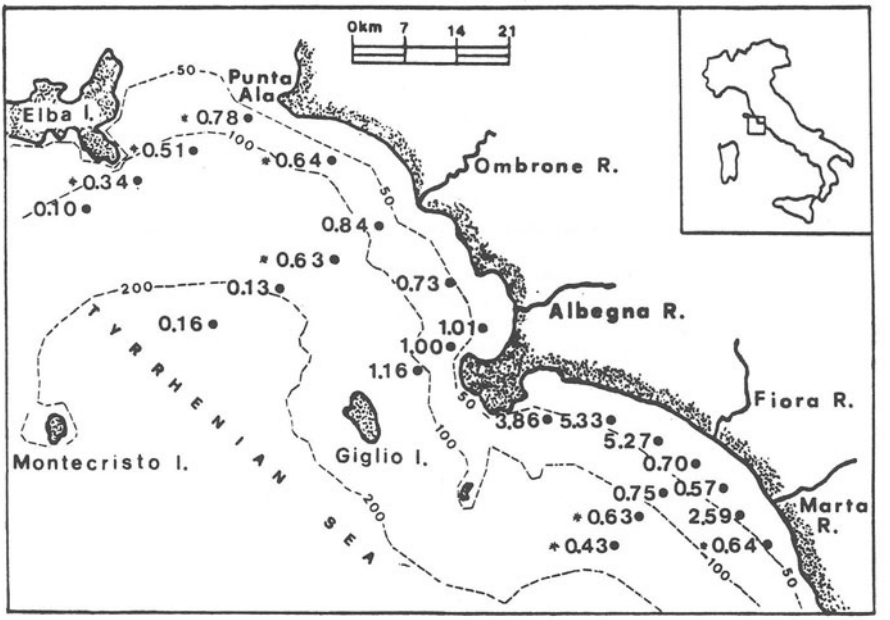

Figure 1 Study area and sediment sampling stations The Hg concentrations (μg g^{-1} dry wt) are reported in the <20 μm grain-size fraction of the sediments The starred values refer to samples collected with the grab

The analyzed species were the following: *Eledone cirrhosa* (octopus-like cephalopod), *Nephrops norvegicus* (Norway lobster), *Parapenaeus longirostris* (shrimp), *Lepidorhombus boscii* (flatfish), and *Citharus linguatula* (flatfish).

2.2. SAMPLE TREATMENT AND MERCURY ANALYSIS

The top layer of sediment, 1 cm thick, was collected from the core samples.

The <20 μm grain-size fraction was separated by wet sieving and analyzed for the content of Hg.

The organisms were measured as dorsal mantle, carapace or total length, depending on the species. A sample of muscle tissue was then taken from each specimen for the analyses.

The sediment and muscle tissue samples were digested with HNO_3 in a Mileston 1200 microwave decomposition system and analyzed for Hg by cold vapor atomic absorption spectrometry using a Perkin Elmer 50B mercury analyzer.

The dry weight was determined on subsamples by bringing them to constant weight at 60° C in an oven. The analytical procedures were tested by DORM-1 (dogfish muscle: 0.798±0.074 μg g^{-1} Hg) and BEST-1 (marine sediments: 0.092±0.009 μg g^{-1} Hg) of the National Research Council of Canada.

3. Results and Discussion

3.1. MARINE SEDIMENTS

The results for the total Hg concentration in the sediments are reported in Figure 1. The metal levels were generally lower than those found by Baldi and Bargagli (1982) in the same area on the total fraction of sediment digested with the Agemian and Chau's method (1976). It was not possible to make comparisons with values of the same area or other areas of the Mediterranean sea as data are lacking on the levels of the metal in the <20 μm grain-size fraction. High Hg concentrations were found facing the mouths of the rivers. Seawards from the mouth of the Albegna the values remain high and are among the highest in the zone. A very high value was also found facing the mouth of the Marta river, the outflow of Lake Bolsena, south of Monte Amiata. The concentrations in the sediments offshore from the Ombrone and Fiora rivers decrease out to sea. The values measured along the coast north of the Ombrone and Albegna rivers are also lower, while those north of the Fiora are the highest of the area, perhaps due to currents, which in this zone should have a prevailing northward trend, and possibly also to the presence of numerous small watercourses that reach the sea in this section of coast.

It should be pointed out, however, that the levels of the metal also decrease along the transect running southwest from Punta Ala.

Thus, while the studied rivers can be reasonably considered responsible for the high Hg levels in the sediments of this area, it is hard to estimate their contribution because the whole area is strongly mineralized, and consequently, marine sediments have a high natural background Hg concentration.

3.2. BENTHIC ORGANISMS

It is known that pelagic predators of the Mediterranean, such as the tuna, display high Hg concentrations (Buffoni *et al.*, 1982).

Table I shows that the benthic organisms analyzed in this area also display very high metal concentrations. This confirms and supplements, with the data on *P. longirostris*, what was observed in previous works (Barghigiani *et al.*, 1986, 1991). Also Leonzio *et al.* (1981) found high Hg concentrations in some benthic species from this area, such as *Mitilus galloprovincialis* (mussel) and *Mullus barbatus* (mullet). In Norway lobster these

TABLE I

Mercury concentration in benthic organisms. Average values ± S.D. are given.

Species	Hg ($\mu g\ g^{-1}$ dry wt.)	Length range (cm)	Sample no.
E. cirrhosa	3.64±1.36	8.5-10.5	82
N. norvegicus	6.81±4.20	3.5-4.5	25
P. longirostris	3.14±1.07	2-3	47
L. boscu	2.83±1.13	16.5-18.5	22
C. linguatula	5.40±2.61	14.5-26.5	22

authors found concentrations of the metal comparable to or even higher than those found by us. It can be said in conclusion that this area deserves more in-depth study on the presence of Hg in sediments and edible organisms and that it would be suitable to extend the investigation to other areas in order to get a detailed view of the situation of Hg levels in the Mediterranean basin and to allow comparison between the area studied by us and other areas.

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MERCURY CONTAMINATION IN NORTHERN QUÉBEC ENVIRONMENT AND WILDLIFE

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Abstract. It has been well documented in Northern Québec and elsewhere that levels of mercury (Hg) in fish from natural lakes often exceed the Canadian marketing standard (0.5 mg/kg). However, little information is available on the presence of Hg in wildlife other than fish or in abiotic compartments of the environment. Hydro-Québec has conducted a study to assess the nature and the extent of the present Hg contamination in Northern Québec and to acquire baseline data to monitor long term temporal changes. The results indicate that the levels of Hg observed in the environment are generally within the background levels reported for comparable pristine environments. However, total Hg concentrations in biota do reach high levels in piscivorous fishes, birds and mammals

1. Introduction

During recent years, several studies have confirmed the presence of contaminants in the Northern Canadian environment and wildlife. Numerous metals and organic compounds have been measured in surface water (McCrea and Fisher, 1986; Langlois, 1987), in snow (Gregor and Gummer, 1989) and in several species of wildlife (Thomas *et al.*, 1992; Muir *et al.*, 1992). Based on its occurrence in aquatic fauna of the Hudson and Ungava regions and on its potential toxicity, Hg was identified as one contaminant of most concern.

In Northern Québec, the levels of Hg in fishes are well documented, both in natural water bodies and in aquatic systems affected by industrial effluents or hydroelectric development (Brouard *et al.*, 1990; Langlois et Sloterdijk, 1989). However, little information is available on the presence of Hg in wildlife other than fish and in abiotic compartments of the environment. Therefore, in the context of the environmental studies of the Great Whale and Nottaway–Broadback–Rupert hydroelectric projects, Hydro-Québec initiated a study to assess the nature and the extent of Hg contamination in the environment and in wildlife and to acquire baseline data in order to monitor temporal changes.

2. Methodology

The study areas comprise the Great Whale (GW) project study area, north of 55°N on the east coast of Hudson Bay, and the Nottaway–Broadback–Rupert (NBR) project study area, between 49°N and 52°N, on the south-east coast of James Bay. The Great Whale study area extends over 70,000 km^2, whereas the Nottaway–Broadback–Rupert study area covers 146,000 km^2. Local sources of Hg pollution are restricted to a few sites in the Nottaway river bassin, in the southern part of the NBR study area, where chloralkali plants and pulp and paper mills have discharged significant quantities of Hg in some adjacent rivers until the mid seventies.

The wildlife sampled in Great Whale include fishes, aquatic and terrestrial birds, terrestrial and marine mammals and freshwater seals. All samples were collected in 1989 and 1990 and, except for marine mammals, the animals were most often provided whole. In the NBR study area, sampling was limited to fish and waterfowl and was conducted in 1990 and 1991. In both study areas, surface water was also sampled, as well as seston and bottom sediments in Great Whale area.

The samples were taken with appropriate tools and all standard precautions were followed to avoid contamination (SOMER, 1993). In some instances, tissues from several individuals of the same species were pooled in a single sample. Surface water was sampled in boro-silicate glass bottles with teflon-lined caps.

In unfiltered water and in seston, the total Hg analyses were done by Atomic Absorption Spectrophotometry (Robertson *et al.*, 1987). The MeHg analysis were done by Gas Chromatography with electron capture detector for unfiltered water (Lee *et al.*, 1989) and

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by Atomic Absorption Spectrophotometry after solvent extraction for seston (Capelli *et al.*, 1979). In sediments and in wildlife, total Hg and MeHg were both analyzed by cold vapor Atomic Absorption Spectrophotometry.

3. Results and Discussion

3.1. BIOACCUMULATION IN THE ENVIRONMENT

The levels of total Hg found in unfiltered fresh water from Great Whale and NBR study areas (Table I) are within the background levels reported in comparable pristine environments (St. Louis *et al.*, 1993). The MeHg usually accounts for less than one tenth of the total Hg present in water. The proportion of MeHg was higher in the NBR study area in summer than in winter.

TABLE I

Total Hg and MeHg concentrations in freshwater (ng/L), in sediments (mg/kg DW) and in seston (mg/kg DW)

Study Area	Total Hg Mean ± S.D.	MeHg Mean ± S.D.
NBR		
Water, Winter (N=20)	4.45 ± 1.73	0.46 ± 0.83
Water, Summer (N=25)	3.07 ± 1.71	0.94 ± 0.54
Great Whale		
Water, Summer (N=18 and 22)	4.8 ± 6.62	0.453 ± 0.37
Seston, Fall 1989 (N=7)	0.11 ± 0.07	0.02 ± 0.02
Sediments (N=12)	0.07 ± 0.05	—

In fresh water sediments from lakes and rivers, the mean concentration of Hg was 0.07 mg/kg and the maximum reached 0.18 mg/kg (N=12). Those values are comparable to some measured in other pristine environments such as Labrador (Lockerbie, 1987), but they are much lower than some measured in industrialized areas of the St. Lawrence river, where maximum concentrations reach 4.8 mg/kg in Lake St. Louis (Jarry *et al.*, 1985).

In lake seston, composed of particulate organic matter collected with a plankton net of *150 µm* mesh size, the mean levels of total Hg and MeHg measured were respectively 0.11 mg/kg (DW) and 0.02 mg/kg (DW). In industrialized areas such as the Niagara river in southern Ontario, mean levels of total Hg in suspended particulate matter were up 2.3 mg/kg (DW) (Nriagu, 1983).

3.2. BIOCONCENTRATION IN WILDLIFE

Although the results presented above show relatively low levels of Hg in the various physical components of the Northern Québec environment, the level of contamination measured in wildlife was relatively high. The total Hg concentration did reach high levels (>0.5 mg/kg FW) in several piscivorous species of wildlife, including fishes, birds and terrestrial and marine mammals (Table II). Fish, which constitute an important food resource for native people, show significant levels of Hg, particularly piscivorous species such as Northern pike, Lake trout and Walleye. Some species, such as Northern pike, show higher levels in the NBR study area, closer than Great Whale to North American industrialized areas, suggesting a south-north latitudinal gradient in Hg concentrations. However, the levels found in NBR Northern pikes (mean of 0.93 mg/kg FW) are comparable or higher than in fishes from most watersheds of Southern Québec, including the St. Lawrence river (Lake Saint-Pierre) (mean of 0.63 mg/kg FW) (Langlois and Sloterdijk, 1989). In other biota, the levels of Hg observed are comparable and sometimes higher than those

reported in the literature for other remote areas of Northern Hemisphere (Muir *et al*., 1992; Wageman and Muir, 1984).

TABLE II

Levels of total Hg (mg/kg FW) in muscle tissue of selected wildlife species

Species	Great Whale		NBR	
	Mean ± S.D.	N	Mean ± S.D.	N
Northern pike	0 63 ± 0 46	75	0 93 ± 0 51	636
Walleye	—	—	0 78 ± 0 46	789
Lake trout	0 77 ± 0 66	504	—	—
Common merganser	1 27 ± 0 48	13	1 41 ± 1 26	19
Herring gull	1 03 ± 0 80	28	1 59 ± 1 32	13
American mink	2.40 ± 2 24	6	—	—

In some tissues, the levels measured were much higher than those observed in muscle, particularly in liver and in feathers of birds (Table III) and in liver and kidneys of marine mammals (Table IV). However, the mean ratio of MeHg/total Hg in ringed seal, beluga and freshwater seals tends to be higher in muscle (respectively 0.34, 0.39 and 0 95) than in liver (respectively 0.20, 0.36 and 0.16).

TABLE III

Levels of total Hg (mg/kg FW) in various tissues of selected bird species

Species	Great Whale			NBR		
	Mean (mg/kg)	Standard deviation	N	Mean (mg/kg)	Standard deviation	N
Common merganser						
• Liver	17 53	12 06	13	10 9	7 5	15
• Feathers	9 97	2 88	12	7 31	2 91	15
Herring gull						
• Liver	2 91	2 35	27	3 63	2 52	13
• Feathers	11 54	8 55	27	19 1	15 3	13
• Eggs	0 28	0 12	2	—	—	—

TABLE IV

Levels of total Hg and MeHg (mg/kg FW) in various tissues of marine mammals from Great Whale study area

Tissue \ Species	Mean ± S.D. (mg/kg FW)		
	Ringed Seal (N=2 to 8)	Beluga (N=3 to 6)	Freshwater seal (N=2)
Muscle			
• Total Hg	0 32 ± 0 19	2 60 ± 2 06	1 10 ± 0 37
• MeHg	0 11 ± 0 08	1 01 ± 0 58	1 04 ± 0 37
Liver			
• Total Hg	5 12 ± 4 64	20 34 ± 19 60	28 80 ± 37 06
• MeHg	1 01 ± 0 87	7 26 ± 5 21	4 55 ± 4 60
Brain			
• Total Hg	0 19 ± 0 09	2 63 ± 2 87	0 36 ± 0 20
Kidney			
• Total Hg	0 49 ± 0 07	—	6 13 ± 1 65

Although it has been demonstrated that Hg of atmospheric origin has been deposited in Northern Québec since the 1940's (Lucotte *et al*., 1993), there is no clear latitudinal

gradient in the Hg concentrations in wildlife from both study areas The variability observed may be related to a combination of factors including growth rate, water quality nature of soils and sediments (e g organic carbon content), geochemistry of substrate atmospheric transport and the presence of industrial effluents (Nottaway basin)

4. Conclusion

The results obtained confirm the occurrence of relatively high levels of Hg in Northern Québec wildlife For some species, such as piscivorous fishes, birds and marine mammals the levels often exceed the Canadian Fish Marketing Standard of 0 5 mg/kg (Health and Welfare Canada, 1985) in muscle and other tissues, which could represent a health risk if those organs/tissues constitute an important part of traditional native diets Although atmospheric transport was identified as a major source of Hg to Northern Quebec the spatial distribution between the two study areas (NBR and Great Whale) has not shown a clear latitudinal variation and the spatial variability within each zone has yet to be examined

Acknowledgments

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COMPARISON OF MERCURY CONCENTRATIONS IN MODERN LAKE SEDIMENTS AND GLACIAL DRIFT IN THE CANADIAN SHIELD IN THE REGION OF OTTAWA/KINGSTON TO GEORGIAN BAY, ONTARIO, CANADA.

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Abstract. An ongoing problem in evaluating the significance of mercury (Hg) in surficial materials is distinguishing sources of natural (spatial) variation of the geological/geochemical environment from sources (airborne, waterborne, etc) of anthropogenic (temporal) variation The Geological Survey of Canada (GSC) has carried out a series of sampling programs, including one in the southeastern part of the geologically complex Canadian Shield in order to link the easily observable lithological variations of bedrock with the chemical composition of overlying glacial deposits and lake sediments This research aims to provide a base against which observed variations in life systems can be judged as natural or anthropogenic In the study area, high concentrations of Hg and other trace elements in lake sediment and glacial sediments can be related to glacial dispersal from mineralized bedrock and/or bedrock with high natural background concentrations of these elements

1. Introduction

Geochemists and geologists routinely gather and compile data that can provide important baseline information on the natural chemical status of the environment It is only with an appreciation of natural compositional variations of the geological substrate, on which life systems are superimposed, that any attempt can be made to evaluate the extent to which humans have affected the chemistry of these systems

Separation of natural geologically controlled (spatial) variations, sometimes referred to as the "status" of a landscape, from anthropogenic (temporal) variations is difficult Lakes in geologically complex terrains, such as the Canadian Shield, have a wide natural range of metal concentrations that are clearly related to their geological setting (Hornbrook *et al*, 1986, Kettles *et al*, 1991) The challenge for geoscientists, then, is to devise strategies for distinguishing among natural and anthropogenic factors that influence the metal content of the surficial environment

Geochemical surveys which map the natural variation of Hg and other metals in terrestrial and aquatic systems may be used to 1) identify where naturally occurring metal enrichments may lead to environmental problems, and 2) predict where the worst effects due to any anthropogenic changes to the environment may occur

Patterns of natural distribution of metals in lakes and soils aid in evaluating the extent to which these same metal species are deposited as airborne or waterborne pollutants Likewise, it is important to understand the natural processes leading to elevated levels of metals near the sediment-water interface in lakes Increasingly, these enrichments are cited as evidence of anthropogenic deposition (Norton *et al*, 1990, Lindquist *et al*, 1991, Swain *et al*, 1992) Though deposition of metals from the atmosphere undoubtedly is widespread, natural areal and vertical variations make evaluation of the relative magnitude of the anthropogenic component problematic

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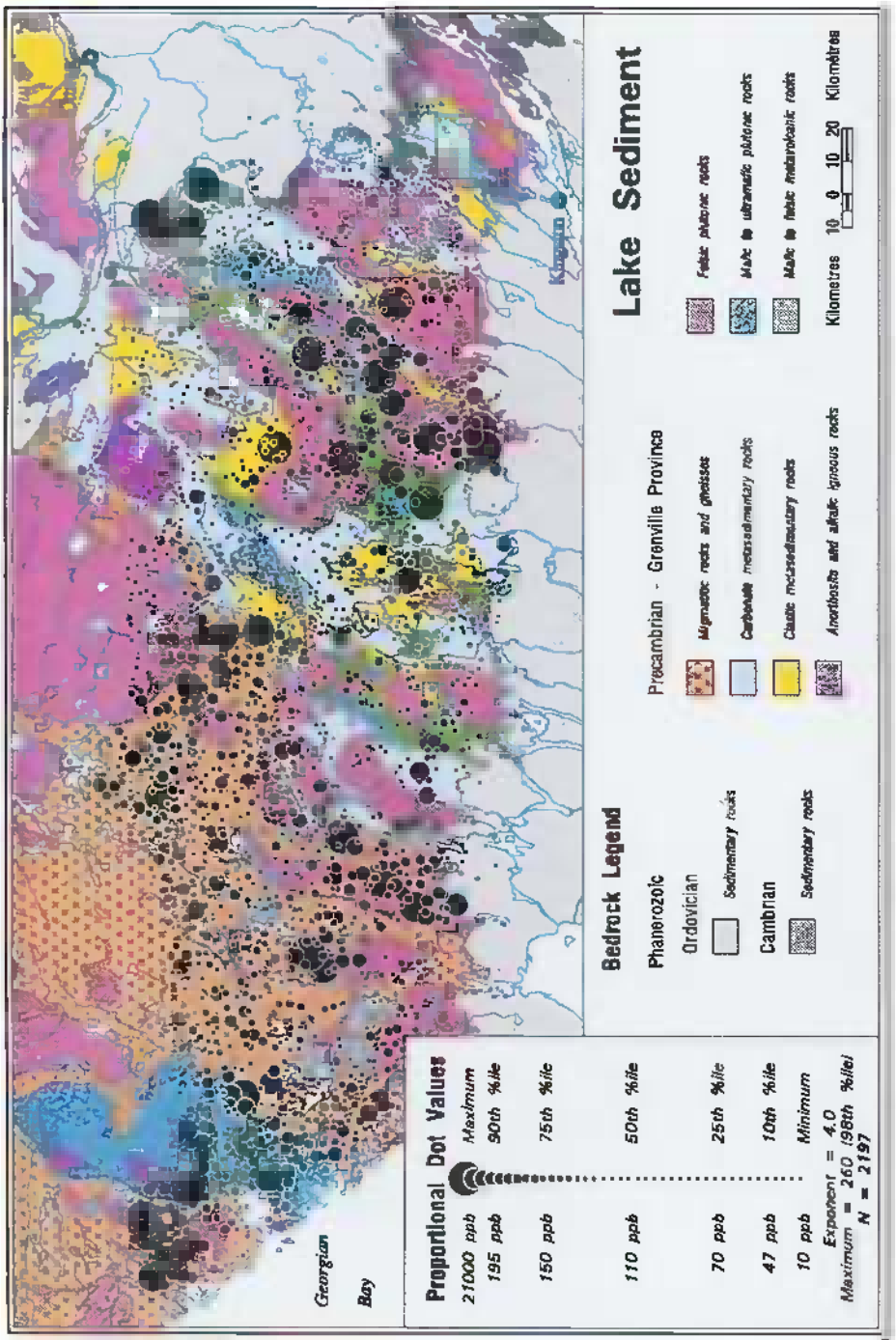

Figure 1 Natural, geologically controlled, levels of Hg (ppb) in the <180 μm fraction of modern lake sediments in the

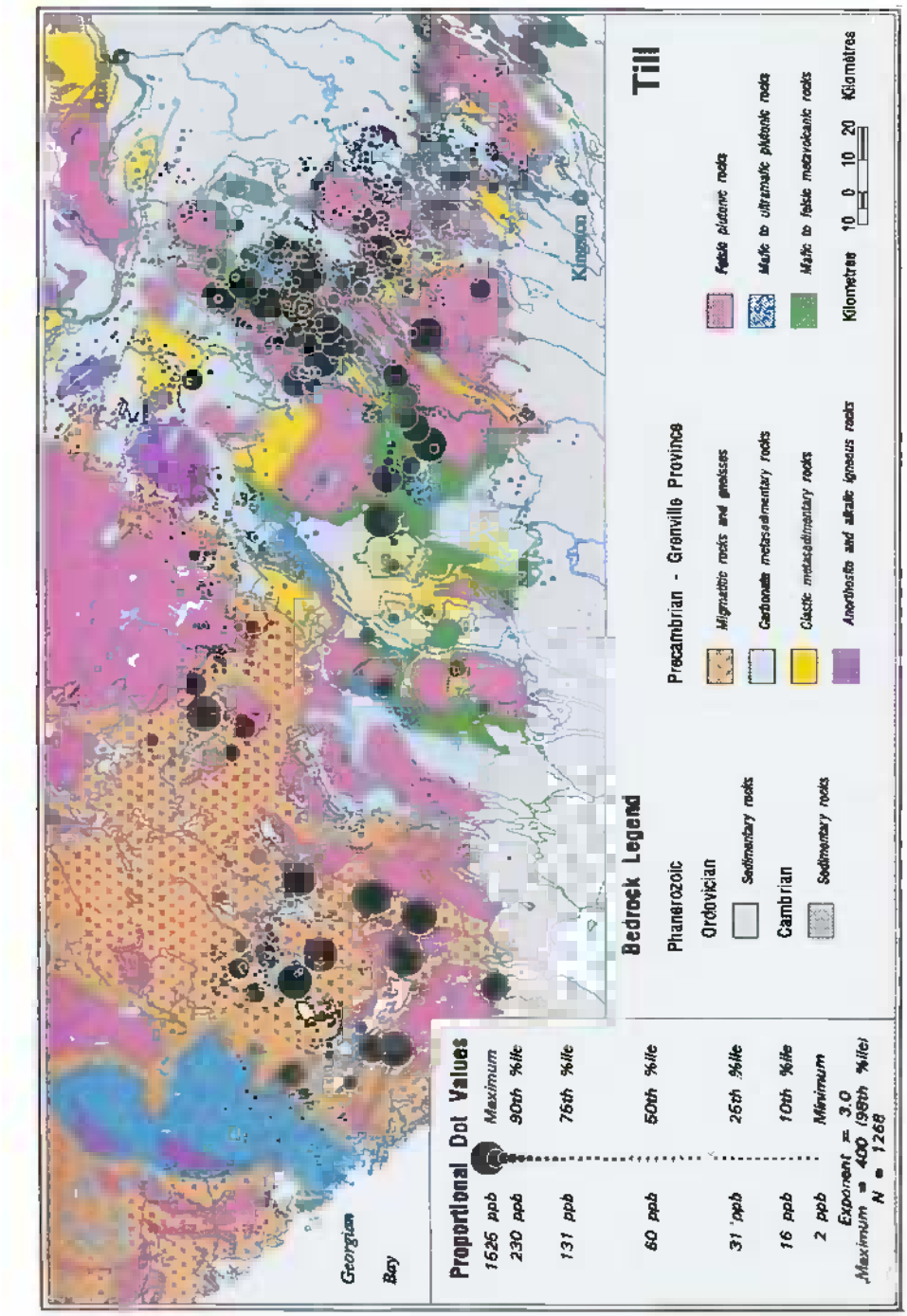

Figure 2 Natural geologically controlled levels of Hg (ppb) in the clay sized (<2 μm) fraction of glacial sediments primarily till in the Canadian Shield region of Ottawa/Kingston to Georgian Bay Ontario Canada

2. Sample collection, preparation and analytical methods

In southeastern Ontario, modern lake sediment samples were collected from approximately 2200 lakes (1 site per 13 km^2) (G S C , 1977a,b, Hornbrook *et al* , 1984a,b) (Figure 1) Sample collection, preparation and analyses followed National Geochemical Reconnaissance (NGR) protocols (for details see Friske and Hornbrook, 1991) Surficial (top 5-10 cm) sediment, which is physicochemically active and potentially anthropogenically impacted, was automatically excluded through sampler design so that the organic-rich sediment (gyttja) samples obtained were generally from >30 cm depth in the sediment column (Coker *et al* , 1979) and thus the reported data represent natural (pre-industrial) levels of total Hg in lake sediments The natural distribution of Hg and other trace elements, as determined by lake sediment geochemistry, has been used for several decades to successfully explore for and locate new mineral deposits (Coker *et al* ,1979, Friske and Hornbrook, 1991)

Over the same area, glacial sediments (n = 1268), primarily till, were sampled at irregular intervals (1 site per 23 km^2) from below the postglacial solum to avoid the effects of postglacial weathering and potential anthropogenic modification (Kettles and Shilts, 1994) (Figure 2)

After air drying, the <180 μm fraction of the lake sediment samples and the clay-sized (<2 μm) fraction separated by centrifugation from undried glacial sediments were analyzed for a wide range of elements Mercury was determined by the cold vapour atomic absorption technique (Jonasson *et al* , 1973) Quality control of all analytical data was monitored using reference standards and blind duplicates inserted at a frequency of 5% for lake sediments and 10% for glacial sediments Precision and accuracy for total Hg measured in both media were in the $\pm$ 10% range

The distribution and composition of various bedrock lithologies and mineralization influences regional element distributions within the secondary environment The cover of glacial drift has a chemical composition that is related to local bedrock and to bedrock "up ice" from the sample site

In the eastern and southern parts of the area sampled, flat lying, unmetamorphosed Ordovician limestones, dolomites, and shales crop out In the west, crystalline igneous and metamorphic bedrock of the Grenville Structural Province of the Canadian Shield crop out (Baer *et al* , 1977) (Figure 1) Sangster (1982) describes a wide variety of important mineral deposit types in the area

The predominant ice flow direction during the last glaciation was towards the south-southwest and carbonate bedrock debris derived from Ordovician terrane has been transported in that direction over Precambrian bedrock Along the Ottawa and St Lawrence valleys and in low lying areas near Georgian Bay, glaciomarine and glaciolacustrine sediments form a fairly continuous surface cover

3. Results

The dispersal and dispersion patterns of Hg in surficial media are a predominately, although sometimes glacially distorted, reflection of the composition of underlying bedrock The large areas of natural Hg enrichment in drift (Figure 2) broadly outline the prominent belts of metavolcanic and metasedimentary rock (Shilts, 1984, Kettles and

Shilts, 1989, 1994) as do areas of high Hg in modern lake sediments (Figure 1) (Hornbrook *et al.*, 1986). Though mercury-bearing minerals are known to occur in widely scattered quartz vein-hosted sulphide deposits within the metavolcanic and sedimentary rocks of the area (Sangster, 1982), individual deposits are small. Moreover, detailed studies of drift dispersal in the region (Sinclair, 1979; DiLabio *et al.*, 1982) show that detectable dispersal from sulphide occurrences is only on the order of 1 km. The observed elevated Hg concentrations in drift over such a large area (Figure 2) may indicate that there are many small, but overlapping Hg dispersal trains and/or Hg-rich mineral phases in the metasedimentary and metavolcanic host rocks, themselves.

4. Discussion and conclusions

Variation of Hg in deep, pre-industrial lake sediments and glacial sediments over the study area illustrates the strong and predictable influence of geology on patterns of chemical variation. These data are essential for evaluating the nature and extent of anthropogenic modifications of natural chemical systems. For example, knowing areas where Hg is naturally enhanced in lakes, glacial drift, and/or bedrock, offers some hope for identifying areas where this potentially toxic element may naturally lead to elevated levels of Hg in fish (e.g. Loukola-Ruskeeniemi, 1990: Rasmussen, 1993; Shilts and Coker, 1995) or where the landscape may be most likely to be most severely impacted by anthropogenic phenomena (i.e. acid rain, etc.) (e.g. Coker and Shilts, 1979; Shilts *et al.*, 1981). It also may lead to a realistic evaluation of the extent to which Hg, and other elements, are enriched in the surficial environment from airborne or waterborne pollutants.

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BINDING OF METHYLMERCURY COMPOUNDS BY HUMIC AND FULVIC ACIDS

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Abstract. Humic and fulvic acids were isolated from Fawn Lake in Ontario and investigated by membrane dialysis for their ability to bind CH_3Hg^+. By measuring the distribution of methylmercury compounds in and outside of the dialysis membrane, for the first time, binding capacities and conditional stability constants for CH_3Hg^+ and humic acids could be calculated. Equilibrium between inner and outer dialysis solution was reached within 24 hours without losses of CH_3Hg^+ in humic solution. The ratio of bound to unbound CH_3Hg^+ increased with decreasing total CH_3Hg^+ levels in the system. The percentage of free methylmercury compounds increased with decreasing pH. Fawn Lake humic acid showed two different binding sites. The conditional stability constant of the stronger site was calculated as 1.3×10^{12}. This site was able to bind 0.2 ng CH_3Hg^+ per mg of humic acid.

1. Introduction

In many southern Ontario lakes with no obvious source of mercury contamination, Hg concentrations in muscle tissue of sport fish exceed health advisory limits (0.5 mg/kg) (OMOE and OMNR, 1993). Total mercury concentrations in the water are very low, typically in the order of a few ng/l. A significant fraction of the total mercury in the water is in the form of methylmercury compounds, the mercury species that is predominantly accumulated in the food web (St. Louis *et al.*, 1994). The dominant source of Hg for remote lakes is apparently through direct precipitation or runoff. It is now well established that the mercury concentration in runoff water is strongly correlated with organic matter (Mierle and Ingram, 1991). The same is assumed for methylmercury compounds. But little is known about their partitioning in the presence of humic substances.

The capability of humic material to bind metal ions is commonly called "complexing" or "binding capacity" and has been measured by various methods, including ion-sensitive electrodes (Giesy *et al.*, 1978), chromatographic (Steinberg, 1980), voltametric (Powell and Town, 1991), ultrafiltration (Chakrabarti *et al.*, 1993) and dialysis techniques (Truitt and Weber, 1981; Van Loon *et al.*, 1992). An advantage offered by dialysis is the ability to make in situ measurements of natural metal ion abundance. Furthermore, it avoids the addition of complexing agents or electrolytes and leaves chemical equilibria as far as possible undisturbed.

Laboratory experiments with lake humic and fulvic acids were carried out to investigate their binding capacity for CH_3Hg^+ and to determine the stability constants and size distribution of CH_3Hg^+ - humic matter complexes. The individual size fractions of humic substances were separated together with the bound CH_3Hg^+ by membrane dialysis with cellulose ester membranes. The smallest molecular weight cut off used was 500. It was assumed that only free methylmercury species would permeate this membrane, while those bound to humic material would not. The effect of pH on binding of CH_3Hg^+ to humic acid was also examined.

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2. Material and Methods

Humic and fulvic acids were isolated from Fawn Lake by adsorption on XAD–8 resins (Thurman and Malcolm, 1981). They were redissolved in 1 mM KNO_3 at a level of 10 mg HA/l and a pH of 6.5. The humic solutions were spiked with CH_3HgCl at concentrations from 0.5 to 100 ng/l. Cellulose ester dialysis membrane tubings (MWCO's of 500, 2000 and 10 000, Spectrum) were filled with 1 mM KNO_3 and put into the humic acid solutions. After equilibration for 24 h, the tubing was opened and the inside solution as well as the outside humic acid solution was analyzed for CH_3Hg^+ after distillation and aqueous phase ethylation followed by preconcentration of volatile methylethylmercury on Tenax with subsequent GC-CVAFS determination (see e.g. Bloom and Fitzgerald, 1988).

3. Results and Discussion

The time needed to reach the equilibrium between the outside feeding solution, spiked with methylmercury chloride, and the receiving solution inside the membrane tubing was investigated in experiments with distilled water. The time series is shown in Figure 1.

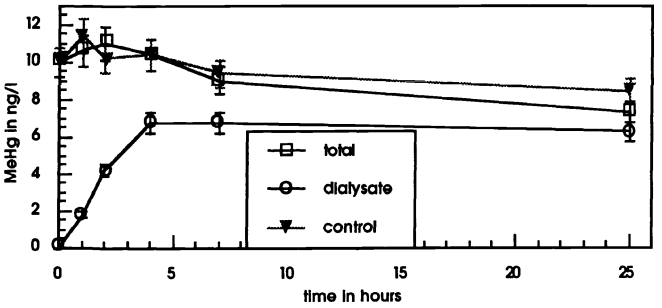

Fig. 1. Equilibrium dialysis of CH_3HgCl (10 ng/l) in 1 mM KNO_3 through a 500 MWCO cellulose ester membrane. The control shows the stability of a 10 ng/l CH_3HgCl solution in 1 mM KNO_3 over 24 h.

Within 24 hours dialyzing time, equilibrium is established. The maximum concentration inside the membrane was reached after 4 h. The experiments with 1 mM KNO_3 showed recoveries of only 80 %, probably due to losses to the container walls. However, with humic material present, the recovery was usually between 90 and 105 %.

Figure 2 illustrates a series of dialyzing experiments with different concentrations of methylmercury chloride. In our experiments, we assumed that only free methylmercury species and not that complexed by humic material, is able to permeate the 500 MWCO membrane. The curve indicates a saturation of humic acids with CH_3Hg^+ at higher levels. The amount of free, uncomplexed methylmercury species, probably CH_3HgCl or CH_3HgOH, decreased with lower concentrations of total methylmercury compounds.

By applying the Scatchard method of analysis to these data (Scatchard, 1949), two different binding sites on Fawn Lake humic acid were identified. The calculated conditional stability constants were 1.3×10^{12} and 5.0×10^{10} with binding capacities of 0.2 and 1.2 ng

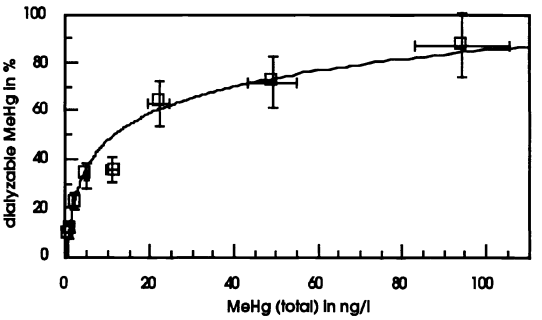

Fig. 2. Dialyzable CH_3Hg^+ as a function of methylmercury chloride concentration. Experiments were performed in 10 mg/l humic acid with 500 MWCO cellulose ester membranes at pH 6.5.

CH_3Hg^+ per mg humic acid, respectively. These stability constants are very high compared to values found for Cu^{2+} or Pb^{2+} (Guy and Chakrabarti, 1976), and fall in the range calculated for Hg^{2+} (Lövgren and Sjöberg, 1989). Comparison with literature data (Rabenstein, 1978) shows that only sulfur ligands exhibit log K_L-values greater than 10. It is therefore assumed that CH_3Hg^+ is bound to sulfidic binding sites. This is in agreement with earlier findings for sediment samples (Hintelmann and Wilken, 1994).

The calculated binding capacity of the stronger binding sites on Fawn Lake humic acid of 0.2 ng CH_3Hg^+ per mg HA is lower than expected, but still high enough to complex all of the dissolved methylmercury cations present under typical environmental concentrations. However, one has to bear into mind that the constants obtained are conditional constants for the pH and ionic strength conditions employed. They might differ from actual constants, but nevertheless show the general influence of humic acids on CH_3Hg^+ binding.

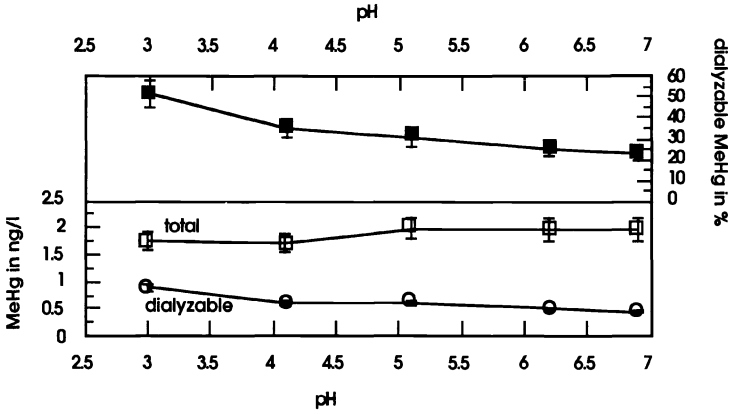

Fig. 3. Dialyzable CH_3Hg^+ (2ng/l) as a function of pH in the presence of 10 mg/l humic acid.

The effect of pH on the binding of methylmercury compounds to humic acids is shown in Figure 3. The amount of free unbound CH_3Hg^+ increased at lower pH's. This kind of conservative behavior is usually observed with other heavy metals. This would imply, that methylmercury bound to sediment humic material can be released into the aqueous phase upon acidification and would be readily available for bioaccumulation processes observed

in acid stressed lakes (Winfrey and Rudd, 1990; Wright *et al.*, 1993).

The distribution of methylmercury species with respect to different size fractions of the humic material is illustrated in Figure 4. For comparison, the well characterized Suwannee river fulvic acid is included. Surprisingly, most of the CH_3Hg^+ did not permeate the 10 000 MWCO membrane, although the average molecular weight of fulvic acids is supposed to be smaller than that. UV determination of the dialyzed solution was carried out to determine the amount of humic material which passed the individual membranes. A similar distribution pattern as shown in Figure 4 was also found for the dialysis of the pure humic material. This would suggest, that CH_3Hg^+ binding is evenly distributed over the whole molecular weight range and not specific to a particular size class.

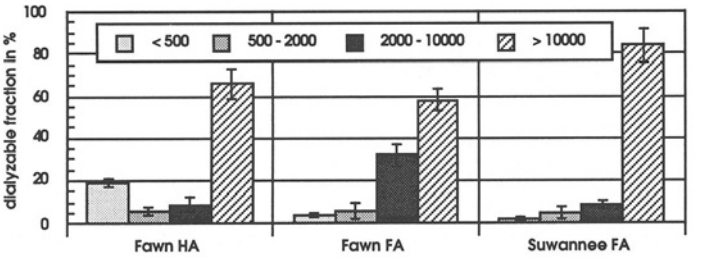

Fig. 4. Fractions of CH_3Hg^+ bound to different size fractions of humic material separated by various cellulose ester membranes. Experiments were carried out at pH 6.5 with 10 mg/l humic material and 2ng/l CH_3Hg^+.

Acknowledgments

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DISTRIBUTION OF MERCURY IN THE SEDIMENTS OF ONONDAGA LAKE, N.Y.

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Abstract. Sediment cores and surface grab samples were collected throughout Onondaga Lake, New York, to determine the concentrations and distribution of mercury (Hg) in the sediments. Horizontal distribution patterns show the effect of sediment focusing and localized sources, with generally low Hg concentrations in the littoral zone sediments, higher concentrations in the profundal sediments, and highest concentrations near known sources of Hg Several cores were dated and reflect historical loading patterns, with low-level increases in Hg concentration starting in the early 1800s and a large increase in 1947 and decrease in 1970 related to the local chloralkali industry These cores indicate that Hg has low mobility in profundal sediments and that the contaminated sediments are effectively being buried

1. Introduction

Onondaga Lake is a hypereutrophic, marl lake located in Syracuse, New York, and has received wastewaters including sewage, PCBs, calcium chloride, mercury (Hg), and other heavy metals. As part of a remedial investigation, 77 sediment cores and 114 surface grab samples were collected and analyzed to determine the concentrations of Hg in the sediments. The purpose of this paper is to summarize and interpret the distribution of Hg with respect to sources and transport processes.

2. Materials and Methods

Sediment cores were collected with a 3-in.-diameter gravity corer lowered at 1 ft/s. Seventy-three cores were sectioned every 30 cm to a depth of 90 cm or more. Four cores about 2.5–3 m long were collected for stratigraphic analysis and sectioned at 2.5, 5, or 10 cm intervals. A stainless-steel 0.06-m^2 van Veen grab sampler was used to collect the 0-2 cm surface sediments. Samples were dried and analyzed for Hg using CVAFS, and lead by GFAAS. Pollen analyses were performed in accordance with standard methods. ^{137}Cs analyses were performed on dried samples using direct gamma spectrometry. ^{14}C analyses were performed on the organic carbon fraction of the sediments by AMS with $^{13}C/^{12}C$ correction.

3. Results and Discussion

Two of the stratigraphic sediment cores were from the deepest regions of the north and south basins, and two were from shallow areas near Ninemile Creek and Bloody Brook. These cores were dated using the following time markers: automobile lead peak and Hg decrease - 1970; ^{137}Cs peak and appearance - 1963 and 1955; Hg increase - 1947; pollen changes - 1915, 1822, and 1786.

Figure 1 shows Hg concentration profiles from the south and north basins, where the sediment accumulation rate is about 1 cm/year. Hg concentrations rose in the 1800s from a background of 0.1 mg/kg to about 0.6 to 2.2mg/kg by the early 1900s. A similar Hg increase around 1835 was observed in a core from Lake Erie and was attributed to early industrialization (Walters *et al.*, 1974). A sharp increase in Hg concentration is observed at a depth of 45 cm in both cores and corresponds to 1947 when AlliedSignal Inc. started a Hg-cell chloralkali plant. In 1953, a second plant was built, which doubled production. It was estimated (U.S. EPA, 1973) that Hg discharges for the periods 1946–1953 and 1953–1970, were about 5 and 10 kg/day, respectively. In 1970, Hg discharge was decreased to 0.45 kg/day, and is recorded in both cores at a depth of about 22 cm,

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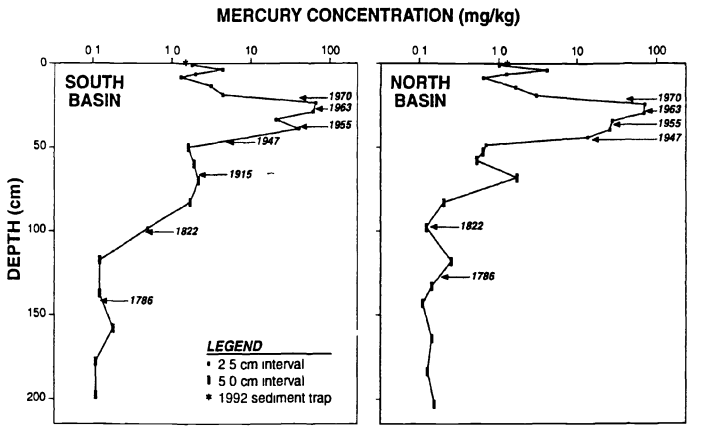

Figure 1 Concentration profiles of mercury in Onondaga Lake

where the concentrations drop from about 70 to 4 mg/kg across a 2.5-cm-thick interval. The sharp concentration gradients show that Hg is not significantly mobile. In 1974 AlliedSignal Inc. was issued a permit to discharge 0.63 kg/day of Hg. In 1977, one chloralkali plant was closed and Hg discharge from the second plant was reduced to 0.013 kg/day. In 1979, this plant was sold to LCP. Assuming a constant solids flux to the sediments since 1970, the lowest concentration at 10 cm corresponds to the early 1980s, shortly after AlliedSignal ceased Hg-cell chloralkali production. The peak at 2.5-5 cm corresponds to about 1988, the last year of Hg-cell chloralkali production. The top sample (0-2.5 cm) from both cores show concentrations of 1 to 1.8 mg/kg, which is consistent with average Hg concentrations in sediment trap material collected in the hypolimnion of the north (1.2 mg/kg) and south (1.5 mg/kg) basins in 1992. In 1988, Rowell (1992) collected 1.5-inch diameter cores from the north and south basins. Mercury profiles were similar to Figure 1, except the abrupt concentration changes were at shallower depths in the 1988 cores. The differences in profiles can be attributed to core compaction and sediment burial.

The sediment core collected near Bloody Brook (not diagramed) showed uniformly low Hg concentrations (0.15 ± 0.04 mg/kg, n=21), and no vertical pattern that could be related to historical sources. Preliminary ^{14}C dating suggests that the sediment accumulation rate is about 0.2 cm/year. The core from near Ninemile Creek (not diagrammed) had low Hg concentrations (<2 mg/kg) to a depth of 100 cm (≈ 1970) and a high average concentration (28 mg/kg) between 100 and 280 cm, indicating a sediment accumulation rate of about 5 cm/year.

The horizontal distribution of Hg was determined for depth intervals of 0-30, 30-60, 60-90, and 90-120 cm and is shown in Figure 2. Distributions in Figure 2 show low Hg concentrations (<0.5 mg/kg) in the littoral zone along the north and east shores. The profundal sediments show higher concentrations extending to a depth of less than 90 cm. The highest concentrations, which extend to depths of over 120 cm, occur near Ninemile Creek and East Flume, both of which received wastewater from chloralkali plants. In 1972 the U.S.EPA (1973), and in 1986 and 1987 the New York Department of Environmental Conservation (NYDEC, 1989) each collected 43 cores. Horizontal Hg distributions in both studies were similar to Figure 2, with highest Hg to greatest depth near sources, and focusing to profundal sediments.

Figure 2 Mercury concentrations in sediment core samples taken at four different depths

The Hg distribution in the 0-2 cm interval is shown in Figure 3. Concentrations are uniform (approximately 2.5–3 mg/kg) in the profundal region and are generally low (0.2–2 mg/kg) in the littoral zone. The high concentrations near East Flume may be due to current sources, or exposure of older deposits. Data from 1992 indicate that the largest current sources of Hg to the lake are Ninemile Creek (7.1 kg/year), the sewage treatment plant, Metro (3.8 kg/year), and Onondaga Creek (1.8 kg/year). Harbor Brook and East Flume are currently negligible sources of Hg (0.2 kg/year each). High concentrations were not observed near Ninemile Creek, which is likely due to dilution of the Hg by the high sedimentation rate.

The disparity in the concentrations in the 0–2.5 cm interval from the sediment cores (1–1.8 mg/kg), and the 0–2 cm interval from the surface grab samples (2.5-2.9 mg/kg) is probably due to draining the water from the van Veen sampler to expose the sediment. The surface sediment probably was also dewatered causing it to compact, so when a 2-cm interval was then collected, it may have included deeper strata that have higher Hg concentrations (4–4.4 mg/kg).

The accumulation (g/m^2) of anthropogenic Hg (concentrations >0.1 mg/kg) in the sediments is shown in Figure 4. This figure integrates the effects of concentration and sediment accumulation rates and shows that 1) the highest accumulations occur near known Hg sources, 2) accumulation in the littoral zone is generally near background, and 3) sediment focusing has contributed to Hg accumulation in the profundal sediments.

3.3. Mass of Mercury

A preliminary estimate of the total mass of anthropogenic Hg in the sediments was made by assigning the median accumulation between the contours in Figure 4 to the areas between contours. The estimated mass of anthropogenic Hg, about 40,000 kg, is an underestimate because in some cores pre-anthropogenic sediment strata were not reached (as shown in Figure 2(d)), and sediments dredged near Ninemile Creek were disposed on land. In 1972, EPA collected sediment cores and estimated the total mass of Hg to be about 13,000 kg. They reported that this value seemed low with respect to the estimated discharge by the chloralkali plants (75,000 kg), and attributed it primarily to the coring method, dredging losses, and errors in the estimate of Hg discharged (U.S. EPA, 1973).

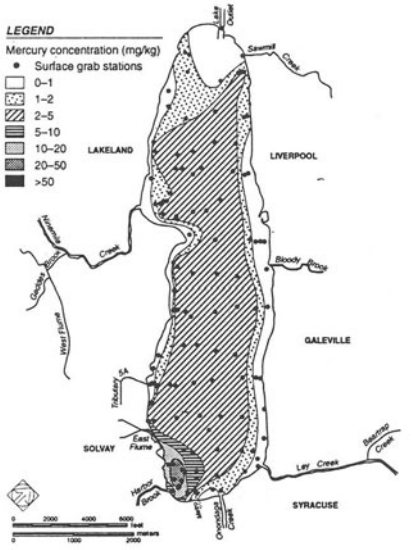

Figure 3 Mercury concentrations in surface sediment, 0–2 cm depth

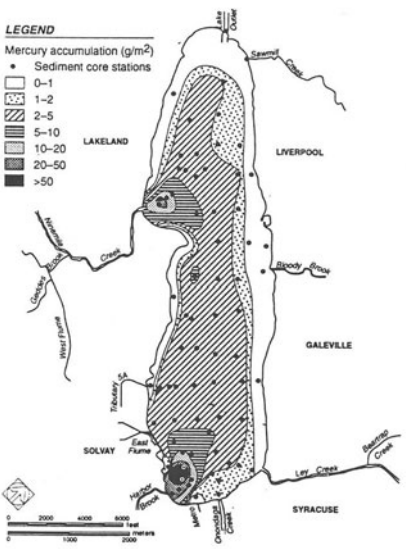

Figure 4 Total anthropogenic mercury accumulation

4. Conclusions

The data show that the distribution of Hg in the sediments is controlled by localized sources and sediment focusing. The vertical profile of Hg concentration shows the effect of industrialization in the 1800s and more recently by local mercury-cell chloralkali plants. These cores also show low mobility of Hg in the sediments, as well as recovery of surface sediments towards pre-chloralkali plant concentrations.

Acknowledgments

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TEMPORAL VARIATION OF MERCURY IN VEGETATION

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Abstract. Temporal changes in the Hg content of balsam fir needles (*Abies balsamea*) and white spruce needles (*Picea glauca*) were monitored at a control site over two growing seasons Results indicated a significant increase in the Hg content of needles of both species over the course of a growing season and from one year to the next The Hg content of new foliage more than doubled within each growing season, and was 5-10 ng g^{-1} higher in the 1990 growing season than in the previous year These results indicate that temporal variation is a potential source of error when mapping the spatial variation of Hg concentrations in vegetation To minimize this source of error, field surveys should be completed as quickly as possible (i e , within two or three weeks)

1. Introduction

Mapping the spatial variation of Hg concentrations in vegetation is a surveying technique used for determining the radius of influence of Hg released from industrial sources and in prospecting for mineral deposits (Siegel *et al.*, 1985; Shaw and Panigrahi, 1986; Kovalevsky, 1986). Consistency in sample collection is essential in order to properly interpret changes in Hg concentration between sites, as Hg concentrations within a plant vary significantly (>10%) with tissue age and type (Barakso and Tarnocai, 1970; Siegel *et al.*, 1985; Kovalevsky, 1986; Shaw and Panigrahi, 1986; Rasmussen *et al.*, 1991; Rasmussen, 1994). Observations of seasonal and annual changes in the trace element content of various plant tissues indicate that temporal variation is another potential source of error that must be considered when conducting a vegetation survey (Dunn, 1991).

The purpose of this study was to monitor temporal changes in the Hg content of vegetation by sampling the foliage of two trees at a control site over the course of a field study (1989-1990) in which the spatial variation of Hg was assessed in more than two dozen plant species over an area of approximately 150 km^2 (Rasmussen *et al.*, 1991; Rasmussen, 1994).

2. Materials and Methods

The study area is located in the southern Canadian Shield, west of the town of Huntsville, Ontario, Canada (long. 79°20' lat. 45°20'). Details of the study area and analytical method have been published previously (Rasmussen *et al.*, 1991; Rasmussen, 1994).

A balsam fir tree (*Abies balsamea*) and a white spruce tree (*Picea glauca*) located 2 m apart were sampled six times over a 23 week period from May to October 1990. Results of sampling the same two trees during the previous growing season (six times from June to August 1989) have been reported previously (Rasmussen *et al.*, 1991). Samples were

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collected from boughs at waist height using unpowdered vinyl gloves and stainless steel clippers. Samples were triple-bagged in the field using Zip-Loc polyethylene bags, and stored frozen until time of preparation and analysis.

The samples were rinsed with distilled deionized water and oven-dried for 24 hr at 60°C. Analysis consisted of a 6-hr hot digestion using HNO_3 and H_2SO_4 in a 1:4 ratio, followed by dilution, $SnCl_2$ reduction and cold-vapor AAS detection. The analytical work was performed in a clean laboratory facility outfitted with gold air filters to adsorb airborne contaminant Hg. The detection limit, defined as three times the standard deviation of the blank, was 1.3 ng g^{-1} calculated for a dry sample weight of 0.100 g. Accuracy and precision were monitored using NBS#1575 Pine Standard (certified value $0.15\pm.05$ μg g^{-1}) and NBS#1572 Citrus Standard (certified value $0.08\pm.02$ μg g^{-1}). Results were consistently within the certified range and reproducibility was within 5% RSD based on 13 duplicate analyses.

3. Results and Discussion

An increase in the Hg content of needles from both species occurred over the 23 week sampling period in 1990 as shown in Fig. 1. Needles produced in the 1990 growing season are labelled "1st year growth", and needles produced in the previous two years (1989 and 1988) are labelled "2nd year growth" and "3rd year growth" respectively (Fig. 1). Temporal variation was most pronounced in new growth: from July to October, the Hg content of 1st year needles approximately doubled in both species (Fig. 1). Temporal variation was significant compared to variation in the Hg content of needles collected from different parts of the same tree on the same day, which was 10% or less (Rasmussen *et al.*, 1991).

Wyttenbach and Tobler (1988) observed similar increases in the Hg content of 1st and 2nd year needles of Norway spruce (*Picea abies (L.) Karst)* over the course of the growing season. Such evidence of temporal variation underscores the importance of restricting sampling to short time periods (Dunn, 1991). To minimize this source of error, Dunn (1991) recommended that vegetation surveys be completed within two to three weeks. The data reported in this study also indicate that it is best to conduct surveys in the late summer or early fall to take advantage of the higher Hg concentrations in samples relative to the analytical detection limit.

A comparison of 1st, 2nd and 3rd year needles (Fig. 1) indicates that the Hg content of the older tissue increases by about 5-10 ng g^{-1} yr^{-1}. Such variations with tissue age, caused by Hg accumulation within the plant, have been reported previously (Rasmussen *et al.*, 1991; Barghigiani *et al.*; 1987; Barakso and Tarnocai, 1970) and illustrate the importance of consistency when collecting living tissue. Based on the observation that older tissue contains higher Hg concentrations, Barakso and Tarnocai (1970) recommended the use of 2nd or 3rd year growth for surveying conifers.

A comparison of the 1989 data (Rasmussen *et al.*, 1991) and the 1990 data (Fig. 1) indicates significant annual variation. For example, the Hg content of 2nd year growth sampled in August 1990 (28 ng g^{-1} in spruce, 26 ng g^{-1} in balsam fir) was double that of

2nd year growth sampled from the same trees in August 1989 (12 ng g^{-1} in spruce, 15 ng g^{-1} in balsam fir). A similar increase from 1989 to 1990 was observed in leaves of deciduous species growing in the same study area (Rasmussen, 1993). For example, in 1989 the Hg content of sugar maple foliage (*Acer saccharum* Marsh) ranged from 6 to 25 ng g^{-1} (median 9 ng g^{-1}), sampled at 95 sites over an area of 150 km^2 (Rasmussen *et al.*, 1991). In 1990, however, Hg content in foliage of the same species ranged from 17 to 41 ng g^{-1} (median 24 ng g^{-1}), sampled at 18 sites across the same watershed (Rasmussen, 1994). The increase from 1989 to 1990 could reflect annual variation in factors affecting growth rate, such as temperature and rainfall, or it could reflect annual variation in the amount of Hg available to the trees in the study area.

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Field assistance by Andrew Devaney and use of the clean lab facilities at the Dorset Research Centre, Ontario Ministry of the Environment and Energy (MOEE) were greatly appreciated. This study formed part of the author's PhD thesis which was jointly funded by the MOEE, an NSERC Strategic Grant (P. Welbourn P.I.) and two Ontario Graduate Scholarships.

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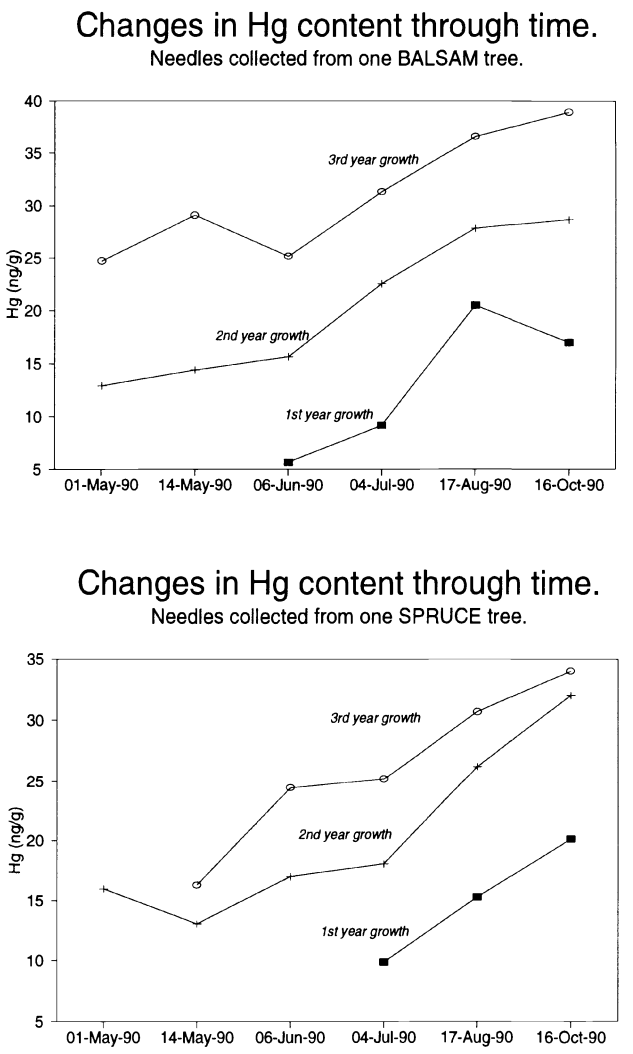

Fig. 1. Temporal variation in Hg concentration (dry wt.) of 1st, 2nd and 3rd year needles of a balsam fir tree (top) and a spruce tree (bottom) sampled in 1990. Variation between needles was 4.3%RSD for balsam (22 duplicate pairs) and 6.4% RSD for spruce (11 duplicate pairs). Variation between different boughs sampled on the same day was within 10% RSD.

MERCURY DISTRIBUTION IN HUMUS AND SURFICIAL SEDIMENTS, FLIN FLON, MANITOBA, CANADA

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Geological Survey of Canada Contribution No. 25594

Abstract. Regional humus and surficial sediments were collected in the vicinity of a base metal smelter in Flin Flon. Results of total mercury (Hg) analyses indicate that enrichment in humus is related to emissions from the smelter stack up to a distance of 40 km. In the immediate vicinity of the point source, total Hg values reach as much as 250 times the regional background (400 ppb). This enrichment is not reflected in the underlying surficial sediments. The Hg distribution pattern is similar for other known metal pollutants emitted from the smelter.

1. Introduction

Humus and surficial sediment samples were collected in the Flin Flon-Snow Lake area, northern Manitoba and Saskatchewan, as part of a regional surficial geological mapping and drift prospecting project undertaken by the Geological Survey of Canada. The Flin Flon area is of particular interest geologically and environmentally since it is the site of a base metal mining and smelting complex. The smelter in Flin Flon produces, on site, zinc, copper, and cadmium from ore extracted from local mines. Particulate emission tests in the smelter stack have indicated that various amounts of Zn, Pb, Fe, Cu, Cd and As are discharged into the environment.

Numerous studies have demonstrated that smelters act as point sources of airborne pollutants that are concentrated in soils and vegetation (Freedman and Hutchinson, 1980a,b; Hutchinson and Whitby, 1974, 1976; Lagerwerff et al., 1972; Little and Martin, 1972). In the Flin Flon area, known pollutants emitted from the smelter have been found in increasing concentrations toward the smelter both in forest soils (Hogan and Wotton, 1984) and in peat (Zoltai, 1988). The emitted metals are deposited as dustfall and rainfall, mainly in the form of metal particulate, metal oxide and probably metal sulfates (Franzin et al.; 1979). Mercury, which is a volatile metal, is mostly emitted as very fine particles of its oxide.

Mercury has never been considered in regard to smelter emissions in the Flin Flon area. The purpose of this paper is to evaluate the distribution of total mercury in the humus and in the glacially derived sediments of the region.

2. Regional setting

The study area straddles the Paleozoic/Precambrian contact near the Manitoba-Saskatchewan border (Figure 1). The northern half is underlain by rocks of the Flin Flon-Snow Lake greenstone belts and their high grade metamorphic equivalent in the Canadian Shield; the southern half by flat-bedded Paleozoic dolostones of the Manitoba Plain. The bedrock is covered by discontinuous Quaternary and Holocene deposits, including till, glaciolacustrine sediments and peatlands. The dominant wind direction recorded in Flin Flon is towards the southeast and southwest, with strong components towards the north-northwest and south (Environ. Canada, 1990). The area is forested by a mixed coniferous deciduous boreal community comprised of jack pine, black spruce, white spruce, balsam fir, trembling aspen and balsam poplar (Hogan and Wotton, 1984).

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Fig.1. Study area showing location of transects and sections.

3. Methods

Humus and till samples were collected in the study area during the summers of 1992-93. The well decomposed, dark organic part of the uppermost soil horizon (A1) was preferentially sampled for humus. At some sites, however, both partially decomposed forest litter and mineral soil may constitute part of the humus sample since organic soil horizons are thin in areas of extensive logging or forest fires. For this study, approximately 50 to 100 g humus was collected from directly over or in an area immediately adjacent to a till sample. Till was collected from hand dug pits and exposed sections at a spacing of 1 to 5 km depending on access. Pits were dug to bedrock or 1 m maximum depth and, in nearly all cases, a 3 kg sample was collected below the upper B soil horizon in order to minimize local weathering effects.

Humus samples were air-dried and sieved to <35-mesh (0.425 mm); the clay-sized fraction (<0.002 mm) of till was separated by centrifuge and decantation. Geochemical analyses for a number of major and trace elements were conducted on these fractions using inductively coupled plasma atomic emission spectrometry, following an aqua regia digestion. Mercury was analyzed by cold vapour atomic absorption spectrometry, following aqua regia digestion. Loss on ignition (LOI) was used to assess the organic content. Analyses of duplicate samples and laboratory standards were used to monitor analytical accuracy and precision.

4. Results and discussion

On a regional basis, results show that Hg concentrations in the humus are consistently higher than those in the till. Statistical compilation gives a median value of 266 ppb in the humus and 50 in the clay size fraction of till. In humus, anomalous samples are as

much as 250x higher than background values (400 ppb); in till, only 7x higher (60 ppb). Anomalously high Hg concentrations in humus are found in the vicinity of the smelter, with values decreasing towards background levels at distances greater than 35 km. From our study, this general pattern is also reflected in the distribution of other emitted metals such as Zn, Pb, Cu, As, and Cd.

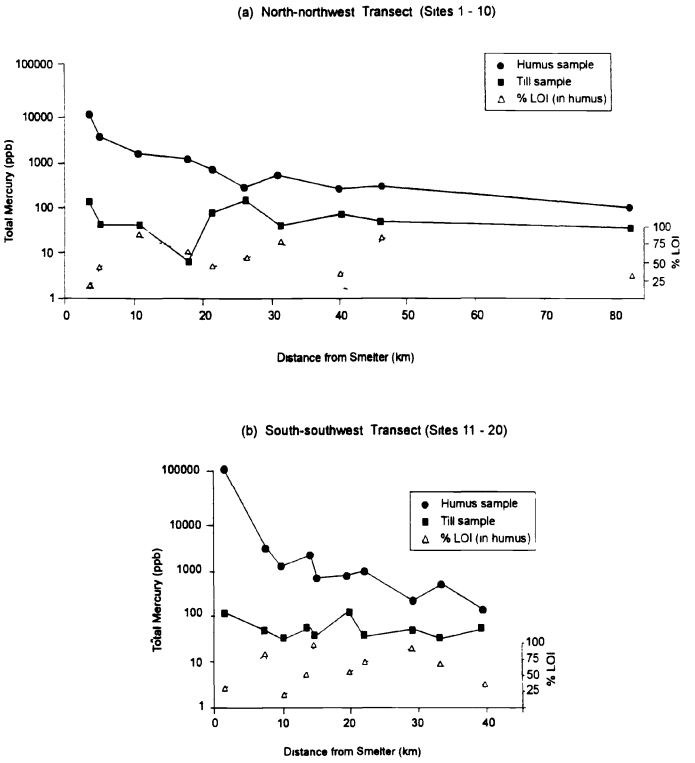

Fig.2. Total Hg concentrations in humus and till along transects. Total Hg is plotted on a log scale. Organic content in humus (% LOI) is shown with a dashed line.

The regional distribution in total Hg concentration is illustrated in two transects: one extending approximately 80 km north-northwest, the other extending 40 km south-southwest from the smelter stack (Figure 2). In both cases, total Hg concentrations in humus exceed those in till for all sites. Values in humus decrease markedly with distance from the smelter while Hg concentration in till remains fairly constant. Although the organic content of the humus, as indicated by %LOI, varies in the samples taken along the transects, the Hg concentrations appear unrelated to these variations. This suggests that the distribution of Hg in humus near Flin Flon is related to contamination associated with the smelting activities. In the immediate area of the smelter, the low organic content of the humus suggests that Hg concentrations may be linked more to fallout of particulate matter than incorporation into organic complexes.

Two till sections within the area were also sampled in detail in order to examine vertical variations in trace element concentrations through humus and the underlying till. Section A (Table I) consists of homogeneous, massive, sandy diamicton, located on

Precambrian terrane 8.75 km south of the smelter. Section B is located 40 km southeast of Flin Flon and forms a vertical exposure on the Paleozoic bedrock. It consists of calcareous massive sandy-silty diamicton. Results show an enrichment in humus for both sections although concentrations are much higher in section A, exceeding those in till by more than a factor of 10. In section B, the value in humus is more consistent with the regional background. Although Hg has a tendency for adsorption by organic matter and secondary hydrous oxides within humus, the magnitude of the enrichment in Section A must reflect deposition of smelter emissions. Enhanced Hg concentrations in the upper portion of the mineral soil in both sections suggest migration of Hg from the surface layer to a depth of 40 cm approximately.

TABLE I

Vertical distribution of total Hg in two soil profiles

Section A		Section B	
Depth (cm)	Hg (ppb)	Depth (cm)	Hg (ppb)
Humus	2800	Humus	260
5	270	15	70
15	190	30	90
25	130	80	50
35	100	130	50
45	60	180	40
55	50	230	50
65	70	280	50
75	50	320	50
85	50	380	50
95	70	430	50
		480	40
		530	50

5. Conclusion

In the vicinity of Flin Flon, the enrichment of mercury in humus is clearly related to emissions from the smelter. This enrichment is not reflected in the underlying glacially derived sediments, as seen both in the transects and in the soil profiles. Hg concentrations appear unrelated to variations in organic content of the humus, as indicated by %LOI.

Acknowledgments

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THE IMPORTANCE OF GEOLOGICAL CONTROLS ON THE NATURAL DISTRIBUTION OF MERCURY IN LAKE AND STREAM SEDIMENTS ACROSS CANADA

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Abstract The Geological Survey of Canada (GSC) has surveyed a significant portion of Canada using systematic stream and lake surveys under the National Geochemical Reconnaissance (NGR) program Total mercury (Hg) data, available for most of the sites, reveal significant natural variation Much of the observed variation in Hg concentration can be directly related to the composition of the bedrock, regolith and glacial deposits in the surrounding watershed Some of the highest Hg values within the sediments of Ontario lakes occur southwest of Thunder Bay in an area underlain by shales known to be naturally enriched in Hg and other trace metals

1. Introduction

Since 1973, a significant part of Canada has been covered by systematic stream and lake surveys under the National Geochemical Reconnaissance (NGR) program designed to establish and maintain a nationally consistent geochemical database To date (1994), more than 200 surveys have been completed to NGR standards, representing over 180,000 sites, covering 2 2 million km^2 throughout Canada (Figure 1) A detailed description of NGR survey methodology is given by Friske and Hornbrook (1991) Data for up to 35 elements are available for many of the sediment samples The purpose of this paper is to draw attention to the voluminous amount of NGR data available on the natural distribution of Hg and other elements and to illustrate the relevance of these data to environmental issues

2. Sample collection, preparation and analytical methods

All sample collection, preparation and analyses follow the stringent NGR protocols (Friske and Hornbrook, 1991) The organic-rich lake sediments (gyttja) were generally collected from >30 cm depth in the sediment column to exclude the surficial sediment which is physiochemically active and potentially anthropogenically impacted Stream sediments were collected from the active part of first and second order streams Both media were air dried, and a <63 μm fraction prepared Mercury was determined by the Hatch and Ott (1968) cold vapour atomic absorption technique, with some modifications (Jonasson *et al*, 1973) Quality control of all analytical data was maintained by monitoring control reference standards and blind duplicates, inserted at a frequency of 5%

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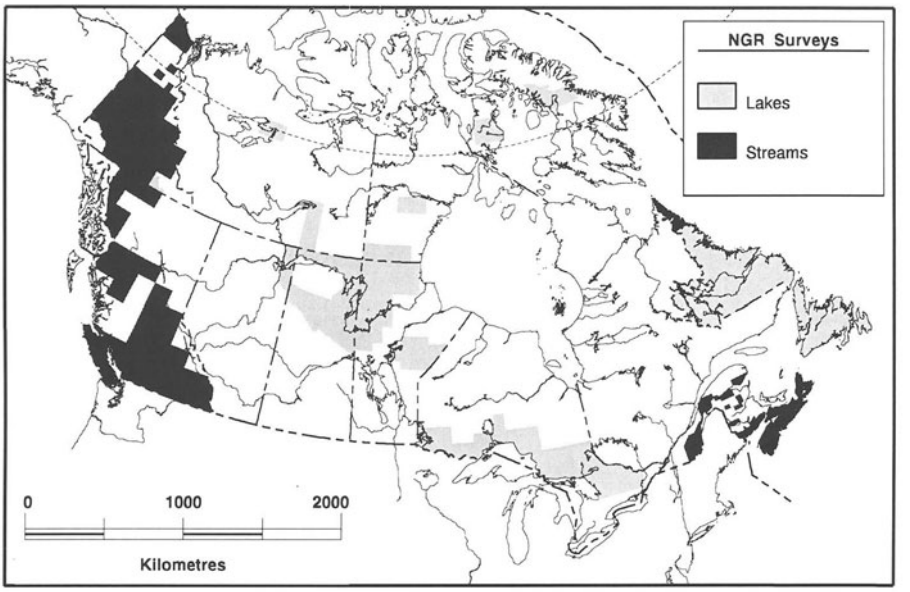

Fig. 1. National Geochemical Reconnaissance (NGR) stream and lake survey coverage (1973 to 1994) in Canada

3. Results and discussion

Mercury, like other elements, is preferentially concentrated in certain rock types through igneous, metamorphic and sedimentary processes. In Cannon's (1978), tabulation of the concentration of 21 elements in 10 natural materials, average Hg concentrations vary from 40 to 50 ppb in limestones and sandstones up to 500 ppb in black shales.

There are many examples in the literature illustrating the effects of changing bedrock chemistry on the composition of related lake sediments (c.f., Hornbrook and Garrett, 1976; Jonasson, 1976; Cameron and Ballantyne, 1977; Maurice, 1977, Coker and Shilts, 1979; Friske, 1985; Johnson *et al.*, 1986; Kerr and Davenport, 1990; Fortescue and Vida 1990; Garrett *et al.*, 1990). Table I summarizes the distribution of approximately 100,000 analyses for Hg in stream and lake sediments. Assuming that the 5th and 95th percentiles are reasonable estimates of the range of background variation, the contrast between the lower and upper limits of background is almost 9 times for lake sediments (N=69,884; 5th=20 ppb, 95th=175 ppb); and 23 times for stream sediments (N=26,124; 5th=10 ppb, 95th=230 ppb). Table I shows how geological factors affect the distribution of Hg in drainage basins in Ontario. Using a lower value of 5 ppb (5th percentile for marble) and an upper value of 305 ppb (95th percentile for shale), 'normal' background values

within the survey area range from 5 to 305 ppb depending on the local bedrock geology (a range of 61 times the lower background value) This illustrates the importance of determining 'local background' values for an area For example, a sample with a concentration of 200 ppb Hg coming from a lake underlain by marble is highly enriched (anomalous), whereas the same concentration from a lake over shales is well within the range of normal background variation

TABLE I
Hg (ppb) summary statistics for lake and stream sediment data from the NGR database and for lake sediments for specific rock types within Ontario

	Total Dataset		Ontario Lake Sediments			
				Rock Type		
	Lakes	Streams	Total	Shale	Marble	Diabase
Number of Values	69,884	26,124	13,813	38	38	277
Mean	74	72	119 4	169 2	54 7	190 4
Std Deviation	99	114	198 3	70 5	36 4	366
5th Percentile	**20**	10	**35**	**90**	**5***	**45**
10th Percentile	30	15	47	90	19	60
25th Percentile	40	25	70	110	28	97
50th Percentile	**60**	**40**	**110**	**165**	**45**	**140**
75th Percentile	90	80	150	192 5	80	199
90th Percentile	140	151	195	291	110	251
95th Percentile	**175**	**230**	**222**	**305**	**132**	**295**

* Detection limit for Hg is 10 0 ppb Values less than 10 0 set to 5 0 for calculations

Figure 2 is a 'smoothed' contour plot of Hg data for sediments from Ontario lakes The area of elevated Hg southwest of Thunder Bay coincides with shales known to be enriched in Hg (Coker and Shilts, 1979, Friske, 1985) The discontinuous band of elevated Hg, extending east from Sault Ste Marie and then northeast to New Liskeard, is associated with sporadic exposures of diabase sills and dykes that are relatively enriched in Hg Some of the lowest Hg levels encountered in Ontario lake sediments occur west of Ottawa in areas underlain by marble It is particularly noteworthy that some of the highest Hg concentrations occur in relatively isolated areas, while some of the lowest values are encountered in southeastern Ontario, the more highly populated and industrialised region

4. Summary

Anthropogenic inputs of Hg and other trace elements into the environment are superimposed on a highly variable natural geochemical background Variations in the natural abundance levels in bedrock vary widely, and can range over severals orders of

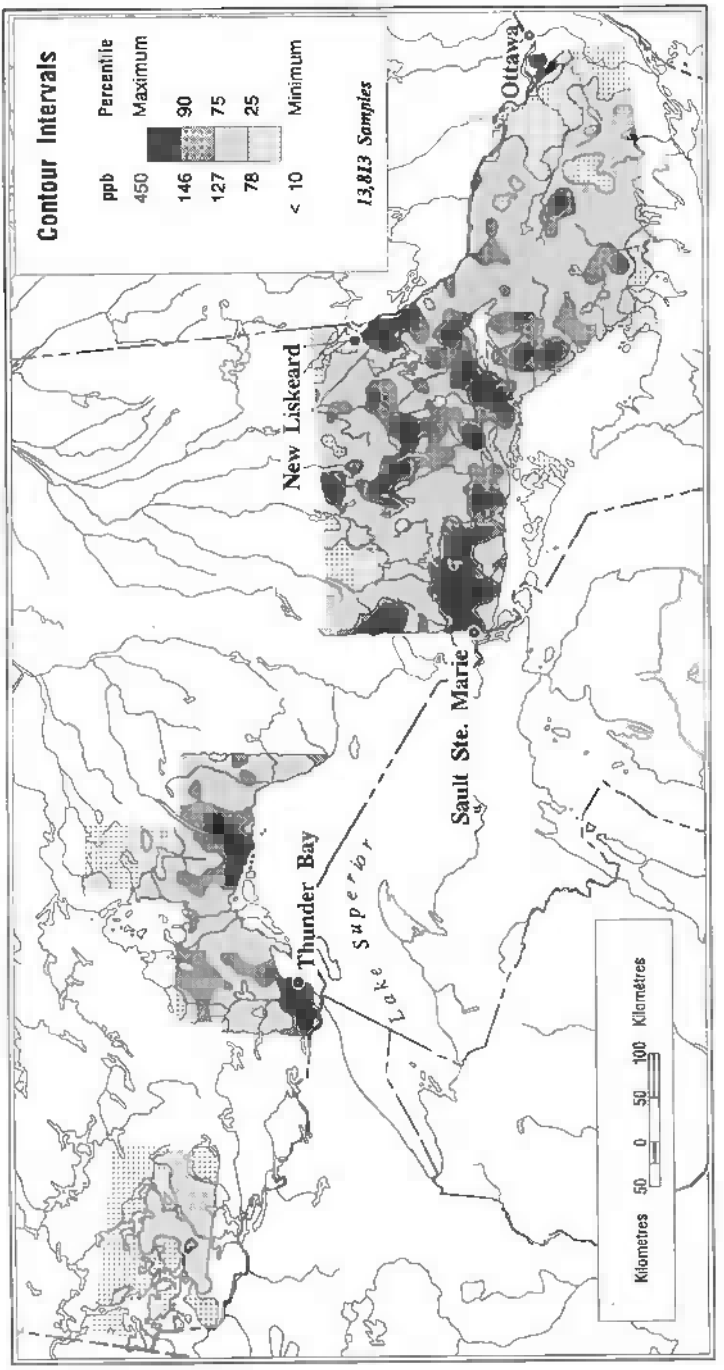

Fig 2 Regional distribution of Hg in Ontario lake sediments

magnitude. These natural geochemical variations are reflected in the chemical composition of the waters, soils, drainage and glacial sediments associated with each bedrock type.

Distinguishing Hg and other trace element contributions from natural sources from those related to anthropogenic inputs is a major challenge, particularly for agencies charged with developing sediment quality guidelines. Any assessment of possibly 'contaminated' areas needs to be evaluated in the context of the local natural background. The NGR database provides a voluminous amount of data pertinent to establishing this background for many elements in the surfical environment.

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SOLUBILITY OF CINNABAR (RED HgS) AND IMPLICATIONS FOR MERCURY SPECIATION IN SULFIDIC WATERS

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Abstract. New experiments have been conducted to determine the speciation of dissolved mercury (Hg) over wide pH (1-12) and sulfide concentration ranges (0.5-30 mM) and in the presence of elemental sulfur (S^0) or Hg^0, conditions that encompass those of near-bottom and pore waters of sediments. Samples containing synthetic red mercuric sulfide (HgS, cinnabar), buffer solution, aliquots of bisulfide (HS^-) solution, and, in special cases, S^0 or Hg^0 were prepared anaerobically and allowed to equilibrate for several months. Filtered samples were analyzed for pH, total sulfide (ΣS^{2-}), and total mercury $[Hg]_{tot}$. Plots of $[Hg]_{tot}$ values vs. pH at varying ΣS^{2-} verified the formation of three previously known mercury-sulfide complexes ($HgS_2H_n^{n-2}$) and revealed that a new Hg_2SOH^+ complex is important at low pH and low ΣS^{2-}. Our constants for ionic strength (I) 0.7 and 25° C are as follows: $K_1=10^{-5.76(+0.71,\ -1.02)}$ for $HgS_{cinn} + H_2S \leftrightarrow HgS_2H_2^0$; $K_2=10^{-4.82(+0.72,\ -1.10)}$ for $HgS_{cinn} + HS^- \leftrightarrow HgS_2H^-$; $K_3=10^{-13.41(+0.76,\ -0.93)}$ for $HgS_{cinn} + HS^- \leftrightarrow HgS_2^{2-} + H^+$; $K_4=10^{-8.36(+0.71,\ -0.93)}$ for $2HgS_{cinn} + H^+ + H_2O \leftrightarrow Hg_2SOH^+ + H_2S$. With decreasing pH, below 1, Hg solubility decreased sharply, indicating the formation of a new solid phase, inferred to be corderoite ($Hg_3S_2Cl_2$). From our solubility data, we calculated the free energy of formation (ΔG_f^0) of $Hg_3S_2Cl_2$ to be -396 (+3, -11) kJ/mol. In experiments where excess $S^0(s)$ was present, a new mercury-polysulfide dimer was identified; its formation constant is $K_5=10^{-1.99(+0.69,\ -1.27)}$ for $2HgS_{cinn} + 2HS^- + nS^0 \leftrightarrow Hg_2S^{II}_4S^0_nH_2^{2-}$. Data from experiments where $Hg^0(aq)$ was added confirmed the reversibility of HgS dissolution. An application of our mercury-sulfide speciation model to a natural anoxic basin, Saanich Inlet, British Columbia, is discussed.

1. Introduction

Owing to bacterial sulfate reduction, hydrogen sulfide (H_2S) and bisulfide (HS^-) are common components of anaerobic waters such as found in the hypolimnion of lakes, in sediment pore waters, and in confined marine basins. Mercury (Hg) combines with sulfide to form HgS, which crystallizes in two polymorphs. The most stable polymorph at low temperatures is cinnabar (red HgS). Additionally, Schwarzenbach and Widmer (1963) showed that Hg can combine with sulfide to form soluble aqueous complexes. As a consequence, sulfide has a dual effect on Hg; small sulfide concentrations act to precipitate it from aqueous solution, whereas large sulfide concentrations act to redissolve it. Quantitatively predicting the behavior of Hg in anaerobic waters requires, among other information, accurate values for stability constants for the Hg complexes likely to form in such environments.

Schwarzenbach and Widmer's stability constant determinations were made in solutions covering a narrow sulfide range and involved an incompletely characterized solid phase. The goals of this work were to measure cinnabar solubility over wide pHs (0-12) and sulfide concentrations (0.5-30 mM). We have also investigated the effect on solubility of the presence of elemental sulfur (S^0) and elemental mercury (Hg^0). In principle, these components can combine with dissolved Hg complexes to form

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polysulfide (S_n^{2-}) and polymercury (Hg_n^{2+}) complexes, respectively. Stability constants for such species, if indeed they exist, have not been determined previously.

2. Materials and Methods

Cinnabar (red HgS) was synthesized by mixing a 1:1 molar ratio of triply distilled Hg(l) (Baker Analyzed) and a slight excess of 99.999% pure sulfur powder (Aldrich Gold Label) in an evacuated quartz tube and gradually heating it to 400-450° C. X-ray diffraction and energy dispersive spectra of the solid verified that it was pure, synthetic, crystalline cinnabar.

Solubility experiments to determine mercury-sulfide speciation were prepared in a nitrogen-filled glove box by placing 0.3 g HgS, 50 ml of deoxygenated buffer solution (buffers were prepared at pH 1-13 and brought to I=0.7 with KCl), and the appropriate aliquot of a 1 M stock bisulfide solution to produce a 0.5, 1, 3, 10, or 30 mM total sulfide (ΣS^{2-}) concentration into a glass ampoule. The ampoules were fusion-sealed and allowed to equilibrate for several months. Experiments to determine mercury-polysulfide and polymercury-sulfide speciation were prepared identically except that they contained 0.3 g S^o (activity S^o=1) or Hg^o(l)-saturated buffer solution, respectively. The Hg-saturated samples did not contain HgS initially.

Filtered samples were analyzed for pH, ΣS^{2-}, and total dissolved mercury, $[Hg]_{tot}$. Total sulfide was measured by iodimetric (4% precision) or potentiometric titration (8% precision). Mercury was analyzed by cold vapor Hg atomic absorption (AA) spectrophotometry on a homemade stannous chloride reduction, gold amalgamation apparatus attached to a Perkin-Elmer Model 2380 Spectrophotometer. We observed a detection limit of 0.3 ppb Hg, a dynamic range of 0.3-20 ppb, and an average precision of 6% with this method. Some $[Hg]_{tot}$ measurements were done commercially on an LDC Analytical Model 3200 cold vapor Hg analyzer (Skinner and Sherman Laboratories, Waltham, MA).

3. Results and Discussion

Reactions based on pH and ΣS^{2-} were written for possible species, starting with three identified by Schwarzenbach and Widmer (1963), and equilibrium constants (K) were allowed to vary in a modeling program until the best least squares fit to the data was found. New species were added as needed to improve the fit. A Monte Carlo simulation was conducted on each K to determine its uncertainty. Table I lists the complexes determined and their equilibrium constants. We have designated reactions for K_1, K_2, K_3, and K_4 the mercury-sulfide speciation model (MS). Reactions for K_1, K_2, K_3, K_4, and K_5 occurred when S^o was present; we have designated them the mercury-sulfide, -polysulfide speciation model (MSPS).

No evidence of polymercury-sulfide species was observed in the samples saturated in Hg^o. We observed a rapid (< 1 day), significant drop in Hg solubility from the initial $[Hg]_{tot}$ values for the buffer solution at low pH. Over time (3 weeks), the $[Hg]_{tot}$ values

TABLE I

Reactions and equilibrium constants for MS and MSPS speciation models, I=0.7, 25° C

$HgS_{cinn} + H_2S(aq) \leftrightarrow Hg(SH)_2^o$	$K_1=10^{-5\ 76(+0\ 71, -1\ 02)}$
$HgS_{cinn} + HS^- \leftrightarrow HgS_2H^-$	$K_2=10^{-4\ 82(+0\ 72, -1\ 10)}$
$HgS_{cinn} + HS^- \leftrightarrow HgS_2^{2-} + H^+$	$K_3=10^{-13\ 41(+0\ 76, -0\ 93)}$
$2HgS_{cinn} + H^+ + H_2O \leftrightarrow Hg_2SOH^+ + H_2S$	$K_4=10^{-8\ 36(+0\ 71, -0\ 93)}$
$Hg_3S_2Cl_2 + H_2S \leftrightarrow 3HgS_{cinn} + 2H^+ + 2Cl^-$	$K^*=10^{-1\ 26(+0\ 61, -1\ 92)}$

$$a_{HgS} = (K^* (K_{1a})^{-1} [HS^-] (a_{H^+})^{-1} [Cl^-]^{-2})^{1/3}$$

$2HgS_{cinn} + 2HS^- + nS^o \leftrightarrow Hg_2S^{II}{}_4S^o{}_nH_2^{2-}$	$K_5=10^{-1\ 99(+0\ 69, -1\ 27)}$
$HgS(s) + H^+ \leftrightarrow Hg^{2+} + HS^-$	$^{**}K_{sp}=10^{-36\ 73}$
$H_2S(aq) \leftrightarrow HS^- + H^+$	$^{**}K_{1a}=10^{-6\ 68}$
$[HS^-] = \Sigma S^{2-}/\alpha$ $\quad \alpha = 1 + a_{H^+}/K_{1a}$	$a_{H^+} = 10^{-pH_{NIST}}$

$$[Hg]_{tot} = [Hg(SH)_2^o] + [HgS_2H^-] + [HgS_2^{2-}] + 2[Hg_2SOH^+] + 2[Hg_2S^{II}{}_4S^o{}_nH_2^{2-}] + [Hg^{2+}]$$

**Indicates literature values used in the model. K_{sp} -- Schwarzenbach and Widmer (1963), K_{1a} -- Williamson *et al.* (1992). Temperature corrections were made, where possible, with reaction enthalpies (ΔH_{rxn}^o), and K values were extrapolated to I=0.7 with the Davies/Setchenow equations.

increased and came close to matching those predicted by our MS model for HgS solubility. The initial drop in $[Hg]_{tot}$ was due to HgS formation from Hg(II) ions generated by oxidation of Hg^o at low pH. The gradual increase in $[Hg]_{tot}$ was due to the slow production of soluble MS species. A similar effect was observed at high pH, but in that case, Hg^o reduced water to form HgS, a slower process (2 days) than HgS formation from Hg(II) ions. Soluble MS species began to form after 3 weeks. At both high and low pH, Hg^o was oxidized to form HgS, and after 3 weeks, the solubility began to conform to our MS model. This served as evidence that HgS dissolution is reversible.

At low pH, HgS solubilities declined in a manner that suggested formation of a solid more stable than cinnabar. We infer this to be corderoite, $Hg_3S_2Cl_2$. We were able to calculate the free energy of formation (ΔG_f^o) of corderoite: -396 (+3, -11) kJ/mol. The transition from HgS to $Hg_3S_2Cl_2$ occurs at pH 2.13 for 0.5 mM ΣS^{2-}, 1.98 for 1.0 mM, and 1.24 for 30.0 mM, all at 0.7 M chloride concentration $[Cl^-]$, 25° C. Corderoite occurs naturally, and Foord *et al.* (1974), found that it forms easily under acidic conditions. The prevalence of chloride in hot springs and groundwaters led them to suggest that corderoite is a "low temperature supergene mineral." Our K* value supports these conclusions; however, the high chloride and acid levels required to form corderoite would rarely be found in lakes.

The following diagram is an application of our MS speciation model to data collected by Lu *et al.* (1986), from Saanich Inlet, British Columbia, a seasonally anoxic fjord. Anoxia is at its peak in August, so we selected that month's data for modeling. Lu *et al.* reported depth (220 m), temperature (9.2° C), salinity (31.3‰), ΣS^{2-} (0.02 mM), and $[Hg]_{tot}$ (.020 nM). From those values, we estimated $[Cl^-]$ and ionic strength. Since no

pH was reported, we covered a wide range of possible pHs in the plot. The most likely values were pH 6 to 8.

The $[Hg]_{tot}$ values predicted by the MS model are 1.5 orders of magnitude higher than observed. This is partly due to temperature and pressure differences between our laboratory and the inlet. The K values could not be corrected for temperature because ΔH_f^o values are not available for the mercury-sulfide complexes. A more likely explanation is that Saanich Inlet is undersaturated with respect to cinnabar. Another possibility is that part of the measured sulfide was adsorbed to dissolved organic carbon or particulate matter in the natural environment, which may have inhibited it from reacting with HgS.

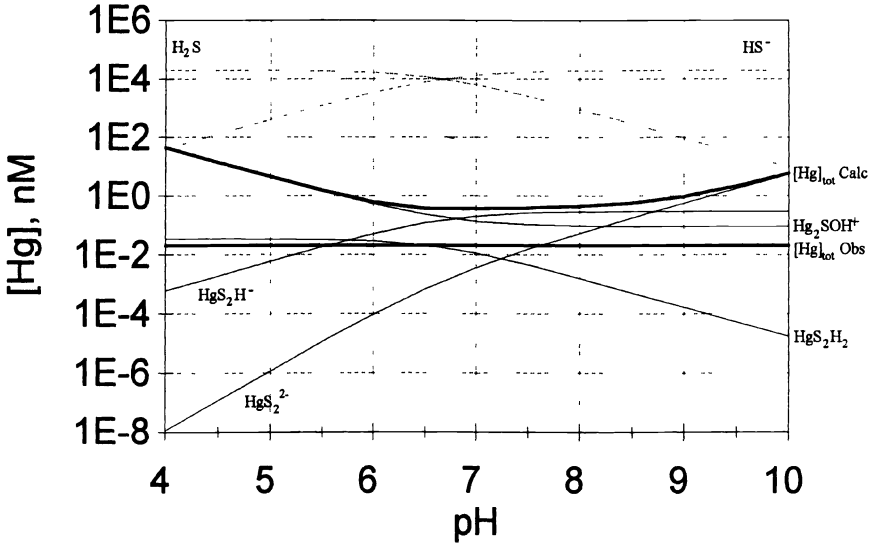

Fig. 1. Application of MS model to Saanich Inlet data from August -- depth=220 m, I=0.6, $[Cl^-]$=0.5 M, ΣS^{2-} =0.02 mM, and $[Hg]_{tot}$=.020 nM (Lu *et al.*, 1986).

4. Conclusion

Mercuric sulfide reversibly dissolves in sulfidic solutions to form $Hg(SH)_2^o$, HgS_2H^-, HgS_2^{2-}, and Hg_2SOH^+ within a pH range (4-10) found in natural anoxic basins. A fifth complex, $Hg_2S^{II}{}_4S^o{}_nH_2^{2-}$, forms at high S^o activity within that same pH range. The transition from HgS to corderoite requires much lower pHs and higher chloride concentrations than would be found in natural lakes.

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PART Xb

MERCURY IN SOILS

DESIGN AND INITIAL TESTS OF A DYNAMIC ENCLOSURE CHAMBER FOR MEASUREMENTS OF VAPOR-PHASE MERCURY FLUXES OVER SOILS

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Abstract. In an effort to establish reliable methodologies for measuring fluxes of mercury (Hg) across the soil-air interface, we have developed a field flux chamber built with FEP Teflon. To evaluate our field flux chamber system, a series of laboratory and field tests were performed. The observations of relatively low chamber blanks and low blank-to-sample ratios for the FEP Teflon chamber suggest its potential in Hg flux investigations. Despite its potential, Hg exchange rate measurements using the field flux chamber method must be made with great caution since it can be subject to contamination problems associated with the selection of chamber materials.

1. Introduction

The transfer of various pollutant chemicals across the biosphere and atmosphere interface is influenced by both anthropogenic and natural processes. It is known that, compared to the generally intense, localized anthropogenic processes, natural processes tend to occur over large areal scale with low flux density. As in the case for many other trace gases of biological origin, the world oceans have been identified to be a major component of the global atmospheric mercury (Hg) budget, with an annual emission rate of approximately 2 Tg yr^{-1} (Fitzgerald, 1989). Terrestrial sources are also suggested to play an important role in the global atmospheric Hg cycling. However, previous estimates of the total terrestrial flux of Hg are highly uncertain due to lack of reliable methodologies and of published data.

Only a small number of experimental techniques have been used for direct exchange rate measurements of atmospheric Hg in terrestrial environments. The pioneering field flux measurements for Hg were conducted using flux chamber techniques (Schroeder *et al.*, 1989; Xiao *et al.*, 1991). Application of a micrometeorological approach, which is generally considered as a more reliable method, has not been attempted

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until recently (Kim *et al.*, in press; Lindberg *et al.*, submitted). Previous dynamic flux chamber studies performed in a boreal forest (Xiao *et al.*, 1991) indicate (1) similarly important roles of both emission and deposition processes over daily cycles and (2) seasonal variabilities in exchange patterns (e.g., emission-dominant summer and deposition-dominant winter). By contrast, initial results from micrometeorological studies in a background, temperate forest environment in Tennessee have shown somewhat opposing features characterized by (1) the generally enhanced magnitude of and frequent occurrences of emission (vs deposition) over daily cycles and (2) consistently emission-dominant trend over seasonal cycles (Kim *et al.*, in press). Kim *et al.* concluded that the level of difference in measured fluxes and temporal exchange patterns may still be explainable considering all different environmental and methodological factors involved in different studies.

In the initial stage of our MASE (Mercury Air/Surface Exchange) project, we have been extensively involved in establishing accurate experimental methods of measuring Hg exchange rates, in particular the micrometeorological modified Bowen ratio (MBR) method. The results of our initial application of the MBR approach to Hg flux measurements have been reported elsewhere (Kim *et al.*, 1993, in press; Lindberg *et al.*, submitted). As a part of our extended effort to accurately quantify Hg exchange rates, we have also been involved in development and application of flux chamber measurement techniques. Here we present and discuss some preliminary results of our flux chamber studies obtained during evaluation periods.

2. Materials and methods

The stainless steel chamber of Xiao *et al.* (1988, 1991), which was built on the basis of their studies of chamber material evaluation (between stainless steel and pyrex glass), still suffered from quite substantial chamber blank problems. Noting the good performance of FEP teflon in various trace gas flux chamber studies (e.g., reduced S: Kuster and Goldan, 1987), we selected it as a chamber material. An FEP-Teflon chamber was constructed with an open bottom and deep stretching skirts (dimension of 60x20x20 cm) and was supported by an external Al frame (Figure 1). This chamber was built to facilitate

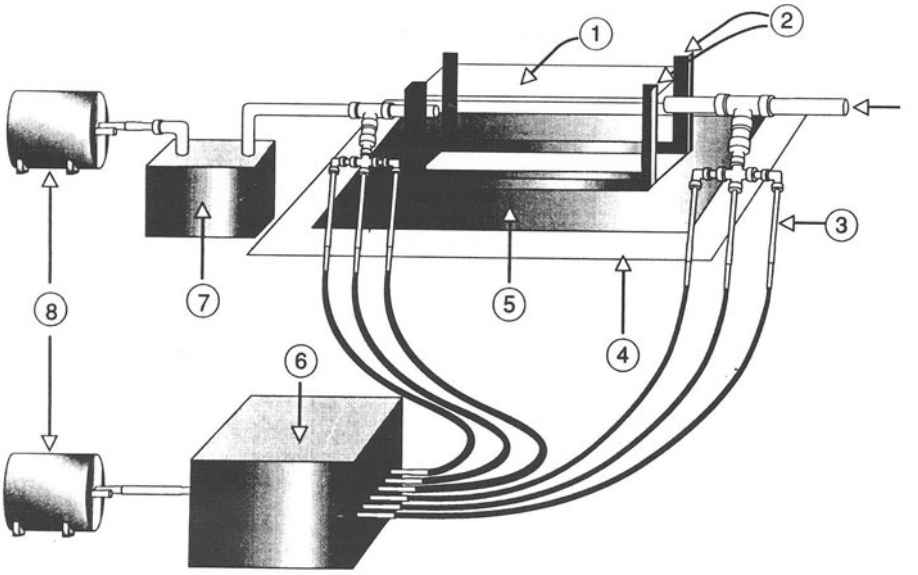

Figure 1. A schematic diagram of flux chamber system: (1) FEP enclosure chamber, (2) external Al-supporting rod, (3) Au-coated sand amalgamation trap, (4) bottom skirt of chamber, (5) frame of Al-supporter, (6) ORNL MFC system for six-replicate sample collection (maximum capacity for each individual MFC unit ~0.5 l min^{-1}), (7) MFC for flushing rate calibration (~15 l min^{-1}), and (8) vacuum pump.

simultaneous collection of three replicate air samples from both inlet and outlet ports to better characterize the true mean concentrations of Hg^0 entering and exiting the flux chamber. For each experiment, the air stream at the inlet and outlet port was sampled simultaneously at constant flow rate of about 400 ml min^{-1}. Air samples were drawn for periods of approximately 2 h using a multiple replicate sampling system equipped with six seperate mass flow controllers (MFCs) (Kim and Lindberg, 1994). Flow into and out of the chamber was also maintained at a constant flow rate of 5 l min^{-1} using a high-capacity MFC (corresponding to about 5 min of turnover time for the internal volume of the flux chamber). The traps for Hg collection were made of gold-coated sand absorbers. To achieve a tight seal between chamber and soil surfaces, the four edges of the chamber-skirt were firmly pressed into the soil by lead bricks. The blank levels of our flux chamber were routinely measured by sealing the chamber over a large, clean sheet of FEP Teflon. The

measurements of field chamber blanks and bias tests between different sampling methods were performed at the Walker Branch Watershed (WBW) in Oak Ridge, TN during June 1993 through June 1994. A detailed description of the experimental site has been presented by Kim *et al.* (in press). For the quality assurance of our flux chamber measurements, ambient air samples were occasionally collected during the same period using an independent sampling system designed to measure the vertical gradients of Hg at two heights (i.e., 10 and 165 cm). The sampling and analytical procedures used in our gradient measurements are detailed in the companion paper in this volume (see *Lindberg et al.* this volume).

The total amount of vapor-phase Hg collected from each flux chamber measurement was determined using a two-stage gold trap analysis technique (Fitzgerald and Gill, 1979) by cold-vapor atomic fluorescence spectrophotometry (CVAFS). The detection limit for the system, calculated as three times the standard deviation of typical mean blank levels of the Hg-collection traps, is typically found at 1 to 2 pg of Hg. The analytical system was standardized by measuring known volumes of a Hg-saturated atmosphere via an air tight gas syringe using a system of our own design. From our measurements of replicate air samples, we routinely achieved a combined sampling plus analytical precison in the range of 1 to 3 % (expressed in terms of relative standard error, RSE). Statistical outliers from each set of samples collected at the inlet and outlet were eliminated using the statistical method of Skoog *et al.* (1992). Since total gaseous Hg collected by our sampling system is predominantly in elemental form (~98%), the concentration and flux values of Hg in this paper are operationally defined as Hg^0.

The rate at which Hg^0 exchanges through the chamber was computed using the following equation:

$$F = \frac{(C_o - C_i)}{A} \times Q$$

where F is Hg^0 flux in ng m^{-2} h^{-1}, C_i and C_o are the Hg^o concentrations in ng m^{-3} at the inlet and outlet ports, A is the bottom surface area of chamber in m^3, and Q is the flushing flow rate through chamber in m^3 h^{-1}.

3. Results and discussion

Previous flux chamber studies to measure Hg fluxes over environmental surfaces indicated that the major problem associated with application of this technique was the presence of large chamber blanks which occasionally exceeded the magnitude of sample fluxes (Xiao *et al.*, 1991). To offer insights into the significance of chamber blank problems, the results of blank/soil flux measurements performed by Xiao *et al.* (1991) are summarized in Table I. To facilitate the comparison of chamber blank vs. sample fluxes, chamber blank values expressed in terms of ng min^{-1} of sampling time were converted into units that are comparable to actual sample fluxes (i.e., ng m^{-2} h^{-1}). The mean and 1 SD of chamber blank are 2.13 ± 1.20 ng m^{-2} h^{-1}. The results shown in Table I clearly indicate that chamber blank values are in many cases larger (up to an order of magnitude) than the flux values.

Noting the significance of chamber blank problems as acknowledged by Xiao *et al.* (1991), we began a series of laboratory and field chamber blank measurements as a first step toward the evaluation of our flux chamber system. To check the extent of initial contamination on our chamber system, the flux chamber was tested as delivered (April 10, 1993) without pre-cleaning. Table II shows a summary of seven laboratory and five field blank measurements made during the initial evaluation period. The mean and 1 SD of our laboratory blank fluxes are 0.5 ± 0.3 ng m^{-2} h^{-1} (n = 7), while those of field blank fluxes are 1.0 ± 0.3 ng m^{-2} h^{-1} (n=4). Although our chamber did not go through a complicated chemical cleaning process like that of Xiao *et al.* (1988), the mean chamber blank values derived from both of our laboratory and field tests are approximately two to four times lower than those seen from studies of Xiao *et al.* (1991). From our previous flux measurements using the MBR method (Kim *et al.*, in press), we quantified the mean and 1 SD of the WBW soil emission rates to be 7.5 and 7.0 ng m^{-2} h^{-1} (n=30). Thus, a combined effect of generally low blank values from our flux chamber system and the observations of enhanced emission rates of Hg^0 from our field study site (relative to the boreal forest site studied by Xiao *et al.*: refer to Kim *et al.*, in press) suggest that more reasonable blank-to-sample ratios may be obtained from our flux chamber measurements at WBW.

TABLE I

Comparison of chamber blanks and blank-to-sample ratio from previous soil-to-air flux measurements of Xiao *et al.* (1991) using stainless steel flux chamber.

Date	Chamber blank* ($ng\ min^{-1}$)	Chamber blank** ($ng\ m^{-2}\ h^{-1}$)	Hg fluxes ($ng\ m^{-2}\ h^{-1}$)	B/S ratio*** (%)
12/17/87	0.0036	1.35	1.4	96
2/9/88	0.0022	0.83	-1.3	63
2/11/88	0.0032	1.20	-1.4	86
4/14/88	0.0099	3.71	-2	186
4/14/88	0.01	3.75	-1.1	341
4/15/88	0.006	2.25	-0.3	750
5/30/88	0.0042	1.58	2.5	63
5/30/88	0.0037	1.39	0.5	278
5/24/89	0.011	4.13	-0.8	516
5/24/89	0.008	3.00	-1	300
6/12/89	0.0042	1.58	0.14	1125
6/12/89	0.0022	0.83	0.17	485
Mean	.0057	2.13		357
1 SD	.0032	1.20		322

* Chamber blanks are presented as originally reported by Xiao *et al.* (1991).
** Chamber blank values of Xiao *et al.* are converted into flux units.
*** Blank-to-sample ratios are expressed in terms of absolute percentage.

To further test the reliability of our flux chamber system, we performed a series of bias tests in which Hg concentrations measured at the inlet and outlet of the chamber system were directly compared with those collected by an independent Hg sampling system. To collect more replicate samples for each sampling system, we modified our typical sampling procedures of each sampling system. For the chamber system, air samples were drawn from both inlet and outlet ports with the bottom of the chamber slightly open to the ambient air. Six replicate samples were collected simultaneously near the chamber inlet using our gradient sampling system for the purpose of comparison. These bias tests between two sampling techniques were performed at both laboratory and

TABLE II

Results of laboratory and field blank flux measurements of Hg^o using ORNL FEP flux chamber.

Date	Hg^o concentrations Mean ± 1 SE (ng m^{-3})		Statistical significance* (P < x)	Blank Flux (ng m^{-2} h^{-1})
	Inlet	Outlet		
	(1) Flux chamber blanks (Laboratory measurements)			
6/23/93	17.35±0.17	17.78±0.02	0.1	0.7
10/27/93	7.69±0.04	7.61±0.14	ns	-0.2
10/27/93	7.37±0.29	6.95±0.02	0.15	-0.9
11/1/93	6.47±0.13	6.60±0.09	ns	0.3
11/1/93	7.36±0.22	7.16±0.10	ns	-0.4
11/1/93	7.13±0.10	7.20±0.06	ns	0.1
11/1/93	7.52±0.16	7.02±0.03	0.15	-0.7
Mean ± 1 SD of chamber blank fluxes (in absolute terms) = 0.5 ± 0.3 ng m^{-2} h^{-1}				
	(2) Flux chamber blanks (Field measurements)			
3/11/93	3.21±0.14	3.68±0.15	0.05	1.4
11/2/93	2.75±0.23	3.20±0.36	ns	1.0
11/2/93	2.36±0.10	2.62±0.15	0.15	0.6
11/12/93	4.17±0.09	4.61±0.07	0.05	1.0
Mean ± 1 SD of chamber blank fluxes (in absolute terms) = 1.0 ± 0.3 ng m^{-2} h^{-1}				

* denotes the probability that two variables are not significantly different

field site. Results from three laboratory bias tests showed that differences between two sampling methods were not statistically significant. (During these tests, Hg^o concentrations in lab air generally ranged from 15 to 23 ng m^{-3}.) In contrast to these observations, statistical analysis on our field bias test results showed discernible differences between the two methods (Table III). The initial tests performed on June 15, 1994 (Table III) show that the concentrations of Hg^o collected by the chamber system are measurably larger than those measured by the reference sampling system and suggest that the extent of disagreement may decrease with time (probably due to enhanced system flushing with extended operation). The differences between laboratory and field bias tests

suggest that our flux chamber system can be more easily subject to contamination under clean conditions (Hg^0 concentration from background field site ~1.5 ng m^{-3}) than under high Hg^0 levels associated with the laboratory air. In an effort to eliminate the possible contamination of the chamber system, we detached, acid-washed, and oven-dried all Teflon connectors attached to the body of the flux chamber. The effect of acid-washing was quite dramatic as seen from our June 21 tests (Table III). The bias between chamber/gradient system decreased from 40 to 90% (before washing) to approximately $\pm$ 5 % (after washing). Similarly, the results of our statistical analysis also show the effect of acid-washing such that differences between two methods become less significant between before and after acid-washing ($P < 0.05$ to $P < 0.10$).

TABLE III

Results of field bias tests between flux chamber and an independent gradient sampling system on June 1994

Date	Time (EST)	Mean Hg^0 (ng m^{-3})	Method	N	SE	RSE (%)	Sig (P < x)
			(1) Before acid-washing				
6/15/94	0949/1119	2.41	G*	6	0.08	3.1	0.05
6/15/94	0949/1119	4.57	FC**	6	0.11	2.3	
6/15/94	1128/1256	2.19	G	6	0.03	1.6	0.05
6/15/94	1128/1256	2.96	FC	6	0.06	2.1	
			(2) After acid-washing				
6/21/94	1055/1240	5.49	G	4	0.18	3.3	0.10
6/21/94	1055/1240	5.83	FC	5	0.14	2.4	
6/21/94	1247/1419	3.50	G	4	0.11	3.0	0.10
6/21/94	1247/1419	3.33	FC	5	0.03	1.0	

* denotes gradient sampling system.
** denotes flux chamber system.

Despite the potential problems of creating artificial environmental conditions, flux chamber techniques may still be favored over other flux measurement techniques due

to: (1) highly senstive measurements of exchange rates; (2) high portability in assessing the spatial variabilities; and (3) allowance of replicate measurements coincident in space and/or time. Its applicability can be further extended to various controlled studies of trace gas behavior (e.g., measurements of Hg^o exchange rates under wet/dry conditions or with/without leaf litter). A series of laboratory/field evaluation tests of the field flux chamber shows a great potential of an FEP Teflon flux chamber for its applications to quantification of Hg fluxes over environmental surfaces. However, as indicated by the test results summarized in Table III, our initial tests suggest that measurements of the environmental Hg mobility by Teflon flux chamber must be made with great caution due to the potential for contamination under clean, background conditions.

Acknowledgements

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THE BIOGEOCHEMICAL CYCLING OF Hg IN FORESTS: ALTERNATIVE METHODS FOR QUANTIFYING TOTAL DEPOSITION AND SOIL EMISSION

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Abstract. A biogeochemical cycling approach to the Hg cycle is explored using existing data from the literature in order to begin to identify important processes that might be studied in detail and extrapolated to a regional scale. If it is assumed that all foliar Hg is taken up from the atmosphere, then estimates of total Hg deposition are rather easily made from measurements of leaf litterfall and throughfall. This assumption needs absolute verification before such an extrapolation can be made, however, because litterfall is a major Hg flux to the forest floor. Hg^0 evolution from soils can be an important process and needs to be measured in more ecosystems. The diffusion model for soil gaseous efflux may be useful in this regard and deserves testing. There is a critical need for a systematic analysis of Hg cycles using common protocols so as to minimize artifacts associated with sampling methodology (i.e., soil Hg efflux). This should be done in several soil and forest types, given the high degree to which Hg transformations in and emissions from soils are dependent upon soil organic matter content, redox potential, and temperature.

Key Words: Diffuson model, litterfall, total deposition, Hg cycling

1. Introduction

There are serious questions as to how to extrapolate from site-specific studies to a regional and global scale with regard to mercury as well as any other regional/global pollutant. Is infeasible to make a sufficient number of measurements to scale up on to either a regional or global scale on a statistical basis; however, it may be possible to relate certain key processes to mapped ecosystem or soil parameters. For example, regional assessments of ecosystem-level S retention have been related to soil classification systems on the basis of detailed S cycling studies showing that soil sulfate adsorption was the key ecosystem S retention process and that it, in turn, could be related to soil Fe and Al hydrous oxide concentrations (Johnson et al 1982; Johnson and Todd 1983; Rochelle et al 1987; Harrison et al 1989; Johnson and Lindberg 1991). Similarly, the observation that foliar sulfate leaching was trivial allowed easy estimation of total S deposition using simple throughfall measurements (Lindberg et al 1986; Lindberg and Garten 1988). Thus, detailed information about S cycling at a few sites facilitated extrapolation to a regional scale based upon process-level understanding; it is possible that the mercury issue can be attacked in the same manner.

In our opinion, there are two critical unknowns which must be addressed before we can understand the cycling and fate of Hg in forest ecosystems: 1) the role of dry deposition as it relates to the source of Hg in litterfall, and 2) the importance of soil emission of Hg into the atmosphere. In the following discussion, we attempt to apply known models used in carbon and nutrient cycling analyses to the Hg problem to see if insights can be gained as to the importance of different processes and the potential for their extrapolation to regional or global scales.

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2. Terminology and Assumptions Used in Forest Biogeochemical Cycling Studies

The traditional method of calculating uptake, requirement and translocation is as follows (Cole and Rapp, 1981): requirement (R) = nutrients used in new tissue [= nutrients in new foliage (F) + wood increment (W) + root increment (RO)]; uptake (U) = nutrient return + nutrient increment in perennial (woody) tissues (W) [= litterfall (LF) + foliar leaching (FL) + root turnover (RT) + W]; foliar leaching (FL) = [throughfall + stemflow - total deposition]; translocation (T) = R - U. This model was developed for nutrients which are actively taken up (i.e, taken up in excess of what would occur if soil solution simply entered the transpiration stream) and recycled both within the vegetation and within the ecosystem. We can safely assume that requirement for Hg is zero, and that any Hg uptake from the soil is passive (i.e., follows the transpiration stream). Thus, for a typical soil solution Hg value of 2-4 ng l^{-1} (Lindqvist et al 1991) and a transpiration rate of 50 -80 cm yr^{-1}, uptake would be on the order of 1 - 4 $\mu g\ m^{-1}\ yr^{-1}$. Iverfeld (1991) measured wet Hg deposition at Gårdsjön, Sweden as 12 $\mu g\ m^{-2}\ yr^{-1}$, throughfall as 16-19 $\mu g\ m^{-2}\ yr^{-1}$, and estimated 25 $\mu g\ m^{-2}\ yr^{-1}$ as litterfall return. Thus, it would seem that uptake through the soil at this site, at least, is trivial and that most foliar Hg originates from dry deposition. Iverfeld (1991) made the latter assumption, and estimated a total Hg deposition on the order of 40 $\mu g\ m^{-2}\ yr^{-1}$, most of which entered the forest floor as litterfall. Several studies have shown that Hg taken up from soils is largely bound in root tissue (perhaps in part as surface contamination in some cases) and translocation to foliage is negligible (Lindberg et al 1979; Hogg et al 1978a; Godbold and Hütterman 1988; Iverfeld 1991). Thus, current evidence suggests that foliar Hg originates from atmospheric deposition, making it extremely convenient and cheap to estimate total Hg deposition to forested ecosystems: only littertraps and throughfall collectors are needed.

It is important to check the validity of the assumption that no Hg is translocated from roots to foliage. If this assumption can be proven true, many more measurements of Hg deposition can be easily and inexpensively made. Lindberg et al (1991) measured wet deposition at Walker Branch, Tennessee as 12 $\mu g\ m^{-2}\ yr^{-1}$ and dry deposition as 20 $\mu g\ m^{-2}\ yr^{-1}$ using an inferential model for a total deposition of 32 $\mu g\ m^{-2}\ yr^{-1}$. Litterfall measurements are currently being made to determine how closely dry deposition measurements match litterfall Hg fluxes.

3. Soil Hg Transformations and Fluxes

Several excellent review chapters and papers have been written on soil Hg chemistry (Lindsay 1979; Andersson 1979; Schuster 1991) and the reader is referred to them for detail. Only the most general features are reviewed here.

The proportion of total Hg as Hg^{o} in soil is a function of a number of chemical factors, including redox potential, adsorption to organic matter and minerals, I^{-}, Cl^{-}, and Br^{-} concentrations (Lindsay 1979; Andersson 1979; Schuster 1991). Schuster (1991) argues adsorption - desorption reactions with organic matter and soil minerals control soil solution Hg concentration and solubility equilibria. Apparently, the high affinity of Hg for organic matter is due to its high affinity for S, and adsorption-desorption reactions with organic matter control soil solution Hg concentrations, keeping them at very low levels. Andersson (1979) reported on a series of experiments adding 10^{-5} M $HgCl_2$ to

kaolinite, bentonite, lillitic clay, and two organic soils adjusted to pH levels ranging from < 3 to > 8. He found that $HgCl_2$ was the dominant Hg species in solution at pH < 4.75, and that adsorption to organic matter controlled total soil solution Hg. Above this pH adsorption by the inorganic soils increased substantially. He concluded that "the only effective sorbent for inorganic Hg in acid soils (pH < 4.5 - 5.0) is the organic material, whereas in neutral soils (pH > 5.5 - 6.0), iron oxides and clay minerals may become much more effective". Interestingly, neither author mentions complexation or precipitation with I^-, perhaps reflecting a lack of data on soil solution I^-.

Due to the high affinity of Hg for organic matter and minerals, soil Hg leaching rates are very low and mostly associated with dissolved organic matter (Andersson 1979; Schuster 1991; Lindqvist et al 1991; Mierle and Ingram 1991; Xiao et al 1991; Krabbenhoft and Babiarz 1992). Mierle and Ingram (1991) report that Hg leaching at Harp Lake in Ontario is 20-30% of wet deposition input and closely associated with dissolved organic matter. Similarly, Krabbenhoft and Babiarz (1992) calculate 92-95% retention of atmospherically-deposited Hg in the soil surrounding Palette Lake, Wisconsin (not accounting for volatilization). Lindqvist et al (1991) estimate that 75 to 80% of atmospherically-deposited Hg accumulates in the upper, organic horizons of soils in Swedish ecosystems. Hg leaching has also been found to be very low in laboratory column studies (e.g., Hogg et al 1978a and b).

Very few studies have been conducted on the volatilization of Hg from soils under field conditions. Dudas and Pawluk (1976) concluded that the cause of lower Hg concentrations in surface than in subsurface soils in Alberta was due to volatilization, suggesting that this is an important process in the long-term. On the other hand, Xiao et al (1991) found that Hg volatilization from forest soils in Sweden using chambers was quite small (ranging from 1.4 to -1.2 ng m^{-2} hr^-, the negative sign indicating net deposition) and often not significantly different from zero. For the warm season, their estimate would correspond to a maximum of about 1 μg m^{-2} yr^{-1}, whereas Iverfeld (1991) estimated total Hg deposition at this site as approximately 40 ng m^{-2} yr^{-1}. In contrast, Kim et al (in press) found that Hg emission episodes (average = 7 ng m^{-2} hr^{-1}) to be more frequent and stronger than soil uptake espisodes (≈ 2 ng m^{-2} hr^{-1}) on Walker Branch Watershed, Tennessee using micrometeorological techniques. It appears that Hg volatilization from soils is approximately of the same order of magnitude as atmospheric deposition at this site (Kim et al in press; Lindberg et al 1991), and further work is now in progress to refine estimates of both fluxes.

In that Hg volatilization is known to be strongly temperature dependent, it is logical to expect it to be of greater significance in soils in warmer climates. However, the differences in the magnitudes of Hg flux may also be due in part to methodological differences: Xiao et al (1991) used closed chambers overlaying the soil, and discussed the potential artifacts that this method may introduce (i.e., reduction of solar radation inputs). Lindberg et al (in press) used the modified Bowen ratio gradient technique, which is probably the least invasive but most expensive and time-consusuming method. A third possibility, described below, is the soil gas profile method (de Jong and Schappert 1972).

4. Factors affecting Hg emissions from soils

Many authors have noted that Hg volatilization from soils is highly dependent upon temperature (Siegel and Siegel 1988; Xiao et al 1991; Lindberg et al 1979, 1991; Klusman and Webster 1981). Using Arrhenius plots, Siegel and Siegel (1988) found that

the release of Hg^o from the soils they studied paralleled closely the vaporization curve for Hg^o, suggesting that evaporation was the primary process controlling soil Hg evolution. The soils used (from the Sulfur Bank fumarole area of the Hawaii Volcanoes National Park) were not representative of typical forest or agricultural soils, however: they had very low pH (2.8 to 3.7) and organic carbon concnetrations (300 to 1100 $\mu g\ g^{-1}$). In the Walker Branch study (surface soil pH ≈ 4.5 and organic matter concentrations ≈ 36,100 $\mu g\ g^{-1}$), Kim et al (in press) found a somewhat lower activation energy for soil Hg volatilization (≈ 17 kcal mol^{-1}) than that obsrved by Siegel and Siegel (1988) (≈ 28 kcal mol^{-1}), and concluded that Hg volatilization could not be accounted for solely by the vaporization of Hg^o.

Assuming that the majority of Hg emission from soils is in the form of Hg^o, such emissions would logically be a function of the concentration of Hg^o in the soil atmosphere and the diffusivity of Hg^o in the soil. Lindsay (1979) gives a useful example of the effect of redox potential (defined, according to his preference, as pe + pH, rather than Eh; but note that Eh in millivolts = 59.2 x pe) (Table 1). Clearly, the condition of greatest interest for gaseous Hg emission interest is in the pe + pH range of 12.3 - 5.27. For the Walker Branch soil (pH = approximately 4.5), this corresponds to a pe of 7.8 to 0.77 (Eh range of 462 to 46 mv), which is well within the conditions expected to be encountered under field conditions. Lindsay (1979) does not consider organic Hg interactions in his analysis however, which are of paramount importance to soil Hg transformations, including the potential for reduction of Hg^{2+} to Hg^o (Andersson 1979; Schuster 1991). Unfortunately, no clear set of equations exist describing the form of Hg as affected by organic matter in soils; thus, models of soil Hg^o efflux will probably have to start with soil Hg^o as an input variable.

The diffusion model has been used successfully to describe the efflux of various gases from soils (de Jong and Schappert 1972; de Jong et al 1979; Solomon and Cerling 1987; Amundson and Davidson 1990; Sheppard et al 1994; Johnson et al 1994). If soil Hg^o efflux is assumed to be a diffusion process, then the following equations apply:

$$q = D\frac{dC}{dz} \qquad \text{Diffusion equation} \qquad 1)$$

and

$$\frac{dG}{dt} = -\frac{dq}{dz} + a \qquad \text{Conservation of mass} \qquad 2)$$

where q= Hg efflux (ng Hg $m^{-2}\ h^{-1}$), C = soil gaseous Hg concentration (ng m^{-3}), z = depth (m), D = diffusion coefficient ($m^2\ sec^{-1}$), G = amount of Hg gas per unit soil volume = (C)(Pore volume, Va), a = net source of sink of Hg (absorption or desorption). Combining equations 1) and 2) (de Jong and Schappert 1972):

$$\frac{dc}{dt} = \frac{1}{Va}\left[-\frac{dq}{dz} + a\right] \qquad 3)$$

At steady-state,

$$\frac{dq}{dz} = a \qquad 4)$$

TABLE I

Hg distribution for a soil with total Hg concentration of 0.1 μg g^{-1}, pH = 7, $(Cl^-) = 10^{-3}$ M, $Br^- = 10^{-5}$ M, $(I^-) = 10^{-6}$ M (after Lindsay, 1979)

pe + pH	Hg distribution
>13.19 (Eh > 366 mv)	All in solution; major species are ion pairs HgI^0 (97.45%), $HgClI^0$ (0.93%), and $HgBrI^0$ (1.62%)
13.19 - 12.30 (Eh = 366 to 314 mv)	HgI precipitates and forms a stable phase
12.3 - 5.27 (Eh = 314 to -102 mv)	Elemental Hg forms; Hg^0 in solution = $10^{-6.52}$ M (6.2% of total Hg); Hg(l) = 93.8% of total Hg. Vapor pressure of $Hg^0(g)$ is $10^{-5.58}$ atm, or 24,000 μg m^{-3}.
< 5.27 (Eh < -102 mv)	$Hg^0(g)$ and $Hg^0(l)$ decrease; HgS forms.

Equation 1) combined with either 3) or 4) can be used to calculate respiration from any desired soil horizon or from the entire profile, if z_o is set at the soil surface.

Because $Hg^o(g)$ diffusion through water is much lower than in air, D is strongly affected by soil water content. There are several formulations for D (Collin and Rasmuson 1988), all of which take soil moisture content into account. In our work with CO_2 evolution (Johnson et al 1994), we used a modification of the equation given by that of Millington (1959) (as quoted by Rolston 1986):

$$D = (\partial)(D_a)(P_{eff}^{10/3})/E^2 \qquad 5)$$

where D_a = diffusion coefficient of Hg^o in air (cm^2 sec^{-1}), E = voids ratio, or total soil porosity, P_{eff} = effective porosity = total porosity (E) minus volumetric water content (V_w), and ∂ = a coefficient to account for non-ideal pore shape and dead-end pores (Collin and Rasmuson 1988).

For our studies of CO_2 evolution in a California Ultisol, the value of ∂ was determined to be 0.1 based upon comparisons of soil atmospheric CO_2 concentrations with measured CO_2 efflux using dynamic chambers (Vose et al 1994; Johnson et al 1994). A similar approach could be taken for Hg^o emissions, whereby simultaneous measurements of the concentration of Hg^o in soil atmosphere, soil water content, and measured Hg^o emissions could be used to obtain ∂. From that point, Hg^o emissions could be calculated for any time when soil atmospheric Hg^0 and soil water content are measured. In our CO_2 work, we found that measurements of atmospheric CO_2 and water content were much easier than measurements of CO_2 flux with chambers, and so we use the calculations to obtain seasonal variations and annual values, with the chamber

measurements as reality checks (Vose et al 1994; Johnson et al 1994). With the micrometerological gradient methods of Lindberg et al (in press) and Kim et al (in press), a similar approach could be used to model Hg^0 emission from soils.

Some idea of the sensitivity of soil Hg^0 concentration to soil moisture can be obtained by combining equations 1) and 5), integrating, and solving for C:

$$C_z = \frac{(q)(z)}{(Da)[(E - V_w)^{10/3}/E^2]} + C_0 \qquad 6)$$

where C_z = Hg^0 at depth z and C_0 = Hg^0 (in the atmosphere above the soil). A plot of $C_{0.1m}$ as a function of Hg^0 flux and soil moisture content typical for the Walker Branch, Tennessee soil are given in Figure 1. D for the Walker Branch soil was calculated from published values of bulk density (Johnson et al 1985) and moisture release curves (Luxmoore and Huff 1989), assuming a mineral phase density of 2.65 g cm^{-3}. It can be seen that calculated Hg^0 concentrations are very sensitive to soil moisture content at the high moisture range due to the greatly reduced diffusion coefficient (D). Unfortunately, there are no soil Hg^0 values from Walker Branch to compare to these calculations. Klusman and Webster (1981) found much lower Hg^0 concentrations in soil atmosphere (<1 to 53 ng m^{-3}) in a 1 m deep, 2 m^3 soil vault in a Colorado forest soil. However, the authors also noted that increased soil moisture caused increased soil Hg^0 concentration at their site, which is consistent with the diffusion model. This was complicated by the fact that they also found soil Hg^0 concentration to be correlated with temperature (soil and air), barometric pressure, water table, and frozen or thawed state of the soil, however. Thus, for example, an increase in soil moisture due to a precipitation event which caused reduced soil temperature might create significant complications for simple model calculations.

The concentration of Hg^0 in the soil atmosphere will likely be a function of the amount of Hg^0 present, which in turn is a function of a number of chemical and biological factors (Lindsay 1979; Andersson 1979; Schuster 1991). Measurements of actual soil atmospheric Hg^0 concentrations in association with measurements of Hg^0 flux with eddy correlation (Kim et al in press), soil water, pH, and redox potential would allow testing of the applicability of basic chemical and physical models for the chemistry of Hg and gaseous evolution. If these models prove applicable, either in part or in total, they can then be applied on a broader regional scale with appropriate measurements.

5. Summary and Conclusions

There is a critical need for a systematic analysis of Hg cycles using common protocols so as to minimize artifacts associated with sampling methodology (i.e., soil Hg efflux). This should be done in several soil and forest types, given the high degree of temperature dependence of Hg transformations in soils and importance of soil organic matter in Hg retention and loss.

The classic biogeochemical cycling model can be greatly simplified and used to assess atmospheric Hg deposition if the assumption that no foliar Hg is derived from soil is valid. Litterfall is apparently a major Hg flux, and thus it is critical to apply rigourous tests to this assumption before taking the calculations any further in either time or space. Comparisons of calculated passive Hg uptake from (soil solution Hg concentrations and

evapotranspiration rates) with measured Hg return in litterfall would provide useful indicators of the potential importance of soil vs atmospheric Hg uptake as a source of Hg in litterfall.

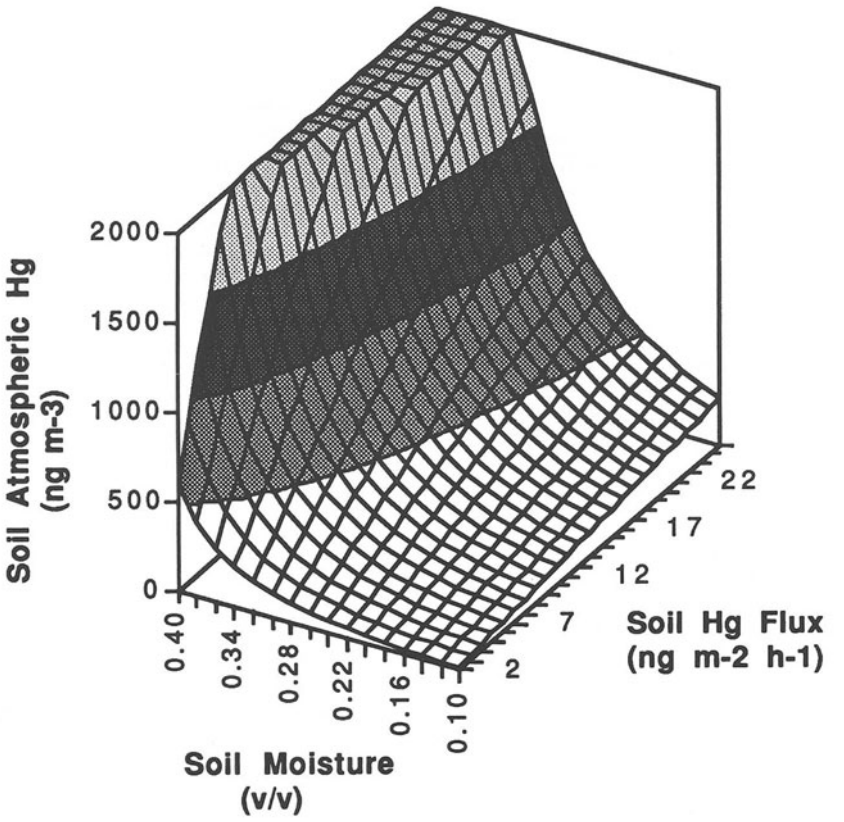

Figure 1. Calculated soil atmospheric Hg^0 concentratration at 10 cm depth as a function of soil moisture and surface Hg^0 flux using the diffusion equation. (See equation 6)

Sub-models of element flux may be useful from a methodological perspective; eddy correlation already has been, and the soil gas diffusion model may also be. Some simple

measurements of soil atmospheric Hg^0 concentration as a function of measured fluxes, soil porosity, and soil water content at the current intensive study sites (Gårdsjön and Walker Branch) could serve as a test of this model. This model has the decided advantage of allowing calculation of gaseous fluxes between horizons within the soil, and is therefore very much worth exploring. Also, the source of soil Hg^0 could be explored by classic litter raking experiments (does Hg^0 originate directly from newly-deposited litter or from the soil itself?)

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GEOCHEMISTRY OF MERCURY IN PRISTINE AND FLOODED FERRALITIC SOILS OF A TROPICAL RAIN FOREST IN FRENCH GUIANA, SOUTH AMERICA

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Abstract. In ferralitic soils of the dense Guianese forest, mercury (Hg) concentrations of the surface horizons varied from 122 to 318 ng/g d.w. The behaviour and accumulation of Hg is not related to the accumulation of organic matter but to the penetration of humic substances and the progressive adsorption onto iron (Fe) oxy-hydroxydes in the mineral horizons. The flooding of such soils with the creation of a small reservoir has lead to a release of 20% of the Hg initially present. This observation is related to the reduction of the Fe oxy-hydroxydes and to the migration of the organo-metallic complexes to the water column. Although physico-chemical conditions are appropriate for bacterial methylation, methyl Hg (MeHg) levels of these soils are very low. The process regulating MeHg production and its possible loss from the soil are unknown.

1. Introduction

Fish taken from reservoirs far from point sources of anthropogenic contamination, be they in temperate (Meister *et al.*, 1979), sub-boreal (Verdon *et al.*, 1991), or tropical environments (Yincharoen and Bodaly, 1993), bear Hg concentrations up to 6 times greater than fish caught in neighbouring lakes and rivers. In the Amazon region, Hg in the biota of large hydroelectric reservoirs such as the Tucurui (Para, Brazil) may have been enhanced during the last decade by local upstream dumping of substantial quantities of Hg from gold mining activities (Aula *et al.*, 1994). In sub-boreal reservoirs, the release of Hg from flooded forest soils represents the primary source of this contaminant to aquatic organisms (Bobaly *et al.*, 1984; Johnston *et al.*, 1991). The Hg found in soils appears to have both natural and anthropogenic origins (Grondin *et al.*, 1995). In equatorial South America, Hg released into the atmosphere by the abovementioned gold mining activities could also be responsible for increased precipitation of Hg onto soils (Pfeiffer *et al.*, 1993). The effects of flooding on the biogeochemical behaviour of Hg in the Amazonian forest soils remain unknown. The purpose of this investigation was to study the principal processes by which Hg is incorporated into the upper horizons of pristine ferralitic and hydromorphic soils in French Guiana and, subsequently, released to the overlying water following several years of flooding.

2. Materials and Methods

The study site is a former fresh water shrimp farm located approximately 60 km south of Cayenne in French Guiana, and includes a reservoir developed in 1984 which floods 37 ha of dense primary forest (Roulet, 1994). The reservoir is similar to the littoral zone of the large Amazonian hydroelectric reservoirs in the following ways: water temperature (29-32°C), water depth (3.5 m maximum), dead submerged tree trunks, dendritic shape, and the absence of strong advection currents. During August 1992, duplicate cores were taken from six stations representing three pristine forest soils (UF1, UF2, UF3) and three

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flooded equivalents (FF1, FF2, FF3) in 1.5-2 m of water. Each core was taken by manually inserting a 15 cm diameter PVC tube to a maximum depth of 30 cm. The surficial flocculated material (floc) of the FF cores was sampled *in situ* with 60 mL syringes. The soils of stations 1 and 2 were typical yellow ferralitic soils (oxisols of the U.S. soil classification), while station 3, at the base of a slope, was characterized by hydromorphic soils. Profiles of pH and redox potential (Eh) were determined for the FF cores. All cores were sliced at one centimetre intervals, and the subsamples, stored in plastic bags, were immediately frozen, and later freeze-dried. Following the digestion of 1-2 g of dry matter in a 10:1 mixture of concentrated nitric acid and 6N quartz-distilled hydrochloric acid, total Hg analyses were conducted by cold vapour atomic fluorescence spectrometry (CVAFS) using a modification of the method of Bloom and Fitzgerald (1988) (Montgomery *et al.*, 1995b). MeHg in the soils was extracted by distillation conducted at 85°C (Horvat *et al.*, 1988), whereby 10-20 mg of dry matter were added to a distillation tube together with 0.7 ml NANOpure water, 0.2 ml 2M sulfuric acid, and 0.1 ml 4M potassium bromide (Mucci *et al.*,1995). The recuperated MeHg was then treated with a solution of potassium persulfate, oxidized for 30 minutes via exposure to U.V. lamps, and then analysed by CVAFS. The carbon (C) and nitrogen (N) contents of the soils were measured using a Carlo Erba analyser. The stable C isotope concentrations in carbon dioxide obtained after combustion of the samples were measured by the Prism VG mass spectrometer. The $^{13}C/^{12}C$ isotopic ratio, $\delta^{13}C$ (‰) is expressed relative to the PDB standard. Reactive Fe (operationally defined as Fe oxy-hydroxides), Fe_{cdb}, was extracted using the citrate-dithionite-bicarbonate buffer (Lucotte and d'Anglejan, 1985), then analysed by atomic absorption.

3. Results

3.1. INTACT AND FLOODED FERRALITIC SOILS

The organic (O2, noted OH) and humic (A1, noted HH) horizons of the ferralitic soils, UF1 and UF2, are limited to 1-6 cm in thickness and are rich in C (>10%), while in the underlying humic penetration horizon (A3, noted HPH) the levels of C fall dramatically, and stabilize at 2-8 % (Figure 1). The variation of the atomic C/N ratio follows the profile of C. The C/N ratio changes from a value of 20-30, which is in equilibrium with the litter and forest vegetation (C/N=20.9 and 25.1, respectively), to a value of humic matter (C/N=10-15). This illustrates the more rapid mineralization of C compared to that of N in soils (Fanning and Fanning, 1989). The evolution of C and C/N in soils is accompanied by a progressive enrichment in ^{13}C from the OH (-29 to -30‰) to the underlying horizons (-28 to -26‰) (Figure 2). The amount of Fe_{cdb} increases dramatically from the HH to HPH (+200 µmol/g), then progressively (600-800 µmol/g) along the entire length of the latter (Figure 2). The Fe_{cdb} content reaches a maximum at the surface of the nodular zone which delineates the bottom of the HPH. The concentration of Hg is not linearly correlated with C content ($r<0.70$) as OH's contain less Hg than the underlying mineral horizons (HH and HPH). Two cores (UF1-1 and UF2-2) show an accumulation of Hg just beneath the OH. This is accompanied by rapid mineralization and a sudden decrease in C at the surface of the cores. In contrast to these observations, both mineralization and Hg levels of the UF1-2 and UF2-1 cores, increase progressively through the HH.

The flooded soil-water interface (not represented in the figures) is characterized by a 1 cm layer consisting of fine and coarse plant debris (C/N=27, $\delta^{13}C$=-31.2‰), and is overlain by 1-1.5 cm of floc composed of nearly pristine terrestial plant matter (C/N=19, $\delta^{13}C$=-30.1‰) (Bird *et al.*, 1992). The C values of the HPH for flooded soils appear to be less rich than those of the pristine ones (2.2±2.1% *vs* 6.2±4.4%). The lower C contents

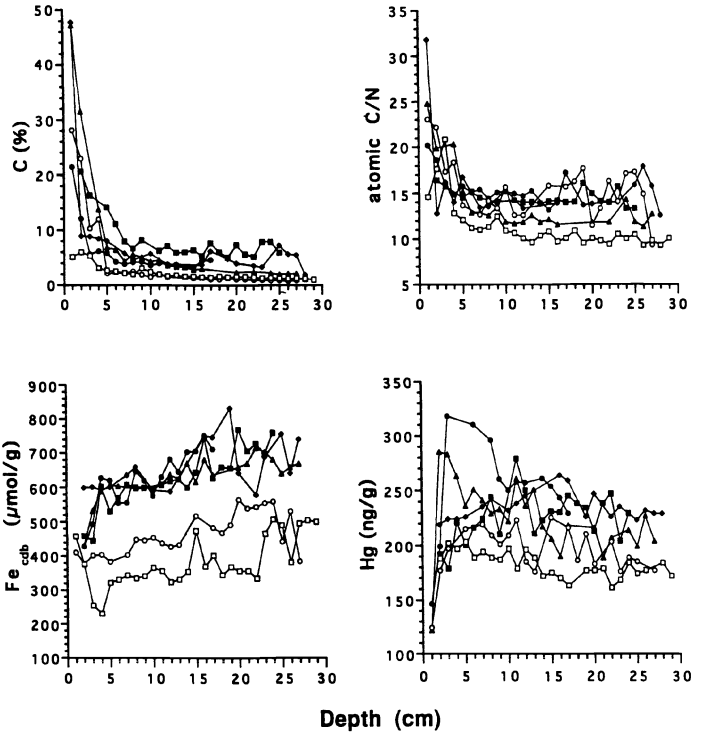

Fig. 1: Profiles of C, atomic C/N, Fe_{cdb} and total Hg for the pristine ferralitic soils UF1-1 (●), UF1-2 (■), UF2-1 (◆), UF2-2 (▲), and their flooded equivalents FF1-1 (○), FF2-1 (❑).

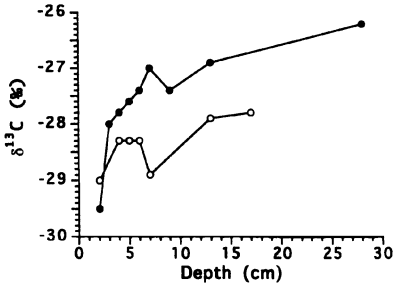

Fig 2: Profiles of $\delta^{13}C$ for the pristine ferralitic soil UF2-2 (●) and the flooded ferralitic soil FF2-2 (○).

are accompanied by a >1‰ reduction of the $\delta^{13}C$ ratios (Figure 1). Flooding leads to increasingly reducing conditions for Fe (Ponnamperuma *et al.*, 1972) in the OH (+80<Eh<+260mV, 5.4<pH<5.8) and HPH (-20<Eh<+40mV, 5.3<pH<6). Comparison of the intact and flooded soil profiles shows that, while the trends are similar, the latter contains 200-300 µmol/g less Fe_{cdb} in the HPH (Figure 1). No accumulation of Fe_{cdb},

however, is observed at the flooded soil-water interface in comparison with the pristine soils. After flooding, although Hg concentrations (Figure 1) remained elevated in all horizons, they were about 20% less than those of the intact soils (189±16 ng/g *vs* 235±26 ng/g). The Hg concentrations of flooded ferralitic soils are fairly strongly correlated with Fe_{cdb} (r=0.8) but not with C (r<0.5).

3.2. INTACT AND FLOODED HYDROMORPHIC SOILS

The hydromorphic soils (i.e., those which experience water table fluctuations up to their surface but are never submerged) (UF3) were represented by gley soils. Below a thin OH lies an impoverished HH, as indicated by C values less than 5% (Figure 3). In the underlying grey eluviated horizon (E, noted EH), the amount of C quickly falls to less than 0.5%. For the HH and the top of the EH, C/N values (15-20) suggest little humification of the organic matter. Water saturation of hydromorphic soils produces reduced conditions (Vizier, 1971) which in turn results in 15-30 times less Fe_{cdb} than in drained ferralitic soils. Profiles for Fe_{cdb}, like those of Hg, show little variability with depth. Hg concentrations are low (<100 ng/g) and not correlated to C content (r<0.5).

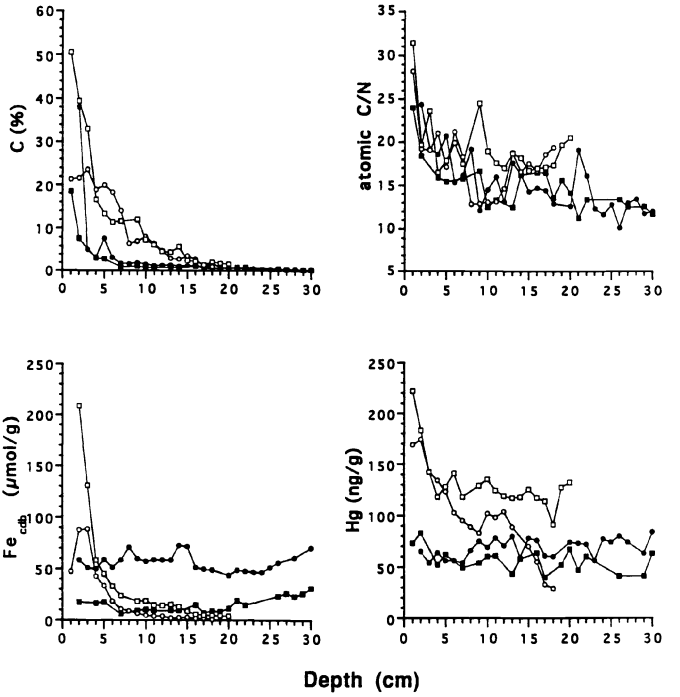

Fig. 3: Profiles of C, atomic C/N, Fe_{cdb} and total Hg for the pristine hydromorphic soils, UF3-1 (●), UF3-2 (■), and their flooded equivalents FF3-1 (○), FF3-1 (□).

Prior to inundation, the FF3 soils, being at a lower elevation than the UF3 soils, were frequently saturated, and often completely submerged. The humification of accumulated organic matter is not advanced since can still be plant debris detected and the clayey texture increased toward the bottom. The OH (C>10%) is up to 7-8 cm thick (Figure 3), and the HH of the FF3 soils is richer in C than the UF3 equivalents, while C/N levels are

identical. In the EH, C contents are negligible, as is typical of all intact hydromorphic soils. In contrast, C/N values increase towards the base of the EH horizon (>15). Fe_{cdb} is almost completely absent in the FF3 soils (Figure 3), where Eh and pH are higher near the surface as compared to flooded ferralitic soils (Eh=+380 mV, pH=6.6). Reducing conditions are, however, observed in the EH (-30<Eh<+50mV, 4.8<pH<5.7). Fe_{cdb} and Hg profiles are characterized by surface accumulation (r=0.8). The Hg concentration is linearly correlated to C content (r=0.76 and 0.86, for FF3-1 and FF3-2, respectively).

4. Discussion

4.1. THE DISTRIBUTION OF MERCURY IN FERRALITIC SOILS

In the ferralitic soils of dense forests, plant litter is rapidly mineralized in the OH. The C/N and $\delta^{13}C$ profiles (Figures 1 and 2) indicate an important change in the quality of organic substances from the OH to the HPH. The observed increase of $\delta^{13}C$ with depth corresponds to a migration of fulvic acids rich in ^{13}C, as has been previously suggested for Brazilian ferralitic soils (Volkoff and Cerri, 1988). In fact, the deeper penetration of humified matter is made up of about 40% fulvic acid in these soils. Fe_{cdb} is much less mobile than humic substances. The leaching of Fe is moderate and, in large part, associated with that of clay (Fanning and Fanning, 1989). The precipitation of illuvial Fe_{cdb} can lead to the formation of neogenic nodules (Muller and Bocquier, 1986) as observed at the base of the HPH of the sampled soils.

There is no accumulation of Hg associated with organic matter in ferralitic soils. In fact, Hg is less abundant in the thin OH than in the mineral horizons. Similarly in the Tucurui region of Brazil, Aula *et al.* (1994) observed the same relationship in ferralitic soils heavily leached of clay (solos podzolicos vermelhos-amarelos or ultisol). The behaviour of Hg in such soils is thus very different from that observed in sub-boreal acidic organic soils, such as podzols and histosols, in which the accumulation of Hg is correlated with the abundance of C in the OH (Andersson, 1979; Grondin *et al.*, 1995). Hg, as well as numerous other heavy metals, can be adsorbed on mineral surfaces (Schuster 1991). Free Hg ions can be complexed by goethite (Forbes *et al.*, 1974) and adsorbed by Fe_{cdb} gels (Kinniburgh and Jackson, 1978), or even co-precipitated (Inoue and Munemori, 1979). In this study, the absence of a correlation between Hg and Fe_{cdb} suggests that the retention of Hg in ferralitic soils is not controlled solely by Fe.

As noted in sub-boreal podzols, acidic conditions are favourable to the formation of organo-Hg complexes (Andersson, 1979; Lodenius *et al.*, 1987). It has been experimentally recognized that Hg has a greater affinity for humic substances, in particular fulvic acids, than for inorganic ions such as chlorine (Cl^-) and hydroxide (OH^-) (Schuster, 1991; Xu and Allard, 1991). Concomitant with the deposition of Hg associated with litterfall is it's liberation by the mineralization of plant matter and subsequent migration to the HPH. This leads to the supposition that the penetration of Hg in ferralitic soils is controlled by the mobility of humic-Hg complexes (Fulvic acid-Hg complexes, in particular). Under certain conditions humic and fulvic acids have a strong affinity for metallic oxy-hydroxides (Tipping, 1981). Soluble humic-Hg complexes which penetrate these soils can thus be readsorbed by Fe_{cdb} which are increasingly abundant (Figure 1). This corresponds with the experiments of Xu and Allard (1991) which show that Hg complexes appear more readily adsorbed on mineral surfaces than do free Hg^{2+} ions. The same phenomenon can probably explain the progressive Hg immobilization in the soils of

Aula *et al.* (1994). Fe nodules may be responsible for further Hg immobilization as they were found to contain 218±206 ng/g of Hg.

4.2. THE DISTRIBUTION OF MERCURY IN HYDROMORPHIC SOILS

In spite of water saturated conditions which generally slow down bacterial activity, there is no accumulation of organic matter (Ponnamperuma, 1972) in hydromorphic soils. Elevated C/N ratios are consistant with the formation of under-polymerized humic acids which remain soluble in these soils (Volkoff and Cerri, 1988). Under the ambiant reducing conditions, most of the Fe is dissolved in pore waters as ferrous ions. Fluctuations of the water-table allow the most soluble of the organic substances, as well as Fe, to be uniformly distributed in the soil profiles and entrained with water (Vizier, 1978). In hydromorphic soils, the reduction of Fe_{cdb} thus cancels out most of the adsorption capacity of soil solids. Hg linked to humic substances, following its release from organic plant matter, is thus further leached by runoff, as suggested by its weak retention in the soil (limited to 50 to 90 ng/g in the EH).

4.3. THE GEOCHEMISTRY OF MERCURY IN FLOODED SOILS

Upon inundation of ferralitic soils, physico-chemical reactions and biodegradation of soil organic matter leads to reducing conditions through the entire soil profile (Vizier, 1978; Gunnison *et al.*,1985) and results in a net loss of 25-40% of the initial Fe_{cdb} content. Differences in both the quality and quantity of C in the HPH before and after flooding is observed in horizons where organic matter, in intact soils, is already degraded (Volkoff and Cerri, 1988). The $\delta^{13}C$ ratios measured in flooded soils correspond to humus less degraded or more enriched in refractory compounds than the intact soils (Benner *et al.*, 1987). Bacterial degradation alone is likely not responsible for such a drastic change in the composition and distribution of the organic matter. On the other hand, loss of free humic substances, rich in ^{13}C, would allow for the heavy isotope impoverishment of organic matter in the soil. The FF1-2 soil (Figure 4), atypical since leaf debris and decomposed twigs are identifiable in the accumulated humus, clearly illustrates this migration. The C content, elevated in all horizons (≈10%), does not follow the same trend as the C/N values, which increase from 15 to 30 with depth. This increase represents a relative enrichment in refractory organic matter which remains following the loss of mobile humic substances due to upward migration.

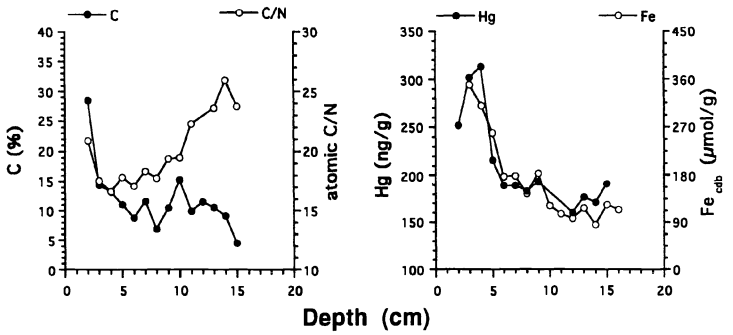

Figure 4: Profiles of C, atomic C/N, Fe_{cdb}, and total Hg for the flooded ferralitic soil, FF1-2.

The remobilization of Fe and mobile humic substances permits nearly 20% of complexed Hg, initially adsorbed onto Fe_{cdb}, to escape the ferralitic soils. This process has also been observed in Hg-poor mineral horizons of flooded soils in sub-boreal reservoirs (Dmytriw *et al.*, this issue; Grondin *et al.*, 1995). These authors propose that the reprecipitation of Fe_{cdb} at a thin oxic layer at the flooded soil-water interface limits the release of Hg. No such zone, however, was observed in our FF1-1 and FF1-2 ferrilitic soils. Diffusion of the complexed Hg toward the water column is therefore likely. In contrast, Hg concentrations at the surface of the humic soil, FF1-2, (Figure 4), where Fe precipitated, reach 313 ng/g.

Fe_{cdb} is fairly abundant in ferralitic soils (300-500 µmol/g) even after 8 years of inundation, while concentrations in unflooded hydromorphic soils are negligible. The fraction of the Hg (189 ng/g on average) immobilized by or co-precipitated with the remnant Fe phase appears to stay in the soil matrix. This fact is well illustrated by the FF2-2 flooded soil (Figure 5), where the HPH, composed of humus caracteristic of typical ferralitic soils (C<10%, C/N≈10), is relatively poor in Fe_{cdb} (125-200 µmol/g). The Hg in this soil accumulates in the middle of this horizon, corresponding to an important zone of newly precipitated Fe nodules.

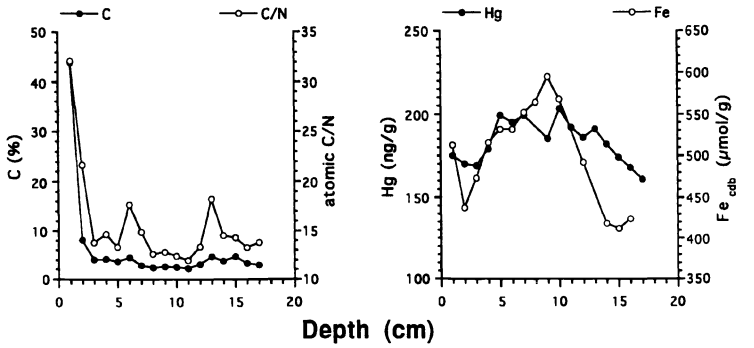

Fig. 5: Profiles of C, atomic C/N, Fe_{cdb}, and total Hg for the flooded ferralitic soil, FF2-2.

In flooded hydromorphic soils, remobilized Fe reprecipitated at the oxic soil-water interface corresponds to a maximum accumulation of Hg. Although it is difficult to distinguish Hg associated with Fe from that which was originally present in the former OH's of the two sampled soils, we found a two-fold difference in Hg concentrations between flooded and pristine soils (200 ng/g *vs* 100 ng/g). This observation suggests that a good portion of the surficial Hg present in the flooded hydromorphic soils may be attributed to adsorption by Fe_{cdb}.

4.4. METHYLATION OF MERCURY IN FLOODED SOILS

Despite warm temperatures and slightly anaerobic conditions, factors favourable for the production of MeHg (Callister and Winfrey, 1986), no increase in concentration was noted following flooding. Methyl Hg levels, in fact, remained very low (1% of total Hg) (Table I). In flooded ferralitic soils this may be attributed to three different causes: (1) MeHg production is insignificant compared with demethylation, (2) methylation is slowed, or (3) MeHg is released to the overlying water column. In contrast, the flooding of

hydromorphic soils, initially containing little Hg, leads to a significant accumulation of MeHg (5-20% of total Hg).

TABLE I. : Total Hg (ng/g d.w.), MeHg (ng/g d.w.), and % of MeHg in the pristine soil, UF2-2, and the flooded soils, FFI-1, FF2-2, and FF3-1.

	UF2-2			FF1-1			FF2-2			FF3-1		
Depth	Hg tot.	MeHg	MeHg (%)	Hg tot.	MeHg	MeHg (%)	Hg tot.	MeHg	MeHg (%)	Hg tot.	MeHg	MeHg (%)
Floc				162	4,4	2,7	146	6,8	4,7	142	3,4	2,4
0-1	-	-	-	172	7,4	4,3	-	-	-	155	7,7	5
1-2	285	2,3	0,8	177	1,6	0,9	175	0,6	0,3	152	29,3	19,3
2-3	283	2,9	1	197	2,5	1,3	170	1,5	0,9	142	14,1	10
5-6	251	2,7	1,1	-	-	-	-	-	-	103	7,4	7,1
6-7	241	2,8	1,2	219	3	1,4	195	0	0	-	-	-
7-8	-	-	-	-	-	-	199	0,8	0,4	89	1,4	1,6
9-10	222	0,9	0,4	-	-	-	185	0,5	0,3	-	-	-
10-11	-	-	-	-	-	-	203	0,8	0,4	98	1,5	1,5
14-15	217	1	0,5	225	2	0,9	182	1,1	0,6	-	-	-

5. Conclusions

The concentrations of Hg in Guianese ferralitic soils are elevated compared to presently published data for the background levels of Amazonian soils, which vary from 30 to 100 ng/g d.w. (Pfeiffer *et al.*, 1993; Aula *et al.*, 1994). These values do not reflect, however, one type of soil nor a specific region. For example, Aula *et al.* (1994), in the Tucurui region, studied strongly leached and desaturated ferralitic soils, Malm *et al.* (1991) sampled humic-rich soils in the Madeira River region, and the results of Lacerda *et al.* (1991) are for unidentified forest soils of the Poconé region. The soils of this investigation are typical ferralitic soils with no surface accumulation of organic matter. On the contrary, humic matter penetrates to the mineral horizons, drawing Hg with it. The behaviour of Hg is thus neither linked to amounts of C nor to those of Fe_{cdb}. The absence of this correlation suggests that the quality of organic matter (breakdown products: humic and fulvic acids) and its adsorption by Fe_{cdb} controls the retention of Hg in ferralitic soils. In regions of the Amazon where soil Hg concentrations surpass background levels (30 to 100 ng/g d.w.), Hg accumulated with organic matter has, until now, been interpreted to be the direct result of atmospheric contamination due to gold mining activities (Pfeiffer *et al.*, 1993). Aula *et al.* (1994), however, stated that atmospheric inputs were negligible in the Tucurui region as Hg concentrations in their sampled soils were <100ng/g d.w. and showed no surficial accumulation. Although Malm *et al.* (1991), while studying humic soils (organic matter >27%), considered airborne contamination to be important due to surface accumulation, we do not feel this to be justified for our case since we find similar concentrations in the mineral horizons. In our opinion, without more systematic studies to quantify background levels in the various soils, it is impossible to confirm that mining activities in Guiana, and in the rest of Amazonia, are responsible for the high Hg levels observed in the soils.

In the small reservoir, composed of flooded ferralitic soils, we found that approximately 20% of the Hg was released to the water column following the reduction of 25 to 40% of the Fe oxy-hydroxides Organic matter at the surface of flooded soils contained very little Hg compared with mineral horizons. The release of Hg linked to the decomposition of

surface organic matter is thus a negligible process compared with that observed along the entire length of the mineral horizons (to a depth of at least 30 cm). The problem of Hg contamination in temperate and sub-boreal reservoirs has often been linked to the decomposition of organic matter in flooded soils (Morisson and Thérien, 1991; Jackson, 1988). It was recently demonstrated that bio-decomposition is not important in the case of flooded sub-boreal soils, and that the release of Hg by diffusion is a relatively limited phenomenon (Montgomery *et al.*, 1995a). In these reservoirs, the principal processes leading to the contamination of the food chain are due to shore erosion (Louchouarn *et al.*, 1993; Mucci *et al.*, 1995), and bioaccumulation in biota living at the surface of flooded soils (Tremblay *et al.*, 1995). Although these processes can also be present in tropical reservoirs, the reduction of Fe oxy-hydroxides play a major role in the liberation of Hg.

Evangelista (1993) observed important quantities of dissolved Fe on the bottom of the Tucurui reservoir following the dissolution of Fe oxy-hydroxides from soils and sediments in the anoxic hypolimnion. In an isolated area of the same reservoir, Aula *et al.* (1994) concluded that elevated levels of Hg in the aquatic biota could be attributed to its release from vegetation and soils, while the principal contaminant sources for the whole reservoir must be gold mines located upstream. Because 75% of the advection current passes through the former riverbed in the Tucurui reservoir, anthropogenic Hg coming from upstream zones should be less important in lateral zones, and almost negligible in isolated arms. The process of Hg release from the mineral horizons of the lateral zone soils could thus be much more important for the contamination of the reservoir than Aula *et al.* (1994) suggest. Contamination observed by Yincharoen and Bodaly (1993) in Thai dams is probably also the result of this phenomenon. Finally, the partial absence of MeHg in flooded ferralitic soils necessitates further study into mechanisms which may regulate the formation and transfer of this contaminant to the food web.

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MERCURY CONTAMINATED SITES - BEHAVIOUR OF MERCURY AND ITS SPECIES IN LYSIMETER EXPERIMENTS

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Abstract. In a polluted site in Germany not only metallic, ionic and MeHg could be detected, but also organomercurials such as methyl- ethyl- and phenyl-mercury. In addition sometimes other organomercurials could be separated but up to now not identified. Extraction of the organomercurials from soil and percolating water was performed by dithizone, differentiation and detection by High-Performance-Liquid-Chromatography and atomic fluorescence detection, respectively. Differentiation between gaseous organic and gaseous elemental mercury was done by adsorption on Carbotrap® and gold filters, thermal desorption and detection by atomic fluorescence

The behaviour of 8 organomercurials in soil is described. For this a lysimeter of a new design was filled with polluted soil. The top layer of the soil was spiked with 8 organomercurials. The percolating water and the air above the soil. were analyzed. Different layers of the soil were also investigated after the experiment. By synthetic rain the movement of Hg species is low: the compounds stay in the first centimeters. Ethoxyethylmercury$^+$, tolylmercury$^+$, and nitromersol were not detected in the percocolate. Concentrations of phenylmercury$^+$ and hydroxymercurybenzoicacid decreased. Methoxymethylmercury$^+$ increased. In the head of the lysimeter, volatile Hg(0) concentration increased during 150 hours by a factor of 5, while volatile organic mercury decreased during this time by a factor of 10. The organomercurial-content in soil decreased.A transformation of organic to inorganic Hg is therefore presumed.

1. Introduction

Many different organomercurials were produced as pesticides and pharmaceuticals in the past in Germany. Several sites are contaminated now by these compounds. It could be expected, that each of these Hg species behave differently in the environment [Wilken et al., 1993]. Aqualified analytical procedure was not available for all compounds. So, first, this has to be developed (Hempel *et al.*, 1992; Hintelmann & Wilken, 1993). Some of these species could be regarded as unstable in sunlight or during the chemical separation steps. Their degradation products could be other organomercurials or Hg(0) and could be absorbed on the soil particles or could remain as volatile species(Craig, 1986; Adam *et al.*, 1980).

In soil and sediments Hg is mainly bound to organic matter. Mobilization often takes place by degradation of the humic substance. Mercury is bound in the water phase to humic and fulvic acids and shows positive correlation to DOC (dissolved organic carbon) (Mierle, 1991; Borg and Johannson, 1989; Iverfeldt and Johansson, 1988). Very little is known about the mobility and sorption of mercury-species. Sorption of Hg decreases as follows: $HgCl_2$ >> CH_3HgCl >> $C_6H_5HgOCOCH_3$ [Hogg *et al.*, 1978]. The aim of this investigation was to assess the risk of sites contaminated by the organomercurials mentioned.

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2. Materials and methods

The analysis of Hg species in soil and water consists of different steps, outlined in Figure 1.

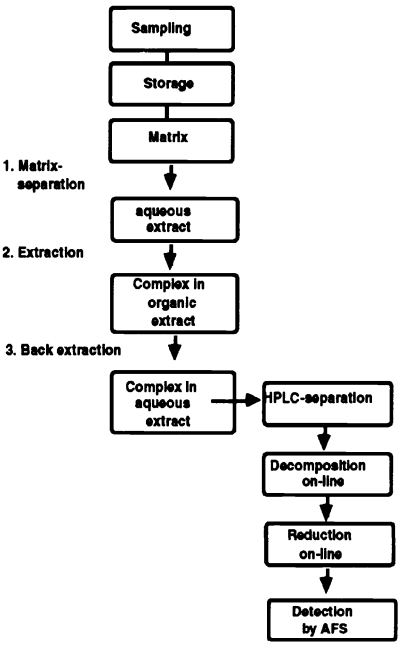


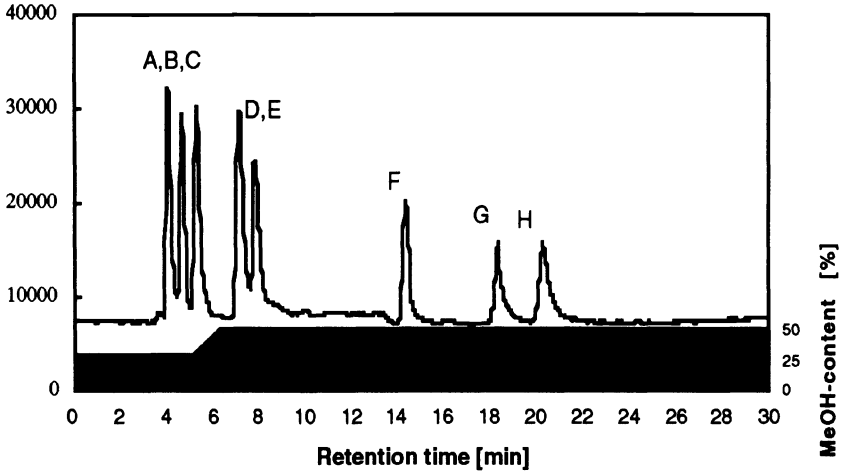
Fig. 1. Strategy to isolate organomercurials with HPLC separation and AFS detection

The soil samples for the lysimeter experiments were taken undisturbed directly in the lysimeter. For the Hg analysis, the samples taken were stored without any sample pretreatment. They were not dried, in order to avoid losses of volatile Hg and Hg compounds. The influence of storage on the stability of mercury species was investigated. The methylmercury concentrations showed no statistical ly significant differences after 8 months at temperatures of 4° and -30 °C (Hintelmann and Wilken, 1993).

The total Hg concentration was determined by decomposition in quartz vessels. 1-2 g of sample were digested in 10 ml HNO_3 conc, suprapur, for 4 hours at 80°C under reflux. The digested samples were diluted by water and measured by Atomic Absorption Spectroscopy, AAS (Perkin Elmer), or by Atomic Fluorescence Spectroscopy, AFS (Brooks Rand). If the dilution was not complete due to organic substances, these were oxidized by 1 ml 0.2 M BrCl solution.

Analysis of Organomercurials

Extraction of Methylmercury: 50 ml of hydrochloride acid (6 mol dm^{-3}) were added to 10 g wet soil sample. The sample was extracted by shaking for 60 min. After centrifugation the supernatant solution was shaken two times with 5 ml toluene. Subsequently, both toluene portions were extracted with 1 cm^3 of a sodium-thiosulfate (1 mmol dm^{-3}) buffered with ammonium acetate (0.05 mmol dm^{-3}).



Extraction of Organomercurials except methylmercury: a 5 cm^3 portion of a citrate buffer (21 g dm^{-3} citric acid, 8 g dm^{-3} sodium hydroxyde, was adjusted to pH 2 by adding 0.1 mol cm^{-3} dithizone in chloroform for 60 min. The sample was centrifuged and the organic phase was transferred to a test-tube, where the dithizone-mercury-complexes were destroyed by shaking with 1 cm^3 of a nitrite/acid-mixture until the colour of the solution changed from green to yellow. Afterwards, the chloroform-phase was extracted with 1 cm^3 of a sodium-thiosulfate solution (1 mmol dm^{-3}) buffered with ammonium acetate (0.05 mmol dm^{-3}).

Determination of the Organomercurials by HPLC/AFS:

A Beckman 126 pump module equipped with a Beckman model 501 autosampler running a 200 mm x 3 mm i.d.column with 10 mm x 3 mm i.d. guard column packed with Chromspher RP /18 material (3 µm, Chrompack) was used for the analysis. The mobile phase consisted of mixtures of methanol/water (30:70, after 10 min. 50:50) buffered with ammonium acetate (20 mmol dm^{-3}) and modified by 2-mercaptoethanol (0,1 mmol dm^{-3}). The flow rate was 0.5 cm min^{-1}. The HPLC was connected with an oxidation /reduction interface. In the first step the oxidizing solution (0.25 mol dm^{-3} sulphuric acid; 0.008 mmol dm^{-3} copper sulfate; 2,5 % potassium peroxodisulfate) was added to the mobile phase to oxidize all organomercurials leaving the HPLC. In the second step, the reducing agent (1.5 % tin(II)chloride; 1.2 mol dm^{-3} sodium hydroxyde) was added to generate elemental mercury. The oxidation/reduction interface was connected to a gas-liquid-separator, followed by a water-removal-membrane (PSA, USA). Afterwards the Hg-containing gas-stream (Helium, 5.0) entered the atomic fluorescence spectrometer (CVAFS 2, Brooks Rand Ltd, Seattle, USA) (Hintelmann and Wilken, 1993).

A HPLC-chromatogram with the separation of different organomercury species is demonstrated in Figure 2.

Fig. 2. Gradient-HPLC/AFS-chromatogram of different organomercury species. Methylmercurychloride (A), Methoxyethylmercurychloride (B), p-(Chloromercuri)benzoic acid (C), Ethylmercurychloride (D), Ethoxyethylmercurychloride (E), Phenylmercurychloride (F), Nitromersol (G) und Tolylmercurychlorid (H), amount added: 2,5 ng Hg absolute each

The detection limit was calculated for MeHg on the basis of 2 g dw soil, recovery rate after HCl / toluene extraction 83 %, thiosulfate extract 1 ml, enrichment factor 5, volume injected: 25 µl, detection limit of the AFS: 20 pg Hg: DL 0.1 µg Hg / kg d.w. soil.

Experiments with lysimeters were performed for the investigation of the mobility of pollutants in soil (Berstrom, 1990). The dynamic behaviour of substances could often be seen in the percolate when artificial rain is added at the top of the column. For mercury investigations, the volatility of this element and its compounds must be taken into consideration and therefore the volatile species should also be measured. The material used must allow no adsorption of Hg, so memory effects, contamination and losses could be avoided.

The lysimeter used is shown in Figure 3.

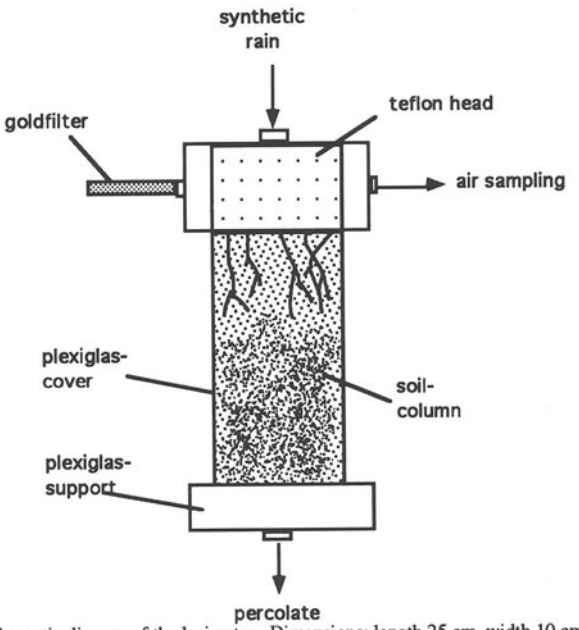


Fig. 3. Schematic diagramof the lysimeter . Dimensions: length 25 cm, width 10 cm. Materials as indicated.

Artificial rain could be added through a valve on top of the teflon head. Cleaned air could be drawn across the top of the soil. The lysimeter foot has a valve for sampling the percolate water.

The soil sample was taken undisturbed from the banks of a small Hg contaminated river in Bavaria, Germany. The mercury species concentrations in a mixed soil sample of the top 20 cm layers are 65.3 mg/kg dw ± 9.5, 7 ± 3 µg/kg dw methylmercury$^+$, and 4 ± 3 ethylmercury$^+$.

Other Hg compounds were brought on top of the soil column in an acetone solution. The compounds added and their concentrations are given in Table I.

TABLE I

Organomercury compounds added to the lysimeter experiment

	mg Hg/ 14 ml acetone		mg Hg/ 14 ml acetone
Methylmercurychloride	10.5	Ethylmercurychloride	11.2
Methoxy-ethylmercurychloride	13.9	Ethoxyethylmercury-chloride	11.3
4-Hydroxymercuribenzoic acid	14.2	Phenylmercurynitrate	13.7
Tolylmercurychloride	10.9	Nitromersol	7.6

3. Results and Discussion

The experiment was run for 14 days; the amount of artificial rain water was 800 ml in total. In the percolate the Hg species were determined. The results are shown in Figure 4 for organomercurials other than MeHg, and in Figure 5 the results for MeHg are presented.

The MeHg concentration lies about 1 μg/l in the percolate and remains more or less constant. The differences by a factor of 2 between the results obtained could be explained by the inhomogenety of the samples collected from the sites.

Of special interest is the behaviour of the other mercurials. They can be divided into three groups:

i Those, which could not be detected in the percolate: methoxyethylmercury$^+$, tolylmercury$^+$, and nitromersol. Ethylmercury could only be detected in one sample at 0.01 μg/l.

ii Those with decreasing concentrations: phenylmercury$^+$ and hydroxymercurybenzoic acid

iii With increasing concentrations: methoxyethylmercury$^+$ only.

It is obvious that the differences between total Hg (Σ Hg tot) and organic Hg (Σ Hg org) were low at the beginning of the experiment whereas with increasing time and amount of percolating water the inorganic Hg dominates.

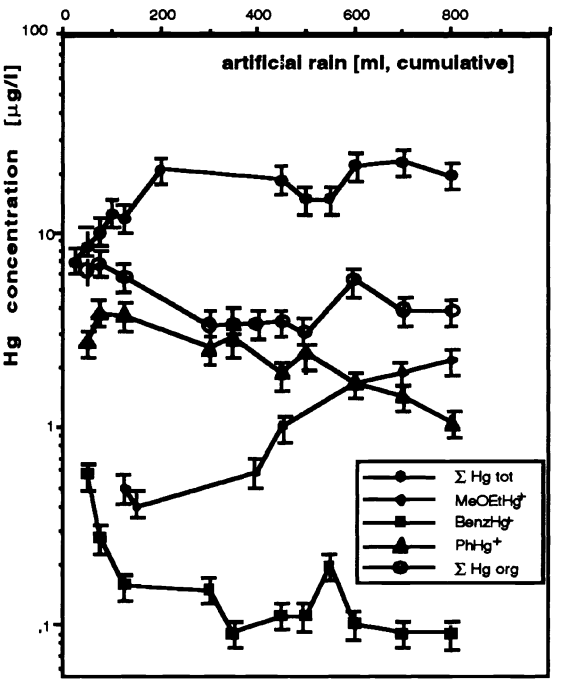


Fig. 4. Concentration of organic Hg species (without MeHg and total Hg in the eluate of a soil. abcissa see also figure 5. The error is the confidence interval Δx of the t-distribution of P = 0.95 and f = 2.

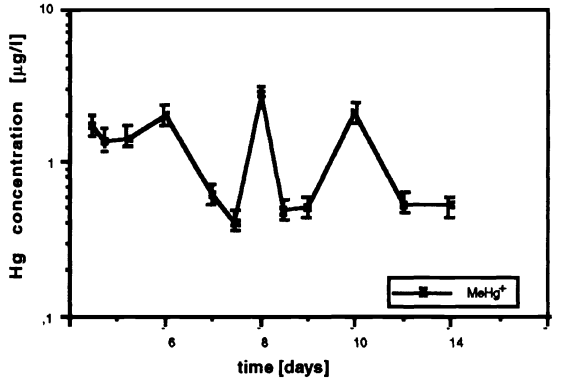


Fig. 5. Concentration of MeHg in eluate of a soil. Abcissa see also figure 4. The error is the confidence interval Δx of the t-distribution of P = 0.95 and f = 2.

After the experiment the soil column was taken out of the lysimeter and cut into slices of 2 to 3 cm thickness. In these different layers, the Hg species were analyzed together with some basic parameters. The results for the organomercurials are given in Figure 6.

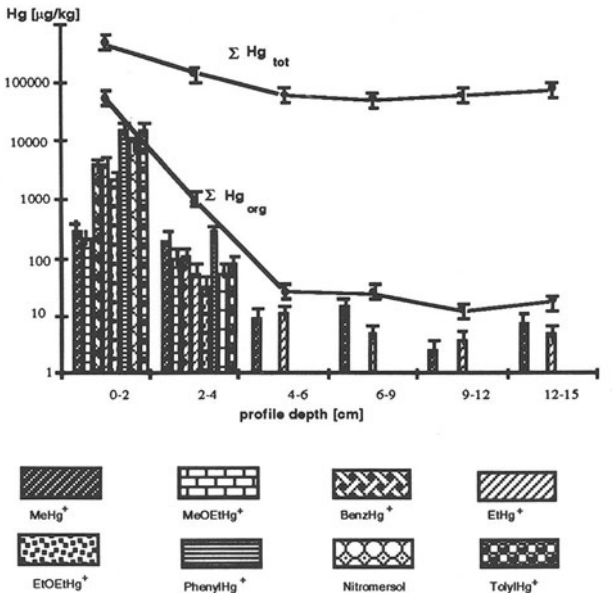


Fig. 6. Depth distribution of 8 different organomercurial species after percolation through a soil column. The errors describe the confidence interval Δx of the t-distribution for P = 0,95 and f = 2.

The loss on ignition and the sulphur content are given in Table II.

TABLE II

Sulphur content and loss on ignition in the soil column after completing the lysimeter experiments.

Depth [cm]	loss on ignition [%]	S [%]
0-2	12.2 ± 0.3	0.10 ± 0.01
2-4	12.0 ± 0.3	0.08 ± 0.01
4-6	10.4 ± 0.1	0.09 ± 0.01
6-9	10.7 ± 0.3	0.04 ± 0.01
9-12	8.8 ± 0.1	0.04 ± 0.01
12-15	7.8 ± 0.3	0.02 ± 0.01

The total Hg concentration decreased from 467 ± 13 mg/kg to 80 ± 4 mg/kg. The evaporation of mercury and its compounds into the lysimeter head is shown in Figure 7.

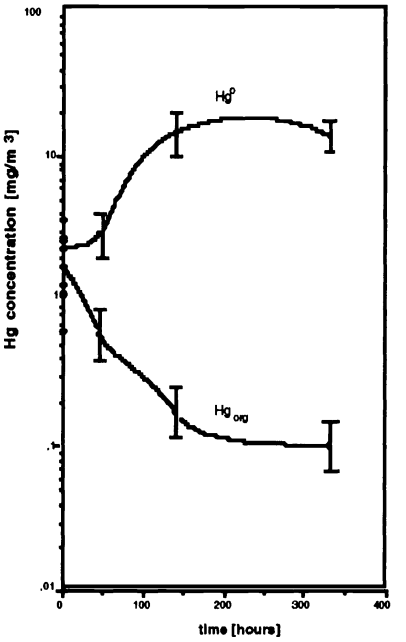


Fig. 7. Concentration of gaseous organic and elemental mercury during the lysimeter experiment above a soil column.

The total Hg concentration in the air increased from 4 to 15.2 mg/m^3. The organic Hg species decreased from 1.7 to 0.1 mg/m^3 at the end of the experiment. Elemental mercury concentration increased from 2.3 to 14.1 mg/m^3 during the first 130 hours. The concentrations therefore are a factor of 50 - 200 higher than those values, which we measured in the field, where we found 47 and 68 ng/m^3 of total Hg, and a variation of organic mercury concentrations between 8 and 29 ng/m^3.

The total budget of the Hg contents is summarized in Table III.

Table III

Balance of Hg contents and concentrations in soil, water and air in the lysimeter experiment. The error is estimated from the recovery rate and lies in the range of < 5 %. < dl: < 0.001

	Hg_{tot}	Hg_{org}	$MeHg^+$	MeOEt Hg^+	Benz- Hg^+	$EtHg^+$	EtOEt Hg^+	$PhHg^+$	Ni-trom.	Tolyl- Hg^+
basic contamination	52.4	<0.01	0.006			0.005				
spike [mg]	93.3	93.3	10.5	13.9	14.2	11.2	11.3	13.7	7.6	10.9
recovery-rate in										
soil [mg]	149.0	7.97	0.08	0.04	0.57	0.58	0.33	2.60	1.48	2.31
air [mg]	0.009	0.001								
water [mg]	0.0077	0.002	0.0004	<dl	<dl	<dl	<dl	0.0016	<dl	<dl
total [mg]	**149.0**	**7.98**	**0.08**	**0.04**	**0.57**	**0.58**	**0.33**	**2.60**	**1.48**	**2.31**
recovery [%]	**102.3**	**8.5**	**0.7**	**0.3**	**4.0**	**5.2**	**2.9**	**19.0**	**19.4**	**21.1**

4. Conclusion

As a result, the main amount of Hg in the lysimeter experiment was found in the soil. The amounts in the air and the percolating water were only a few µg. Most of the spiked Hg was found in the first centimeters, probably fixed on soil compartments like organic matter and clay minerals.

In the soil only 8.5 % of the organomercurials were found, although the total Hg content was recovered completely. The incomplete recovery of the organomercurials is probably caused by transformation processes to inorganic and elemental mercury. These processes lead to increasing volatilisation of Hg^0 and strong fixation of Hg^{2+} on organic matter and clay minerals in the top layer of the soil.

The results of the investigations indicate that Hg is transferred between different matrices and transformed to various species. These processes change the chemical, physical and toxicological nature of Hg and its mobility.

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THE PARTITIONING OF MERCURY IN THE SOLID COMPONENTS OF DRY AND FLOODED FOREST SOILS AND SEDIMENTS FROM A HYDROELECTRIC RESERVOIR, QUEBEC (CANADA)

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Abstract Upon inundation, the soils in a hydroelectric reservoir are subjected to several years of physical, biological, and chemical changes as the transition from a terrestrial to an aquatic ecosystem is achieved. It is suspected that changes in soil Eh and pH alter the metal binding capacity of organic matter, reactive iron (Fe) oxides/oxyhydroxides, and clay minerals, and may cause the mercury associated with these phases to be remobilized. Four cores were collected along a transect from an unflooded forest soil to a pre-impoundment lake bottom sediment. They were subjected to a customized sequential extraction procedure to determine the distribution of Hg between three operationally-defined solid compartments: organic carbon, reactive Fe oxides/hydroxides, and the solid (clay and sulfide) residue. Results indicate that up to 80% of the Hg in the O-horizon of forest soils and flooded soils and up to 85% of the Hg in lake sediments is bound to the NaOH-extractable organic carbon fraction. Furthermore, it was observed that the highest Hg concentrations are associated with degraded organic matter. In the B-horizon of a podzol, 40-60% of the total Hg was found associated with reactive Fe minerals. In contrast, the flooded podzol contains almost no reactive Fe at any depth and associated Hg concentrations are low. We propose that upon inundation, Fe oxides are reduced and Hg released to the pore waters where it is rapidly bound to other available substrates. Analyses of the extractions residues suggest that there is an enrichment of Hg in this fraction immediately above the B-horizon in a flooded soil.

1. Introduction

Mercury (Hg) is transported over long distances from sites of industrial and urban activity and is deposited uniformly on lakes and forests by wet and dry aeolian processes (Verta *et al.*, 1989; Lucotte *et al.*, 1994). Following the flooding of soils in the hydroelectric projects of northern Québec, aquatic organisms living in the impounded areas have been shown to exhibit elevated mercury levels (Brouard *et al.*, 1990). Mercury is believed to be released from inundated soils as a result of increased bacterial activity promoted by the flooding of terrestrial organic matter (Jackson, 1988a; 1988b).

In soil profiles and lake sediments, it is well established that Hg preferentially resides with organic matter (Louchouarn *et al.*, 1993; Lucotte *et al.*, 1994). The Hg adsorptive properties of poorly crystalline Fe oxides (Barrow and Cox, 1992; Forbes *et al.*, 1974) and clay minerals (Farrah and Pickering, 1978) in soils have also been documented. Iron oxides which accumulate in oxic surficial sediments can also retain Hg (MacNaughton and James, 1973).

Upon inundation of the soils, migration of the O_2 penetration depth towards the surface, and the reduction of the oxyhydroxides in the B-horizon, metals can be released to the pore waters and diffuse as soluble complexes both vertically and horizontally (Ponnamperuma, 1972). If a redox boundary is present near the sediment-water interface, soluble reduced iron may be reoxidized and precipitated as authigenic Fe-oxyhydroxides in this horizon where they can scavenge remobilized Hg.

In order to help characterize the geochemistry of mercury in terrestrial and aquatic systems, a sequential extraction procedure was devised and applied to determine the

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partitioning of Hg between three operationally-defined solid compartments: organic matter, reactive Fe and Mn oxyhydroxides, and a residual clay and sulfide fraction. The proportion of total mercury associated with each phase was determined on both dry and flooded soils in order to document the redistribution (if any) of mercury between these compartments resulting from a diagenetic remobilzation upon inundation.

2. Materials and Methods

Four sites, representing pre- and post-impoundment conditions of the LG-2 Reservoir (inundated in 1982), were sampled. They include: (1) a forest podzol, (2) a flooded forest podzol, (3) a gleysol, and (4) a pre-impoundment lake sediment now part of the reservoir.

The forest podzol, flooded forest podzol and gleysol were recovered using a beveled 15 cm diameter PVC tube inserted into the forest (or flooded forest) floor. The lake sediment, collected at a water depth of 22 m, was retrieved using a spring-loaded box corer subsampled with a 15-cm diameter PVC tube. Each core was manually extruded and subsampled at 1 cm intervals as it was exposed. Cores collected under water were subsampled under a nitrogen atmosphere. Subsamples were stored in individual plastic bags which were heat-sealed and frozen until analyzed in the laboratory in Montréal.

Total mercury [Hg(tot)] was determined following digestion/reaction of approximately 0.15 g of freeze-dried, homogenized sediment for six hours at 120°C with a 10:1 nitric:hydrochloric acid solution (SPEQ, 1979). After cooling and dilution, Hg concentration was determined by cold vapor atomic fluorescence (CVAF) following a modification of the procedure of Bloom and Fitzgerald (1988) (Pichet *et al.*, 1994; Montgomery *et al.*, 1994). When applied to NRC DORM standards, both the reproducibility (the variance divided by the mean) and the accuracy (difference between the measured and reported values, divided by the reported value) was between 4-5%.

Each 1 cm interval of the cores was analyzed 2-5 times. Reproducibility was ≅10% in the upper organic horizon where Hg concentrations are high, ≅5-20% in the lower mineral horizons where Hg concentrations approached the detection limit, and ≅5% in the finely divided homogeneous lake sediment.

A dilute alkali solution [1N sodium hydroxide (NaOH)] was employed to extract soil organic matter (Schnitzer and Khan 1978). Ten mL of the reagent were added to 0.15 g of freeze-dried homogenized sediment. The solutions were shaken for one hour, centrifuged, and the supernatant poured off. The process was repeated once and the supernates combined. Five mL of the combined supernates were digested using the acid digestion procedure described above, and the resulting solution was analyzed for Hg by CVAF. Carbon analyses performed on the solids before and after NaOH extraction indicated that >85% of the carbon in the B-horizon of both the dry and the flooded forest soil had been solubilized. In the upper organic horizons of forest and flooded forest soils, a residual 25-30% carbon remained. The lake sediment residue contained < 5% of the original C content after two extractions.

Reproducibility (s) for NaOH-extractable Hg [Hg(NaOH)] analyses fell between 15-30% for the podzol, flooded podzol, and gleysol. Lake sediment results were more consistent (s ≅ 7%) owing to its homogeneous nature.

Mercury associated with reactive Fe and Mn phases, Hg(HCl), was determined by CVAF following an extraction with 10 mL of 1N HCl for 24 hours. After dilution, the solutions were

analyzed for Fe by flame atomic absorption spectrophometry (Perkin-Elmer 3000). Reproducibility of Hg(HCl) analyses was ≅10% in the carbon-poor residues of the lake sediments and the B-horizons of pristine and flooded soils.

The amount of Hg retained by the solid residue, Hg(res), after the above extractions was determined following an acid digestion using the method described for Hg(tot). Owing to the low levels of mercury contained in this residue (often less than 10 $ng\,g^{-1}$), reproducibility was also low (s ≅ 20-40%).

Total organic carbon (%C) was determined using a Carlo-Erba elemental analyzer. Total sulfur (%S) was determined following combustion of solids in a LECO induction furnace and titration of the evolved SO_2 with an ALPHA sulfur titrator. Inorganic carbon was determined by coulometric titration of the CO_2 evolved following acidification of the sample with 2N HCl. In all cases, the inorganic carbon content did not exceed 0.06% and is therefore not reported.

3. Results and Discussion

3.1. Mercury-organic associations

Mercury is predominantly associated with the NaOH-extractable organic fraction (Figure 1), and thus correlated to the distribution of organic carbon in all four profiles. The NaOH digestion isolated 60-80% of the total Hg contained in the organic horizons of both the podzol and the flooded podzol, and >80% of the total mercury in the organic layer of the gleysol. At least 85% of the Hg(tot) in the former lake sediment was found to be extractable with 1N NaOH, suggesting that inorganic substrates are of minor importance in sequestering Hg in lake systems below the redox boundary.

Maximum Hg(NaOH) concentrations in the podzol, gleysol, and flooded podzol are found near the bottom of their respective organic horizons. These concentrations are associated with black, decaying, undifferentiated organic material.

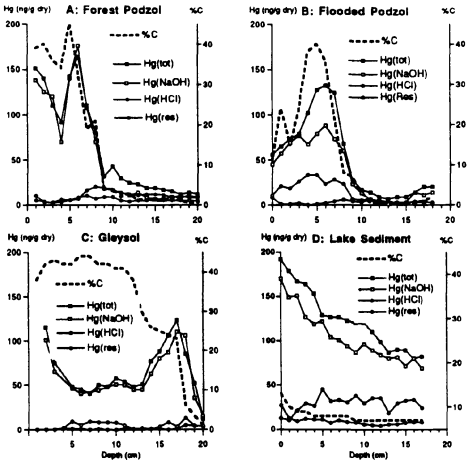

Fig. 1. Association of mercury to each operationally-defined substrate with depth. (A) Forest Podzol, (B) Flooded Podzol, (C) Gleysol, (D) Lake Sediment.

3.2. HCL-EXTRACTABLE IRON AND MERCURY

Between 40% and 60% of Hg(tot) residing in the B-horizon of the forest podzol is associated with HCl-extractable phases (Figure 1). The highest Hg(HCl) concentrations appear in the upper B-horizon, and are closely correlated with elluviated Fe(HCl) (r= 0.80) and visible rust-colored grains in the sample core.

There is three to four times more Hg(HCl) and Fe(HCl) in the forest podzol than in its flooded equivalent. The flooded soil contains little reactive Fe at any depth and associated Hg concentrations are low (2-5 $ng\,g^{-1}$). Immediately above the old "B-horizon" of the flooded podzol, lies a zone where the residual fraction is enriched in mercury [Hg(res) = 25-30 $ng\,g^{-1}$]. These data may indicate that Hg liberated by the reduction of Fe oxyhydroxides after inundation was incorporated onto clay minerals and/or sulfides, as the redox boundary migrated towards the sediment-water interface.

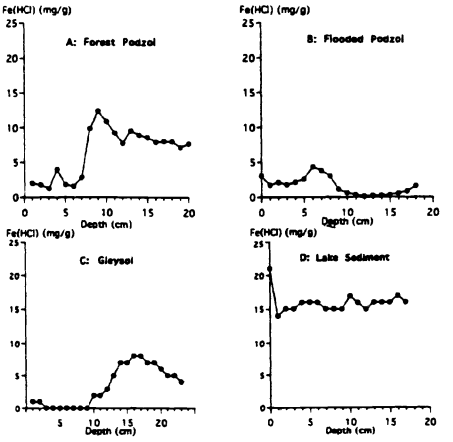

Fig.2: Distribution of 1N HCl-extractable iron, Fe(HCl), with depth.
(A) Forest Podzol, (B) Flooded Podzol, (C) Gleysol, (D) Lake Sediment.

Significant Fe(HCl) concentrations are found in the gleysol only at depths greater than 14 cm (Figure 2C). This corresponds to the top of the B-horizon and may represent a poorly developed zone of mineral accumulation. The gleysol sequesters no appreciable Hg(HCl) at any depth (Figure 1C).

The highest Fe(HCl) and Hg(HCl) values are found at the sediment-water interface of the former lake sediment, where authigenic and detrital Fe oxyhydroxides readily adsorb Hg (Figure 1D & 2D).

4. Conclusions

Up to 80% of the Hg in the organic-rich horizon of aerially-exposed and flooded forest soils and up to 85% of the Hg in lake sediments collected along a transect on the shores of a hydroelectric reservoir is bound to NaOH-extractable organic matter.

Between 40 and 60% of Hg(tot) residing in the B-horizon of the forest podzol is associated with HCl-extractable phases. The absence of HCl-extractable iron and mercury in a flooded

podzol indicates that these phases, and the associated Hg, are liberated to the interstitial waters as a result of a change in the geochemical environment. The availability of other Hg-binding substrates and the presence of authigenic Fe-oxyhydroxides near the sediment-water interface, make it unlikely that Hg thus liberated will escape to the overlying waters. Although the clay and sulfide fraction of the inundated podzol does contain significant Hg concentrations, it is more likely that Hg liberated upon the reduction of reactive iron is accommodated by the highly reactive degraded organic matter immediately above the B-horizon. Since organic matter degradation rates under the anaerobic conditions in this region are extremely low, it serves as a geochemically stable and long term sink for anthropogenic Hg.

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CHARACTERIZATION OF MERCURY SPECIES IN CONTAMINATED FLOODPLAIN SOILS

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Abstract. The chemical form or speciation of mercury (Hg) in the floodplain soils of the East Fork Poplar Creek in Oak Ridge, Tennessee, a site contaminated from past industrial activity, was investigated. The speciation of Hg in the soils is an important factor in controlling the fate and effect of Hg at the site and in assessing human health and ecological risk. Application of three different sequential extraction speciation schemes indicated the Hg at the site was predominantly relatively insoluble mercuric sulfide or metallic Hg, though the relative proportions of each did not agree well between procedures. Application of X-ray and electron beam studies to site soils confirmed the presence of metacinnabar, a form of mercuric sulfide, the first known evidence of authigenic mercuric sulfide formation in soils.

1. Introduction

During the 1950s, approximately 100 t of Hg were discharged from the U. S. Department of Energy facilities in Oak Ridge, Tennessee to East Fork Poplar Creek (EFPC). Much of the Hg has remained trapped in the floodplain soils which are currently being investigated under U.S. Superfund legislation. The chemical form or speciation of Hg in the soils is a controlling factor in the fate and effect of Hg at the site and influences the site risk assessment and required remedial actions.

A sequential extraction methodology for the speciation of Hg in soils (method 1) indicated the Hg in the floodplain soils was almost entirely inorganic, of which approximately 85% was mercuric sulfide (Revis *et al.*, 1989 a,b). Since several investigators have shown mercuric sulfide is a relatively insoluble and non-bioavailable form of Hg (Fagerstrom and Jernelov, 1971; Gillespie and Scott, 1971; Engler and Patrick, 1975; Rogers, 1979; Willett *et al.*, 1992), the study was considered significant in terms of the fate and effect of Hg at the site. Subsequently, X-ray fluorescence (XRF) dot maps obtained from a scanning electron microscope (SEM) examination of twenty soils revealed a consistent elemental association between Hg and sulfur (S) (Harris *et al.*, in press). To support the characterization effort, another sequential extraction methodology in development for characterization of Hg in soils was applied to twenty floodplain soils (method 2) (Miller, 1993). The results of this analysis indicated that although mercuric sulfide was a significant form, elemental Hg (or Hg amalgams) was the predominant form of Hg in the floodplain (Dobb *et al.*, 1994).

Although the speciation results from two different sequential extraction methodologies did not agree, the analyses were not performed on the same soils. In order to resolve the discordance, the two previously utilized sequential extraction methodologies as well as a third method (method 3) (Sakamoto *et al.*, 1992) were each tested on five soils. In addition, supplemental X-ray and electron beam studies were initiated to further characterize the species of Hg in the floodplain.

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2. Methods

Soil samples were collected from the floodplain, composited in stainless steel bowls and refrigerated in the laboratory in sealed containers until use. Small (<100 g) subsamples of five soils were taken and further homogenized. One portion (approximately 3 g) of each soil was air dried to determine percent moisture, ground and analyzed for Hg by SW-846 Method 7470. Field-moist portions of each soil were sequentially extracted in 50 ml centrifuge tubes by the methods outlined in each of the three procedures. The determination of organic Hg in each analysis was omitted because the results of all studies have consistently indicated organic Hg is an insignificant fraction in EFPC soils. The supernatant from each extraction was filtered and analyzed for total Hg by SW-846 Method 7471. In addition, one soil was spiked with metacinnabar, the form of mercuric sulfide identified in EFPC soils as discussed below.

For the X-ray and electron beam studies, one of the most Hg-contaminated soils was selected because of the relatively high minimum detectable concentrations of some of the methods (i.e. nominally 1% for X-ray diffraction). Further enhancements of Hg concentration were achieved by particle size separation by differential sedimentation/centrifugation (Jackson, 1975). Soils were characterized by a JEOL 840 SEM, a JEOL 2000FX transmission electron microscope (TEM) with select area electron diffraction (SAED) using an accelerating voltage of 100 kV and a beam current of 15 μA and a Phillips high angle diffractometer with a graphite crystal monochromator using CuKα (λ=1.5418 angstroms) radiation operated at 40 kV and 40 μA.

3. Results and Discussion

The concentration of Hg in the five soils ranged from 42 to 2400 μg/g. The results of the sequential extraction studies are shown in Figure 1. Metallic Hg and mercuric sulfide accounted for greater than 70% on average of the total Hg in the five soils in all methods. The percentage of metallic Hg detected in each of the soils by methods 1 and 2 are not in agreement (method 3 did not have a determination for metallic Hg). The average percentage of metallic Hg in the soils by method 1 was 28% compared to 72% by method 2 and differences within individual soils were even more pronounced. The percentage of mercuric sulfide detected by the three procedures also did not agree. For the five natural soils, method 1 detected an average of 46% mercuric sulfide compared to 25% for method 2 and 83% for method 3. For all five soils, the percentage of mercuric sulfide detected was highest for method 3 followed by method 1 and then method 2. The recoveries of the metacinnabar spike were 87% for method 1, 84% for method 2 and only 24% for method 3.

A series of X-ray/electron beam studies were initiated to further refine the Hg speciation at the site. Hg-rich soil fractions with a concentration of 0.89% (2 - 5 μm) and 0.96% (<2 μm) were obtained by particle size separation from a 2670 μg/g soil and further analyzed by SEM energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS), X-ray diffraction (XRD) and TEM with SAED. EDS/WDS of numerous Hg-rich soil particles showed consistent stoichiometric relationships between soil Hg and mercuric sulfide standards, particularly metacinnabar. TEM with SAED confirmed the presence of sub-micron crystals of metacinnabar, often in close association with the clay matrix (Stevenson *et al.*, 1994). As shown in Figure 2, the XRD patterns of the enriched soil fractions have peaks indicative of metacinnabar. The relatively small, broad peaks are caused by the sub-micron crystallite size and concentrations of Hg near the

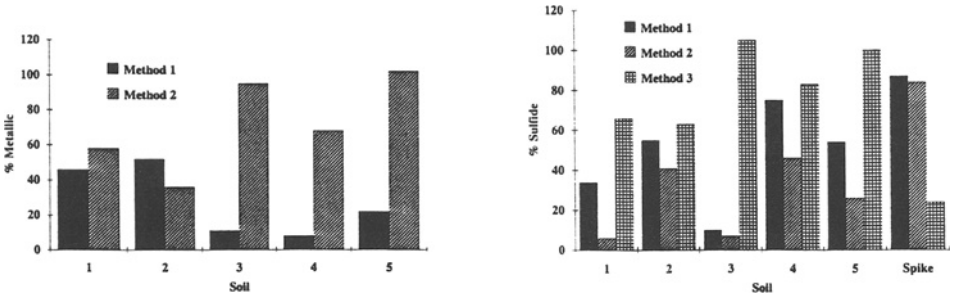

Fig. 1. Comparison of speciation from different sequential extraction procedures for metallic Hg (left) and mercuric sulfide (right)

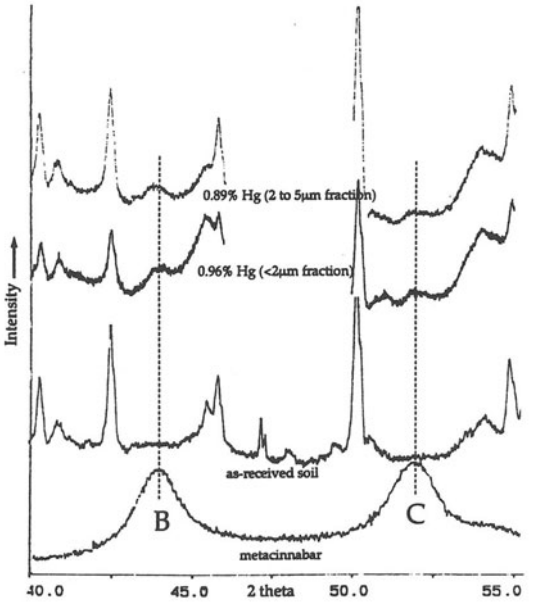

Fig. 2. Comparison of XRD patterns for Hg rich size fractions with as-received soil and with synthetic metacinnabar.

nominal detection limit, but are pronounced when compared to the as-received soil.

The causes for the differences in the results of each sequential extraction procedure is unclear. The methods were developed with the use of pure Hg compounds spiked in soils, though the behavior of Hg in soils may not be well represented by pure compounds. The behavior of sorbed Hg, in particular, was not investigated in either of the methods. There is supporting evidence of the presence of mercuric sulfide from X-ray/electron beam studies, while there has been no additional evidence of metallic Hg. Nonetheless, X-ray/electron beam studies have been limited to a few soils making extrapolation of the results for validation of the sequential extraction schemes difficult.

4. Conclusions

The results of three different sequential extraction studies concurred the Hg in EFPC soils consists primarily of inorganic metallic Hg and mercuric sulfide, though the relative percentages of each did not agree well between methodologies. Therefore, the use of sequential extraction procedures alone for the speciation of Hg in soils is considered problematic at present (further development is underway). The presence of sub-micron, crystalline mercuric sulfide (metacinnabar) in soils was confirmed by TEM with SAED and XRD. This is the first known evidence of the formation of authigenic mercuric sulfide in soils.

Acknowledgments

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GLACIAL DISPERSAL OF MERCURY FROM BEDROCK MINERALIZATION ALONG PINCHI FAULT, NORTH CENTRAL BRITISH COLUMBIA

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Abstract. Mineralized occurrences of Hg in bedrock are abundant along Pinchi Fault, in north central British Columbia, two of which have been mined in the early to mid 20th century. Distribution patterns of mercury concentrations measured in the clay sized fraction (<2 μm) of till reveal anomalous levels on and down-ice from the fault Mercury in the till is interpreted to be of detrital origin. In other words, during glaciation, glacier ice eroded bedrock and older sediments enriched in mercury and transported them in a down-ice direction, finally depositing the sediment load at a distance from the source. Consequently, the area with anomalous mercury concentrations in the till is several orders of magnitude larger than the area of mercury mineralization in bedrock.

1. Introduction

As ice flows over a substrate, it erodes bedrock and older unconsolidated sediments and transports debris from those sources in a down-ice direction. Subsequently, debris is deposited from the ice, as till, at a certain distance from the original source. If bedrock with a distinctive character (lithology, color, geochemical signature, etc.) is eroded by ice, it will result in a perceivable train of debris in the till, i.e. a dispersal train (DiLabio, 1990; Shilts, 1973). Concentrations of fragments from that rock type will be high in the till near the source and will eventually get diluted by debris from other sources, further down-ice.

The purpose of this paper is to present a case where mercury concentrations in the till are anomalously high on and down-ice from a fault (Pinchi Fault) in central British Columbia. Patterns of mercury concentrations in the till are attributed to glacial erosion, transport and deposition of debris derived from cinnabar (HgS) mineralization located along the fault.

2. Setting

Pinchi Fault is a major NW-SE oriented structural lineament which extends over 450 km through central British Columbia (Armstrong, 1949; Paterson, 1977). The fault separates Cache Creek Terrane to the west from Triassic Takla Arc Terrane to the east (Fig. 1). Mercury occurrences, with cinnabar as the principal mineral, are abundant along the fault (Fig. 2) (Armstrong, 1948; 1949). Two mercury mines (Pinchi Lake and Bralorne Takla) were active in the early to mid 20th century.

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Previous work indicated that chemical analysis of plant materials reflects mercury mineralization along Pinchi Fault (Fig. 2) (Siegel et al., 1985; Warren et al., 1983a; 1983b).

During the last glaciation, ice advanced onto lower areas of interior British Columbia with ice flow directions depicted on Figure 1.

3. Results and conclusion

As part of the Canada-British Columbia Agreement on Mineral Development (1991-1995), a geochemical sampling program was implemented by the Geological Survey Canada in the central part of the province in an area which includes a long section of

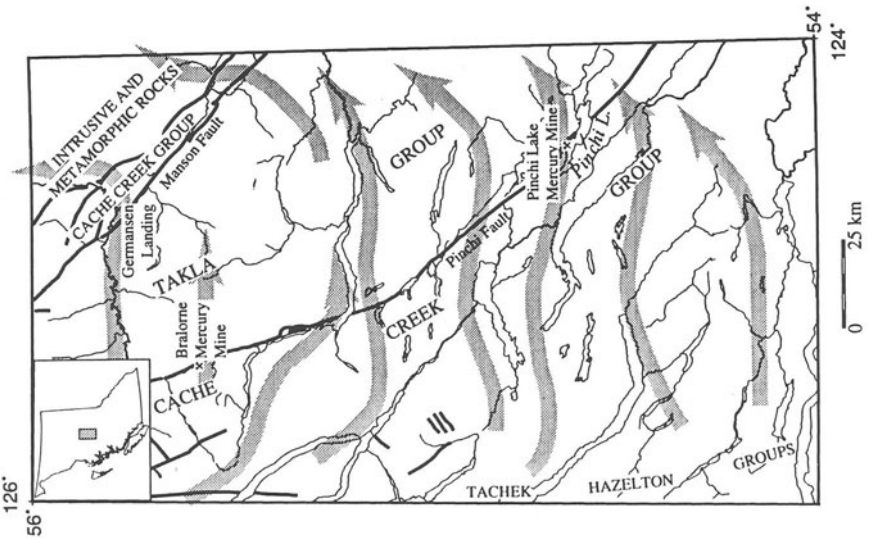

Figure 1. Generalized bedrock geology and ice flow patterns of the study area. All faults are shown as thicker black lines.

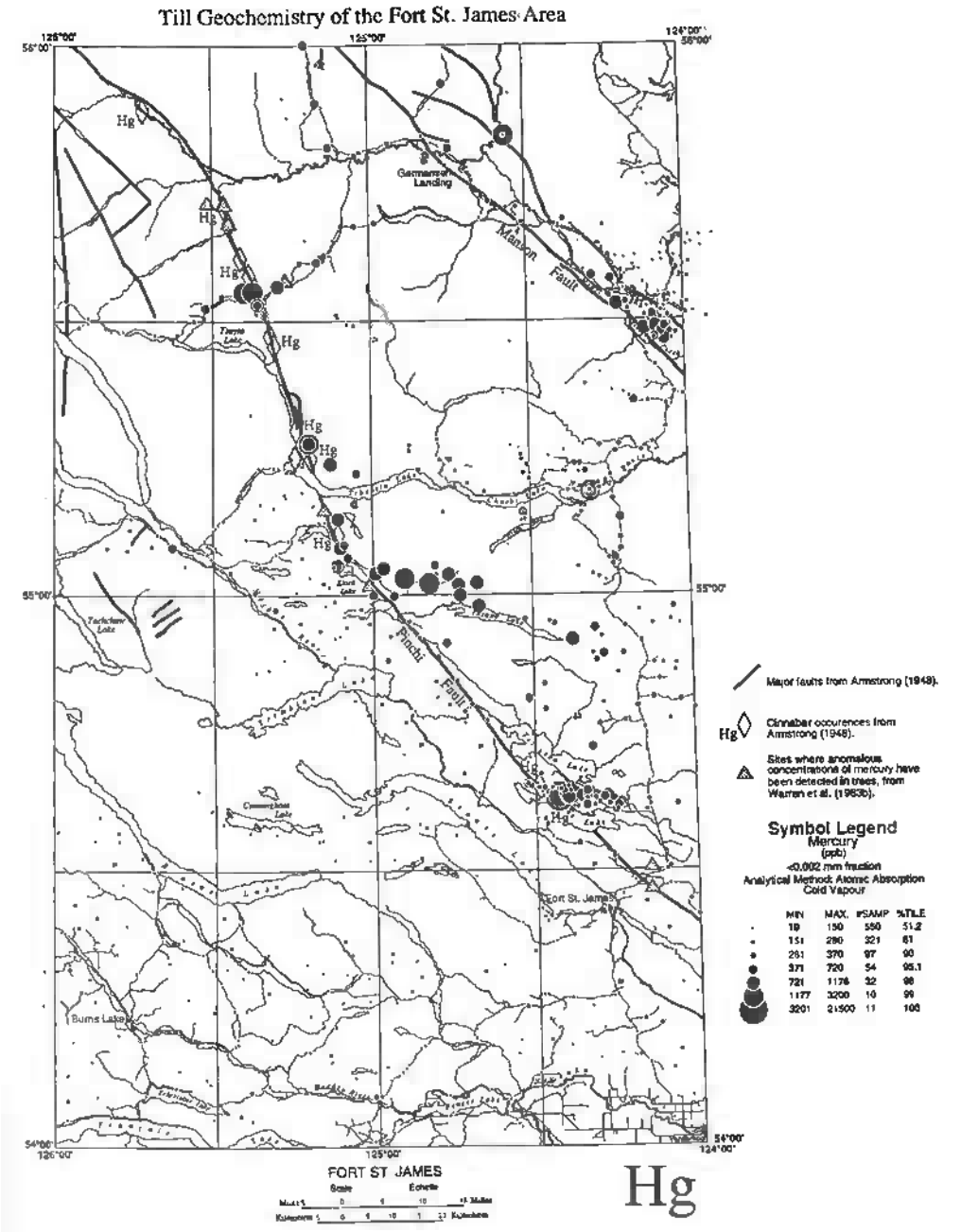

Figure 2. Geochemical map for mercury concentrations measured in the clay size (<2 μm) fraction of till. Dot sizes are proportional to the mercury concentration present in the till.

Pinchi Fault (Plouffe and Ballantyne, 1993). The clay sized fraction of till samples collected from the C soil horizon or the transition zone between the B and C horizons (depth greater than 1 m) from sections found along roads and river banks was analyzed for mercury by cold-vapor atomic absorption. Results indicate that natural mercury concentrations in till on and down-ice (east) from the fault zone are 4 to 100 times higher than concentrations in till on the up-ice side (west). Such mercury distribution in the till is attributed to the effect of glacial erosion, transport and deposition. In other words, during glaciation, glacier ice eroded bedrock and older sediments enriched in mercury, transported them in a down-ice direction, finally depositing the sediment load at a distance from the source. Detailed sampling completed north of Pinchi Lake (Fig. 2) showed that the measurable length of the glacial transport of mercury-bearing debris is in the range of 12 to 18 km. This implies that the area of till that is anomalous in mercury is several time larger than the surficial expression of bedrock mercury mineralization.

Total mercury detected in the till is thought to be primarily derived from a natural source and not from airborne pollution since : (1) till, a pre-industrial sediment, was sampled at a depth of one meter, (2) enrichment patterns are on and down-ice from Pinchi Fault, and (3) other studies conducted in areas polluted by airborne contaminants revealed minimal or no downward leaching of metals (Henderson and McMartin, 1994).

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EFFECTS OF ROOT MORPHOLOGY AND HG CONCENTRATION IN THE SOIL ON UPTAKE BY TERRESTRIAL VASCULAR PLANTS

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Abstract. Vascular plant tissues of various species growing on flood plain soils along the South River at Waynesboro, VA. have previously been shown to contain Hg. These soils characteristically contain 10-20 μg Hg g^{-1}. In the field, root/rhizome Hg content in *Asclepias syriaca* and *Solidago* sp. ranged from undetectable amounts at low Hg control sites to 1.96 μg Hg gdw^{-1} at contaminated sites, with the association being inversely related to subterranean organ size. Within each size class, tissue Hg was directly related to soil Hg concentration. The relationship of subterranean organ size and enhanced Hg association was further substantiated by high levels of Hg in the fibrous root systems of grasses grown under greenhouse conditions.

1. Introduction

Mercury contamination of ecosystems on flood plains downstream from E. I. duPont de Nemours and Company (DuPont), at Waynesboro, VA, has been investigated since 1983 by the James Madison University Terrestrial Mercury Research Group. Both old-field and flood plain forest communities have been examined (Cocking *et al.*, 1991). The soils in these systems contain high levels of total mercury (Hg) that are characteristically 10-20 μg Hg g^{-1}, but soil with concentrations up to 84 μg Hg g^{-1} has been found in some locations. Primary producers in these ecosystems contain up to 5.5 μg Hg g^{-1}dw, and there are up to 16 μg Hg g^{-1}dw in consumers such as earthworms (Cocking *et al.*, 1995). The plant tissues will either be consumed by herbivores, or ultimately become constituents of detritus. The detritus pathway is responsible for significant energy flow in most terrestrial ecosystems and is likewise a major route for the bioaccumulation of Hg. The uptake of Hg by plants has been studied by various workers including Beauford *et al.* (1977), de Temmerman *et al.* (1986), Elsokkary (1982), Huckabee *et al.* (1983)

The purpose of this report is to illustrate properties of plant roots and Hg availability in soil that may have a bearing on the large amount of variability in Hg uptake that is often found between individuals and species.

2. Materials and methods

Field data were obtained from several studies carried out at the sites described in Cocking *et al.* (1991). A total of 15 *Asclepias* (milkweed) sample points in four populations growing in the sites and nearby old fields were used as a source of material to study Hg uptake in response to soil Hg concentration and root size. Sample size at most points was three plants which were analyzed separately. Soil samples were obtained from the top 25 cm, and in the case of the study of Hg uptake by *Asclepias*, were obtained from three cores at the base of each plant which were composited for analysis

A greenhouse study was carried out on the James Madison University campus in Harrisonburg, VA. Grass plants were grown from seed in 15 cm plastic pots interspersed on a greenhouse bench in a randomized block experimental design. Homogeneous soil samples were collected from a Hg contaminated site in Waynesboro and mixed 1:1 by volume with Pro-lite potting soil to serve as Hg contaminated potting medium. Unsupplemented Pro-lite served as the "control-potting soil." These plants were part of a study examining the effects of altered soil pH on Hg uptake, but the data presented in this report were from plants exhibiting no significant pH effects.

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Harvesting involved removal of plant material from the soil or pots and dividing it into root and shoot components. Plant tissues were sequentially washed in tap water (H_2O), 1.5% nitric acid (HNO_3), tap H_2O, and deionized H_2O. Subsequently they were air dried and ground through Wiley Mill sieve #40. Plant and soil samples were digested with HNO_3, sulfuric acid (H_2SO_4), and vanadium pentoxide (V_2O_5) (Knetchel and Fraser, 1979; Ward, 1986). Total Hg was measured with a Perkin-Elmer 3030 atomic absorption spectrometer equipped with a MHS-10 hydride system using sodium borohydride ($NaBH_4$) as a reductant. The accuracy of these determinations was verified with NBS orchard leaves, river sediment and comparison with analyses carried out by CMI Environmental Laboratory, Harrisonburg, VA, as described in Cocking *et al.* (1991).

3. Results and Discussion

3.1 BIOACCUMULATION OF HG IN FLOOD PLAIN ECOSYSTEMS

Roots and/or leaves of over a dozen old-field species from contaminated sites (11 to 31 μg Hg g^{-1}) contain Hg (Cocking *et al.*, 1991); however, increased spatial and temporal sampling of several of these species in subsequent years did not reduce sample variability. Differences in tissue Hg concentration of graminoids and milkweed (*Asclepias syriaca*) growing in contaminated and uncontaminated soil are shown in Figure 1. Examination of individual sample data correlated with soil Hg implied direct relationships between soil Hg and tissue concentrations; however, small sample sizes and high variability limited regression analysis.

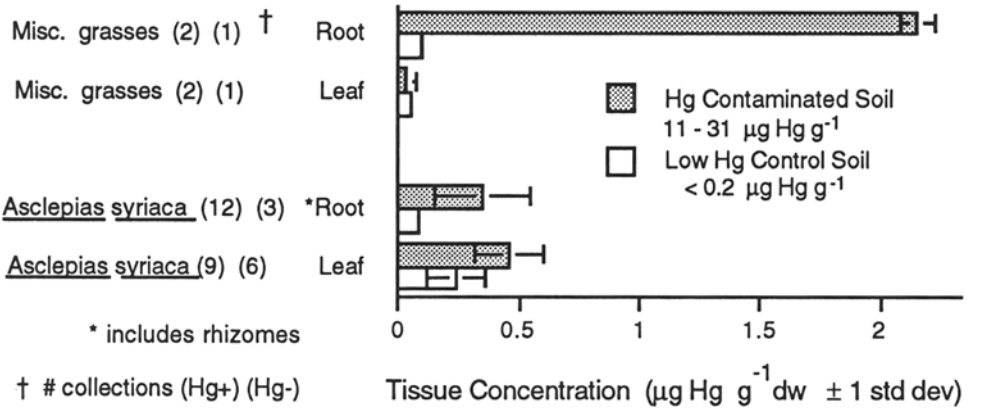

Fig. 1. Root/shoot distribution of Hg in whole plant samples under field conditions.

A more detailed study revealing two of the sources of variability was also carried out in the field. In this case, the soil Hg content immediately in the vicinity of *Asclepias* (milkweed) and *Soludago* (goldenrod) plants was determined along with the tissue content of the individuals. The underground organs (roots or rhizomes) of were sub sampled by grouping the tissues in different diameter classes. Fine roots have the greatest surface area and exhibited the highest Hg concentration. Figure 2 illustrates the inverse effect of subterranean organ diameter (direct effect of surface area) on the association with Hg in *Asclepias*. A similar, but much less pronounced pattern was found for *Soludago,* with

the maximum concentration being <0.3 μg Hg g^{-1}dw in the <0.5 mm fine roots when the plants were growing in soils having 10 - 25 μg Hg g^{-1}.

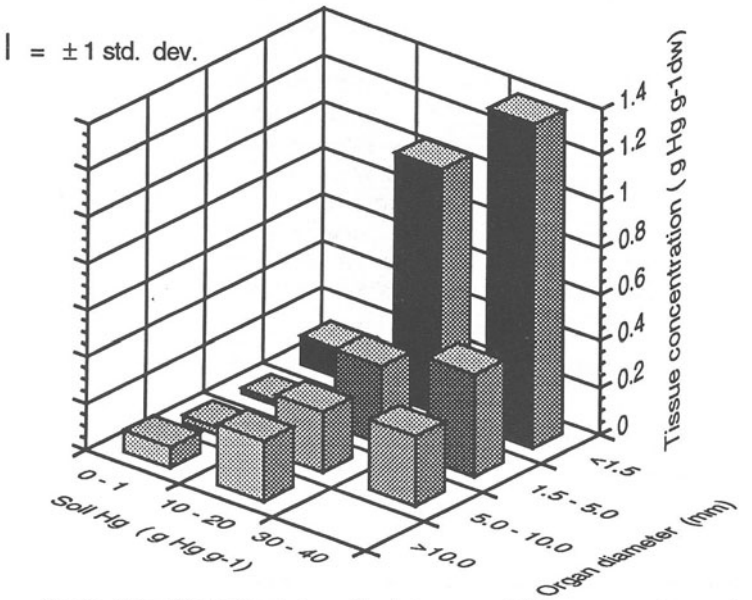

Fig. 2. The effect of an interaction between soil Hg concentration and root/rhizome size on tissue concentration in *Asclepias syriaca*.

Persistence of Hg after thorough acid washing of these tissues to remove unbound Hg indicates a close association of Hg with the organ, but does not conclusively indicate uptake within the cells. We do know, however, that some Hg is absorbed into the cellular matrix of the plants since a separate study of the larger *Asclepias* underground organ sizes (~3-10 mm) showed that about 25% of the total Hg content was in the core that remained after shaving the outer cortex. The role of these organs as a pathway for Hg into higher trophic levels is probably not greatly affected by differences between adsorption and absorption for consumer species when animals eat fragments of the entire root.

In this study, tissue Hg concentration was directly related to soil Hg and regression of the concentration in individual plants on the Hg content of adjacent soil produced a significant positive correlation for all sizes of *Asclepias* organs (<1.5 mm, $r = 0.71$ $p<0.001$; 1.5-5.0 mm, $r = 0.54$, $p<0.001$; 5.0-10.0 mm. $r = 0.46$, $p<0.025$; and >10.0 mm, $r = 0.68$, $p <0.05$). The two smaller size classes for *Solidago* were also positively correlated (<0.5 mm, $r = 0.93$, $p<0.001$; and 0.5-1.0 mm, $r = 0.75$, $p<0.05$), but no significant dependency was observed with the larger roots which had very low Hg content.

3.2 UPTAKE OF HG BY PLANTS UNDER GREENHOUSE CONDITIONS

The field studies indicated that the greatest amount of Hg was associated with fibrous root systems that are characteristic of monocots including *Allium* (onion) (Cocking *et al.*, 1991) and various graminoids (grasslike species). These organs are masses of relatively small roots, which is consistent with the finding that tissue content is directly dependent

on surface area and inversely related to organ diameter in *Asclepias* and *Solidago*. The overall results of a greenhouse study (Figure 3) where two grasses, *Festuca ovina* and *Poa pratensis*, were each grown in 60 randomized pots containing high and low Hg content soils confirmed this field observation.

Fig. 3. Hg association with fibrous root systems

4. Conclusion

Uptake from the soil is a significant route for the entrance of Hg into vegetation in terrestrial ecosystems. The Hg concentration of plant tissues is dependent on soil Hg concentration, species differences, tissue type, and subterranean organ size (surface area). The large number of potential interactions between these variables illustrate the difficulties involved in the prediction of Hg levels in the vegetation of Hg contaminated terrestrial ecosystems from soil concentration data. Similarly, vegetation Hg content alone is not a precise indicator of the degree of soil contamination.

Acknowledgments

This study and the presentation of a more extensive poster at the Whistler conference, including results of a study of the effect of soil pH on Hg uptake which will be published separately, was supported entirely by James Madison University, Harrisonburg, VA. Special thanks to Dr. Peter Nielsen for his help in the conception and implementation of this project.

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PART Xc

MERCURY RISK ASSESSMENT AND MANAGEMENT OF ANTHROPOGENIC SOURCES

MERCURY IN SOILS AND CROPS FROM FIELDS RECEIVING HIGH CUMULATIVE SEWAGE SLUDGE APPLICATIONS: VALIDATION OF U. S. EPA'S RISK ASSESSMENT FOR HUMAN INGESTION

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Abstract. The Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) has owned and operated a 6320 ha Dedicated Beneficial Sludge Utilization Site in Fulton County, Illinois since 1971. The site consists of calcareous strip mine spoil intermingled with placed land. Sewage sludge from Chicago is barged to the site, located approximately 185 miles southwest of the city, and utilized to reclaim the strip mined soils and to fertilize the corn and wheat crops grown on them. Fields have received as much as 1317 dry Mg ha^{-1} of sewage sludge since 1971. Sludge Hg concentrations have ranged from 1.1 to 8.5 mg Hg kg^{-1} with mean concentration of 3.31 mg Hg kg^{-1}, and maximum cumulative Hg loading rates are approximately 4 kg ha^{-1}. Sludge applications have significantly increased extractable soil Hg concentrations, and regression analysis indicates that from 80 to 100% of the Hg applied to soils in sewage sludge since 1971 still resides in the top 15 cm of soil. Since 1985 the MWRDGC has been monitoring Hg concentration in corn leaf and grain, wheat grain and soils at the Fulton County site. Monitoring data indicate that 98.8% of the corn grain samples, 93.0% of the wheat samples and 50.7% of the corn leaf samples collected from 1985 through 1992 had Hg concentrations below detectable limits (<25 μg kg^{-1}). Cumulative Hg loading rates are utilized along with crop tissue concentrations to compute crop uptake response slopes (UC) for Hg into plant tissues at the Fulton County site. The UC for corn and wheat grain was zero and for corn leaf was -0.0014 (mg Hg/kg tissue)/(kg Hg/ha soil), which indicate that sewage sludge additions did not increase plant tissue Hg concentrations at the Fulton County site. The negative UC obtained for corn leaf may actually indicate that sewage sludge applications decreased Hg uptake from mined soils possibly due to organic carbon and sulfides in the anaerobically digested sludge binding native Hg. The United States Environmental Protection Agency (U. S. EPA) has recently promulgated their 40 CFR Part 503 regulation for sewage sludge use and disposal. The rule sets risk based limits on ten metals, including Hg, in sludges that are land applied. Exposure pathways involving plant uptake of Hg are briefly discussed and it is shown that the UC used in U. S. EPA's risk assessment models for these pathways overpredict uptake of Hg by crops when compared with the UC derived from the MWRDGC's monitoring data at Fulton County.

1. Introduction

The United States Environmental Protection Agency (EPA) recently promulgated their 40 CFR Part 503 *Standards for the Use or Disposal of Sewage Sludge* (USEPA, 1993). The regulation sets concentration limits on ten metals, including Hg, in sludges that are applied to land based on an extensive, detailed, risk assessment that determines exposure to

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humans, plants, animals and soil biota through 14 terrestrial, atmospheric and aquatic pathways (USEPA, 1992). Computation of a plant uptake slope, defined as the change in plant tissue metal concentration (mg metal/kg tissue) per unit of metal applied to the soil in sewage sludge (kg metal/ha soil) is a component of four of the terrestrial pathways: Sludge→ Soil→ Plant→ Home Gardener, Sludge→ Soil→ Plant→ Produce Consumer, Sludge→ Soil→ Plant→ Animal→ Human, Sludge→ Soil→ Plant→ Animal (USEPA, 1992).

For the home gardener and produce consumer pathways the following algorithm was used to compute soil metal loading limits:

$$RIA = \{(RfD \cdot BW/RE)-TBI\} \cdot 10^3, \quad (1)$$

where RIA is the adjusted reference intake of pollutant in humans (the maximum allowable intake from exposure to sludge through the given pathway during a lifetime of exposure, for Hg U. S. EPA determined this to be 17.8 μg/day), RfD is the oral reference dose (the maximum allowable intake of pollutant from all sources at the acceptable risk level, U. S. EPA determined this to be 0.0003 mg Hg/kg body weight), BW is the body weight (assumed to be 70 kg for the entire 70 year exposure period), RE is the relative effectiveness of ingestion exposure (unitless and assumed to equal one) and TBI is the total background intake rate of pollutant from all sources of exposure other than sludge (U. S. EPA determined this to be 0.0032 mg Hg/day), and:

$$RP_C = RIA/\Sigma(UC_i \cdot DC_i \cdot FC_i), \quad (2)$$

where RP_C is the reference cumulative application rate of pollutant (the regulatory metal loading limit, expressed in kg pollutant/ha soil), UC_i is the uptake response slope of pollutant in plant tissue for food group$_i$ (mg pollutant/kg plant tissue)/(kg pollutant/ha soil), DC_i is the daily dietary consumption of food group$_i$ (g/day), and FC_i is the fraction of food group$_i$ produced on sewage sludge amended soil (unitless). U. S. EPA considered several food groups, which are discussed later, for these pathways.

For the pathway in which humans consume animal meat, the algorithm consisted of Equation (1) above and:

$$RF = RIA/\Sigma(UA_i \cdot DA_i \cdot FA_i), \quad (3)$$

where RF is the reference concentration of pollutant in the animal diet (the maximum concentration of pollutant in the animal's diet that will produce meat safe for human consumption, U. S. EPA determined this to be 174.4 μg Hg/g forage), and UA_i is the uptake response slope of pollutant in animal tissue food group$_i$ (the coefficient of pollutant transfer between forage and animal tissue expressed as (μg pollutant/g animal tissue)/(μg pollutant/g forage)). U. S. EPA considered a number of animal tissue food groups including: beef, beef liver, lamb, pork, poultry, dairy products, and eggs. DA_i is the daily human dietary consumption of animal tissue food group$_i$ (g animal tissue/day), and FA_i is the fraction of food group$_i$ assumed to be derived from animals that ingest forage grown on sludge amended soil (unitless), and:

$$RP_C = RF/UC, \quad (4)$$

where UC here is the uptake response slope of pollutant in the forage tissue eaten by the animal (mg pollutant/kg plant tissue)/(kg pollutant/ha soil)(USEPA, 1992).

The EPA utilized only data from studies where Hg was applied to soils as an indigenous constituent of sewage sludge to compute the plant uptake response slopes (UC) utilized in the Part 503 risk assessment. Unfortunately, there are very few studies in the scientific literature which meet this criterion and so the UCs calculated for Hg in Part 503 are based on only four studies (USEPA, 1992). The UC of Hg for garden fruits, root crops and legumes was based on data from Cappon (1981) and Furr *et al.* (1976a). The UC of Hg for grains, potatoes, and animal forage was based entirely on data from Furr *et al.* (1976a), and the UC of Hg for leafy vegetables was based on data from Cappon (1981), Furr *et al.* (1976a, b) and Chaney *et al.* (1978).

The Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) has operated a 6320 ha dedicated land reclamation site in Fulton County, Illinois since 1971. The site has received in excess of 1,000,000 Mg of sewage sludge which is barged to the site, 185 miles southwest of Chicago, and applied to strip mined soils on the site to reclaim them and fertilize the corn and wheat crops that are grown for animal feed and alternative fuel production. The concentration of Hg in crop tissue and soils from the sludge application fields has been monitored since 1985. These data along with cumulative Hg loading rate data may be used to compute UC for Hg into corn and wheat grain and corn leaf for the Fulton County site. These UC for Hg, derived from a large scale field project, may then be compared to the Part 503 UC for the same plant tissues, which were computed from a limited number of research plot-scale experiments.

2. Materials and Methods

2.1. DESCRIPTION OF THE FULTON COUNTY SITE AND MWRDGC SLUDGE

From 1970 through 1975, the MWRDGC purchased 6,289 ha of land in Fulton County, Illinois (50 km SW of Peoria, Illinois) and approximately 2,219 ha of the property is currently being used for crop production. The major soils on site are typic hapludalfs and aric ochraqualfs, however, much of the site consists of calcareous strip-mine spoil. The reclamation area is divided into approximately 50 fields having a mean area of 20 ha each. Field design, soil characteristics, and environmental monitoring are discussed by Peterson *et al.* (1979, 1982), Pietz *et al.* (1978).

All material applied to the site was waste activated anaerobically digested sludge processed at the MWRDGC's Stickney and Calumet Water Reclamation Plants. The sludge Hg concentration ranged from 1.1 to 8.5 mg Hg kg^{-1} with mean concentration of 3.31 mg Hg kg^{-1}, and had pH between 6.5 and 7.5. Granato *et al.* (1991) provide a more detailed description of sludge chemical composition and land application methodology.

2.2. SOIL AND PLANT TISSUE SAMPLING AND ANALYSIS

Duplicate composite corn leaf samples consisting of 20 leaves were taken from each field. One composite sample consisting of grain from 15 randomly sampled ears was also taken from each field. Winter wheat was sown in September and harvested in July of the following year and one grab sample was taken from the grain harvested from each field after combining. Corn and wheat samples were dried at 65°C for 48 hr and ground in a Wiley mill.

Fields were divided into halves and 20 cores of the surface 15 cm of each half of the field were composited. The composited samples were air dried and ground to pass a 2 mm stainless steel sieve.

Both plant tissue and soil samples were analyzed by digesting 0.300 g subsamples in a solution containing 21.6 mL of 0.014 M $K_2S_2O_8$, 2.0 mL concentrated H_2SO_4 and 1.0 mL concentrated HNO_3 in sealed 50 mL plastic culture tubes which were placed in a water bath at 98°C for 16 hours. After cooling, 1.2 mL of hydroxylamine sulfate solution (0.75 M hydroxylamine sulfate in 2 M NaCl) was added to each tube. Samples were then filtered through Whatman 934-AH glass microfibre filters into 18x150 mm disposable culture tubes. Samples from 1985 through 1991 were analyzed by cold vapor atomic absorption spectroscopy on a Varian model AA10/VGA76. Samples for 1982 were analyzed by cold vapor atomic absorption spectroscopy on a Leeman model PS200. In both cases, acidic stannous chloride solution was used to reduce Hg^{+2} to elemental Hg to promote vaporization.

3. Results and Discussion

3.1. EFFECT OF CUMULATIVE SLUDGE APPLICATIONS ON SOIL Hg CONCENTRATION

The MWRDGC has been monitoring for Hg in soils, corn and wheat at their Fulton County site since 1985 and data presented here were collected from 1985 through 1992. Since sludges had been applied, and hence Hg had been loaded, on soils at the Fulton County site since 1971, we related extractable soil Hg with cumulative soil Hg loading rates for each field from which a plant tissue sample was taken from 1985 through 1992, there were 231 samples in all, to determine whether the Hg applied still remained in the soil surface (Figure 1).

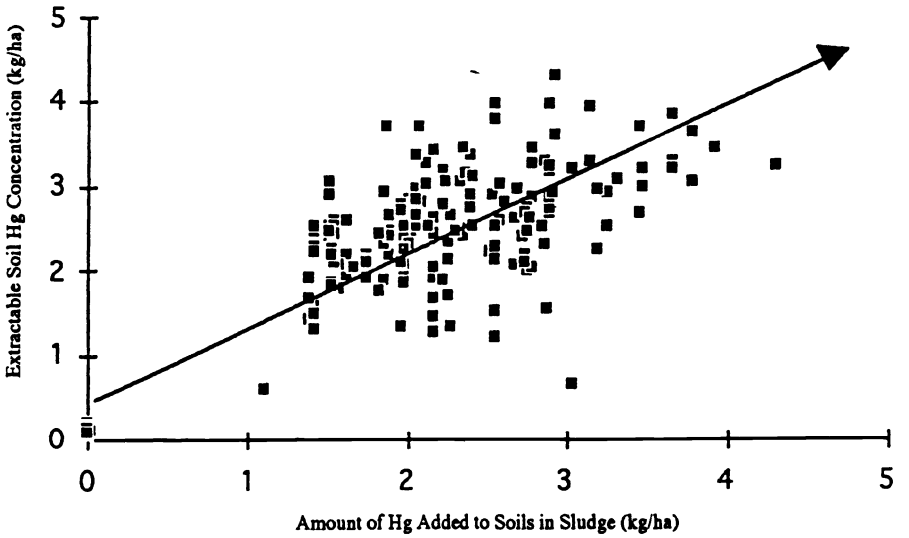

Fig. 1. Effect of sewage sludge Hg additions on extractable soil Hg concentrations.

We converted extracted soil Hg concentrations from $\mu g\ kg^{-1}$ to $kg\ ha^{-1}$ by multiplying them by 0.00224. This assumes that the top 15 cm of a ha of soil weighs 2240 Mg (bulk density = 1.493 $g\ cm^{-3}$). Regression analysis indicates that:

$$\text{Extractable Soil Hg Concentration} = .9 \cdot (\text{Soil Hg Loading Rate}) + .4 \quad (5)$$

This regression had $r^2 = 0.7$ and the slope was significant at $p = .05$. The regression line is represented by the arrow in Figure 1. The 95% confidence interval about the regression slope indicates that 80 to 100% of the Hg loaded in the soil by addition of sewage sludge was extractable. Thus we feel that nearly all of the Hg loaded into the soils at the site over its 20 year period of operation has remained in the surface 15 cm.

3.2. EFFECT OF CUMULATIVE SEWAGE SLUDGE APPLICATIONS ON PLANT TISSUE Hg CONCENTRATIONS

The U.S. EPA computed the UC they utilized for various plant tissues by relating plant tissue concentration to soil loading rate (Table I). The UC for potatoes, legumes, peanuts and sweet corn, 0.001 (mg Hg/kg plant tissue)/(kg Hg/ha soil), is a conservative default value assigned to tissues having UC determined to be <0.001. The UC computed for grains and animal forage by U. S. EPA are conspicuously high (Table I). We utilized corn leaf, corn grain and wheat grain Hg concentration data to compute site specific UC values for the Fulton County site and compared these site specific values with the UC utilized for grain and animal forage in the Part 503 risk assessment models for the home gardener, produce consumer and animal meat consumer pathways.

TABLE I

Crop Hg uptake response slopes (UC) utilized in U. S. EPA's Part 503 sewage sludge regulation risk assessment

Crop	UC (mg Hg/kg tissue)/(kg Hg/ha soil)
Potatoes	0.001
Leafy Vegetables	0.004
Legumes	0.001
Root Vegetables	0.007
Garden Fruits	0.005
Peanuts	0.001
Sweet Corn	0.001
Grains and Cereals	0.043
Animal Forage	0.043

For the samples analyzed from 1985 through 1992, 50.8% of the 177 corn leaf samples, 98.8% of the 174 corn grain samples, and 93% of the 57 wheat samples had Hg concentrations below the analytical detection limit. For samples analyzed from 1985 through 1991, the detection limit was 25 $\mu g\ kg^{-1}$ and samples analyzed in 1992, on new instrumentation, had a detection limit of 17 $\mu g\ kg^{-1}$. This suggests that Hg uptake into plant tissue at the Fulton County site is very minute, especially into corn and wheat grain.

For the purposes of computing UC, a concentration equal to the appropriate detection limit was assumed for all tissue samples in which Hg was not detected.

The effect of Hg loading through land application of sludge on corn leaf Hg concentration at Fulton County is illustrated in Figure 2. Each of the 177 points in Figure 2 represents data from one reclamation field from one year. Regression analysis indicates that:

$$\text{Corn leaf Hg concentration} = -1.4 \cdot (\text{Hg Loading Rate}) + 30.6 \quad (6)$$

The regression had $r^2 = 0.05$ but the regression slope was significantly different from zero at p= .05. The regression line is represented by the arrow in Figure 2. The slope of the regression line can be converted to UC by multiplying by .001 (to convert the plant tissue concentration units from μg/kg to mg/kg). Thus UC for Hg into corn leaf at Fulton County is -0.0014 (mg Hg/kg tissue)/(kg Hg/ha soil) and the 95% confidence interval associated with this UC, derived from the regression analysis above is from -0.0025 to -0.0005 (mg Hg/kg tissue)/(kg Hg/ha soil). The negative sign in this UC implies that increased Hg loading or, more acurately, increased sludge loading into Fulton County soils actually diminishes Hg uptake into corn leaves. While we cannot state unequivocally that this is actually happening it may be true since increased Hg loading is accompanied by increased organic carbon loading which may decrease availability of native Hg for plant uptake. Since the sludges applied to Fulton County soils were anaerobically digested they contained sulfides which can also serve to bind native Hg.

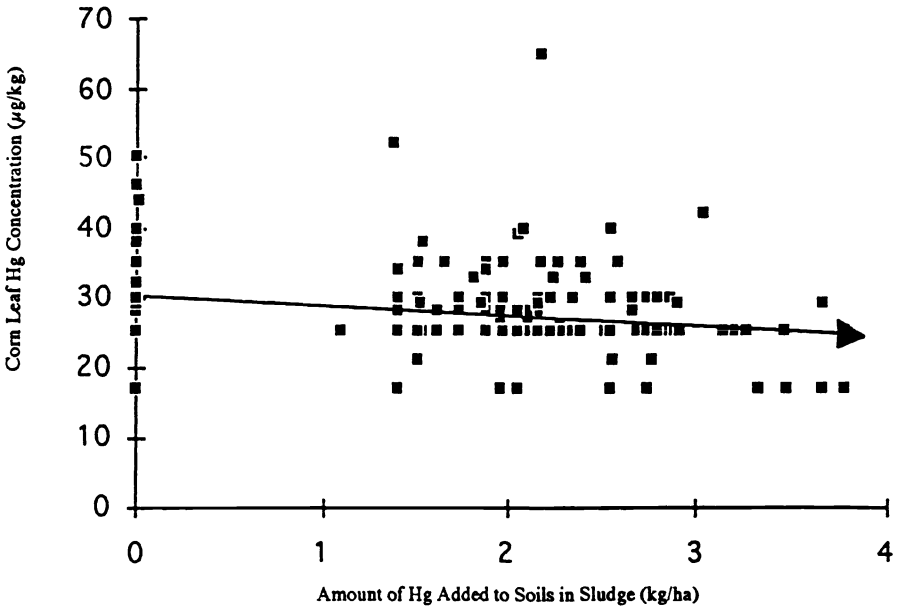

Fig. 2. Effect of sewage sludge Hg additions to soil on corn leaf Hg concentration.

Figure 3 illustrates corn and wheat grain Hg concentrations and corresponding soil Hg loading rates for each of the fields sampled from 1985 to 1992. Each of the 231 points in

Figure 2 represents data from one reclamation field from one year. It should be reemphasized that 98.8% of the corn grain and 93.0% of the wheat grain samples had Hg concentration below detectable limits so the vast majority of the data points are clustered at the tissue concentration equal to the 1985-1991 detection limit (25 $\mu g\ kg^{-1}$). The regression slope for these data (soil Hg loading rate was independent variable and grain Hg concentration was dependent variable) was not significantly different from zero at p= .1, which indicates that UC for corn and wheat grain at Fulton County is zero. This result is not surprising considering that 93.0% of the wheat grain samples and 98.8% of the corn grain samples had less than detectable concentrations of Hg.

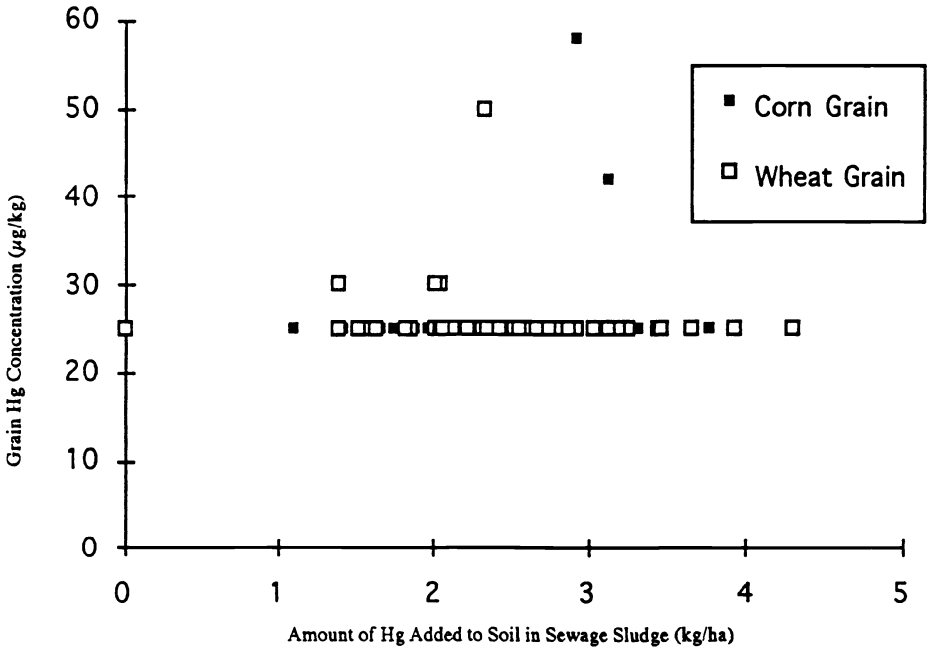

Fig. 3. Effect of sewage sludge Hg additions to soil on corn and wheat grain Hg concentration.

These results indicate that the UC utilized for grain and animal forage by the U. S. EPA overpredicts the uptake of Hg into these crops at the MWRDGC's Fulton County, Illinois site. The U. S. EPA's UC for grain and animal forage predicts that for each kg of Hg loaded onto a ha of soil, the concentration of Hg in the grains and animal forages grown on that soil should increase by 0.043 mg kg^{-1} or by 43 $\mu g\ kg^{-1}$. This, clearly, is not happening at Fulton County. Even if crop tissue contained no Hg on fields prior to sludge applications, the U. S. EPA's UC predicts that at Hg loading rates of 4 kg ha^{-1}, the grains and animal forages grown on these sludge amended soils should contain 172 μg Hg kg^{-1}. This tissue Hg concentration is nearly three times higher than the highest tissue Hg concentrations ever observed at the site (Figures 2 and 3).

4. Conclusions

The monitoring data from our Fulton County site indicate that repeated applications of sewage sludge to land will significantly increase the concentration of Hg in surface soils. We estimate, from the 95% confidence interval about the slope of the regression of extractable soil Hg with sludge applied soil Hg, that between 80 and 100% of the sludge applied Hg remained in the top 15 cm of soil on fields at the Fulton County site.

The concentration of Hg in crop tissue at the Fulton County site was low despite cumulative sewage sludge applications in excess of 1000 Mg ha^{-1} on many fields. The concentration of Hg was particularly low in grains as we observed that 98.8% of the corn grain samples and 93.0% of the wheat samples had Hg concentrations below the analytical detection limit (25 μg Hg kg^{-1} for samples from 1985 through 1991 and 17 μg Hg kg^{-1} for samples from 1992).

We computed UC for Hg uptake into corn leaf and corn and wheat grain utilizing crop tissue data and soil loading rate data. The UC derived from our Fulton County monitoring data indicate that the UC utilized in Part 503 overpredict the transfer of Hg from sludge amended soil into grains, and animal forage. The UC utilized by U. S. EPA for these tissues was 0.043 (mg Hg/kg tissue)/(kg Hg/ha soil) (Table I) while our monitoring data indicate that UC for grains is zero and for corn leaf is -0.0014 (mg Hg/kg tissue)/(kg Hg/ha soil). We have concluded from these UC that there is no significant uptake of Hg into plant tissue resulting from sewage sludge applications to the soil at the Fulton County site. In fact, the negative UC for corn leaf may indicate that sewage sludge applications are reducing the uptake of Hg into corn leaf at the site possibly due to organic carbon and sulfides in the anaerobically digested sludges binding native Hg in the mined soils.

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MERCURY FROM POWER PLANTS: A PROBABILISTIC APPROACH TO THE EVALUATION OF POTENTIAL HEALTH RISKS

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Abstract. Estimating the impacts of mercury (Hg) power plant emissions on the environment and human health involves the prediction of chemical concentrations in the different environmental media and the foodchain. As calculations show the ingestion pathway to dominate Hg risk, the reliable characterization of the processes influencing Hg concentrations in environmental media other than air is of particular importance. In this context, we present and implement an approach for the evaluation of Hg multimedia risks associated with power plant emissions. The approach is based on the investigation of four critical components influencing Hg ingestion risk: (1) Hg deposition; (2) hydrologic environment; (3) Hg uptake by fish; and (4) Hg uptake by vegetation. To capture the variability in the conditions affecting Hg risk, the problem is handled in a probabilistic way, where the influential parameters are assigned probability distributions or possible value ranges that cover a wide spectrum of emission possibilities and environmental conditions. Particular emphasis is given to the aquatic environment.

1. Introduction

While for some chemicals inhalation can be considered the pathway of concern for airborne emissions, for others noninhalation pathways may dominate the risk. The importance of noninhalation pathways depends on certain physical and chemical characteristics of the compound which determine the amounts at which this chemical will enter and accumulate in environmental media other than air and the various components of the foodchain. Chemicals with significant noninhalation risks can be referred to as "multimedia chemicals".

Among the various chemicals emitted by fossil-fueled power plants, mercury requires special attention, as it possesses particularly strong multimedia characteristics (e.g., high bioconcentration tendency in fish). In addition to its strong multimedia characteristics, mercury is a chemical whose behavior is particularly sensitive to environmental conditions, and especially the characteristics of the aquatic environment. Due to this sensitivity, risks associated with mercury emissions are anticipated to exhibit great variability among different sites located in different environmental settings.

Since a multimedia assessment typically requires extensive resources, it may not always be possible to perform such an assessment for each power plant evaluated for Hg risks. Therefore, it is useful to develop an alternative approach that allows us to approximate multimedia risks without having to perform a complete multimedia assessment for each one of these sites. We present and implement an approach for the development of

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approximating factors for the prediction of multimedia risks associated with mercury power plant emissions. This approach is based on the investigation of four critical components influencing Hg multimedia risk: (1) Hg deposition; (2) hydrologic environment; (3) Hg uptake by fish; and (4) Hg uptake by vegetation. To capture the variability in the conditions affecting Hg multimedia risks, the problem is handled in a probabilistic way. Two major sources of variability are evaluated: (1) emission speciation; and (2) environmental characteristics. Of the various environmental parameters, particular emphasis is given to the characteristics of impacted water bodies which may be used for public water supply and fishing.

2. Mercury Fate and Transport

The fate, transport and toxicity characteristics of mercury may be significantly affected by the physical phase and speciation of the chemical. Consequently, it is important that these parameters are taken into account when studying the cycling of mercury in the environment. In the following paragraphs of this section we provide a brief overview of mercury's chemical forms, chemical transformations, intermedia transport and foodchain bioconcentration characteristics.

2.1. CHEMICAL FORMS

Mercury is present in the environment in three oxidation states: elemental mercury, Hg^0; monovalent mercury, Hg(I); and divalent mercury, Hg(II). These forms and their compounds can be present in the atmosphere in either gas, liquid, or solid phases. Mercury compounds found in the environment can be either of inorganic or organic nature. The organic compounds of mercury, which are found primarily in aquatic environments, are of particular environmental interest because they have a tendency to accumulate in biota and particularly large fish.

The total concentration of mercury in the atmosphere is generally dominated by elemental mercury vapor. Lindberg et al. (1991) report a particulate (i.e., mainly Hg(II) inorganic compounds) to total mercury ratio of 0.5%, measured during a study at Walker Branch Watershed in Tennessee. Organic mercury in the atmosphere is also present at low concentrations (Fitzgerald et al., 1991).

2.2. ATMOSPHERIC CHEMICAL TRANSFORMATIONS

As a plume travels downwind, mercury may undergo chemical transformations by reacting with other species present in the plume or in the atmospheric background. Such chemical transformations may occur both in the gaseous and aqueous phases. Gas-phase mercury chemistry involves primarily oxidation of Hg^0 by common atmospheric species (e.g., Cl_2, O_3, H_2O_2, etc.), leading to the formation of Hg(II) inorganic compounds. Aqueous-phase reactions can occur in rain, cloud, or fog water as well as in the moisture associated with

hygroscopic aerosols. These reactions involve the oxidation of Hg^0 to Hg^{2+}, the reduction of Hg^{2+} to Hg^0, and the complexation/dissociation of various Hg^{2+} compounds. The oxidation of Hg^0 by organic acids and the formation of organo-mercurials (e.g., methylmercury) is also possible. A more detailed description of mercury atmospheric chemistry is provided by Seigneur et al. (1994).

2.3. DEPOSITION

Deposition is the intermedia process responsible for the transport of chemicals from the atmosphere to the ground surface. A good understanding and accurate characterization of this process is of particular importance when performing a multimedia risk assessment as this will determine if and to what extent other media get contaminated. The deposition process can be divided into dry and wet deposition.

2.3.1. Dry Deposition

Dry deposition represents the uptake of chemicals at the earth's surface, and combines the effects of gravitational settling and interaction with terrain features. In mathematical models, dry deposition is often parameterized through the use of a deposition velocity, V_d, which represents the ratio of the deposition flux to the ground-level atmospheric concentration. The deposition velocity can vary significantly depending on the speciation and physical state of the chemical. For particulates, V_d is a strong function of the particle size. For gases, dry deposition is dominated by physico-chemical interactions with the subject surfaces. Typically, dry deposition velocities of gases are higher for chemicals that are either soluble or reactive on surfaces than for insoluble inert chemicals.

Dry deposition velocities for Hg^0 have been measured and predicted by various investigators for different types of deposition surfaces. These values are generally low ranging from 0.006 to 0.12 cm/s (Barton et al., 1981; Lindberg et al., 1979; Lindberg et al., 1991). Reported deposition velocities for particulate mercury are also low, ranging from 0.003 to 0.11 cm/s (Lindberg et al., 1991). No measurements or predictions have been reported in the literature for the dry deposition velocity of gaseous Hg(II). However, discussions among experts in the scientific community suggest that since Hg(II) compounds are characterized by high solubility and reactivity, their dry deposition characteristics are expected to be similar to those of comparable reactive gases. Specifically, Hg(II) dry deposition has often been compared to that of HNO_3. Dry deposition velocities reported in the literature for HNO_3 range from 0.06 to 5 cm/s (Seinfeld, 1986).

2.3.2. Wet Deposition

Wet deposition is the removal and subsequent deposition of chemicals in the atmosphere by precipitation. Unlike dry deposition, which occurs in the lower layers of the plume above the deposition surface, wet deposition affects the entire volume of the plume inside the precipitation layer. In mathematical models, wet deposition is often parameterized through the use of a scavenging (or washout) coefficient, Λ. The value of Λ depends on

the intensity of precipitation as well as the particle size for condensed chemicals (Jindal and Heinold, 1991), and solubility and reactivity in droplets for gaseous chemicals (Seinfeld, 1986).

2.4. AQUATIC CHEMICAL TRANSFORMATIONS

Mercury deposited or transported into surface water bodies may undergo a variety of transformations. An extensive understanding and an accurate quantitative estimation of these processes has, however, not yet been achieved. The chemical transformation of greatest interest from a health risk perspective is the methylation of mercury, as this organic form of the chemical has been known to exhibit high toxicity as well as the tendency to bioaccumulate in fish (particularly at the higher levels of the trophic chain). During the process of methylation, bacteria present in the aquatic environment transform dissolved inorganic mercury into methylmercury. The reverse process is also possible and is referred to as demethylation. The rates of methylation and demethylation in a given aquatic environment appear to be a function of certain climatologic and lake water quality characteristics. Such characteristics include temperature, pH, dissolved and particulate organic carbon, calcium, and sulfate concentrations (Hudson et al., 1992).

2.4.1. The Mercury Cycling Model (MCM)

As part of research carried out during the recent years on mercury, the Electric Power Research Institute (EPRI) has developed the Mercury Cycling Model (MCM) (Hudson et al., 1992) which simulates the chemical transformations and uptake of mercury by fish in the aquatic environment. Input to the model consists of mercury input loads (i.e., deposition rates to the lake surface), hydraulic, and water quality characteristics of the lake. The model was formulated based on a combination of theoretical understanding and experimental observation of the chemical transformations of mercury in a lake environment.

2.5. FOODCHAIN UPTAKE

2.5.1. Vegetation

Mercury uptake by vegetation can occur through three major mechanisms: direct deposition from air to the plant surfaces, uptake from the soil through the roots, and uptake from air through the foliage in the case of gaseous forms of mercury. Modeling of vegetation uptake through direct deposition utilizes the deposition rates of Hg as well as factors accounting for the amount of deposited material intercepted on edible plant surfaces and the decay of chemical mass. Modeling of the uptake of vegetation through the foliage is only performed for gaseous mercury species and utilizes the corresponding chemical concentration in the air and the compound's Henry's law constant which expresses its tendency to volatilize or remain in solution (i.e., in the plant). Finally, modeling of the uptake of vegetation from the soil through the roots is usually performed

by means of a bioconcentration factor which expresses the ratio of the chemical concentration in the plant to that in the underlying soil.

2.5.2. Fish

Mercury contamination of fish may occur by means of three distinct processes: bioconcentration, bioaccumulation, and biomagnification. Bioconcentration is the result of direct uptake of chemicals from water across the gill membrane. Bioaccumulation represents the combined uptake of chemicals directly from water and indirectly through ingested food and sediments. Finally, biomagnification is the increase of chemical concentration at the higher levels of the trophic chain. Frequently, when modeling chemical uptake by fish, the effects of these three processes are lumped together in a single factor which relates the concentration of dissolved mercury in water to the resulting mercury concentration in fish. This combined factor is referred to as a water-to-fish bioconcentration factor (BCF_f). The value of the resulting BCF_f depends on the speciation of the chemical (i.e., mercury in this case) as well as the characteristics of the specific water body (Hudson, et al., 1992). Site-specific values of methyl mercury BCF_f can be predicted through use of the Mercury Cycling Model, which was mentioned above.

3. Modeling Approach

3.1. SELECTION OF APPROPRIATE APPROXIMATION FACTORS FOR THE PREDICTION OF Hg MULTIMEDIA RISKS

The multimedia risk from mercury power plant emissions results from the summation of three separate components: inhalation risk, ingestion risk, and dermal absorption risk. Typically, Hg risks from dermal absorption are expected to be insignificant compared to the other two pathways and, therefore, they could be ignored. Estimation of inhalation risks is fairly straightforward as it only requires knowledge of the Hg ground-level atmospheric concentration and the inhalation "Reference Concentration" (RfC), which describes the threshold value for the occurrence of health effects. The estimation of ingestion risks, however, requires significantly more extensive effort and characterization of various environmental parameters. As the goal of this approach is to avoid performing a detailed multimedia analysis for each site, the approximating factors to be developed should be selected to relate multimedia risks to variables that can be obtained either through the sampling data, or from the results of the air dispersion modeling. Also, the variables to be used in the approximating relationship should be selected to provide the most reliable estimates of mercury multimedia risk.

The magnitude of the ingestion risk will depend on the amount of Hg deposited, as deposition will determine the extent to which environmental media other than air, and the foodchain will get contaminated. Deposition consists of two components: dry and wet. For a local assessment, dry deposition is considered directly proportional to the ground-level ambient air concentration (C_a), whereas wet deposition is proportional to the

chemical emission rate (Q_e) (see Section 2.3.2). Therefore, in the case of ingestion risks resulting from dry deposition, C_a is the variable which is most characteristic of the resulting ingestion risk. In the case of ingestion risks from wet deposition, however, use of the emission rate, Q_e is more appropriate.

Since the variables affecting the dry and wet deposition ingestion risks are different, it is appropriate to break the total ingestion risk into two components and develop two separate sets of approximation factors for dry and wet deposition.

Following the above rationale, the equation to be used for the multimedia risk (i.e., hazard index (HI))[1] approximation can be formulated as follows:

$$\text{Multimedia HI} = RCF_{dry} * C_a + REF_{wet} * Q_e + C_a/RfC \quad (1)$$

where: C_a = the ground-level air concentration; Q_e = total Hg emission Rate; RfC = reference concentration (i.e., toxicity parameter) for Hg inhalation; RCF = "Risk per unit Concentration Factor"; REF = "Risk per unit Emission Factor."

The three terms in the above equation represent ingestion risk from dry deposition, ingestion risk from wet deposition, and inhalation risk, respectively. It should be noted that the ingestion toxicity of mercury (i.e., the ingestion reference dose (RfD)) is incorporated in the RCF and REF parameters.

3.2. SETUP OF CALCULATION ALGORITHM

The algorithm for the calculation of the above described RCFs and REFs was developed following a sensitivity analysis of the "Total Risk of Utility Emissions" (TRUE) multimedia risk assessment model. A detailed description of TRUE is provided by Constantinou and Seigneur (1993). The purpose of the sensitivity analysis was to identify the environmental and mercury physico-chemical parameters and mechanisms having the highest influence on the resulting multimedia risks. The effect of other parameters for which regulatory recommended values exist (e.g., exposure parameters, toxicity values etc.) was not evaluated. The fish consumption rate assumed in the calculations was 37g/d (EPA, 1989).

We recognize that a great deal of uncertainty is associated with these parameters and that their inclusion is essential when performing a thorough uncertainty analysis of mercury risk. The purpose of the study presented here, however, was not the performance of uncertainty analysis for Hg risks, but rather the evaluation of the variability of these risks under different assumptions regarding the environmental conditions as well as mercury speciation and physical behavior. Inclusion of other parameters, which are not related to environmental conditions and Hg speciation, would make it difficult to separate the effect of the variability in these conditions from the effect of other parameters on the

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[1] *The hazard index is defined as the sum of the individual hazard quotients (HQs) from the different pathways of exposure to a chemical. The HQ for a given chemical and pathway is defined as the ratio of the estimated exposure dose to the "Reference Dose" (RfD), which represents a threshold value for the occurrence of health effects.*

resulting distribution for Hg risk. A parameterized version of the risk assessment model including only the most influential mechanisms and parameters was setup in a spreadsheet format and was linked to the probabilistic software Crystal Ball (Decisioneering, Inc., 1992) for the performance of synthetic simulations.

3.3. EVALUATION OF THE RESPONSE OF THE AQUATIC ENVIRONMENT

Since the fish pathway is critical in the evaluation of Hg multimedia risks, it is essential that a comprehensive approach be used for the evaluation of aquatic chemical transformations and Hg uptake by fish. For this purpose, EPRI's Mercury Cycling Model was used to simulate chemical transformations and Hg bioconcentration factors for a total of 15 lakes in the country covering a variety of sizes, types (i.e., seepage, drainage, reservoirs), and water quality characteristics (e.g., pH, chlorophyll a, dissolved organic carbon (DOC), particulate organic carbon (POC), chlorides, calcium, and sulfates). The geographic diversity of the lake set included 11 states representing New England, Upper Mid-West, Southwest, Southeast, and Rocky Mountain regions. A separate sensitivity analysis was performed on MCM to parameterize the model in such a way that it could be incorporated in the previously described spreadsheet risk assessment model. The results of MCM for the different lakes were analyzed to provide probability distributions characterizing the variability of the fish bioconcentration factors and chemical transformation parameters.

4. Findings

4.1. MERCURY CYCLING SIMULATIONS

For the purposes of the present study, we used the steady-state version of the MCM model to simulate the dynamics of Hg in lakes. The values of the predicted CH_3HgX BCF_fs for the various lakes varied widely from a minimum of 12,000 l/kg to a maximum of 9.8×10^6 l/kg, with a geometric mean of 3.0×10^5 l/kg (expressed with respect to the fresh weight of fish). The fish species assumed in the calculations was yellow perch.

The critical parameter for the assessment of human health risk is the concentration of mercury in fish. The fish flesh concentration of mercury is dependent upon both the concentration of mercury in water and the estimated BCF_f. The predicted methylated fractions of mercury in lake water for the various lakes analyzed ranged between 0.2% (in an alpine drainage lake) and 47% (in a small seepage lake). It should be pointed out that the semi-empirical nature of the MCM model raises some uncertainty in the accuracy of its predictions for systems where no calibration has been performed. However, the use of the model here was deemed appropriate as the purpose of the study was the evaluation of the variability in risks caused by the characteristics of the aquatic environment, rather than the accurate simulation of the dynamics of a specific system. Further theoretical understanding of the kinetics of Hg transformations in the aquatic environment, and

additional calibrations of the model to a variety of systems and geographic regions would help reduce this uncertainty.

4.2. DEPOSITION MODELING

The calculation algorithm employed in the analysis was based on the use of deposition velocities for dry deposition and scavenging coefficients for wet deposition. As the deposition characteristics of the various physical states and chemical species of Hg may vary significantly, separate calculations were performed for each possible mercury form. For the purposes of the probabilistic analysis, the deposition parameters were assigned appropriate probability distributions or value ranges found in the literature. The study area considered was that enclosed by a 50 km radius around the power plant. The lakes analyzed were assumed to be located within this study area. The speciation of Hg in the emissions was also considered. As studies have shown the presence of methyl-mercury in power plant emissions to be rather insignificant, speciation considerations were limited between elemental Hg^0 gas, and inorganic Hg^{II} gas and particulate compounds. The numerical data used in the analysis for Hg emission speciation were based on the results of EPRI's PISCES sampling program. These results suggest a broad range of 0 to 80% of Hg in the emissions present in the elemental Hg^0 form (Chu, 1994).

4.3. MULTIMEDIA Hg RISK APPROXIMATION FACTORS

A total of 15 parameters was considered in the probabilistic analysis, consisting primarily of speciation and deposition parameters as well as parameters characterizing the Hg cycling in the aquatic environment. All other parameters incorporated in the calculations were held at fixed values (i.e., regulatory defaults). A total of 15,000 "Latin Hypercube" iterations was performed on the parameterized model to provide distributions for the RCF and REF multimedia risk approximation factors. The derived distributions for the RCFs and REFs are highly skewed to the right (i.e., the occurrence of high values is possible at a lower probability). Sensitivity analysis indicated that the extensive variation in the results of the synthetic simulations is attributed primarily to the variability of the methyl-mercury fish bioconcentration factor (i.e., CH_3HgX in fish-to-CH_3HgX in water). Other factors which appear to have a significant influence on the results are: (1) the flushing rate of the lake; (2) the dry deposition velocity of $Hg^{II}(g)$; (3) the contribution of the watershed to the Hg loading of the lake; and (4) the fraction of inorganic Hg input load to the lake which gets converted to CH_3HgX.

The statistical parameters and percentiles of the derived RCF and REF distributions are summarized in Table 1. To make the numbers more meaningful (i.e., directly representative of Hg ingestion risks), the emission and dispersion characteristics of a 700 MW coal-fired power plant were used, as an example, to derive hazard indexes (HIs) corresponding to the RCF and REF factors. These HIs are presented along with the RCFs and REFs in Table 1.

TABLE1

Statistical Parameters of RCF and REF Distributions

Parameter	RCF (m^3/g)	Dry Deposition HI for Site A	REF (s/g)	Wet Deposition HI for Site A
Mean (expected value), μ	1.5×10^{10}	2.4×10^{-3}	2.6	7.8×10^{-4}
Standard Deviation, σ	2.3×10^{11}	3.7×10^{-2}	20.7	6.2×10^{-3}
Percentiles:				
$F_{5\%}$	1.2×10^{8}	1.9×10^{-5}	0.03	9.0×10^{-6}
$F_{25\%}$	2.9×10^{8}	4.6×10^{-5}	0.07	2.1×10^{-5}
$F_{50\%}$	7.6×10^{8}	1.2×10^{-4}	0.17	5.1×10^{-5}
$F_{75\%}$	3.0×10^{9}	4.8×10^{-4}	0.67	2.0×10^{-4}
$F_{95\%}$	3.3×10^{10}	5.3×10^{-3}	6.93	2.0×10^{-3}

RCF: Risk per Unit Concentration Factor
REF: Risk per Unit Emission Factor

* The dry and wet deposition HIs for Site A are provided as an example to transform the RCFs and REFs to Hg HI units

The characteristics of Site A are as follows:
- Emission Rate, $Qe = 3.0 \times 10^{-4}$ g/s
- Average ground-level air concentration, $C_{av,g} = 1.6 \times 10^{-13} g/m^3$

Table 1. Statistical Parameters of RCF and REF Distributions.

It should be pointed out that the resulting distributions for the RCF and REF risk factors are anticipated to provide rather conservative results of Hg multimedia risk. The reason for the conservatism is that the set of 15 lakes used in the derivation of these distributions was more representative of "worst-case" rather than average conditions regarding methylation and Hg bioconcentration in fish. This conservatism can be reduced by adding to the set more lakes that cover the entire range of possible values.

5. Conclusion

An approach was presented for the evaluation of multimedia human health risks associated with Hg power plant emissions under different assumptions regarding the speciation of Hg in the emissions and the characteristics of the surrounding environment. The problem was handled in a probabilistic way where the influential parameters were assigned probability distributions that were selected to cover a wide range of possibilities. Particular emphasis was given to the deposition of Hg and the response of the aquatic environment. The results indicated extensive variation in the anticipated Hg risks. This variation is attributed primarily to the variation in the value of the methylmercury water-to-fish BCF estimated for different lake environments.

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AN ASSESSMENT OF ADULT RISKS OF PARESTHESIA DUE TO MERCURY FROM COAL COMBUSTION

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Abstract. This paper presents a probabilistic assessment of the risks of transient adult paresthesia (tingling of the extremities) resulting from ingestion of methylmercury (MeHg) in fish and shellfish. Two scenarios are evaluated: the "baseline," in which the MeHg dose results from the combined effects of eating canned tuna fish, various marine seafoods, and freshwater sportfish, and an "impact" scenario in which the Hg content of the freshwater sportfish is increased due to local deposition from a hypothetical 1000 MW_e coal-fired power plant. Measurements from the literature are used to establish the parameters of the baseline, including atmospheric rates of Hg deposition and the distributions of MeHg in fish. The Hg intake for the impact scenario is then based on linear scaling of the additional annual Hg deposition as estimated from a Gaussian plume dispersion model. Human health responses are based on a logistic fit to the frequencies of paresthesia observed during a grain poisoning incident in Iraq, 1971-2. Based on a background prevalence rate of 2.2% for adult paresthesia, the assessment predicts a 5% chance that the increase in paresthesia prevalence due to either baseline or incremental MeHg doses might approach about 1% of the background prevalence rate.

1. Introduction

Mercury occupies a special place in the hierarchy of environmental pollutants. Unlike many of the "air toxics," adverse health effects from Hg have been convincingly demonstrated in the past, because of several unfortunate poisoning incidents. Although Hg is distributed throughout the environment as an air pollutant, its toxic effects result mainly from ingestion of contaminated fish. Unlike most other air pollutants, there are few permanent sinks for Hg in the environment, and emissions from a given source may eventually be dispersed around the planet. As a result, adverse effects must be considered on scales ranging from local to global.

This paper presents results from a probabilistic assessment of the Hg health risks to adults associated with fish and shellfish consumption and with a hypothetical 1000 MW_e coal-fired power plant (Lipfert *et al.*, 1994). The assessment draws on extant knowledge in each of the important steps in the chain from emissions to health effects, recognizing that, because of the non-linear nature of the dose-response functions, both global background levels and local source increments must be considered. Estimated results at key points in the calculation chain were compared with actual measurements to help validate the modeled estimates. Two scenarios were considered: the "baseline"

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scenario (MeHg from fish consumption without local impacts), and the "impact" scenario (baseline plus maximum local power-plant impact).

The approach strives for realism rather than conservatism throughout the analysis. Existing "reference doses" are not used as an index of health risks because of their embedded conservatism; rather, health risk estimates are based on alternative dose-response models derived from original data on a mild reversible neurological response: adult paresthesia (tingling of the extremities). If substantial impacts on paresthesia were predicted, more severe endpoints could then be analyzed within the same framework. The Monte Carlo methods used in the assessment specifically incorporate the uncertainties in the dose-response functions *per se*, as well as in the intake terms.

2. Materials and methods

The geographic setting for this analysis is assumed to be the upper midwestern United States; an annual precipitation rate of 1 m is assumed. Table I summarizes the risk assessment model that was developed; see Lipfert *et al.* (1994) for details of the model framework and calculations. These features were combined using the computing package @RISK (Palisades Corp., 1988), with Latin hypercube sampling.

2.1 EMISSIONS AND ATMOSPHERIC PROCESSES

The hypothetical 1000 MW_e coal-fired power plant examined in this study was assumed to burn coal having the U.S. average content of Hg (0.08 μg/g). The emission controls (electrostatic precipitator) were assumed to reduce the Hg emissions by about 10%. This results in an estimated total Hg emission rate of 180 kg/y from the hypothetical plant, comprising elemental, reactive, and particulate Hg species. The reactive and soluble portion (Hg^{++}) was assumed to be 75% (Felsvang *et al.*, 1993). A Gaussian plume dispersion model (Lipfert *et al.*, 1985) was used to estimate the local annual average air concentrations of the 3 species and deposition rates were estimated for each within 50 km. In modeling deposition, Hg speciation was important because of the variations in water solubility of the different Hg species. Dry deposition was modeled by assuming a value for the dry deposition velocity, defined as the ratio of the deposited flux to the air concentration. Wet deposition was modeled in two different ways, using either the washout ratio (ratio of concentration in precipitation to air concentration) or a dynamic plume depletion algorithm. The model indicates that only about 5% of Hg emissions are likely to deposit within the first 50 km of travel; the balance is assumed to join the global Hg pool. At 50 km, the local Hg deposition from the plant would be about 1% of background levels.

The model predicted that this reactive Hg would deposit relatively close to the plant, where its impact may be maximized over a relatively small area (assumed to be a sportfishing lake). The maximum additional local wet and dry Hg deposition near the plant is about 0.020 $mg/m^2/y$, which amounts to about a doubling of existing background deposition rates. In the risk calculations, we combined the uncertainties of all the emissions, transport, and deposition processes and used a local deposition increment with a range from 50% to 200% increase over global background.

TABLE I
Features of the BNL Mercury Risk Assessment Model

Hg emissions	Ratio of Hg^{++} to total Hg is estimated based on Cl^- in coal. Effects of air pollution controls are estimated.
Transport, dispersion, and deposition	Gaussian plume transport and dispersion model for 3 Hg species, up to 50 km. Constant V_d and washout ratio for each Hg species. No atmospheric reactions.
Accumulation in surface waters	The incremental wet+dry deposition to the watershed is assumed to enter the water body (conservative assumption).
Contributions to global background	Any Hg not deposited within 50 km is assumed to enter the global pool and to increase global deposition.
Effects of local sources on fish Hg content	Average Hg in each fish species is assumed to increase in proportion to the Hg deposition increment (local plus global).
Background Hg intake from fish, shellfish	The intake distribution is calculated by using probabilistic methods to sum (log normal) distributions of (Hg concentration x consumption rate) for fresh-water and marine species and for canned tuna.
Equilibrium metabolic model	The equilibrium level of the body burden of MeHg is estimated by considering the frequencies of the 3 different types of fish meals, in addition to the total MeHg intake. The distribution of body burden is estimated using probabilistic methods, from distributions of Hg intake, body mass, and half life of Hg, as a baseline and with power plant contributions to MeHg in freshwater fin fish.
Dose-response functions and risk analysis	Distributions of the parameters of a continuous dose-response model are developed from the Iraqi paresthesia data and used to estimate levels of risk for the baseline and for the incremental effects of a 1000 MW_e hypothetical power plant.

These assumptions about the importance of local Hg deposition are supported by measurements in various settings. Anderson and Smith (1977) found an increase of about 33% in lake sediment Hg (but not in soil) due to the start-up of a nearby coal-fired power plant. Ferrara *et al.* (1986) report the influence of anthropogenic Hg emissions on the local scale. Greenberg *et al.* (1992) measured a pattern of increased wet deposition of Hg that resembles model predictions (Figure 1), near a large municipal solid waste facility.

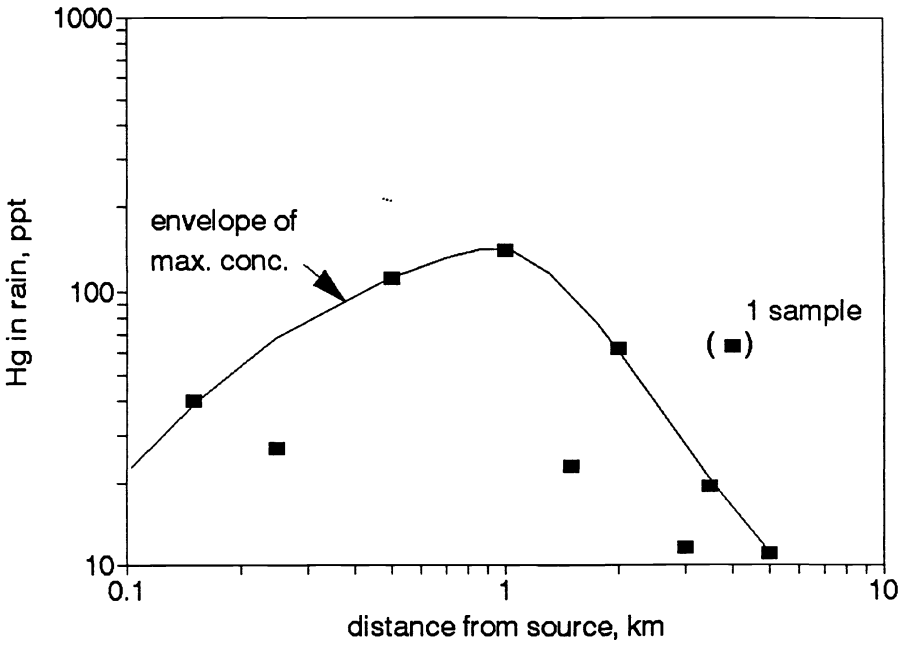

Fig. 1 Average concentrations of Hg in precipitation, measured for 6 rain events, near a New Jersey incinerator. Data from Greenberg *et al.* (1992).

2.2 FISH CONSUMPTION RATES AND THE DISTRIBUTION OF BASELINE MeHg INTAKE

The U.S. population is exposed to MeHg principally through the consumption of fish and shellfish. Hg from dental amalgams is primarily inorganic (Subcommittee on Risk Assessment, 1993). Data on fish Hg content were obtained from various sources, with heavy reliance on the EPA Chemical Residues Study (U.S. EPA, 1992). Fish consumption statistics from various sources were used to estimate the baseline MeHg intake of the population; see Lipfert *et al.* (1994) for details. Surveys and national fishery statistics suggest that the overall average per capita fish consumption rate is about 20 g/d (about 1 meal per week). About 95% of the U.S. population consumes

some fish over the course of a year. Mercury levels tend to be higher in freshwater sportfishing species; the upper Midwest region was selected for study because freshwater fish consumption tends to be higher there; the average daily (baseline) total MeHg intake there was estimated to be about 4.5 μg/d, based on total consumption of about 25 g/d. Table II presents the relevant MeHg intake statistics, which are based on log-normal distributions.

TABLE II
Representative Statistics for Components of the
Fish and Shellfish Diet in Northcentral States

Component	Means		Medians		GSDs*		Apparent Intake
	diet g/d	Hg μg/g	diet g/d	Hg μg/g	diet g/d	Hg μg/g	(mean) μg/d
canned tuna	4.5	0.20	2.7	0.15	2.7	2.2	0.88
freshw. finfish	10.3	0.28	6.8	0.15	2.5	3.0	2.9
other marine	9.9	0.077	7.2	0.06	2.0	2.2	0.76
total fish	24.7 g/d						4.5 μg/d

*GSD = geometric standard deviation

Rates of aquatic methylation processes and bioconcentration are typically very uncertain and depend on many factors. In this assessment, the estimated increase in freshwater fish MeHg due to Hg deposition from the hypothetical plant is assumed to be proportional to the change in local Hg deposition. Thus, that portion of the MeHg intake of the populations consuming locally-caught fish near the plant would increase in proportion to their freshwater fish consumption. Any MeHg resulting from dental amalgams would be considered part of the baseline and would not be affected by changes in fish consumption.

2.3 METABOLIC PROCESSES

In contrast to both carcinogenic and irritant air pollutants, the dose metric of concern for MeHg is neither the total accumulated dose nor the maximum acute level, but the equilibrium body burden that is attained as a balance between steady intake and excretion. Body burden controls health responses and is directly related to measurable levels of MeHg in blood and hair. Because a high body burden of MeHg can only be obtained by eating fish more often, the averaging process that takes place with respect to individual doses obtained from eating disparate meals over time is an important feature that should be included in a risk assessment. Monte Carlo simulations were used to develop an empirical model of this process. Figure 2 shows how the (geometric) standard deviation of body burden decreases as the annual number of meals (and absolute value of MeHg body burden) increase. The resulting body burden

estimates were found to compare satisfactorily with the available measurements on blood and hair Hg, which have GSDs ranging from 1.4 to 2.8; the equivalent values for body burden from our simulations were 1.74 and 2.05, depending on assumptions. If metabolic averaging is not considered, typical GSD values obtained by combining the distributions of Hg concentration and fish consumption can exceed 3.0 (Stern, 1993).

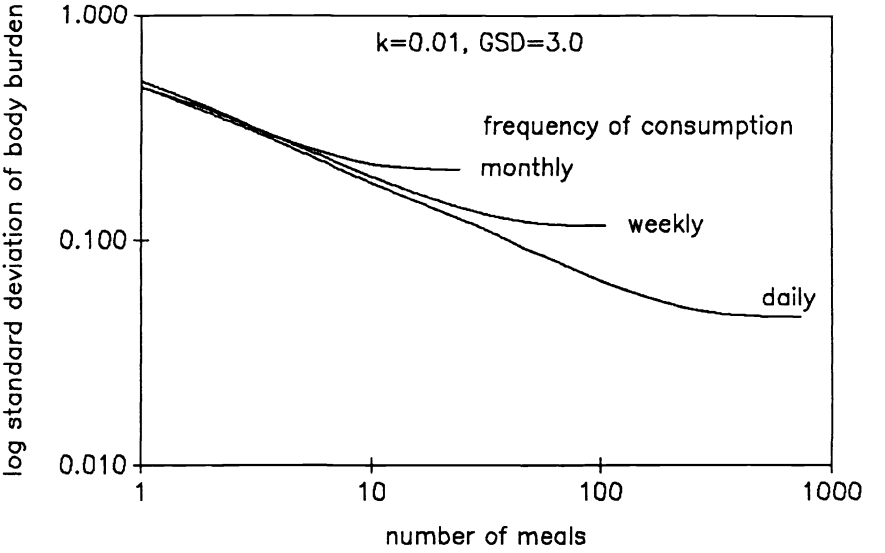

Fig. 2 Reduction in the standard deviation of body burden as a function of number of fish meals consumed in the time to reach equilibrium, with an underlying GSD of 3.0. (k = elimination constant)

2.4 DOSE-RESPONSE FUNCTIONS

A quantitative health risk assessment requires a mathematical dose-response function that predicts adverse health effects in terms of the imputed dose. It must be able to accommodate uncertainties in the (dose) input terms, and the uncertainties of the dose-response model itself must be defined, including those associated with the choice of model parameters or functional form.

The central nervous system is the principal target for MeHg, with the potential for effects on sensory, visual, and auditory functions. Individuals may vary greatly in their responses; paresthesia is perhaps the mildest symptom of MeHg poisoning. Data on 122 Iraqi adults and older children who consumed Hg-contaminated bread in 1971-1972 (Bakir *et al.*, 1973) were used to derive a continuous dose-response function (DRF); 59 cases of paresthesia were observed. It should be noted that paresthesia is not uncommon in unexposed populations; thus some residual or background prevalence rate should be expected, perhaps of the order of a few percent. Bakir *et al.* grouped the patients into 7 MeHg exposure categories. The lowest 2 groups were considered controls (unexposed): the average frequency of paresthesia in these 2 groups was 7.5%.

Blood Hg levels were determined an average of 65 days (about 1 half-life) after the incident and have been used as an index of MeHg exposure in most previous analyses. This means that the relevant (peak) blood concentrations are low by about a factor of 2 (Marsh, 1987). Further evidence for this hypothesis is derived from the dose-response data of Al-Mufti *et al.* (1976). They divided the residents of the consuming village into four groups, by number of loaves consumed. These figures were converted into body burdens by using the group average numbers of loaves consumed, the average MeHg content per loaf (1.27 mg) and the numbers of days of consumption from the data of Bakir *et al.* (1973), either 40 or 50 days. This dose-response function is plotted in Figure 3 (for both time assumptions) along with the data of Bakir *et al.* (1973, frequencies) and Nordberg and Strangert (1978, body burdens derived from the blood data). There is a substantial mismatch between the bread-based data and the original Bakir-Nordberg data. However, if the Nordberg and Strangert body burdens are arbitrarily doubled to account for the 65-day delay in determining the blood chemistry, the two sets of data agree quite well.

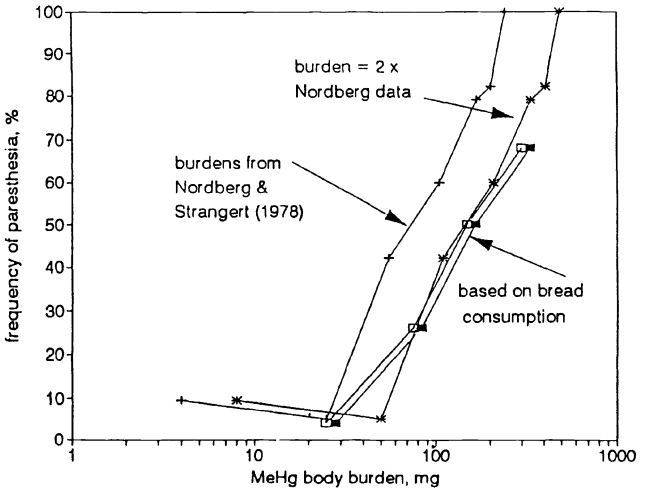

Fig. 3. Dose-response data for paresthesia in the Iraqi poisoning incident, according to various formulations.

A logistic function was used to represent the combined data. This is an "S" shaped curve with asymptotes at both extremes. In this application, predicting paresthesia at low doses is of much more interest than at high values, so that the final DRF model was chosen to fit well in this range. In addition, various background paresthesia prevalence rates were investigated. A background rate of 2.2% was close to the optimum, which was also the background level determined by Al-Mufti *et al.* (1974) from surveys. The final DRF model is given by

$$\ln(p/(1-p)) = 2(3.80 + 2.20\log(\text{body burden}) - 5) \qquad [1]$$

where p is the frequency of paresthesia. The standard errors of the two terms in Eq. [1] were 0.30 and 0.43, respectively.

3. Results: Assessment of Baseline and Incremental Risks

The risk analysis simulations were performed for several different assumptions involved in the metabolic model, two of which are given in Table III. The total range predicted in mean baseline risks was 0.002 to 0.005% (0.2-0.5 chances in 10000), with a 95th percentile risk range of 0.006 to 0.02%, depending on scenario assumptions. Using a uniform distribution of increased Hg deposition (from 50% to 200% increase) due to the power plant, the expected average risk level increased to 0.004 to 0.013% with an upper 95th percentile risk range of 0.013 to 0.052%, again depending on assumptions. The uncertainties in the parameters of the DRF were seen to be the primary source of uncertainty in the overall assessment. If a deterministic hockey-stick DRF had been used instead of the logistic model, the incremental frequency of paresthesia would have had about a 99% chance of being zero.

TABLE III
Probabilistic Risk Assessment Results (5000 trials)

Scenario Assumption meal size linked to body weight		1 No	2 Yes
# of meals consumed	median	44	38
in 5 half-lives	mean	56	43
	95%	132	86
(a) Baseline Simulations			
MeHg intake (μg/d)	median	2.67	2.29
	mean	4.44	3.70
	95%	13.4	11.4
Body burden (mg/kg)	median	0.0034	0.0028
	mean	0.0044	0.0033
	95%	0.0111	0.0070
Paresthesia prevalence	median	2.0	1.3
(cases per million adults	mean	29	19
above background)	95%	110	62
	background	22,000	22,000
(b) Source Impact Simulations			
MeHg intake (μg/d)	median	4.05	3.64
	mean	7.70	6.77
	95%	26.0	21.5
Body burden (mg/kg)	median	0.0052	0.0046
	mean	0.0085	0.0056
	95%	0.026	0.0132
Paresthesia prevalence	median	4.5	3.3
(cases per million adults	mean	73	38
above background)	95%	270	133
	background	22,000	22,000

The effects of power plant Hg emissions on marine species were assumed to be proportional to global background Hg. Assuming a coal Hg content of 0.08 μg/g and annual coal consumption of 800 million tons, the contribution of U.S. utilities to the global pool relative to all other Hg sources would be about 1% (WHO, 1990). We thus assumed that the effect of U.S. utility coal burning on the Hg content of marine species is negligible.

4. Concluding Discussion

This study shows that the effects of Hg emissions from a hypothetical 1000 MW_e coal-fired power plant may approximately double the upper percentiles of exposures to MeHg resulting from consuming game fish obtained from a localized area impacted by the plant. Even at these more elevated exposure levels, the attributable incidence in mild neurological symptoms (paresthesia) is estimated to be quite small, especially when compared with the estimated background incidence of paresthesia in the population. For example, in a population of 10,000 heavy fish eaters (taken here as the 95th percentile of the U.S. population), about one additional case of paresthesia due to fish consumption would be expected in the absence of a power plant, fewer than three additional cases with the plant, and about 220 cases due to all causes other than MeHg poisoning.

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CANADIAN ENVIRONMENTAL QUALITY GUIDELINES FOR MERCURY

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Abstract: CCME Canadian Environmental Quality Guidelines for mercury have been recommended or are under development for soil, water and sediments. These guidelines provide nationally consistent benchmarks for environmental quality across Canada and are intended as decision support tools in protecting and sustaining aquatic and terrestrial ecosystems in Canada and the beneficial uses they support. A Canadian water quality guideline for protection of aquatic life was recommended in 1987 as 0.1 $\mu g \cdot L^{-1}$. Currently, mercury guidelines for soils and sediments are under development. Preliminary calculations indicate that interim marine and freshwater sediment guidelines for the protection of aquatic life will both be 0.14 $mg \cdot kg^{-1}$; and that soil quality guidelines will be 2.0 $mg \cdot kg^{-1}$ (agricultural and residential land uses), and 30.0 $mg \cdot kg^{-1}$ (commercial and industrial land uses). Final recommended values are subject to change pending final approval by the Canadian Council of Ministers of the Environment.

1. Introduction

Goals for environmental quality have evolved from simple human use protection goals such as "drinkable, swimmable" water, to protection of the "ecosystem", including the human and non-human components. In response to an increasing public concern that chemical substances entering the environment were a major factor placing ecosystems at risk, the Canadian Council of Minister's of the Environment (CCME), undertook to develop nationally consistent benchmarks for environmental quality in Canada that would be protective of the long-term sustainable use of Canadian ecosystems. An initial emphasis on water quality lead to the publication of the Canadian Water Quality Guidelines in 1987 (CCREM 1987). National water quality guidelines were developed to protect and sustain not only the important human uses such as drinking water, but also freshwater life, livestock water and irrigation water. More recently, the guidelines have been expanded to encompass other important ecosystem components, mainly marine water quality, marine and freshwater sediment quality, tissue residue guidelines for protection of wildlife consumers, and soil quality guidelines.

The use and interpretation of the terms *criteria, guidelines, objectives* and *standards* vary among different agencies and countries. Environment Canada has generally adopted the term guideline as being a numerical limit or narrative statement recommended to support and maintain designated uses of the environment. This term is used interchangeably with the term criteria in describing the soil quality guidelines.

Canadian Environmental Quality Guidelines (EQGs) are based on a published national protocol which ensures consistent decision-making and quality of scientific data

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in development of national guidelines. Though protocols vary dependent on the specific exposure pathways and receptors of concern for a particular land or water use, the basic philosophy underlying guideline development is the same, i.e. to ensure that levels of contaminants in the environment pose no risk to the potential or existing range of biota, functions and interactions integral to sustaining the integrity of the ecosystem which supports a specified land or water use. To achieve this broad-based protection of a complex system, guidelines are based on conservative assumptions, such as protection of sensitive species and life stages.

Collectively, Canadian EQGs provide an important framework for protecting aquatic and terrestrial ecosystems across Canada and sustaining the many beneficial uses they support. EQGs have broad application in environmental evaluation and management. For example, they can serve as the basis for the development of objectives for the assessment and remediation of contaminated sites, as screening tools for assessing environmental quality and interpreting the significance of contaminant levels in environmental media, as goals for national and regional toxics management or rehabilitation programs, and as environmental benchmarks for international negotiations on emission reductions and trade agreements. These guidelines also play an important role in the Canadian Environmental Protection Act (CEPA) which was proclaimed in 1988 and is the basis of the federal government environmental protection legislation. Under CEPA Part 1, the Minister was given the authority to formulate environmental quality guidelines and objectives.

This paper outlines the current derivation procedures for Canadian Water Quality Guidelines, Soil Quality Criteria, and Sediment Quality Guidelines, and presents the proposed guidelines for mercury. To provide the context for development of mercury guidelines, this paper begins with a brief overview of the major sources, fate, and behaviour of mercury in the Canadian environment.

2. Mercury in the Canadian Environment

Mercury is relatively ubiquitous in the environment and is found in almost every environmental compartment including air, volcanic gases, fresh water, sea water, soils, mineral ores, lake and river sediments, and living organisms. Sources of mercury are both natural, via weathering and degassing of the earth's crust, and anthropogenic (D'Itri 1990).

In Canada, anthropogenic release of mercury to the environment has been estimated at approximately 31 tonnes annually (Jaques 1987). The major form of this release is as atmospheric emissions. Although mercury is no longer mined in Canada, the major source of mercury emissions is base metal recovery (45.2% of the total). Power generation and the combustion of coal, petroleum products, wood and natural gas contribute the second largest source of emissions (25.8% of the total).

In Canada, the general terrestrial concentrations of mercury are in the range of 0.02 to 0.15 $mg \cdot kg^{-1}$, with an average of 0.05 $mg \cdot kg^{-1}$ (Jonasson and Boyle 1972; McKeague and Kloosterman 1974; Environment Canada 1979) with elevated levels adjacent to anthropogenic point sources such as mining sites, reaching several hundred $mg \cdot kg^{-1}$

(Jonasson and Boyle 1972). Naturally elevated levels have also been found in British Columbia due to cinnibar deposits and in areas of Quebec and Ontario near areas of gold, copper or zinc mineralization (Environment Canada 1979). Flooding of terrestrial environments to form hydroelectric reservoirs results in the formation of methylmercury compounds in soil which become available to organisms within the soil, sediment, and water column (Louchouarn *et al.* 1993).

Sediments are often a major sink for mercury compounds in aquatic environments where it can be rendered virtually inactive (deep sediments) or converted to methylmercury, principally by sulphur-reducing bacteria (Bigham and Henry 1993; ENVIRO TIPS 1984). Mercury levels in Canadian lakes are generally below 0.3 $\mu g \cdot g^{-1}$ except in the Flin Flon area in Manitoba where Harrison and Klaverkamp (1990) reported high levels of 3.77 to 6.39 $\mu g \cdot g^{-1}$. Background sediment concentrations of mercury in Canada have been found to range from 0.01 $mg \cdot kg^{-1}$ to 1.6 $mg \cdot kg^{-1}$ with the mean concentration being 0.075 $mg \cdot kg^{-1}$ (Friske 1994). However, elevated concentrations have been noted in Ontario, Labrador, Northern Manitoba and in Yukon streams due to a variety of factors including the presence of massive sulfide and black shale deposits, glaciations resulting in transport and deposition, and faulted and techtonically-active terrains.

Several recent studies indicate that background mercury concentrations range from 1 to 20 $ng \cdot L^{-1}$ in freshwater (Kudo et al. 1982; Bloom 1989; Mierle 1990). In an acidified watershed in central Ontario, Mierle (1990) observed a positive correlation between aqueous mercury and dissolved organic carbon with total mercury concentrations below 5 $ng \cdot L^{-1}$ except during low flow periods when they exceeded 20 $ng \cdot L^{-1}$. Anthropogenic sources may elevate these levels considerably. For example, the Wabigoon River in Ontario received an estimated 10 metric tons of mercury from chlor-alkali operations with total mercury levels in water reaching up to 370 $ng \cdot L^{-1}$ reported near the outflow (Jackson et al. 1982), with levels typically in the 20-40 $ng \cdot L^{-1}$ range (Parks et al. 1989).

3. Canadian Environmental Quality Guidelines for Mercury

Mercury has been identified as a priority toxic substance in the Canadian environment, both through CEPA and by the CCME, and national environmental quality guidelines for mercury have been finalized, or are currently under development, for water, sediment and soil. Mercury has become an increasingly important issue in recent years since it is not only toxic in its inorganic form, but methylation greatly enhances it mobility and bioavailability. Since the primary site of methylation appears to be the sediments, and the sediments also act as a significant sink for this contaminant, the need for sediment quality guidelines has become apparent. In the following section, we briefly outline the derivation procedure for each of these guidelines using mercury as an example. Unless these values have been approved and published under the auspices of the CCME, they are not to be considered as final, recommended national guidelines.

The procedure and minimum toxicological data required to derive full and interim guidelines is specified in national protocols which have been developed for water,

sediment, and soil (CCME 1991, 1994a,b,c). Each protocol includes criteria used to assess the acceptability of data, specified minimum data requirements for both full and interim guidelines, the derivation method and supporting rationale. Before a guideline is recommended for a substance, a complete assessment of that substance is conducted including production and uses, sources to the Canadian environment, environmental concentrations, behaviour in the environment, bioaccumulation, toxicity to both aquatic and terrestrial organisms and existing guidelines from other jurisdictions.

3.1 WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE

Methods

Guidelines for the protection of aquatic life are developed both for protection of sediment benthos and biota in the overlying water column. The guidelines are defined as numerical limits designed to protect all forms of aquatic life during complete life cycles and indefinite exposure periods. The water quality guideline is derived by determining the lowest observed effect level (LOEL) for the most sensitive species and endpoint. Once the LOEL has been determined, an appropriate safety factor is applied such that the derived guideline represents a maximum concentration in water which should not be exceeded for the protection of aquatic organisms and designated uses.

Results for Mercury

Although the formal protocol for the development of Canadian water quality guidelines was established in 1991, mercury guidelines for water were adopted from other jurisdictions and published in the 1987 version. It was recommended that the total concentration of mercury in water was not to exceed 0.1 $\mu g \cdot L^{-1}$ based on the data of Reeder *et al.* (1979). In this study, toxic effects were examined for the most sensitive fish species identified in the literature review, the fathead minnow (*Pimephales promelas*) and the most toxic mercury species, methylmercury. It was found that levels of methylmercury in the edible parts of the fathead minnow exceeded the 0.5 $mg \cdot kg^{-1}$ limit for human fish consumption when exposed to 0.03 $\mu g \cdot L^{-1}$ methylmercury in water (Olson *et al.* 1975). Even though this concentration of methylmercury in the muscle did not cause adverse effects in the fish, the level set for human consumption would be reached before the fish were detrimentally affected. Therefore, in order to prevent this dangerous accumulation of methylmercury, levels of methylmercury in water should not exceed 0.01 $\mu g \cdot L^{-1}$. Assuming that methylmercury is less than 10% of the total mercury content of the water, the guideline for total mercury in water was adjusted to 0.1 $\mu g \cdot L^{-1}$.

Recent data has shown support for the adopted water quality guideline for mercury. Snarski and Olson (1982) have calculated the bioconcentration factor for mercury in the fathead minnow as being 4994. Since the permissible limit of mercury in fish muscle is 0.5 $\mu g \cdot g^{-1}$, the concentration of total mercury in water to protect fish from accumulating to this level is 0.1 $\mu g \cdot L^{-1}$. Chronic toxicity studies for the fathead minnow have indicated that effects occur below 0.23 $\mu g \cdot L^{-1}$. Therefore, the accepted WQG not only is supported by bioaccumulation data but also by chronic toxicity studies.

3.2 SEDIMENT QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE

Methods

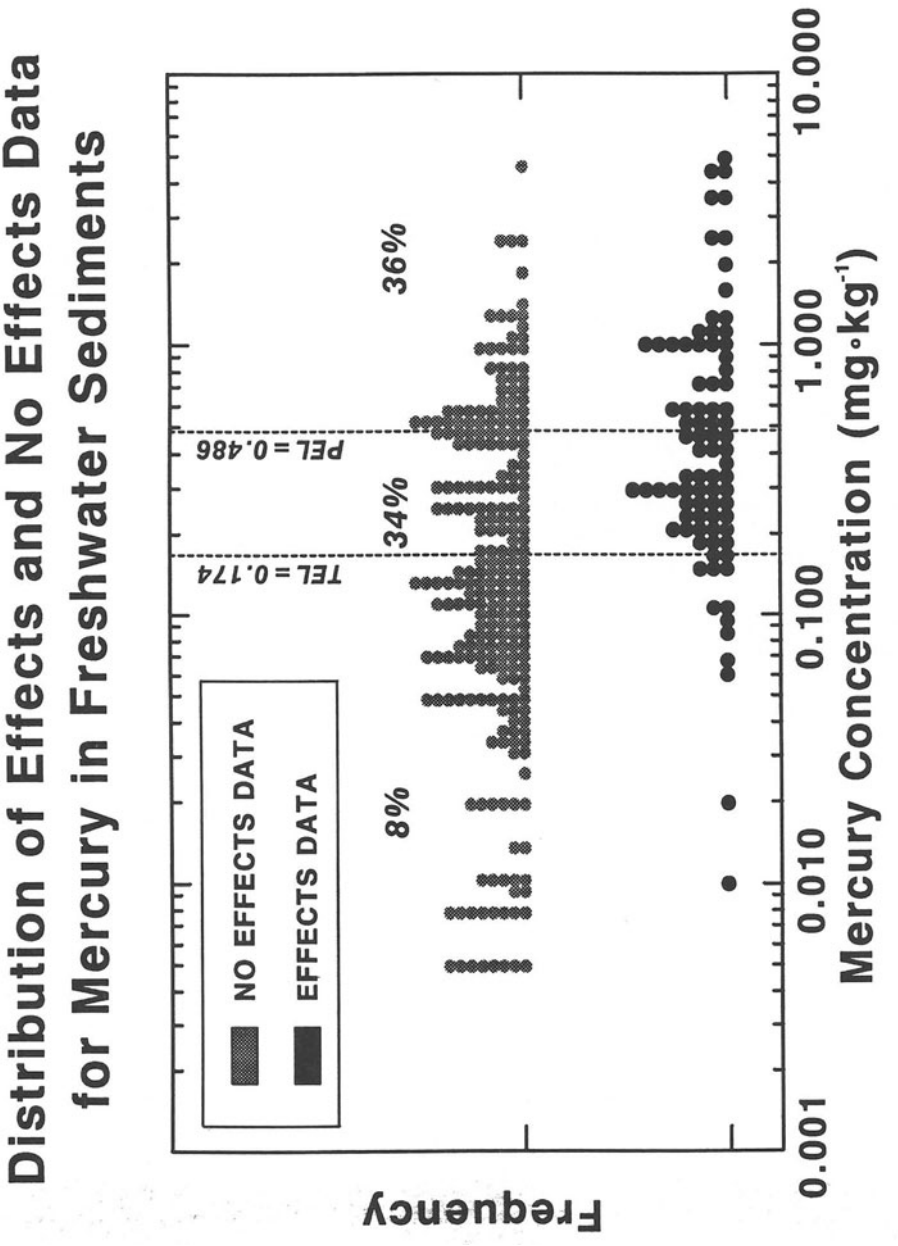
The purpose of sediment quality guidelines (SQGs) is to protect freshwater and marine (including estuarine) aquatic life associated with bed sediments. The protocol is based on two approaches: the National Status and Trends Program (NSTP) approach and the Spiked-Sediment Toxicity Test (SSTT) approach (CCME 1994b). The NSTP approach is a weight-of-evidence approach which includes data for a chemical generated from modelling (equilibrium partitioning theory), laboratory (spiked-sediment bioassay), and field studies (co-occurrence data consisting of matching sediment chemistry and biological effects data) (Long and Morgan 1990; Macdonald 1993; Long *et al.* 1994). This information is used to establish *associations* between concentrations of chemicals in sediments and adverse biological effects. All data is screened for acceptability and entered into a Biological Effects Database for Sediments (BEDS). A threshold effects level (TEL) is calculated as the geometric mean of the lower 15th percentile concentration of the effects data and the 50th percentile concentration of the no effects data set. This TEL consistently determines a range of sediment concentrations that is dominated by no effect data entries and represents the concentration below which adverse effects are not expected to occur.

The Spiked-Sediment Toxicity Test (SSTT) approach is a complementary procedure which will be used in the future to confirm and strengthen guidelines developed using the NSTP approach. The SSTT approach uses information on the response of test organisms to specific sediment-associated chemicals under controlled laboratory conditions (Chapman and Long 1983; Ingersoll 1991; USEPA 1992). SQGs will be developed using this approach once methodological issues have been resolved.

Results for Mercury

The distribution of BEDS data for total mercury for the freshwater environment is shown in Figure 1. The interim TEL for Mercury calculated for freshwater sediments is 0.174 $mg \cdot kg^{-1}$ dry weight. In addition to the TEL, the toxicological data can also be used to calculate a probable effects level (PEL) which represents the lower limit of the range of mercury concentrations that are almost always associated with adverse biological effects. For freshwater ecosystems, the PEL for mercury is 0.486 $mg \cdot kg^{-1}$. In marine ecosystems, the interim TEL and PEL calculated from the data are found to be 0.13 $mg \cdot kg^{-1}$ and 0.70 $mg \cdot kg^{-1}$, respectively.

The range defined by these two limits represents the range in which effects will occasionally be observed. By establishing these ranges, the likelihood of an adverse biological effect occurring at a given concentration can be estimated. This likelihood is calculated on the basis of the frequency distribution of the toxicity data by dividing the number of effect entries in a range by the total number of entries in that range, expressing this value as a percentage (Figure 1). In the case of freshwater ecosystems, only 8% of the mercury concentrations within the no effects range (0 to 0.14 $mg \cdot kg^{-1}$) are associated with adverse effects. In the possible and probable effects range for mercury, the incidence of adverse biological effects is 34% and 36% respectively. In marine ecosystems, the incidence of adverse effects is 8%, 24% and 37% in the no effects, possible effects and


Distribution of Effects and No Effects Data for Mercury in Freshwater Sediments
NO EFFECTS DATA
EFFECTS DATA
TEL = 0.174
PEL = 0.486
8%
34%
36%
Frequency
0.001
0.010
0.100
1.000
10.000
Mercury Concentration (mg•kg-1)

probable effects range, respectively.

A full Canadian sediment quality guideline can only be recommended when the interim guideline is supported by a weight-of-evidence of the available ancillary data that links the interim sediment quality guideline with specific sediment types and/or characteristics of the sediment or overlying water column (e.g. particle size, TOC). At present, since most of the ancillary data represents means for sites, there is no correlation between the sediment concentration of mercury with any sediment or water characteristic. Therefore, only an interim sediment quality guideline can be recommended at this time.

The data presently available for the calculation of sediment quality guidelines are primarily from the United States, although Canadian data are included wherever they are available. However, a wide range of species and endpoints are employed in the tables, as well as broad ranges in sediment type, allowing the interim sediment quality guidelines to be applicable to a broad spectrum of circumstances.

3.3 SOIL QUALITY CRITERIA

Methods

Soil quality criteria (guidelines) are derived to sustain four major categories of land use in Canada - Agricultural, Residential/Parkland, Commercial and Industrial. Ecological guidelines for soil are based on protection of ecological (including domestic biota) receptors exposed either directly or indirectly to soil contaminants. Human health criteria for soil are also developed but will not be dealt with in the current paper. The ecological effects protocol (CCME 1994) accounts for exposure from direct soil contact (SQC_{SC}), contaminated soil ingestion (SQC_{SI}), and ingestion of plants grown on contaminated soil (SQC_{FI}). The ingestion procedures are generally intended to protect terrestrial wildlife and livestock from indirect exposure to bioaccumulating contaminants ($\log K_{ow} > 4$). Within the direct contact procedure, there are three acceptable options for derivation of a criterion: 1) the Weight of Evidence approach; 2) the Lowest Observable Effect Concentration (LOEC) approach and 3) the Median Effects approach. The final determination of a guideline for the different land uses will vary as outlined in the 1994 protocol.

Depending on the available toxicity data and professional judgement, an uncertainty factor from 2 to 5 is applied to the derived value. The preliminary guideline is further "checked" to ensure that it is protective of microbial processes and groundwater. Information on natural background levels in the Canadian environment is also used to evaluate the final recommended value.

Results for Mercury

Sufficient data were available to develop Canadian soil quality criteria according to the CCME protocol (1994c), using the soil contact method but not for the soil ingestion or food ingestion methods (Table 1). Using the LOEC method the preliminary guideline for Agricultural and Residential/Parkland uses was calculated as 12 $mg \cdot kg^{-1}$ dry weight, based on the LOEC for lettuce (Environment Canada 1994, Table 1). Since only three (3) studies were available on only three (3) taxonomic groups, and the LOEC was from an acute toxicity study, a safety factor of 4 was applied to the LOEC resulting in a SQC_{SC} of 3

TABLE 1.

Summary of acceptable bulk soil toxicity data of mercury to terrestrial plants, invertebrates and microorganisms.

Species	Duration	Chemical Used	Test Substrate	Endpoint $mg \cdot kg^{-1}$				Reference
				NOEC	LOEC	EC_{25}	EC_{50}	
Radish (Seed emerg.)	72 h	$HgCl_2$	Artificial Soil: pH 4 to 4.2; Sand 70 to 75%;	51	103	73	103	Environment Canada 1995
Lettuce (Seed emerg.)	120 h	$HgCl_2$	Clay 16 to 22%; Silt 8 to 13%;	7	12	11	15	
Earthworm (survival)	14 d	$HgCl_2$	Moisture 80% WHC; org. matter 4.7 to 10.4%	96	194	130	181	
Microbial Processes (respiration inhibition and ATP synthesis reduction)	6 h/14 d	$HgCl_2$	Soil: pH 6.9; Organic matter 1.9 to 2.4%; Clay 7 to 25%; moisture 50 to 55% WHC	1.4 (g.m.)	14.78 (g.m.)			Zelles *et al.* 1986

g.m. - geometric mean of three studies

$mg \cdot kg^{-1}$. However, the microbial data showed that the mean No Effects Concentration for the effect of mercury on microbial processes is 1.47 $mg \cdot kg^{-1}$. The geometric mean of the two values was used to derive a final recommended guideline of 2.0 $mg \cdot kg^{-1}$ for Agricultural and Residential/Parkland uses.

For the Commercial and Industrial land uses, the geometric mean of all LOECs for ecologically relevant species and endpoints was used to recommend an initial guideline value of 62 $mg \cdot kg^{-1}$. This value was adjusted to reflect the results of the microbial check, resulting in a final recommended soil quality guideline of 30 $mg \cdot kg^{-1}$ for Commercial/Industrial land uses.

Major data gaps were identified for mercury in the terrestrial environment. Although a minimum of data exists to allow for the derivation of soil quality criteria for different land uses, there is still a paucity of data on the toxicity of mercury to soil ecosystem receptors. Thus, a great deal of research into soil mercury toxicity is required not only to improve understanding of the mechanisms, but also to validate the current soil quality criteria and improve upon it. Additional information is also needed on the background concentrations of mercury in soil. Though preliminary data indicate that mercury does not bioaccumulate in the terrestrial ecosystem, further information is required to validate this conclusion.

4. Summary and Conclusions

At present, there is sufficient data to develop water, sediment and soil quality guidelines for mercury. There is also a recognized need to develop tissue residue guidelines for aquatic ecosystems once this protocol has been finalized by the CCME. A variety of data gaps exist including insufficient Canadian data, limited knowledge on uptake of mercury species from soils and biomagnification of mercury up the food web. Further research needs to focus on these areas to expand the database used in developing the guidelines and as a means of field validating the proposed guidelines. In regards to sediment quality guidelines, relationships need to be established between concentrations of mercury in sediments, effects and sediment characteristics in order to derive full guidelines and allow for accurate predictions of toxicity at specific sites.

Environmental quality guidelines for mercury and other priority substances are important tools for environmental management, and there is an increasing emphasis in Canada on the use of environmental quality guidelines in environmental management. CCME guidelines have already been targeted as key elements of national management programs and strategies such as the Ocean Disposal Program and the National Contaminated Sites Remediation Program. These guidelines are not meant to be used independently but in conjunction with other management tools such as environmental effects monitoring, background concentrations and bioassays.

The range and scope of these national guidelines has gradually expanded, and will continue to expand to reflect our evolving understanding of the effects of contaminants in terrestrial and aquatic ecosystems and to ensure the long term sustainable use of Canada's resources.

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A MULTI-MEDIA APPROACH TO PERMITTING MERCURY RELEASES FROM COAL-FIRED POWER PLANTS

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Abstract. The current approach taken by many regulators in protecting the environment involves limiting the emission of pollutants to specific media (land, air, and water) through a permit. These "single media" permits do not take into account the mobility of pollutants, such as Hg, once they enter the environment, nor do they provide the regulated community with incentives to adopt pollution prevention practices. This paper explores multi-media permitting to limit coal-fired power plant releases of Hg; a pollutant that poses significant risk to human health and the environment. Power plant Hg emissions are a function of fuel, combustion regime and emission treatment. The approach presented is based on consideration of the Hg concentrations in various power plant emissions and the regulations governing these emissions. Multi-media permit development involves conducting a mass balance for Hg across the facility. Where pollution prevention is not an option, the permit should act to transfer the Hg to the waste stream in which it presents the least risk to human health and ecosystems. Development of cross-program risk based regulations is also stressed.

1. Introduction

The effects of Hg contamination on the environment have long been documented (Das *et al.*, 1982). Although a number of laws have sought to limit Hg emissions, environmental Hg contamination continues to be a concern (Swain *et al.*, 1992; EPA, 1994a; Nater and Grigal, 1993). For example, 70% of US fish consumption advisories are imposed for Hg (EPA, 1994b). In some lakes, the concentration of Hg in fish is increasing at a rate of 3 to 5% per year (Swain and Helwig, 1989).

Elemental Hg enters the atmosphere naturally as a result of evaporation from water bodies and the degassing of earth's crust. In the atmosphere, Hg is transported as a vapor or deposited back to the Earth's surface (NAS, 1978). Since Hg does not serve any normal metabolic function, increased cellular levels resulting from man's disruption of the natural Hg cycle can lead to toxicity (Eisler, 1987). Mercury entering water bodies can be methylated by bacteria (EPA, 1992). Of all the forms of Hg, methylmercury (MeHg) is most toxic, lipophilic and stable; the biological half life in fish being estimated at 2 to 3 years (EPA, 1985).

There are a number of risk-based benchmarks for Hg. The World Health Organization (WHO) has set an average daily intake level of 0.471 μg MeHg/kg body weight, although some studies suggest that this level may be too high (Fitzgerald and Clarkson, 1991). The Reference Concentration (RfC) for inhalation of elemental Hg is $3x10^{-4}$ $\mu g/m^3$ (EPA, 1994c). In terms of ecorisk values, soil concentrations above 1 to 2 ppm Hg (dry weight) may be phytotoxic (Neme, 1991). To protect sensitive species, the US Fish and Wildlife Service recommends that total Hg in consumed aquatic organisms not exceed 0.1 and 1.1 mg/kg (fresh weight) respectively, for birds and small mammals (Eisler, 1987).

There is a need to regulate anthropogenic sources of Hg using a holistic approach that recognizes the total environment. The objective of this paper is to present a prototype multi-media permit for one source of Hg; coal-fired power plants. While literature data on Hg and coal-fired power plants are frequently conflicting, the specific values in this paper are not as important as the overall concepts presented.

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2. Power Plant Mercury Emissions

The source of Hg in power plant emissions is coal, which ranges from <0.01 to 8.0 µg/g by weight, depending on the type of coal, the geographic region and the location within the mine (Malani, 1981). More recent studies indicate that the average concentration of Hg in bituminous and lignite coal samples obtained from US companies is 0.092 and 0.095 µg/g, respectively (UARG, 1994). The Hg content of power plant emissions is also related to the type of operation being conducted. Coal storage and handling operations can affect Hg entering the environment in stormwater runoff or as fugitive particulate matter (PM). Mercury concentrations in coal-pile runoff are likely below the reported values of 0.2 to 2.5 µg/L (EPA, 1982a). PM emissions from handling operations vary greatly, depending on the type and number of coal deliveries, etc. (Kestner, 1987). A conservative estimate for Hg entering the environment as fugitive PM is 6.5×10^{-7} mg/kg coal/yr (Malani, 1981; Chow *et al.*, 1993). The actual value is subject to wind speed, storage pile surface area, coal density and moisture content, precipitation-evaporation factors, and emission controls.

The fate of the Hg in combusted coal is dependent on residual carbon in the fly ash, coal chlorine and the air pollution control system and temperature at which it operates (Meij, 1991). Mercury can remain in the bottom ash, leave the combustion stack as a vapor or be captured by pollution control devices. Upon feeding coal into the furnace, Hg and Hg compounds in the fuel will volatilize. Condensation of Hg may occur as the flue gases cool prior to the particulate control devices. Coal produces 3 to 20% ash, providing a surface for adsorption of the Hg. This process may not be significant due to Hg's low boiling point and because ash particles may cool more slowly than flue gases (EPA, 1993a; Smith, 1980). Mercury oxide is also formed as the flue gases cool; 60% of the Hg in the combustion flue gases may be in the form of Hg^{+2}. The relative distribution of divalent, elemental and MeHg in flue gases may be dependent on the coal's chlorine level (Chow *et al.*, 1993). Elemental Hg in the flue gases may be oxidized by HCl to the divalent species (Meij, 1991).

Air pollution control devices for power plants target nitrogen and sulfur oxides and PM, however, ancillary removal of Hg occurs since it preferentially condenses on the surface of fine ash particles (as opposed to larger particles) (Clarke, 1993: Smith, 1980). Typical control devices for PM (electrostatic precipitators (ESP), fabric filters) remove 10 to 90% of the Hg from flue gases (Chow *et al.*; 1993; Sloss, 1993). This wide range in control efficiencies may be related to sampling/analytical problems, flue gas HCl concentrations, and/or enhanced adsorption to unburnt carbon (Chow *et al.*, 1993). Mercury in fabric filter treated flue gas is reported at 2 to 8 µg/Nm^3 (Chow, 1994). Acid gas controls include wet and dry flue gas desulfurization (FGD) systems, the former removing 15 to 90% of the Hg (EPA, 1981; Chow and Torrens, 1994; Chu, 1989; Meij, 1991; Sloss, 1993). Mercury concentrations in wet FGD sludges and periodic wastewater are in the range of 0.0001 to 6 µg/g and <0.1 to 0.7 µg/L, respectively (Santhanam *et al.*, 1985). The distribution of metals in the sludge and wastewater, which is recycled back into the FGD process, is pH dependent (EPA, 1981).

Minute concentrations of Hg may be found in cooling tower blowdown or once-through cooling water as a result of entrainment of fugitive coal dust particles or because of Hg in the intake water. Other wastewaters, such as bottom ash sluice and coal pile runoff, are often directed to a pond for treatment by sedimentation (EPA, 1982a). Mercury concentrations in the ash pond effluent depend on pH and detention time and are generally <0.2 µg/l (TVA, 1979; EPA, 1994d). The remaining Hg in the ash pond is deposited in the sediment or released to the atmosphere through evasion.

In terms of the overall Hg emission budget for coal-fired power plants equipped with an ESP, 75 to 90% of Hg emissions are in the vapor form in stack gases (Clarke, 1993; KBN, 1992). Most of the remaining Hg emissions from the plant are found in the residual ash. Fly and bottom ash contain 7 to 43% and 2%, respectively, of the Hg entering the furnace, although a number of studies estimate that the concentrations in bottom and fly ash are equal (Meij, 1991; EPA, 1982b; Mersole, 1993; Tripodi, 1980).

3. Prototype Plant

For the purpose of this paper, the prototype 1000 MW (net) plant uses $8x10^6$ kg/day uncleaned, pulverized bituminous coal at 7.34 mg Hg/10^6 Btu (0.21 ppm Hg by weight). The prototype facility maintains a 45-day supply in the lined coal storage area and fugitive PM emissions are controlled with water sprays. Runoff from the coal pile is routed to a lined landfill. The coal produces 14% ash with a carbon content of 60% by weight. The coal is low in chlorine and contains 3.5% sulfur. The distribution of ash in the dry-bottom furnace (front firing) is 15% bottom/85% fly. Fly ash is removed from the combustor flue gases by a cold-side ESP (150°C) with a Hg removal efficiency of 20%. Fly and bottom ash are sluiced at $1.4x10^7$ L/day to a once-through ash pond treated with lime prior to clarification and discharge to a river. The pond has a retention time of one day and is dredged annually to remove sediment which is disposed of in a lined landfill. Given these operating parameters, the Hg flux across the prototype facility is 613.2 kg/yr. Annual Hg emissions for individual waste streams are contained in Table I. The values presented are estimates, based on literature values, used to illustrate the transfer of Hg between media based on different control options.

4. Applicable US EPA Regulations

There are a number of Federal regulations governing emissions from power plants. State agencies, which may have additional or more stringent regulations, are usually delegated the authority to implement and enforce these Federal laws. An example of an additional state law is Florida's power plant siting provisions, which require centrally coordinated permit application, agency review, and approval for proposed electric utilities (State of Florida, 1993) . This streamlined process allows the State to investigate the need for new power production and the potential effects construction and operation will have on human health, welfare, and the environment. The remaining discussion on regulations will focus on Federal regulations and the permitting mechanism used by the various statutes to regulate power plant emissions.

The Clean Water Act mandates that National Pollutant Discharge Elimination System (NPDES) permits be issued to facilities with point source discharges of effluent to any water of the U.S. NPDES permits may contain two types of limits: those that are based on industry-specific best available control technology (i.e. effluent guideline-based) and those that are based on protection of the uses of the receiving water (i.e. water quality-based). The effluent guidelines for steam electric plants apply to facilities that use >50% fossil fuel and derive >50% of their revenue from selling electricity (EPA, 1982a). Wastewaters covered by steam electric plant effluent guidelines include once-through cooling water, metal cleaning wastes, low-volume wastes, coal pile runoff and ash pond discharges; none of these guidelines specifically limit Hg. Water quality-based limits are included in NPDES permits if the effluent guideline-based limits do not protect the

receiving water's uses from adverse effects. The need for water quality-based limits is assessed by determining whether the water quality standards designed to protect the waterbody's uses will be exceeded as a result of the discharge. States typically adopt National Ambient Water Quality Criteria (NAWQC) for pollutants into their water quality standards. The freshwater NAWQC for Hg consist of a one hour maximum of 2.4 µg/L to prevent acute toxicity and a 4-day average of 0.012 µg/L designed to protect the uses of freshwater aquatic life (EPA, 1985). The latter value is set to prevent bioaccumulation to levels that would exceed the US Food and Drug Administration Hg Action Level of 1.0 mg/kg edible fish-tissue (FDA, 1984). It should be noted that the bioconcentration factor upon which this is based may be too low. EPA has set the Hg level necessary to protect humans who consume fish from the waterbody at 0.146 µg/L; this value is set at 0.144 µg/L if the waterbody is also designated as a source of drinking water. If information submitted by the permittee indicates that there is a reasonable potential for the level of Hg in the wastewater to cause the state standard to be exceeded, the NPDES permit must contain a water quality-based limit and monitoring conditions.

The licensing mechanism under the Clean Air Act as amended in 1990 (Act) is the Title V operating permit which is used to integrate applicable requirements of the other titles of the Act for major sources of air pollution (EPA, 1990a). Under Title III of the Act, Hg is identified as a hazardous air pollutant (HAP). EPA is mandated to identify sources emitting more than 9.09 metric tons/year (TPY) of any HAP or 22.72 metric TPY of combined HAPs and designate the maximum achievable control technology (MACT) available to the sources. Individual coal fired power plants fall below these thresholds and therefore are not currently subject to MACT standards for Hg. The Act does, however, allow EPA to establish a lesser quantity threshold based on a pollutant's potency, persistence, and bioaccumulation. Section 112(c) further requires the Agency to regulate sources accounting for 90% of the aggregate emissions of Hg. Power plants receive Title V permits reflecting the Title IV acid rain provisions which do not specifically address Hg but may lead to a reduction in emissions because of the control technology utilized. Mercury has also been targeted as one of the 15 pollutants of concern by the Great Waters program under §112(m) (EPA, 1994a). In its report to Congress, the Agency recommends that reasonable actions be taken now, including investigating lesser quantity emission rates. Under §112(n) of the CAA, EPA is required to identify sources of Hg emissions, their health and environmental effects, and control technologies and costs. The recently completed emission inventory points to coal-fired utilities as one of the largest sources of Hg emissions (EPA, 1994e). Section 112(n) also requires EPA to study whether there is further need to regulate the electric utility industry based on the public health hazards. Both the Hg and utility studies are scheduled for completion in 1995.

In terms of the Federal rules that regulate the other waste streams, the solid by-products from utility coal combustion including fly and bottom ash, slag, and FGD sludge are not currently considered as hazardous wastes per RCRA Subtitle C (EPA, 1990b). The wastes will be considered for inclusion in the Agency's continuing assessment of industrial solid waste under RCRA Subtitle D. Although Hg is on the list of targeted compounds in the Emergency, Planning and Community-Right-To-Know Act of 1986, utilities are exempt from having to report their releases under §313. Such data would, however, make estimates of Hg emissions to the environment more accurate.

As part of EPA's increasing commitment to pursue multi-media approaches, the Agency has begun to develop industry specific "Cluster Rules," the first being for the pulp and paper industry (EPA, 1993b). EPA has jointly proposed control technology-based effluent limitations and air emission standards in order to meet the separate statutory requirements

of the CWA and the CAA by analyzing the environmental and economic impacts of various combinations of controls. By design, Cluster Rules provide greater environmental protection, facilitate pollution prevention and coordinated compliance planning and should reduce the cost of compliance.

5. Multi-media Permitting

Given the number and complexity of regulations that apply to power plants, a coordinated analysis of these various provisions during permit development is desirable. Multi-media permits consolidating the requirements of the various regulations offer a number of advantages. The process of applying for a permit may be much simpler for a permittee who deals with a single regulator at one time rather than applying for each media specific permit at a different time and with a different regulator. Multi-media permits can also increase the efficiency of the process for the regulators. Perhaps the greatest benefit offered by a multi-media permit is the ability to promote pollution prevention. Through the use of a multi-media permit, the regulator can be assured that pollutants are not being moved from one waste stream to another, but are, instead, actually being minimized through process changes, material substitution, etc. For those operations which are less amenable to waste minimization practices, the multi-media permit can be used to direct the pollutant into the waste stream in which it is most easily managed and environmentally inert.

Although EPA has begun considering multi-media permitting, the concept has yet to become a reality. The development of a such a permit entails far more than collating existing permit conditions into a single document. The critical issue is the simultaneous analysis of the various wastestreams relative to environmental goals. In developing a multi-media permit for the prototype plant described earlier, the first step is to establish a Hg budget for the plant. The Hg input for the plant during a given period of time, estimated using coal Hg and consumption data, must equal the sum of the Hg in the resulting emissions to air and water and in the form of solid waste. The monitoring and record keeping requirements of the permit would include the collection of such data at a frequency reflecting the fluctuations in the parameters that effect Hg emissions such as coal chlorine content, ash carbon content, control device efficiency. Because of a lack of regulations mandating Hg monitoring for these streams, very little of this information currently exists for use in developing a multi-media permit.

6. Comprehensive Risk-Based Regulation

The next step in permitting this source is to establish the waste stream specific limits on Hg mandated by Federal, state and local regulations. As alluded to above, currently, this exercise may only lead to a water-quality based limit on wastewaters with significant levels of Hg. Approximately 30% of Florida steam electric plant NPDES permits contain water-quality based limits on Hg for at least one outfall (EPA, 1994d).

The lack of Federal regulatory authority to set Hg limits on power plant waste streams is particularly concerning for air emissions, which contain the vast majority of the Hg leaving the facility. One long-term solution to this situation is the adoption of state or local regulations, more stringent than their Federal counterparts, that mandate the establishment of Hg limits for all waste streams posing significant environmental risk. Many states already have media specific regulations that require pollutants to be limited based on the risk that they pose, once in the environment. As such, it is not inconceivable

that a state could adopt an industry-wide and/or pollutant specific regulation based on risk, similar to Florida's power plant siting provisions. Such a regulation would limit the Hg in each waste stream to a level below which health and environmental effects would not occur. This approach is similar to that already taken in setting water quality based limits which insures that Hg in the combined power plant wastewaters is limited to a level that will not, over time, lead to accumulation of Hg in aquatic life that causes toxicity to humans or wildlife consuming them, or in the organisms themselves. Similarly, the limit on the Hg content of solid wastes from the plant could be based on the level necessary to prevent phytotoxicity or human health effects via dermal absorption. The RfC to protect humans from effects via inhalation could be used in conjunction with modeling to establish an air emission limit for Hg. This risk based, multi-media approach has the advantage of not "over or under regulating" any one waste stream. Each waste stream would be regulated to the same level; that necessary to prevent exceeding the ambient human Reference Dose/Concentration for the particular pathway of concern (inhalation, ingestion, dermal) and the ecological benchmark (plant, aquatic life, and wildlife toxicity). In effect, emission limits would be normalized by risk. For a persistent pollutant such as Hg, these regulations would also need to consider the long term fate and potential for the near and far field accumulation over time. For example, a comprehensive risk based regulation for Hg would need to not only address the concentration in the water column, but the Hg loss to the sediment as well. In addition to considering the human inhalation pathway in limiting Hg emissions to the air, long term deposition of Hg would need to be considered to insure that ecosystems are protected from the toxic effects of Hg transported to soils, streams and lakes. While this aspect of the regulation may be difficult to address given our current understanding of the fate and transport of Hg, it remains an important consideration in developing a comprehensive Hg rule. Given current Federal regulations, it can be argued that power plant wastewater limits designed to protect ecosystems and health are ineffectual if the Hg in the air emissions is transported to the same water bodies, subsequently preventing the achievement of the water quality goals.

7. Pollution Prevention

Development of a risk-based rule that cuts across all media and waste streams would provide the permittee with flexibility in achieving the limits using their own discretion. To be noted however, the rule should be crafted to allow the regulatory agency to promote pollution prevention practices. Options for preventing Hg emissions from power plants include energy conservation and switching to fuels with a lower Hg content (EPA, 1993a). Much about energy conservation has already been made available in the literature and will not be repeated here. In switching to fuels with a lower Hg content, the μg Hg/Btu must be considered rather than the μg Hg/kg coal. Without this comparison, switching to a coal with a lower Hg content could actually lead to higher emissions if the heat content of the coal is substantially inferior. For the prototype plant (Table I), a 70% reduction in Hg emissions is projected when coal with 7.27 mg $Hg/10^6$ Btu is replaced by coal with 2.19 mg $Hg/10^6$ Btu, all other factors remaining the same.

8. Transfer of Mercury Between Waste Streams

When waste minimization is not capable of reducing emissions to acceptable levels, Hg should be transferred to the waste stream/media in which it is most easily

Table 1. Approximate Annual Hg Releases in kg/yr (% distribution between streams), except as noted

Option	Coal Pile Runoff[1]	Storage & Hand. Opert.[2]	Inlet to Furnace	Stack Gas	Bot. Ash[4]	Fly Ash[5]	Fly Ash Conc in ppm	FGD Sludge[6]	Ash Pond Inflnt	Ash Pond Out[7,10]
Proto-Type	0.20 (<0.04)	0.002 (<0.0004)	613.0	481.0 (78.4)	12.3 (2)	120.0 (19.6)	0.35	___	132.0	131.0
1. Wet FGD Scrubber	0.20 (<0.04)	0.002 (<0.0004)	613.0	193.0 (31.4)	12.3 (2)	120.0 (19.6)	0.35	288.0 (47)	12.3	11.2
2. Coal Cleaning	<0.20 (<0.04)	<0.002 (<0.0004)	429.0 [3]	135.0 (31.4)	8.6 (2)	84.1 (19.6)	0.24	201.6 (47)	8.6	7.6
3. Coal Switching	<0.20 (<0.04)	<0.002 (<0.0004)	182.0 [8]	143.0 (78.4)	3.6 (2)	36.0 (19.6)	0.10	---	3.6	2.6
4. Carbon Injection	0.20 (<0.04)	0.002 (<0.0004)	613.0	120.1 (19.6)	12.3 (2)	300.0 [9] (49)	0.86	180.2 [9] (29.4)	12.3	11.2

[1] - *Based on average U.S. annual rainfall of 37 inches and effluent conc. of 0.2 μg/L (New Encyclopedia Britannica, 1991; EPA, 1982a)*
[2] - *(Kestner, 1987; Malani, 1981)*
[3] - *The amount of Hg removed by coal cleaning is 183.96 kg/yr, and is treated at the coal mining facility*
[4] - *Assume Bottom Ash Hg content is 2% of Hg in coal (Meij, 1991)*
[5] - *Assume ESP has 20% Hg removal efficiency (Chu et al., 1993)*
[6] - *Assume FGD System has a 60% Hg removal efficiency (Chow et al., 1993)*
[7] - *Assume Combined and Bottom Ash Ponds have an annual average conc. of 0.2 μg/L (EPA, 1982b)*
[8] - *Based on a Hg content of 2.19 mg/10^6 Btu (Neme, 1991)*
[9] - *Assume overall Hg removal efficiency for ESP and FGD system is 80% (Neme, 1991; Li, 1985); FGD efficiency = 60%*
[10] - *Loss to sediment estimated at 1 kg/yr.*

managed/environmentally inert. Given the relative inability to control the transport and fate of Hg once it is emitted to air and water, it can be argued that Hg should be directed towards the solid waste stream, where, if treated correctly, Hg may be most stable. By moving the Hg from air and water emissions to the solid waste, the natural environmental distribution of the element is more closely mimicked. The Hg in air emissions is least controllable because of the greater potential for dispersion. By adding a wet FGD scrubber after the ESP on the prototype plant, the proportion of Hg leaving the facility via the stack gases is estimated to be reduced from 78 to 31%. The ESP/scrubber combination may achieve 80% Hg removal for utility boilers (Neme, 1991). At the prototype plant, Hg- laden waste sludge from the wet-FGD system and fly ash from the ESP are placed in a pond for further treatment. Mercury can be removed from aqueous solutions through precipitating it as insoluble compound (e.g. HgS), filtering with adsorptive compounds such as activated carbon, graphite powder and powdered zinc, chemical flocculation and ion exchange (EPA, 1974). The efficiency of these methods is a function of the concentration of the Hg, the other pollutants present, and other water quality parameters such as pH. To avoid the need to treat much of the wastewater, the facility can switch to a dry bottom ash handling system, stabilizing the ash and sludge for disposal in a landfill. Fixation can involve mixing FGD sludge, fly ash and lime to produce a stable pozzolanic material (Bishop *et al.*, 1992).

While retrofitting facilities with additional controls can reduce Hg concentrations in the flue gas, the incremental reductions that can be achieved with traditional technologies (ESP, baghouse, scrubber) might not be economically feasible. Carbon injection is a promising treatment technique that may provide up to a 90% removal of Hg from coal-fired boiler stack gases to the solid waste stream (Chow *et al.*, 1993). As important, no significant desorption of the Hg from the waste carbon was noted over a four week period.

Another option for lowering the release of Hg to the air is coal cleaning which removes an average of 30% of the Hg depending on its mode of occurrence (Neme, 1991). This technique moves the Hg in the coal to wastewater, fugitive air emissions and the solid waste stream, thereby preventing it from entering the atmosphere upon combustion of the coal (Table I). Treatment of the coal washing wastewater to further transfer the Hg to the solid wastestream (described above) is required. While coal washing is performed at the mine rather than at the power production facility, these Hg emissions must be considered in the overall mass balance since they indirectly result from the plant's operations.

Although none of the treatment options discussed eliminate Hg from power plant emissions, they do serve to isolate it to the extent possible in the solid waste. Once in the solid waste, it may be possible to recover the metal into a concentrated waste or to treat it so as to minimize its mobility. Because of rising disposal costs and increasingly strict permit limits on ash pond discharges and landfill requirements, power companies have more seriously considered marketing ash. Rather than disposing of ash in a landfill where the possibility exists for heavy metal bearing leachate to contaminate soil and groundwater, it could be marketed for use in products such as cement (Collins, 1992). Any marketing option must of course insure that the Hg in the solid waste is in a stable form that will not re-enter the environment over time.

While permit conditions requiring the transfer of Hg from air and water emissions to solid waste may be justified by a comprehensive risk-based regulation, where such a rule does not exist, the regulator must create incentives for the permittee to move the Hg from one waste stream to another. One possible incentive involves levying a Hg tax that encourages the transfer of Hg to solid waste. The charge on Hg in air emissions could be x times higher than that charged for Hg in wastewater; the charge for the Hg released

in wastewater could likewise be y times the charge for the Hg in the solid waste. The magnitude of the charge for Hg in each waste stream could be based on the relative risk posed. Obviously, such a scheme would likely require rule development on the part of the permitting agency. Additional incentives could include expedited permit issuance and reduced Hg monitoring/reporting requirements for facilities voluntarily submitting a mercury budget which documents the transfer of Hg to the solid waste stream from air and wastewater emissions.

Conclusions

Obviously not all of the tools needed to implement the multi-media permitting scheme described are currently available. Research and development needs to be conducted in the areas of Hg monitoring, modeling, effects, (i.e., risks) waste minimization technology and control devices. To overcome the impediments to multi-media permitting, Congress and EPA must work together to integrate environmental laws or at least make them more comparable. There are too many cases where a wise provision in one law created an environmental problem under a different law. The Agency must also be willing to provide states with guidance regarding the timing of permits and in the development of market-based incentives for directing the fate of Hg.

EPA has made substantial progress in moving towards a more holistic approach to environmental management as indicated by the recently developed Cluster Rule and the Great Waters Report. Trade associations like EPRI are also to be acknowledged for their efforts to understand the fate and control of Hg emissions from utilities.

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A MERCURY MODEL USED FOR ASSESSMENT OF DREDGING IMPACTS

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Abstract. The effects of dredging of contaminated sediments on the mercury (Hg) concentrations of prey and predatory fish were calculated for the Kokemäenjoki River and its estuary in Western Finland. The accumulation of Hg in fish is controlled by the Hg concentrations in water, zooplankton, zoobenthos and by suspended solids. Hg is accumulated into fish mainly through food web, eg. from perch (*Perca fluviatilis*) as prey and to pike (*Esox lucius*) as predator. In addition to dredging, temperature and flood situations have also increased the Hg accumulation and release from the bottom sediments.

The validity of the model has been tested with data recorded from earlier dredgings. Thereafter the model has been used to predict the Hg levels caused by dredging planned upstream in the river. The predictions are supported by the concentrations of total mercury (Tot.Hg) and methyl mercury (MeHg) measured in water and in sediments under several flow conditions. As a result, 30 % increase of Hg in pike - from 0.8 to 1.05 mg/kg - was expected. This was too high, and therefore dredging was not included in the final plan for flood protection.

1. Introduction

River sediments contaminated by mercury (Hg) are problematic since they are often distributed over wide areas and are easily transported and released by flows and floods. With dredging, even higher amounts of total mercury (Tot.Hg) can be released from the sediments. These releases will accumulate through the food web into fish as methyl mercury (MeHg), which can be toxic to birds and mammals, including man (Verta, 1990; Harris, 1991; Sjöblom and Häsänen, 1969; Jernelöv, 1970; Jernelöv and Lann, 1971; Huckabee *et al.*, 1979; Häkkilä, 1987).

The increased understanding of accumulation dynamics in fish, accumulation rates and fish growth dynamics has resulted in bioaccumulation models (Norstrom *et al.*, 1976), bioenergetic growth models (Hewett and Johnson, 1992) and combinations of these in bioenergetic bioaccumulation models (Korhonen *et al.*, 1994), respectively. These are useful aids in planning river management, e.g., dredging, in other construction efforts or regulation, in assessing their potential effects in advance, in designing the operations to mitigate harmful effects, and finally, in deciding their acceptability and ways of execution.

The aim of this paper is to describe the use of a bioenergetic bioaccumulation model in the practical planning, selections and decisions of real management problems. At first the application area, observations and management alternatives are reviewed, then the model is briefly presented and selection of model parameters is described, and the use of the model is explained. Model results are presented and their use and their meaning for decisions are described. More model details and validity tests are presented elsewhere, in Korhonen *et al.* (1994). The work is largely based on the long and strong tradition of environmental Hg research in Finland (Sjöblom and Häsänen, 1969; Häkkilä, 1987; Verta, 1990).

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2. Area of Application

The research area is located in Western Finland in the central parts of the Kokemäenjoki River, up to 60 km from the sea (Figure 1). The surface sediments (0 - 30 cm) are mainly clay and silt (about 85 %). Since the 1950's the sediments have been contaminated by Hg from a chlorine plant. The Hg loading was drastically reduced in the early 1970's and was recently eliminated almost totally. The concentrations of Hg in sediment in the area vary from 0.01 to 16.7 mg/kg (dry weight). The total amount of Hg in the sediment planned to be dredged is about 100 kg.

The Kokemäenjoki River is one of the biggest rivers in Finland. Its mean rate of flow (MQ) amounts to 220 m^3/s, the mean high flow (MHQ) to 600 m^3/s and the mean low flow (MNQ) to 37 m^3/s. The drainage area is 26 000 km^2 and almost 12 % of it is covered by lakes. The catchment of its middle reach and the Loimijoki River, the main tributary, is an important agricultural area. The rivers are regulated by several hydropower plants.

Wide areas around the central part of the river, including the Loimijoki River, often suffer from floods. The areas of planned remediation efforts, observations, estimation of model coefficients and model application are located at the central parts of the river (Figure 1). The model validity has been tested at the downstream parts near the river mouth (northwestern corner of Figure 1, Korhonen *et al.*, 1994).

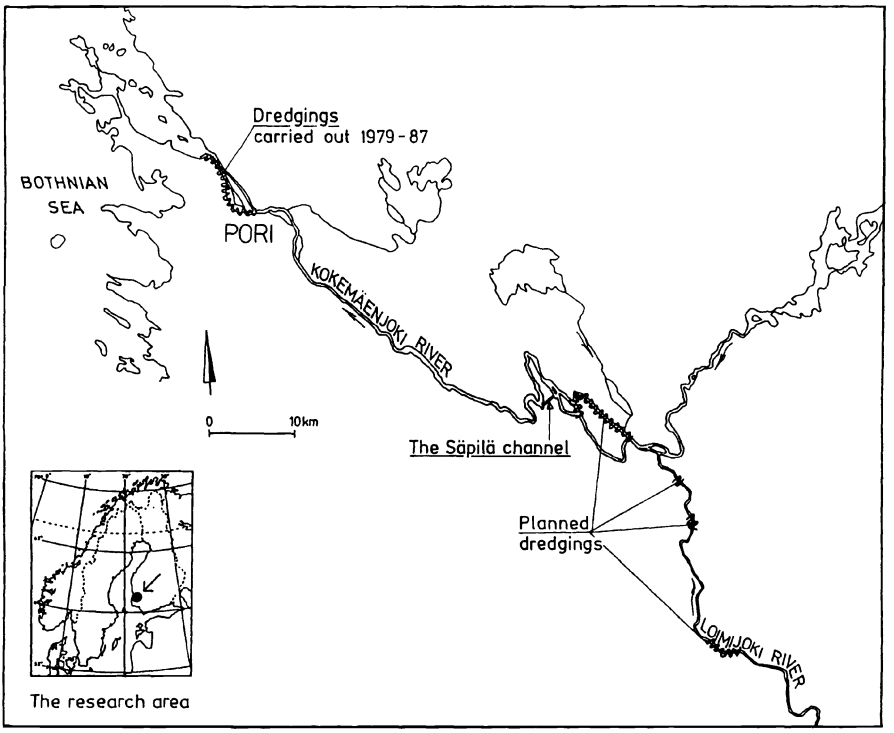

Figure 1. The research area in the central regions of the Kokemäenjoki River in Western Finland. The validity of the model has been tested in the downstream region near the river mouth (Korhonen *et al.*, 1994).

3. Plans for Dredging

Both the Kokemäenjoki River and the Loimijoki River are prone to flooding, which has caused substantial damage to agriculture. Some housing areas have also suffered from flooding. Severe flooding (>20 km^2) in the 1970's created demands for flood protection. The preliminary remediation plan presented in 1987 - 1988 contained dredging of a part of the river, clearing of some rapids and construction of a new artificial channel (the Säpilä channel, Figure 1). The remediation efforts would affect the use of the river for electricity production, because the middle reach of the Kokemäenjoki River is regulated by two hydropower stations. In addition to the desired economic impacts, the project has some controversial effects on the environment. Most important of these are impacts on the threatened fish asp (*Aspius aspius*), increase in the Hg content of fish and lowering of ground water level.

4. The Model Utilized

The model was developed and described by Korhonen *et al.* (1994). Its central elements are based on the bioenergetic calculation of food consumption and fish growth (Bevelhimer *at al.*, 1985; Hewett and Johnson, 1992) and on the bioaccumulation of MeHg into the fish from food and from water (Norstrom *et al.*, 1976). Its main steps and dynamics are schematilly shown in Figure 2.

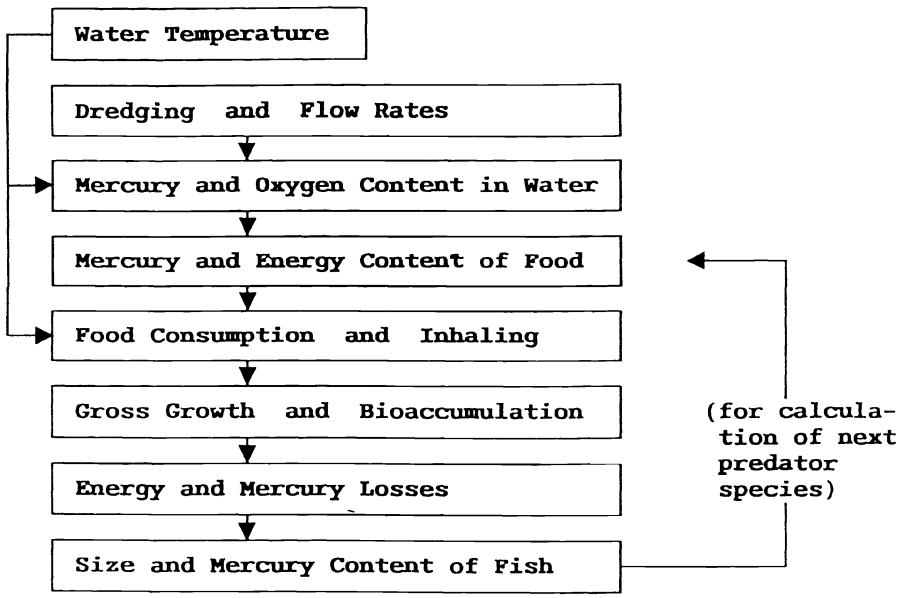

Figure 2. Main calculation steps of the bioenergetic mercury accumulation model.

5. Observations

The growth data for pike (*Esox lucius*) are based on a sample of 344 fish caught 1984 - 1987 in the Kokemäenjoki River and in its estuary (Figure 1). The growth of perch (*Perca fluviatilis*) is estimated from a sample of 761 fish caught 1987 - 1990 in the estuary.

The water temperatures were the monthly averages of 1970 - 1991 at the surface of the river and the estuary. They varied from 0.2 °C in winter to 20 °C at the end of July. The same temperatures were used for model validation (for 1970 - 1992, Korhonen *et al.*, 1994) and the present application. The oxygen concentrations in water varied from 8 in August to 12.6 mg/l in winter, and pH from 6.6 to 7.6.

The estimates of the Hg content in sediments are based on about 50 samples from different depths (0 - 50 cm) obtained between 1985 and 1993 (Häkkilä, 1987; Korhonen and Virtanen, 1993). Typically - but not regularly - the highest values are found near the shore at 10 - 30 cm below the surface of the sediment. In 52 % of the sediment samples there is Hg < 0.1 mg/kg, in 28 % of samples > 1 mg/kg. Hg concentrations in deeper bottom layers, more than 30 cm from the sediment surface, have not exceeded 0.06 mg/kg. The average concentration in the sediments planned to be dredged is about 0.3 mg/kg.

Concentrations of Tot.Hg and MeHg in water were measured 7 times in 1991 - 1992 at 5 places in the river and estuary. The concentrations of Tot.Hg varied from 1 to 20 ng/l and those of MeHg from 0.01 to 0.5 ng/l (Korhonen and Virtanen, 1993).

No recent observations were available from the concentrations of Hg in zooplankton and zoobenthos. In the 1970's and 1980's, Hg concentrations from < 1 mg/kg to > 100 mg/kg dry weight were measured for these groups (Häkkilä, 1987).

Concentrations of Hg in pike have been measured in the region since the end of 1960's. The number of annual samples varied from 2 to 100 fish. Between 1970 and 1992, the concentration of MeHg in 1 kg "standard" pike varied from 0.38 to 1.35 mg/kg fresh weight, depending on the area and time. In 1991 - 1992, the concentration of Hg in prey fish (mainly perch and roach, *Rutilus rutilus*) varied from 0.08 to 0.27 mg/kg, based on a sample of 60 fish of 5 to 20 cm in length (Korhonen and Virtanen, 1993).

6. Parameter Estimation

The coefficients of food consumption by perch are obtained directly from Kitchell *et al.* (1977). The coefficients for pike are modified from those of Bevelhimer *et al.* (1985) to represent the local conditions. The optimum temperature of food consumption has been reduced from 24 to 19 °C, and the maximum temperature from 34 to 26 °C, respectively.

The estimates of food composition and the relations between the sizes of predators and preys are based on detailed investigations by Korhonen and Heikinheimo-Schmid (1993). The coefficients of bioaccumulation are taken directly from Norstrom *et al.* (1976). The only exception was the steepness exponent r coupling Hg removal rate Lp to fish weight W (Lp/P proportional to W^r, when P is Hg concentration). For perch this was changed from -0.58 to -0.8 in order to avoid unnatural fluctuations. All coefficients of bioaccumulation are listed in Korhonen *et al.* (1994).

7. Approximations for Model Input and Use

Based on the observations and the selected model coefficients, the model was applied to earlier dredging under roughly natural flow conditions (Korhonen *et al.* 1994). Comparisons of the model results with the measured mercury levels in pike indicated qualitative similarity in the downstream section of the river (Figure 1 in Korhonen *et al.*, 1994).

With the same assumptions which were used in the validity tests, the model is applied to the planned dredging of the contaminated sediment areas. The concentrations of MeHg in fish used food are of interest mainly during the growth season from May to September. During that time, under the present conditions, the MeHg concentrations in water vary from their spring flood values of 0.5 to 0.1 - 0.2 ng/l for the rest of the summer. In the model input these are estimated as an average 0.2 ng/l for the whole season. Winter concentrations of 0.03 ng/l MeHg in water are not taken into account in the model for mercury accumulation to fish, because fish eat almost nothing during the winter season.

Tot.Hg released from the sediments and mixed to the MQ is estimated to increase the MeHg concentration of water with 50 % during the growth season (from May to September) if the works are carried out throughout all seasons at equal efficiency for three years. The average flow over three years is not expected to deviate very much from the MQ. The flood flows during the dry spell, from June to September, are assumed to increase MeHg in water with an extra 0.1 ng/l when the flow is stronger than twice the MQ (Figure 3).

The effects of dredging include both the direct releases from disturbed sediments and the overflow from the settling and drying areas to which the bottom masses are pumped or transported. In the region where the validity tests were made, suction pumping was used while showel digging has mainly been planned for the central parts of the river. This may slightly overestimate the predictions since the pumped wet masses can be more hazardous for strong overflows than the dryer showel masses, especially since the conditions in the settling basins (as warm, large, slowly flowing, turbid and perhaps anoxic) after pumping can be very favourable for methylation. Due to lack of direct observations no attempt was made to eliminate this possible overestimation from the predictions.

The relative increase of MeHg in water is assumed to appear immediately at equal relative strength in the MeHg of the plankton and zoobenthos perch eat. Compared with the concentration increases in water the effects in the food of younger (0 - 3 year) perch is 250 000 -fold and in that of the older (4 - 7 year) perch 500 000 -fold. From this assumption - i.e. 50 % increase of perch food MeHg for 3 years, and thereafter return to the present values again - the accumulation of MeHg into perch is calculated with its growth using the bioenergetic bioaccumulation model with a time step of one day.

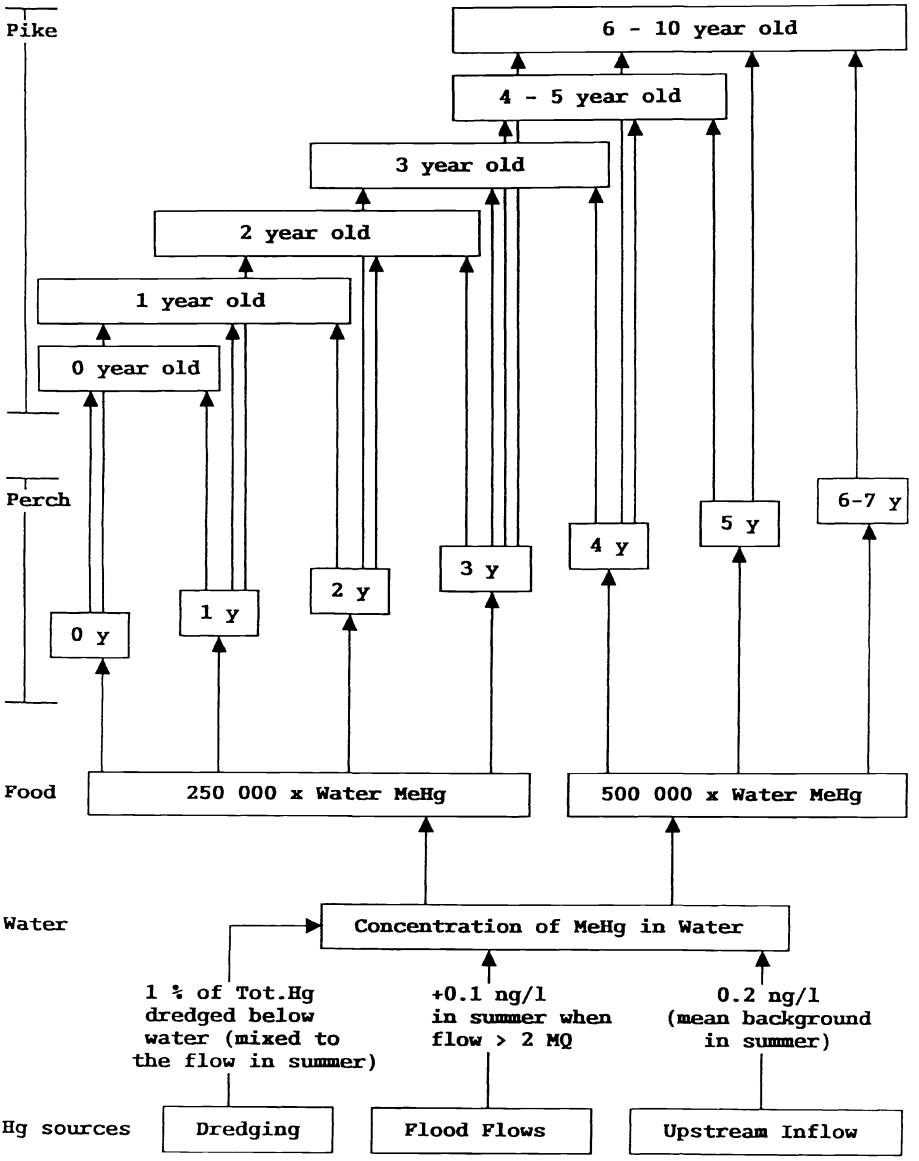

Figure 3. Basic assumptions behind and accumulation paths within the use of the bioenergetic bioaccumulation model (Korhonen *et al.*, 1994).

Based on the investigations of Korhonen and Heikinheimo-Schmid (1993), the perch are assumed to be eaten by pike according to age as follows:

Pike age (years)	0	1	2	3	4 - 5	6-10
Eaten perch age (years)						
0	+	+				
1	+	+	+			
2		+	+	+		
3			+	+	+	+
4				+	+	+
5					+	+
6-7						+.

I.e., pike eat fish already at the age of 0 years. The Hg accumulation to pike and their growth are calculated separately for male and female fish using recursively the bioenergetic bioaccumulation model with one day time steps. Schematic presentation of the accumulation paths within the food web as they are described in the model is shown in Figure 3.

8. Model Results

The highest relative increases of MeHg concentrations in perch, 60 %, are found in the 1 year old individuals during the two last years of dredging. In older perch the highest increases, 40 to 50 %, occur in the last year of dredging. The elevation of MeHg is evident in the oldest perch until 5 years after dredging (Figure 4).

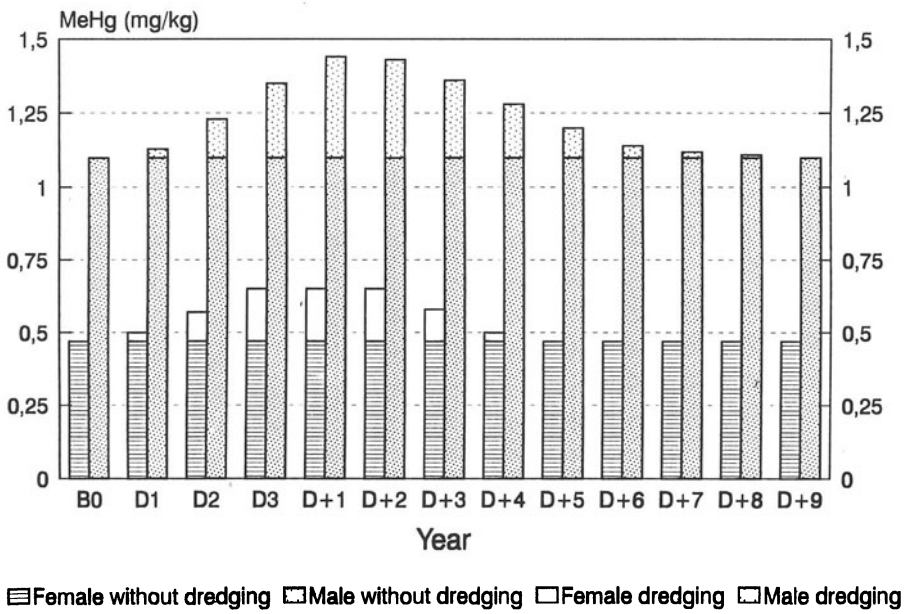

Figure 4 The effects of dredging on the MeHg in 1 year, 3 years, 5 years and 7 years perch in respect of time (years) before (B0), during (D1-D3) and after (D+1-D+7) the dredging

Accumulation of MeHg into the pike is slower than that into perch. In a 1 kg pike the highest increases appear in the year following the three years of dredging. The effects on female and male pike are shown separately in Figure 5. As the average of males and females, the highest increase of MeHg is about 30 %, from 0.8 to 1.05 mg/kg, which is just above the recommended absolute limit of 1 mg/kg for selling and eating. Increased concentrations of MeHg persist in males for 8 years following the termination of dredging, while in females these last for 4 years only. Rapid growth rate of females decreases their Hg increase compared with the Hg increase in males.

In practice, all of the MeHg in fish is from their food. According to the results of the bioaccumulation model (Borgmann and Whittle, 1992; Korhonen *et al.*, 1994; Korhonen and Virtanen, 1993), only a small percentage of Hg is directly from water through gills with inhalation.

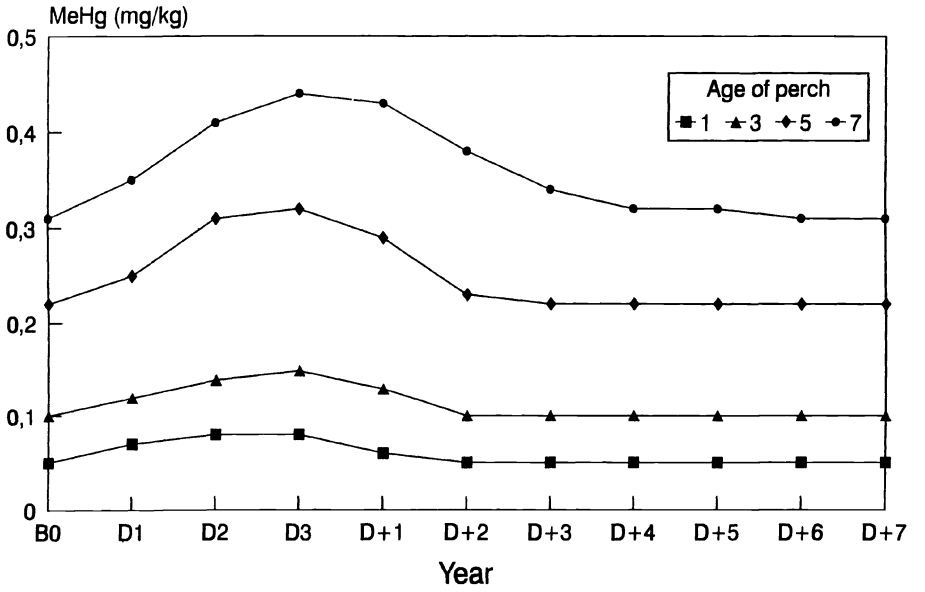

Figure 5. The effects of dredging on the MeHg in 1 kg female (right) and male (left bars) pike in respect of time (years) before (B0), during (D1-D3) and after (D+1-D+9) the dredging. Model results (total columns) compared with the prevailing values without dredging (the lower parts of the columns).

9. Use of Model Results in Impact Assessment

In Finland the Water Act requires that developers of large scale water regulation projects present investigations on the effects on the aquatic environment, fish stocks and fisheries. The assessment of the impacts of the flood protection project started in the late 1980's. In 1991 the National Board of Waters and the Environment decided that the international principles of environmental impact assessment (EIA) should be applied in the project. In Finland the law for EIA will come into force in the fall of 1994.

In the EIA process six different alternatives for flood protection were considered. Two

of them included dredging of Hg contaminated sediments, two others restricted dredging to areas not contaminated by Hg, one alternative contained only opening of a new channel, and one was the zero alternative where nothing was planned to be done nor changed.

Results of the Hg model were used both in the EIA process and in preparing an application for the Water Court. Results of the Water Court Process are not yet known. During the EIA process ecological, social and economic impacts were examined (Hildén *et al.*, 1991; Hildén *et al.*, 1994; Hämäläinen and Marttunen, 1994). Some stake holders were interviewed, to find out their opinions about the impacts and the alternatives of the flood protection project, and to improve their involvement.

The release of Hg from sediments was one of the issues that caused public concern. This lead to development of the model described in Korhonen *et al.* (1994) and in this paper. The results of the model and other extensive investigations were useful in the interviews to assess the relative differences between the alternatives.

10. Conclusion

As a result of the EIA process the National Board of Waters and the Environment decided not to dredge the Hg contaminated sediments as part of the flood protection project. The decision was based on a combination of costs, benefits and potential harmful environmental effects. Thus accumulation of Hg in fish was one of the reasons presented in support of the decision not to carry out the dredging.

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MERCURY PATHWAYS IN MUNICIPAL WASTEWATER TREATMENT PLANTS

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Abstract. A nine-week sampling and analysis program was completed at a large municipal wastewater treatment plant to characterize the fate of Hg entering the plant. Mercury removal in primary treatment averaged 79%, and the average Hg removal across the entire plant was approximately 96%. Mercury loadings on the secondary (activated sludge) treatment process were elevated to near plant influent levels due to the recycle of spent scrubber water from sewage sludge incinerator emissions control equipment. This internal recycle of spent incinerator scrubber water resulted in elevated Hg loadings to the incinerators, and effectively reduced the Hg control efficiency of the emissions control equipment to near zero. Measurements indicate that approximately 95% of the Hg mass entering the plant is discharged to the atmosphere via sludge incinerator emissions. These results indicate that municipal wastewater treatment facilities can remove Hg from wastewater quite effectively; however, where wastewater sludge is incinerated, almost the entire mass of Hg removed from the wastewater can be discharged to the atmosphere.

1. Introduction

Municipal wastewater treatment plants represent the focusing point of modern society's industrial, commercial and domestic liquid wastes. Although treatment plants are designed for BOD and solids removal, they are facing ever more stringent expectations with respect to their removal of heavy metal and synthetic organic pollutants. To the extent that heavy metals are associated with particulate phases, removal with solids is generally good; dissolved species represent more of a problem (Oliver and Cosgrove, 1974; Lester *et al.*, 1979; Stoveland *et al.*, 1979). In the case of mercury (Hg), good liquid-side removals are typically observed, and discharges to receiving waters are minimized (Oliver and Cosgrove, 1974; Goldstone *et al.*, 1990). The removal of Hg from wastewater prior to discharge to receiving waters is necessary to protect those waters; equally important is the ultimate immobilization of the Hg removed. Where sewage solids are incinerated, Hg can be released to the atmosphere, and ultimately deposited in the environment. It has been estimated that Hg discharged to the atmosphere can reside there for months, and it is now clear that atmospheric Hg emissions can result in deposition on local, regional and global scales (Lindqvist and Rodhe, 1985). Mercury deposition and transport to lakes has resulted in fish consumption advisories across North America and northern Europe (Lindqvist *et al.*, 1991; Swain *et al.*, 1992). Elevated Hg levels in fish can represent a threat to the health of sensitive human and animal populations which consume the fish (Clarkson, 1990; Minnesota Pollution Control Agency, 1992a). Chlor-alkali plants, metals smelting and processing, fossil fuel combustion and waste incineration have been identified as major anthropogenic contributors to atmospheric Hg loadings (Lindqvist *et al.*, 1991). Based on recent data, sewage sludge incineration in the United States probably accounts for no more than 3000 kg/year in Hg emissions (EPA, 1990). However, emissions from particularly

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large sewage sludge incineration facilities may exceed those from all but the largest power and waste incineration facilities (Minnesota Pollution Control Agency, 1992b). In order to better understand, and ultimately reduce, the contributions of municipal wastewater treatment plants to environmental Hg loadings, this study undertakes to characterize the fate of Hg in one such plant.

2. Experimental

2.1. Treatment plant description

Sampling and analysis of total Hg concentrations in major process streams were carried out at the Metropolitan Wastewater Treatment (Metro) Plant in St. Paul, Minnesota. The Metro Plant utilizes primary and activated sludge secondary treatment to process 10.0 m^3/s of wastewater from the metropolitan Minneapolis-St. Paul area. Wastewater flow through the plant is divided between east and west treatment trains, the larger east primary process treating approximately 70% of the daily flow. Flow equalization prior to secondary treatment results in approximately equal hydraulic loadings on the east and west activated sludge/final clarification process units. Residual primary and thermally conditioned waste activated sludges are dewatered and incinerated in six multiple hearth incinerators. Emissions from the incinerators are controlled with high temperature quad cyclones, and venturi and packed tower wet scrubbers, in series. Spent scrubber water is returned to the secondary influent stream for treatment. A simplified diagram of the Metro Plant process flow scheme is shown in Figure 1.

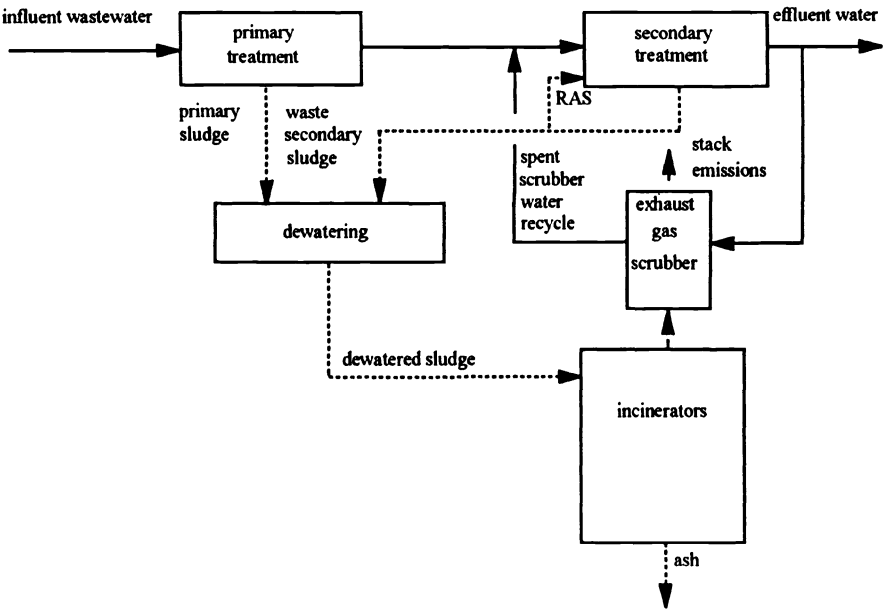

Figure 1. Simplified Metro Plant process flow scheme.

2.2. WASTEWATER AND SLUDGE SAMPLING PROCEDURES

Sampling of major process streams was carried out over a nine week period during which grab samples were collected every third day. Sampling times were randomized to provide a representative picture of daily Hg loadings. Over 200 samples from major target streams were collected and analyzed. Targeted streams were: east primary influent, effluent, and sludge; west primary influent and effluent; east secondary influent, effluent, and waste activated sludge; west secondary influent, effluent, and waste activated sludge; and spent incinerator exhaust scrubber water.

Samples were collected using a modification of the "clean hands/dirty hands" two-person sampling technique (Brooks Rand, 1990). Wastewater samples were collected from open process streams by having the "clean hands" member of the sampling team discard the preservation solution and place the 500 ml Teflon sample bottle on the end of an acid-soaked polyethylene sampling stick, which the "dirty hands" member then placed in the process stream, with the bottle opening about 15 to 30 cm below the water surface. The bottle was rinsed once with sample water, filled again, then "clean hands" capped the bottle tightly, removed it from the sampling stick, and placed it back into its original double zip-lock bags. Samples collected from process weirs were obtained similarly, except that "dirty hands" held the sampling stick so that the bottle opening was placed in the falling nappe of the weir discharge. Liquid activated sludge samples were collected from continuous-flow sampling sinks by having "clean hands" dip the bottle into the flowing stream. Liquid primary sludge samples were collected from a sampling tap which was flushed thoroughly before sampling. Here, "clean hands" held the sample bottle in the flowing stream. Spent scrubber water samples were collected from a sampling tap in the same manner as the primary sludge samples.

2.3. INCINERATOR EXHAUST GAS SAMPLING PROCEDURE

Total Hg in the incinerator exhaust gas was sampled using iodated carbon traps (Metzger and Braun, 1987; Bloom, 1993). The sampling train consisted of, in series, a front trap, a backup trap, Teflon tubing, a silica gel impinger, a dry gas meter and a vacuum pump (see Figure 2). Connections between the traps and the tubing were made with acid-leached Teflon friction-fit connectors. A 112 cm piece of 6.35 mm OD stainless steel tubing was used for support of the in-stack sample train elements (traps and tubing). The function of the metal tubing was for support only; Hg in the sample gas came in contact only with the inside of the traps. The iodated carbon traps (MSA #459003) were affixed to the support so as to point into the sample flow. Samples were collected at 200 ml/min for 50 minutes. The sampling point was downstream of all emissions control equipment. At the end of the sampling period, the pump was turned off, and the probe (traps and Teflon tubing secured to stainless tubing) was removed from the stack sampling port. The front and backup traps were removed, capped individually with plastic caps, and labeled. They were placed in zip-lock bags and immediately transported to the clean analytical laboratory for processing. Ten sampling runs were made, and four of the six incinerators were tested. On seven sampling runs, historical incinerator air flowrate data were used to calculate Hg mass loadings. On the other three sampling runs, flowrate data obtained by pitot tube measurements at the time of the test were used. The two methods of mass loading calculation yielded similar results.

2.4. Analytical reagents and laboratory procedures

Bromine monochloride reagent was prepared by carefully adding, first, 5.4 g of KBr, and then, one hour later, 7.6 g of $KBrO_3$ to 500 ml of low-Hg HCl in a stirred Teflon bottle. A 5% potassium permanganate solution was prepared by adding 5 g of $KMnO_4$ to 100 ml of ASTM Type I water (DDW). A 5% potassium persulfate solution was prepared by adding 5 g of $K_2S_2O_8$ to 100 ml of DDW. Stannous chloride reagent was prepared by adding 20 g of $SnCl_2$ to 10 ml of low-Hg HCl, then diluting to 100 ml with DDW; this reagent was then purged for one hour with Hg-free nitrogen at approximately 250 ml/min. Hydroxylamine hydrochloride solution was prepared by adding 30 g of NH_2OH-HCl to 100 ml of DDW; this solution was purged overnight with Hg-free nitrogen at approximately 250 ml/min. All reagents were prepared weekly, except for hydroxylamine hydrochloride, which was prepared monthly, and stannous chloride, which was prepared daily. Concentrated nitric and sulfuric acids were used as received.

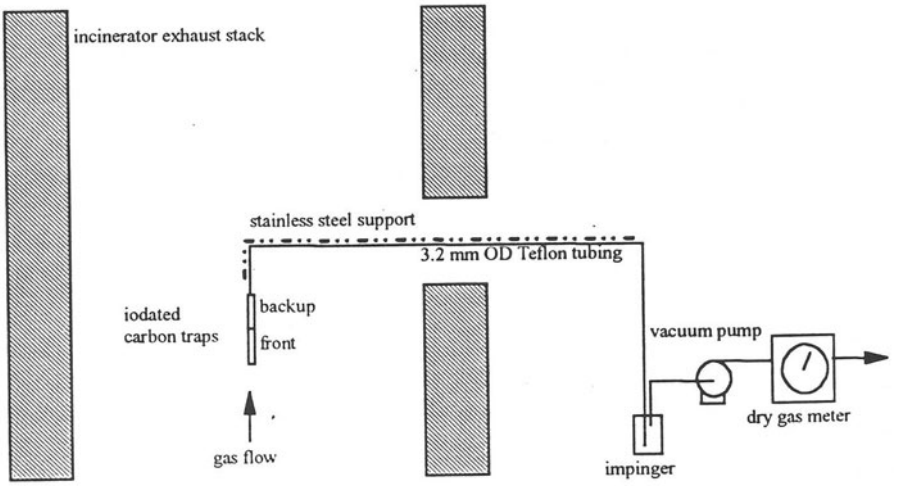

Figure 2. Incinerator exhaust gas sampling train.

New 500 ml Teflon FEP bottles and 30 and 60 ml Teflon FEP vials used in this study were first acid-leached in concentrated nitric acid at 60°C for six days. They were rinsed thoroughly with DDW, then filled with 1% HCl and placed in an oven at 60°C overnight. Following another thorough rinsing with DDW, the bottles and vials were filled once more with 1% HCl, capped tightly, then left in a class 100 HEPA-filtered clean air hood to dry, before being double-bagged with new polyethylene zip-lock bags. The bottles and vials were stored in plastic buckets in the clean analytical laboratory until use.

Following their use, the bottles and vials were rinsed, in succession, with tap water, nitric acid, chloroform, and then tap water again, before being placed in concentrated nitric acid at 60°C for three days of acid leaching. Sample bottles in which the acid permanganate digestion was carried out were pre-rinsed with hydroxylamine hydrochloride solution prior to the rinsing scheme above. Following the acid leaching, the bottles and vials were rinsed with DDW, filled with 1% HCl, left overnight at 60°C, rinsed again, filled with 1% HCl, then double-bagged and stored until further use.

A record of the sampling history of each 500 ml bottle was maintained, and individual bottles were dedicated for use on particular process streams. Bottles used for sampling high concentration streams were not used later for low concentration streams. This, along with the rigorous cleaning program, helped to assure the integrity of the collected samples.

2.5. Sample digestion procedures

After sampling, the double-bagged samples were immediately placed in a cooler, and transported within one hour to the clean analytical laboratory for processing. Once there, the bottles were removed from their bags, rinsed externally with DDW, and placed in the class 100 clean air hood. For wastewater samples, digestion reagents were added directly to the sample bottles, and the bottles double-bagged with new bags. Samples were allowed to sit overnight in the clean room hood, or in a clean plastic bucket. The next day, single-bagged and tightly capped sample bottles were placed in a convection oven at 95°C for two hours. Digestion reagents for various wastewater samples are described in Table I.

TABLE I

Sample digestion methods

sample type	digestion method
primary influent	150 ml/L $KMnO_4$, etc.†
primary effluent	60 ml/L BrCl; 2 hrs at 95°C
secondary influent	150 ml/L $KMnO_4$, etc.†
secondary effluent	20 ml/L BrCl; 2 hrs at 95°C
spent incinerator exhaust scrubber water	60 ml/L BrCl; 2 hrs at 95°C

† 150 ml/L $KMnO_4$, 80 ml/L $K_2S_2O_8$, 50 ml/L H_2SO_4, 25 ml/L HNO_3; 2 hrs at 95°C

Sludge samples were digested differently than wastewater samples. Three-ml aliquots were pipetted into 30 or 60 ml Teflon FEP vials. One-half ml of HCl was added, followed by 3 ml of concentrated sulfuric acid and 7 ml of concentrated nitric acid. The vials were capped tightly and left to sit, double-bagged, overnight in the clean air hood. The next day, 10 ml of the digestion liquor was pipetted into an acid-leached 100 ml volumetric flask. The flask was placed in sand on a hot plate at 250°C for 2-3 hours or until the dark orange-red color had faded. An acid-cleaned 1-inch glass marble was placed atop the flask to minimize air exchange, promote refluxing and relieve pressure buildup. Digested

samples were diluted to 100 ml with 0.5% bromine monochloride solution.

The iodated carbon traps from the incinerator exhaust gas sampling were prepared for analysis by transferring the iodated carbon and cloth particulate filter from the trap to a 30 ml Teflon vial. Two mls of concentrated sulfuric acid and 5 mls of concentrated nitric acid were then added, the vials were capped tightly, double-bagged and left in the clean air hood overnight. The next day, the samples were placed in a convection oven at 110°C for 3 hours (Bloom, 1994). After cooling, the samples were diluted by the addition of 7 mls of DDW.

2.6. Analytical procedures

Aliquots of the digested samples were analyzed using the cold vapor atomic fluorescence technique with dual-trap gold amalgamation (Fitzgerald and Gill, 1979; Brooks Rand, 1990). Samples treated with acid-permanganate or bromine monochloride were prereduced with hydroxylamine hydrochloride. For analysis, a sample aliquot was pipetted into the 250 ml cold vapor bubbler containing approximately 150 ml of DDW and one ml of stannous chloride reagent. Samples were purged for 15 minutes with gold-filtered nitrogen at 250 ml/min. The purged mercury was collected on a gold-coated quartz sand trap (Brooks Rand AF-20). A soda-lime (Mallinckrodt Mallcosorb) acid/moisture pre-trap was used between the bubbler and the gold trap to minimize acid/moisture effects on the gold-coated sand. This procedure was carried out entirely within a clean air hood.

Following the collection of the Hg on the gold trap, the trap was placed in a NiCr coil and heated to 450-500°C for three minutes while under gold-filtered helium flow of 30 ml/min. The desorbed Hg was collected on an analytical gold trap. The analytical trap was subsequently heated similarly, the Hg and carrier gas thus entering the atomic fluorescence detector (Brooks Rand Model CVAFS-2). The detector signal was recorded and integrated with an HP 3395 Integrator. Peak area was used in all calculations.

In addition to frequent calibration checks (at least every six samples), the quality of the data was assured with the daily analysis of NIST 1641c Mercury in Water SRM. The average of twenty daily determinations of this SRM was 1.46 +/- 0.03 μg/ml; the certified value is 1.47 +/- 0.04 μg/ml.

3. Results and Discussion

The measured process stream Hg concentrations were combined with flowrate data to calculate process stream Hg loadings throughout the Metro Plant. Mass balances across individual processes and across the entire plant were evaluated according to the equation

$$\text{mass in} - \text{mass out} = \text{balance}$$

where "balance" represented the mass of Hg found to be either in excess or unaccounted for. Dividing the "balance" by the "mass in" gave a relative measure of the mass imbalance observed. The results of balance calculations performed for the east primary

and east and west secondary processes at the Metro Plant are shown in Table II. No balance was calculated for the west primary process as no sludge samples were taken there. The balance term in Table II is given as a percentage of the influent mass.

The Hg balance across the east primary process showed approximately 11% more Hg coming out than going in. A probable explanation for the excess Hg found leaving this process is the overestimation of the primary sludge Hg loading. Primary sludge stream solids levels vary widely and unpredictably over time, leading to difficulty in getting a representative sample. Plant process monitoring records indicated that the average total suspended solids (TSS) concentration in this stream over the sampling program duration was approximately 6200 mg/L. The average TSS concentration measured in our sampling was approximately 7500 mg/L, or 21% higher. The primary sludge Hg concentration was highly correlated (99% significance level) with the TSS concentration, and the oversampling of solids in this stream resulted in the overestimation of the Hg concentration and loading.

TABLE II

Mass loadings (g/day) and balance values for Metro Plant treatment processes

	influent	effluent	sludge	balance (%)
east primary	171	36	154	-11
east secondary	92	3	83	7
west secondary	160	6	135	12

The average Hg removal in the east primary treatment process was 79%, while total suspended solids removal (average: 71%) and volatile suspended solids removal (average 70%) were somewhat lower. Previous studies have reported that more than 90% of the Hg in raw municipal wastewater is typically associated with particulate phases (Oliver and Cosgrove, 1974; Goldstone *et al.*, 1990), and work in our lab has indicated that approximately 85% of the Hg in Metro Plant primary influent is associated with particle sizes greater than 5 μm. This association with solids accounts for the relatively good Hg removal observed in primary sedimentation processes (Goldstone *et al.*, 1990).

Mercury mass balances across the east and west secondary processes at the Metro Plant come reasonably close to closure. The east side balances within 7%, while the west side result shows 12% more Hg going in than coming out. In part, these discrepancies are thought to be due to overestimation of the secondary influent flowrates, and, thus, the influent loadings. Secondary solids and flow imbalances have previously raised questions about the accuracy of secondary influent and sludge flow metering at the Metro Plant (Tetreault, 1994), and metering accuracy is currently under study. Further evidence suggesting overestimation of the secondary influent loading is that the total primary effluent (67 g/day) and spent scrubber water (153 g/day) Hg loadings do not add up to the

estimated total secondary loading of 252 g/day. These data would suggest that the estimated total secondary influent loading is high by approximately 10 to 15%.

The west secondary influent Hg loading is, on average, 74% higher than that on the east side (160 vs 92 g/day). This is because the heavily-loaded spent scrubber water ordinarily goes to the west side. Effluent and waste activated sludge Hg loadings on the west side are similarly elevated, reflecting the higher inputs.

The Hg loadings of all major process streams are shown on the simplified process flow diagram in Figure 3. Here, east and west side loadings are combined to give overall primary and overall secondary process loadings. The primary sludge mass loading is shown in parentheses to indicate that this value was calculated by difference (balance assumed to equal 0) rather than by direct measurement. Similarly, the dewatered sludge mass loading was calculated by adding the primary and waste activated sludge loadings together.

The Hg balance around the entire treatment plant closed within 2% (balance/mass in < 2%), a good result given the difficulties and variability inherent in such exercises (Goldstone and Lester, 1991). Of the 248 g/day entering the Metro Plant, more than 95% (241 g/day) is estimated to be emitted to the air via incinerator emissions, while only 4% (10 g/day) is discharged to the Mississippi River via the effluent stream. Based on measurements made previously, the incinerator ash stream accounted for negligible Hg output from the plant. The volatilization of Hg species in wastewater treatment processes

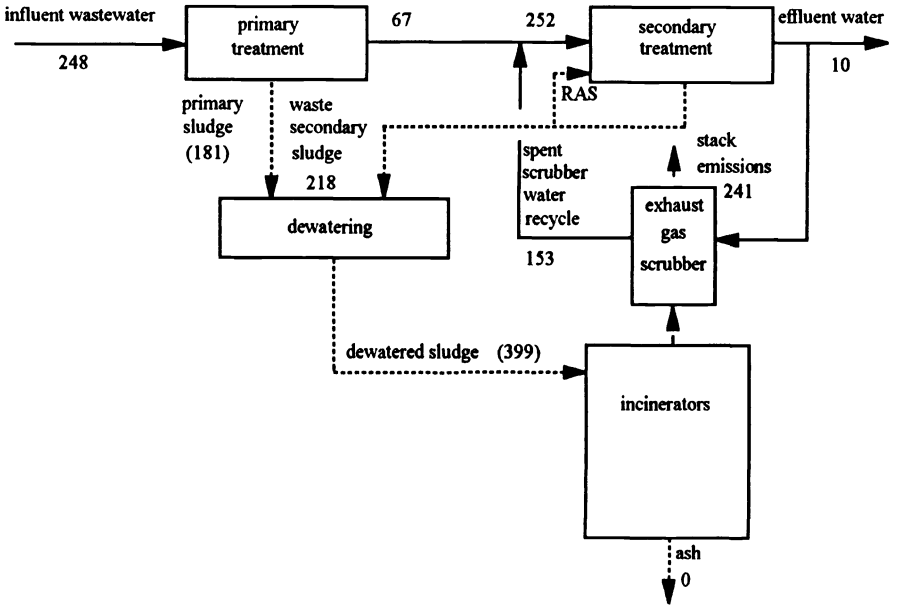

Figure 3. Metro Plant mercury mass flows, grams/day.

(Goldstone *et al.*, 1990) is also apparently of negligible significance at the Metro Plant. Because of the preferential association of Hg with solids, the Metro Plant is very effective in removing Hg from the wastewater stream; however, the incineration process is not effective in controlling or containing the Hg removed.

The difficulty in controlling Hg discharges from the Metro Plant stems from the recycle of the spent scrubber water stream. The scrubbers remove approximately 40% of the Hg mass from the incinerator exhaust stream. That mass is returned to the secondary treatment process, where it associates once more with sludge solids, and returns to the incinerators. The cycle repeats, and the Hg has multiple opportunities to escape the scrubber, until, eventually, it does. A similar situation has been observed for cadmium (Cd) at the Metro Plant; however, because some Cd partitions to the residual ash, all of it is not lost out the stack. This recycle arrangement results in elevated sludge Hg loadings and elevated loadings in all secondary treatment process streams, including the effluent. Both atmospheric emissions and effluent discharges could be reduced by treating the spent scrubber water outside of the wastewater treatment process, that is by not sending it back into secondary treatment, but by handling it elsewhere. A novel sulfide precipitation process designed to remove Cd from spent scrubber water was piloted at the Metro Plant and shown to provide removal of over 90% of the Cd and over 70% of the Hg in this stream (MWCC, 1991); process optimization would likely yield higher Hg removal values. This is one way in which internal Hg loadings and environmental Hg discharges at the Metro Plant might be reduced. Alternatively, a non-water-based emissions control process (activated carbon injection, for instance (EPA, 1992)) could be employed, where the Hg removed from the exhaust stream would be handled outside of the wastewater treatment process.

Metro Plant incineration operations are fairly typical of the industry in the United States. Multiple hearth incinerators and wet scrubber emissions control equipment are normally employed, and the internal recycle and treatment of spent scrubber water is typical (EPA, 1985; EPA, 1990). Thus, it could be expected that other wastewater treatment plants incinerating sewage sludge might display similar process Hg dynamics.

4. Conclusion

Almost all of the Hg entering a large municipal wastewater treatment plant was found to be emitted to the atmosphere via sewage sludge incineration exhaust. While the plant achieved excellent removal of Hg from the wastewater stream, the handling of the residual sludge solids resulted in the loss of that Hg to the atmosphere.

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FIELD-BASED RESEARCH ON ELEMENTAL MERCURY SPILLS

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Abstract. Natural gas industry sites have been contaminated in the past by elemental mercury (Hg) from gas flowmeter manometers. Flowmeters (metering stations) are located throughout the natural gas distribution system at wellheads, at gas processing plants, along gas transmission lines, at underground gas storage facilities, and at points of end use. Field site instrumentation has occurred at six field research sites located in natural gas production areas of the United States. These field research sites, located in Louisiana, Pennsylvania, and New Mexico, are representative of diverse climatic, geologic, and hydrologic conditions. *In situ* hydraulic conductivity measurements on these sites represent a range of 10^{-4} to an estimated 10^{-10} m/s. Mean annual precipitation ranges from near desert (extremely negative annual water budget) to subtropical (extremely positive annual water budget). Geologic materials found on the six sites include stratified alluvial clays, weathered bedrock, and coarse sands and gravels. Each of these sites has had documented spills of elemental Hg and has been instrumented with stainless steel monitoring wells, each of which has a dedicated stainless steel and Teflon® sampling pump. These monitoring points have been sampled quarterly in an effort to develop fundamental information on the transport and fate of Hg in the shallow subsurface, under a range of climatic, geologic, and hydrologic conditions. Both field-filtered and unfiltered groundwater samples have been collected as part of the quarterly sampling effort to determine the potential role of colloid-borne Hg transport in shallow groundwater systems. Data collected from five consecutive quarterly sampling efforts at the New Mexico and Pennsylvania sites suggest that there has been no apparent adverse impact to shallow groundwater in the immediate vicinity of the research sites. A quarterly monitoring program is currently under way at the two Louisiana sites.

1. Introduction

The Energy & Environmental Research Center (EERC) has been contracted by the Gas Research Institute (GRI), with support from the U.S. Department of Energy (DOE), to investigate gas industry sites that have been contaminated in the past by elemental mercury from gas flowmeter manometers. Flowmeters (metering stations), which typically contain 3 to 5 kg of Hg, are located throughout the natural gas distribution system at wellheads, at gas processing plants, at underground gas storage facilities, along gas transmission lines, and elsewhere. Soils in the immediate area of flowmeters have been contaminated because of leakage, spills, equipment failure, pressure surges, vandalism, and operator error.

GRI/EERC field site instrumentation has occurred at six field research sites located in three natural gas production areas of the United States. These field research sites, located in Louisiana, Pennsylvania, and New Mexico, are representative of diverse climatic, geologic, and hydrologic conditions. All of the sites chosen for detailed research have visible elemental Hg contamination in the soil. The sites were investigated with the intent of determining any adverse impact on vulnerable environmental media in the vicinity of the

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metering area. The primary focus of these investigations has been on shallow groundwater, soil, and near surface sediments, all of which have been extensively sampled and analyzed at each of the field sites.

This paper summarizes some preliminary results obtained from an extensive research program that is currently under way.

2. Methods and Materials

While probably no ideal material exists for the construction of monitoring wells for Hg contamination studies, numerous materials may be appropriate, depending on whether Hg is the only contaminant of interest or the groundwater samples will be analyzed for other contaminants as well. This research program utilized 316 stainless steel casings and screens so that samples could be collected for the analysis of both organic compounds and Hg forms. Other materials that may be appropriate for monitoring wells include Teflon® and polyvinyl chloride (PVC) (Bloom, 1994).

All equipment and supplies utilized in site instrumentation and sampling activities were, at a minimum, thoroughly steam-cleaned to minimize the potential for the introduction of Hg and other contaminants into the subsurface. Hollow-stem auger drilling techniques were utilized and allowed the collection of continuous cores, the top 0.6 m of which were analyzed for total Hg, as was the first water-bearing zone encountered in the drilling process. The hollow-stem auger method served to minimize the carrydown of near-surface sediments and soils, which generally exhibited much higher Hg concentrations than their subsurface counterparts.

Sampling devices (pumps) and tubing utilized in this research were constructed of 316 stainless steel and Teflon® and were dedicated to each monitoring well. The utilization of dedicated pumps in each well allowed in-line filtration for the collection of filtered groundwater samples (Harju, 1992). Unfiltered groundwater samples were also collected.

Experience indicates that the best results in collecting representative groundwater samples are achieved only after exhaustive well development activities (purging) and extended aging after placement (weeks to months) (Bloom, 1994). Experience also indicates that Hg concentrations in uncontaminated groundwater systems are typically very low when properly collected, thus making the collection of representative groundwater samples critical to the evaluation of Hg contamination (Krabbenhoft and Babiartz, 1992). Therefore, sampling activities were not conducted until exhaustive well development activities focused on the reduction of turbidity had been conducted.

Each sampling event involved significant purging of the monitoring wells, usually 10 or more casing volumes, except in the cases where lowly permeable materials would not allow that volume. At the end of the purging process, continuous monitoring of pH, conductivity, and temperature were conducted until three consecutive samples would not vary more than 5%.

Initially, U.S. Environmental Protection Agency (EPA)-specified techniques were utilized for the analysis of collected groundwater samples. The EPA technique required 1) the use of either high-density polyethylene (HDPE) or glass containers, 2) preservation with nitric acid, and 3) analysis by cold-vapor atomic absorption spectroscopy (CVAAS) (U.S. EPA, 1986). It was soon discovered that detection limits for CVAAS analyses were not sufficiently low to allow quantification of total Hg in collected samples. Subsequently, two parallel sampling efforts were conducted for each field sampling event, one utilizing EPA methods and the other utilizing ultraclean techniques and low-level analysis. The sampling technique utilized Teflon® sample containers and no preservatives; analysis was done following a procedure that included the addition of bromine monochloride, tin chloride reduction, dual gold amalgamation, and cold-vapor atomic fluorescence spectroscopy (CVAFS). All samples collected for subsequent analysis by CVAFS were acquired using ultraclean methodologies. Filtered samples were collected utilizing high-capacity (700-cm^2) in-line 0.45-μm disposable filters consisting of a cellulose acetate membrane housed in a polycarbonate shell.

3. Results

As of this time, five quarterly sampling events have occurred at the field sites located in Pennsylvania and New Mexico, and wells have been developed and sampled twice in Louisiana. Additionally, 2.5-cm-diameter cores have been collected near the immediate areas of Hg spills on the sites located in Pennsylvania and New Mexico. Slug tests have been conducted on numerous wells at each of the Pennsylvania and New Mexico field sites to determine hydraulic conductivity.

The two New Mexico sites have moderately shallow water tables (5 to 6 m). Both sites are composed of materials that have relatively high hydraulic conductivities (5.0×10^{-6} m/s to 1.3×10^{-4} m/s), consisting primarily of sands and silty sands with minor clay-sized materials and very little organic matter. The two sites are characterized by an extremely negative annual water budget. The summers are very hot and dry, while the winters are cool and dry, though not as dry as summers. Each of the two sites has six monitoring wells located at distances of approximately 11 to 30 m from the metering area. Groundwater pHs, conductivities, and Hg concentrations are summarized in Tables I and II. Geochemically, the major dissolved cations include sodium, magnesium, and calcium, while major dissolved anions include sulfate and carbonate/bicarbonate. Groundwater Hg concentrations, as analyzed by CVAFS, range from less than 1.00 (parts per trillion) to 3.56 ng/L in unfiltered samples, with no apparent differences between upgradient and downgradient wells. Filtered groundwater samples, as analyzed by CVAFS, have displayed Hg concentrations from less than 1.00 ng/L to 3.04 ng/L, again with no apparent differences between upgradient and downgradient wells. All groundwater samples analyzed for Hg by CVAAS have been below the analytical detection limit. One of the sites in New Mexico was remediated at the

TABLE I

New Mexico - Aztec Site

WELL No./ POSITION	FILTERED Hg (ng/L)	UNFILTERED Hg (ng/L)	CONDUCTIVITY (microsiemens)	pH
Upgradient Wells				
AZ-1	0.48–1.25	1.92–2.53	760–790	6.94–7.27
AZ-4	0.37–3.04	1.73–3.56	830–890	7.05–7.23
Downgradient Wells				
AZ-2	0.71–1.35	2.30–3.37	860–940	6.88–7.12
AZ-3	1.25–1.48	1.25–2.45	790–1080	6.91–7.10
AZ-6	0.92–1.52	1.29–1.32	720–760	6.93–7.25

TABLE II

New Mexico - Blanco Site

WELL No./ POSITION	FILTERED Hg (ng/L)	UNFILTERED Hg (ng/L)	CONDUCTIVITY (microsiemens)	pH
Upgradient Wells				
BL-1	1.07–2.14	0.80–1.66	1080–1160	7.10–7.25
BL-4	0.84–1.13	0.89–1.04	1690–1750	6.94–7.06
Downgradient Wells				
BL-2	1.00–1.31	0.84–1.39	1360–1410	7.03–7.16
BL-3	0.67–0.89	0.48–2.16	1160–1170	7.07–7.24
BL-5	0.46–0.78	0.49–1.21	1150–1170	7.03–7.16
BL-6	0.90–1.03	0.58–3.23	1920–2130	6.94–7.32

inception of site instrumentation, while the other was remediated approximately 1 year into the study period.

The two Pennsylvania sites have extremely shallow water tables (1 to 4 m). Both sites are composed of materials with relatively low hydraulic conductivities (1.7×10^{-8} m/s to 3.6×10^{-7} m/s), consisting primarily of silts and clays with a significant fraction of organic matter. The two sites have a positive annual water budget. The summers are warm and wet, and the winters are cold and wet. One of the sites has six monitoring wells surrounding the metering area, while the other has five monitoring wells surrounding the metering area. In both cases, the wells are at distances of about 9 to 27 m from the metering area.

Groundwater pHs, conductivities, and Hg concentrations are summarized in Tables III and IV. Geochemically, the major dissolved cations include calcium, iron, and sodium, while the major dissolved anions include sulfate, carbonate/bicarbonate, and chloride. Groundwater Hg concentrations, as analyzed by CVAFS, range from 1.24 to 90 ng/L in unfiltered samples, with the highest Hg concentrations coming from extremely turbid samples. Well development activities focused on reducing groundwater turbidity have

TABLE III

Pennsylvania - Laurel

WELL No./ POSITION	FILTERED Hg (ng/L)	UNFILTERED Hg (ng/L)	CONDUCTIVITY (microsiemens)	pH
Upgradient Wells				
LR-1	0.14–13.7	1.24–3.20	150–160	6.26–6.57
LR-2	3.85–5.45	22.0–23.5	240–250	6.54–6.64
LR-5	<0.1–0.69	23.8–55.1	310–340	6.58–6.90
Downgradient Wells				
LR-3	2.50–3.71	18.3–35.0	170–190	6.00–6.48
LR-4	0.88–4.20	10.7–12.8	210–280	4.86–5.53

TABLE IV

Pennsylvania - Medix

WELL No./ POSITION	FILTERED Hg (ng/L)	UNFILTERED Hg (ng/L)	CONDUCTIVITY (microsiemens)	pH
Upgradient Wells				
MR-1	<0.1–3.04	4.40–4.66	220–260	6.81–7.51
MR-2	<0.1–0.96	18.2–27.0	250–360	6.32–6.51
MR-4	0.37–3.21	24.5–28.4	140–180	6.62–6.43
Downgradient Wells				
MR-3	0.20–1.29	15.8–19.6	360–470	6.78–7.44
MR-5	1.81–2.91	26.4–31.6	1010–1030	6.67–6.72
MR-6	0.14–3.44	55.3–90.1	400–430	7.21–7.42

presumably been adversely affected by the presence of saprolitic shales, both within the soil profile as well as shallow bedrock, resulting in a constant production of fine grained material within the vicinity of the boreholes, well number MR-6 has been particularly problematic in this regard. Filtered groundwater samples, as analyzed by CVAFS, have displayed Hg concentrations from less than 1.00 to 5.45 ng/L, with no apparent differences between upgradient and downgradient wells. All groundwater samples analyzed for Hg by CVAAS have been below the analytical detection limit. Neither site was remediated before or during the study period.

Preliminarily, we can classify the Louisiana sites as being much less permeable than the others. At the same time, the water table tends to be significantly deeper (6 to 10 m), and the annual water budget is expected to be extremely positive. The summers are hot and wet, and the winters are cool and wet.

4. Conclusions

Preliminary conclusions can be drawn based on the results of research conducted primarily on four sites in New Mexico and Pennsylvania. Elemental Hg was commonly spilled in the past from manometers used to measure flow in natural gas pipelines. Spilled elemental Hg usually breaks into small beads or droplets in the immediate vicinity of the spill. Generally, Hg infiltration is limited to 0.5 to 1.0 m, although deeper migration may occur if fractures or macropores are present (Henke *et al.*, 1993). At the sites investigated, migration appears to be extremely limited, with no apparent adverse impact to shallow groundwater in the immediate vicinity of the site. The results of analyses on both filtered and unfiltered groundwater samples support this position and, interestingly, have not been significantly different, except in cases of extremely turbid samples, suggesting that colloidal transport has not been occurring at the sites studied in detail thus far.

Refinement of these conclusions and/or additional conclusions will likely result from the evaluation of the soil/sediment analyses, as well as from the work at the two Louisiana research sites. Work is scheduled to be concluded in Louisiana in late 1994 or early 1995.

Acknowledgments

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THE ACCELERATED REDUCTION AND ELIMINATION OF TOXICS IN CANADA: THE CASE OF MERCURY-CONTAINING MEDICAL INSTRUMENTS IN QUEBEC HOSPITAL CENTRES.

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Abstract. In Canada, medical instruments containing mercury (Hg) are still widely used in hospitals These are mostly thermometers and sphygmomanometers Mercury present in these instruments does not in itself constitute a risk of contamination since this metal is contained within a closed system However, breakage, inadequate maintenance and disposal of such instruments can expose workers and the public to this toxic substance In Quebec, 80% of the 28 hospitals surveyed still use Hg sphygmomanometers and 45% Hg thermometers Besides, 35% do not have any recovery procedures in case of spillage and most mercury spills are apparently not reported Two main courses of action are recommended the gradual replacement of these medical instruments by aneroid sphygmomanometers and electronic thermometers, and the establishment and communication, in the form of a handbook, of guidelines to handle and dispose of mercury safely

1. Introduction

Voluntary Action (VA) to reduce or eliminate toxic substances is being encouraged in many countries In Canada, one medium being used is a programme called ARET ARET stands for Accelerated Reduction/Elimination of Toxics The goal of this programme is to speed up the reduction/elimination of anthropogenic emissions of selected persistent and bioaccumulating toxic substances In 1993, as part of the ARET activity, Environment Canada funded the MER-MED (MERcury in MEDical instruments) project (Guerrier, Coté, Paul, 1994)

In Canada, an important quantity of medical instruments containing metallic mercury (Hg) are used in hospitals These are mostly thermometers and sphygmomanometers Even if new types of equipment are available, instruments containing Hg are still widely used

Hg present in medical instruments does not in itself constitute a risk of contamination since Hg is contained within a closed system However, because metallic Hg is in liquid form at room temperature, it vaporizes when spilled or left in the open and has a tendency to scatter into small droplets when spilled (Lauwerys, 1990) Breakage, disposal or maintenance of an instrument can expose workers and the public to this toxic substance (McNerney, 1988) Inadequate management of these Hg wastes can lead to their incineration and their disposal in landfills as well as the release of Hg into the environment

In Quebec, regulations require that Hg be disposed of as a toxic waste, whatever the quantity (Commission d'enquête sur les déchets dangereux, 1990, Règlement sur les déchets dangereux,

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annexe II) The Quebec Toxicology Center has been involved several times in recent years after spills occurred in hospitals and has developed an expertise in Hg recovery procedures (Guillot, 1993)

The objectives of this study were to consult suppliers of medical equipment, as well as the personnel of some Quebec hospitals, in order to identify quick actions that could be taken to reduce and eliminate the use in hospitals of medical instruments containing Hg This project also aimed, through a telephone survey, at estimating the quantities of instruments used or stored in hospitals, and identifying disposal methods and existing recovery procedures in case of spillage It has been developed by the Quebec Environmental Health Committee (CSE)

2. Materials and Methods

A sphygmomanometer contains between 18 and 30 cc of Hg (between 245 and 408 g) Usually, in a hospital, there is one sphygmomanometer per two beds, as well as one instrument in each examination and operating room A thermometer normally contains less than 10 g of Hg, depending on its size There is normally one thermometer for each patient, plus a certain number in circulation

In the last few years, new types of instruments or devices have been introduced They do not contain Hg but perform the same functions as conventional thermometers and sphygmomanometers According to the suppliers of medical equipment, as well as the medical personnel consulted, they are essentially

- aneroid sphygmomanometers
- electronic sphygmomanometers

- alcohol thermometers
- electronic thermometers
- tympanic thermometers

A telephone survey was carried out in 28 Quebec hospitals during November 1993

- 18 in the Montreal region
  - 14 in the Montreal Urban Community
  - 4 in the peripheral zone
- 5 in the Quebec City region
- 5 in other regions

3. Results and Discussion

In hospitals, the main medical instruments containing Hg still used and purchased are sphygmomanometers and thermometers According to the study, 80% of the institutions surveyed use Hg sphygmomanometers and 45% use Hg thermometers The study also reveals that only 35% of the 28 surveyed hospitals have recovery procedures in case of spillage

On the basis of the different options currently available, it would appear, according to the medical personnel consulted, that the devices most likely to replace conventional Hg instruments are aneroid sphygmomanometers and electronic thermometers Even though this study did not aim at evaluating the performances of the different types of instrument, it seems that aneroid sphygmomanometers and electronic thermometers have similar performance and costs as conventional instruments

However, it is very difficult to establish a precise inventory of used and stored instruments containing Hg in Quebec hospitals and, as a result, to determine the amount of Hg in circulation Because most Hg spills are currently not reported and because instruments are disposed of in an uncontrolled fashion, it is difficult to estimate the extent to which such Hg finds its way into the environment

The study also reveals that there are no official procedures or notices in the Quebec hospital network for recovery, handling and disposal of Hg The existence of some kind of procedure in one particular hospital is often the result of the initiative of one person in the hospital

4. Recommendations

On the basis of the information obtained, one main action has been identified

• **The replacement in Quebec hospitals of sphygmomanometers and thermometers containing Hg by aneroid sphygmomanometers and electronic thermometers.**

But in today's conjuncture and considering the quantities of instruments used, it appears difficult to recommend an immediate and total replacement in hospitals of all medical instruments containing Hg It seems more realistic to recommend

• **A gradual replacement of those instruments. Each new sphygmomanometer acquired by a hospital should not contain Hg and each hospital should consider the replacement of sphygmomanometers still usable. Through purchase policies, hospitals should replace thermometers containing Hg by electronic thermometers, unless their use involves a risk of infections.**

Until Hg has totally disappeared from hospitals, different courses of actions can be considered for hospitals to reduce the risks of exposure to Hg and contamination of the environment

• **Inform all hospital personnel about the risks and problems associated with the handling and the inappropriate disposal of Hg;**
• **Assure the adequacy of disposal methods of Hg;**
• **Elaborate a recovery procedure for Hg in case of spillage;**
• **Elaborate a handling procedure for Hg.**

In order to estimate the quantities of medical instruments containing Hg used and stored in hospitals as well as to facilitate the follow-up of the reduction of the use of this toxic metal, hospitals should:

- **Keep an inventory of all instruments containing Hg (used and stored);**
- **Keep an inventory of the quantities of Hg stored.**

To facilitate such actions, the CSE recommends:

- **The establishment and communication, in the form of a handbook, of guidelines to handle and dispose of Hg safely in hospitals.**

Acknowledgments

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MERCURY IN THE NATURAL GAS INDUSTRY IN CANADA

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Abstract. There are an estimated 1,500 natural gas facilities across Canada, most of which used mercury (Hg) in metering equipment at one time or another. Although the use of mercury has ceased, many gas industry buildings still contain detectable levels of Hg in air. Air Hg levels are generally low but indoor remediation is suggested. Worker exposure to the air Hg levels is not considered a significant hazard. Very high soil Hg levels have been observed at numerous sites. Soil Hg levels do not pose an immediate human hazard but are sufficient to be hazardous to ecological receptors. The area of soil contamination is generally within the buildings or within a few metres of the nearest door. Downward movement of the Hg does not generally extend more than one metre. Remediation of contaminated soil with on-site thermal desorption is recommended as the appropriate soil clean-up technology.

1. Introduction

Elemental Hg was frequently used in the natural gas industry in manometers to measure gas pressure and flow at wellheads, metering sites along pipelines and other operations. Most commonly, manometers were located in small meter houses often with dirt floors. During the operating life of the instruments, spills of Hg were known to occur as a result of breakage, pressure surges or equipment failure. Spilled Hg was often swept outside of the building. As a consequence, both the building interiors and the soils exterior to the buildings have been contaminated by Hg. The use of Hg for these purposes generally stopped in the early 1980's.

In 1991, the Gas Research Institute (GRI) initiated studies which identified Hg as a potentially significant health, safety and environmental issue within the gas industry. The studies culminated in a workshop on *Mercury Contamination at Natural Gas Industry Sites* in 1992 (GRI, 1992). Canadian natural gas companies have responded quickly and many have investigated the potential for Hg contamination at their sites.

As a result of past practices there are two principal issues of Hg at the gas industry sites: 1) Spilled beads of Hg are trapped inside the buildings in floor cracks, gravel floors, door frames or under machinery. The Hg continues to volatilize posing a potential risk to workers, 2) Mercury swept outside has caused local contamination of soils posing a potential environmental hazard.

The purpose of paper is to present a brief overview of findings from several surveys of Hg contamination at metering and compressor stations within the Canadian natural gas industry.

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2. Methods

Ecological Services for Planning Ltd. has conducted surveys of Hg at natural gas industry sites throughout Manitoba and Ontario. Prior to conducting on-site surveys, information was obtained regarding historical uses of Hg and possible spills, local land uses, proximity to residences, groundwater conditions and occupational use of buildings.

2.1 AIR SURVEY TECHNIQUES

Approximately 375 individual air surveys have been conducted at 175 sites. Indoor Hg levels were measured with a Jerome 431-X meter by Arizona Instruments. The meter uses a gold film sensor to detect Hg in air at levels ranging from 0.001 to 0.999 mg/m^3 Hg, $\pm$ 5% at 0.100 mg/m^3. Inside Hg levels are measured in the ambient breathing zone, as well as near the floor, around cracks, door jams and under equipment. The building floor temperature is measured to ensure that a minimum inside temperature of 5°C is achieved.

In Ontario air criteria for mercury are as follows:

Time Weighted Average Exposure Concentration (TWAEC) = 0.05 mg/m^3

Maximum Exposure Concentration (MEC) = 0.15 mg/m^3

The MEC is also sometimes known as Short Term Exposure Limit (STEL).

If the STEL is exceeded in the breathing zone, the building is evacuated and fully trained personnel are required for site remediation. If the TWAEC is exceeded in either the breathing zone, or near the floor, building clean-up is recommended.

For clean-up the areas were vacuumed thoroughly using a NILFISK model GS90 Mercury Collection Vacuum Cleaner. The contaminated area was then sprayed with 20% sodium thiosulfate solution, allowed to dry and vacuumed again. Air Hg readings were again recorded after this clean-up procedure.

2.2 SOIL SURVEY TECHNIQUES

Two levels of soil surveys were used for the detection of Hg: 1) Reconnaissance or screening level survey where only a few soil samples were collected to determine if Hg is present on a site, and 2) detailed survey to delineate the spatial extent of potential Hg contamination for subsequent remediation.

The choice of sampling strategies depends on the survey goals and objectives. The number of soil samples collected from individual sites can vary from 1 to >100 depending on the site size and required accuracy of delineation of the contaminated zone. Under average conditions we collected between 10 to 20 samples to map soil contamination.

Approximately 300 g of soil was collected using a hand trowel and placed in clean glass jars. Subsurface samples were collected at a depth of 30 to 100 cm. Samples were analyzed for total Hg by flameless atomic absorption spectrophotometry with a working detection limit of 0.1 mg/kg for Hg in soil. Standard reference material and blanks were routinely run every 15 soil samples.

The soil analytical results were compared with the applicable criteria. Criteria differ in Ontario (Ontario Ministry of the Environment and Energy; MOEE) and other jurisdictions regulated by the federal government (Environment Canada). Furthermore, both the provincial and federal agencies have recently proposed revisions to their criteria, with final approval being expected later in 1994.

Commercial/Industrial clean-up criteria	Existing	Proposed
Ontario (mg/kg):	2.0	10.0
Environment Canada (mg/kg)	10.0	30.0

The MOEE also has proposed a Stratified Clean-up approach whereby under certain conditions, soils greater than 1.5 m deep may contain 57 mg Hg/kg soil.

3. Results and Discussion

3.1 AIR MERCURY LEVELS

- At no sites did the breathing zone Hg level exceed the TWAEC or the STEL
- At approximately 40% of the sites, detectable (> 0.005 mg/m^3) Hg concentrations were recorded near floor cracks or under equipment
- At approximately 11% of the sites Hg levels exceeded the TWAEC when the probe was placed near floor cracks or under equipment
- Interior clean-up operations were undertaken at 40 facilities
- The clean up procedure reduced air Hg levels in 75% of the cases
- Air Hg levels actually increased in 25% of the facilities after clean up, likely in response to the removal of caulking, fixtures or paint that exposed trapped Hg to the air

3.2 SOIL MERCURY LEVELS

- Soil Hg levels at the sites ranged from < 0.04 mg/kg to 4,200 mg/kg dry wt.
- Beads of elemental Hg were visible in some soil samples
- The results suggest that the probability of detecting contamination improves with more samples collected.
- There was no correlation between building air Hg levels and outside soil Hg concentrations
- Mercury is deposited as minute particles very heterogenously within the soil. As a result, analysis on split samples often provides very different values. This is not an analytical problem, but a sampling strategy issue
- Mercury was observed as deep as 1 m below the soil surface
- Results of other studies indicate that Hg in soil does not move laterally in groundwater

A brief hazard assessment is useful to classify sites according to level of contamination to determine the need for future remediation, and to identify potential risks to workers and ecological receptors.

Sites Should be Classified According to Regulatory Criteria:

1. Do ambient indoor air levels exceed either the STEL or TWAEC?
2. Do soil levels exceed the applicable remediation criteria?

Attributes of the gas industry sites to be considered when assessing potential hazard: a) the sites are generally small, b) sites are often remote or in an industrial area away from residents, c) metering stations are visited infrequently (i.e. once per week) by workers, d) workers at compressor stations are more frequently (daily) inside buildings, e) there is little or no vegetation at the sites, and f) lateral transport of Hg via groundwater is not expected.

Exposure Pathways

MEDIUM	ROUTE	RECEPTOR	EXPOSURE
Surface Soil	Direct	Workers	Contact likely
		Residents	Contact not likely
		Terrestrial life	Contact possible
Indoor Air exposure	Inhalation	Workers	Intermittent
Groundwater	Direct	Workers, residents	Exposure not likely
		terrestrial life	Exposure not likely

Based on the air Hg concentrations measured, and low exposure periods of workers potentially exposed to these concentrations, there is low potential risk to workers at the gas industry facilities in most situations. Although cases of extreme mercury contamination of building interiors have reportedly been observed, we have not discovered situations of gross contamination.

Soil mercury concentrations greater than 10 to 20 mg/kg may be toxic to some plants and soil invertebrates such as earthworms. Therefore, the levels of Hg observed in many soil samples would be toxic to some ecological receptors.

Thermal Desorption or roasting has been identified by the U.S. EPA as the Best Available Demonstrated Technology (BADT) for use in treating Hg-contaminated soils. In Canada, soil remediation is currently limited to excavation and either storage on-site, or transport to a hazardous waste disposal area. Neither solution is ecologically sound in the long term. Ecological Services for Planning Ltd. is currently investigating the development of a mobile thermal desorption unit to remediate Hg contaminated soil. A mobile unit is well suited to the natural gas industry needs which has many sites widely dispersed across Canada with each site involving relatively small volumes of soil.

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PART XI

MERCURY MEASUREMENT METHODS

DENUDER-BASED TECHNIQUES FOR SAMPLING, SEPARATION AND ANALYSIS OF GASEOUS AND PARTICULATE MERCURY IN AIR

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Abstract. A denuder-based method for sampling and separating gaseous and particulate mercury in the air is described. Two different denuder configurations developed in Vilnius, Lithuania (silver) and in Gothenburg, Sweden (gold) are compared. Data were acquired at different sampling locations around the cities of Vilnius and Gothenburg. The concentration of particulate Hg was found to be 0.04 to 0.40 ng m^{-3} in the Vilnius region, and 0.11 to 0.57 ng m^{-3} in the Gothenburg region. Intercalibration results for the silver and gold denuders are presented. The results obtained by the two different denuder configurations and sampling set-ups display satisfactory agreement.

Keywords: gaseous, particulate, mercury, sampling, silver, gold, denuder.

1. Introduction

It is commonly accepted that about 95% of the mercury (Hg) in the ground layer atmosphere is found in the gas phase with the rest associated to particles. The differences in physical behaviors of these two Hg forms have urged the development of techniques which are suitable for sampling particulate Hg in a simple and accurate way (Lindqvist et al.,1991).

Preconcentrations are generally needed in order to measure Hg concentrations in the air, since the concentrations are very low. Traditional sampling methods use filters for particulate Hg (Kothny,1973; Brosset,1982; Lindqvist et al.,1985; Slemr et al.,1985; Kvietkus,1985). Different sampling media can be used depending on the Hg concentration range of interest, e.g. acidified permanganate solution, activated carbon, silver and gold traps (Hatch and Welland, 1968; Johnson and Braman, 1974 ; Slemr et al.,1979; Fitzgerald and Gill, 1979; Brosset, 1983; Kvietkus, 1986; Xiao et al., 1991). Silver and gold traps of different configurations and sizes are widely used nowadays, due to their basic properties of being quantitative adsorbers of Hg in the gas and being simple to use. Conventionally, quartz wool is used in form of filter or trap for collecting particulate Hg from the air. The particulate Hg so measured was a kind of operational definition, since the wool is not selective for particulate Hg, an unknown amounts of gaseous Hg^0 might also become adsorbed on the wool or filter surface. At the same time, certain small

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size particles could penetrate the filter, since particulate Hg in air was reportedly associated mainly with small particles, i.e. < 0.3 μm (Davies, 1966; Kvietkus, 1985). The ratio of elemental Hg to its particulate form measured using the conventional method, may suffer high uncertainty.

Preliminary experimental results show that it is impossible to collect fine particulate Hg quantitatively using gold wool traps, see Figure 1. Particulate Hg can be efficiently collected by pyrex wool trap only at relative high flow rates, i.e. > 3 L min^{-1}. A particle counting device was connected to a system where gold and pyrex wool traps were used to check the collection efficiency for particulate Hg. It can be seen from Figure 1, that at flow rate of 3 L min^{-1} good efficiency occurs with particle diameters > 0.4 μm and > 0.8 μm for a pyrex wool trap and a gold wool trap, respectively. Lower flow rates result in worse efficiency for both traps. The collection efficiency for particulate Hg can be improved by increasing the flow rates, but the efficiency of gold and pyrex traps for gaseous Hg^o will be, in general, reduced at higher flow rates. Thus, a good sampling method for separating particulate and elemental Hg is still needed. Below, a denuder based technique is presented, that may provide a practical solution to the separation of the two forms of Hg in the air.

The attractive function of a diffusion denuder is the selective removal of gaseous substances from the air. Thus, it appears to be a good solution to the separation of particulate Hg from its gaseous form (Xiao et al., 1991). Denuders of gold and silver with different configurations and sampling set-ups for collecting particulate Hg in the air are compared. Preliminary results using these techniques for Hg measurements are presented, and the environmental significance is discussed.

2. Experimental

2.1. THE AFS ANALYTICAL SYSTEM

An Atomic Fluorescence Spectrometer (AFS) analytical system was constructed at the Institute of Physics, Lithuania (Kvietkus et al.,1983). The detection limit of the device is 0.1 pg in helium. Usually, argon is used as carrier gas due to the significant difference in prices, and the sensitivity is only slightly improved with helium. The measuring results can be displayed directly on the digital screen of the AFS or registered by a chart recorder. The time for one sample analysis is 60 seconds. The two-stages gold trap amalgamation procedure used for analysis of Hg together with its calibrating system using Hg standard gas source have been described previously (Kvietkus,1985).

The gold wool traps used in the analytical system were made by filling a quartz tube with a thin gold wire (20 μm). The tubes are 10 cm in length with an inside diameter of 4 mm. The total amount of gold used was about 100 mg and the effective length of the tube was about 10 mm. Pyrex wool traps were built in the same fashion.

2.2. THEORETICAL BACKGROUND FOR DENUDER MAKING

The fundamental theory of the gas molecular diffusion is the basis for denuder using. Generally, denuders are made from cylindrical tubes, which are coated on the inside surfaces with an active layer that can retain certain gas molecules selectively. Denuders often used in the atmospheric studies to seperate gaseous and particulate phases airborne pollutants. While the gas molecules are adsorbed on the wall of denuders, the particles will pass through the tube, due to their inertial momentum (Lane et al., 1988; Munthe, et al., 1990; Larjava et al., 1990). In this paper, silver and gold coated denuders were made for separating gaseous and particulate Hg in air.

The collection efficiency of a denuder for elemental Hg can be calculated from the following empirical equation, (Davies,1966):

$$E = (1 - c_o/c) = 0.819\exp(-14.6272\partial) + 0.097\exp(-89.22\partial) + 0.01896\exp(-212\partial),\ \partial = \pi DL/V \quad (1)$$

where c and c_o are the concentrations of elemental Hg at the inlet and the outlet of tube respectively, L is the length of tube, V is the volume of air through the tube, and D is the diffusion coefficient for the mixture of Hg^o and air at the atmospheric pressure, which in turn, was described by the following equation (Jost, 1952):

$$D = 2.628\ X\ 10^{-3}\sqrt{\frac{T^3(M_1 + M_2)/2M_1M_2}{p\Omega_{12}^{\ 2}}} \qquad cm^2/s, \qquad (2)$$

where $\Omega_{12} = 1/2\ (\Omega_1 + \Omega_2)$, Ω is the molecule diameter (Angstrom), M is the molecular weight, T is the temperature (^{o}K), p is the atmospheric pressure. The diffusion coefficients of Hg vapor at different temperatures, calculated according to (2), are presented in Table I. These data show that the diffusion coefficients depend on the ambient temperature during the experiments, and this should be taken into account.

Table I. Diffusion coefficient of Hg vapor at different temperatures.

T, °C	10	20	30	40	50	60
D, $cm^2\ s^{-1}$	0,118	0,126	0,132	0,144	0,150	0,159

Figure. 2 presents the adsorption efficiency calculated using formula (1). As can be seen from the figure, optimal conditions are achieved when the effective length of a tube is 20 cm with an inside diameter of 3 mm and an air flow rate of 0.20 L min^{-1}. It can also be seen that at lower flow rate (<0.1 L min^{-1}), a 10 cm denuder would work as effective as a 20 cm one.

2.3. PREPARATION AND TEST OF DENUDER IN LABORATORY

2.3.1. Silver denuders produced in Vilnius.

Quartz and pyrex glass tubes of required length and diameter were washed with 5N HNO_3 first, then the tubes were heated in a furnace for several hours at a temperature of 600-800 °C. This procedure was repeated several times in order to remove Hg accumulated on the walls. For preparing gold denuders, small volume gold solution (Hanovia® bright gold liquid solution, see Azzaragva, 1979) were sucked inside the tubes to the desired level first. Then they were dried by passing air through the tubes at flow rates of 10-30 mL min^{-1}. Subsequently, the tubes were heated to 600 °C in a furnace, while continuing to pass air through them. The tubes thus treated were coated with a very bright thin gold layer. For preparing silver denuders, the well-known organic mirror reaction was applied, i.e. $AgNO_3$ was reduced by glucose, the reductant being silver which was deposited on the surface of the reaction vessel.

Silver denuders with an inner diameter of 3 mm and an effective length of 20 cm were made in this investigation. Typical blank values for such silver denuders were in the range of 0.5-2.0 pg. The collection efficiency of such silver denuders for Hg^0 were tested in laboratory. Results showed that 98% of Hg was collected by a single silver denuder at an air flow rate of 200 ml min^{-1}. 99.96% collection efficiency would be obtained if two such denuders were used in series. The results agreed well with the theoretical calculation.

2.3.2. Gold denuders prepared in Göteborg.

The denuders were 65 cm long with a inside diameter of 0.4 cm. Such denuders were capable of removing >99.95% of Hg^0 in an air stream at a flow rate of about 1 L min^{-1}. A detailed description concerning the preparation, testing and the set-up of gold denuder for Hg collections can be found elsewhere (Munthe et al., 1990; Xiao, et al. 1991).

2.4. ON -SITE SAMPLING SET UP USING SILVER DENUDER.

The sampling set-up is presented in Figure 3. Thus, two silver coated denuders were connected in series as a working group in order to assure the quantitative collection of Hg. Between the two groups a heating device was installed, which can be heated up to 900 °C. Based on the molecules diffusion principle and the collection efficiency of Hg on the silver denuder tested in the laboratory, gas phase Hg should be quantitatively collected by the first denuder group. All Hg species that pass through the first denuder group should be particulate Hg. The heating furnace of 900 °C is able to convert all Hg species (Wang et al.,1994) to its elemental form, which in turn be trapped on second silver denuder group. About 20-60 L of air in the background area usually provides good results for particulate Hg measurement, which correspond to a sampling time from 2 to 5 hours. Generally, 4 hours sampling time was used when measuring particulate Hg in field. The tubes were sealed with Parafilm® after sampling and should be analysed within a few days.

3. Results and Discussion

3.1. ON-SITE MEASUREMENT RESULTS USING SILVER DENUDER

The measurements were performed between July and August 1989 at Aisetas, an air quality monitoring station for measuring pollutants at background level, in eastern Lithuania. The station is located in an open field without much forest and is far away from industrial sources. The results obtained for elemental and particulate Hg are presented in Table II.

Table II. Concentrations of gaseous and particulate Hg in the background station Aisetas, Lithuania.

No.	Hg Concentration, ng m^{-3}		Percentage of
	vapor	particulate	part./gas.(%)
1	4.3	0.14	3.1
2	3.3	0.09	2.6
3	3.0	0.11	3.5
4	3.4	0.05	1.5
5	1.7	0.13	7.5
6	4.0	0.40	10.0
7	2.9	0.10	3.4
8	2.3	0.14	6.0
9	2.2	0.19	8.5
10	2.1	0.14	6.5
11	2.0	0.11	5.7
12	1.5	0.04	3.1
Average	2.70	0.14	5.0

The results are daily averages based on at least 6 measurements. As seen from the table, the average ratio between particulate and elemental Hg is about 5.0%. This is similar to the results obtained by other groups with conventional quartz traps for particulate Hg (Braman and Johnson,1974 ; Slemr et al., 1985), although in a case, as high as 10.0 % was noticed.

Gold-coated denuders have been employed in an investigation in the outskirts of Göteborg in 1990, from February to April. Five different sampling positions were chosen and concentration of particulate Hg was found to vary from 0.11 to 0.57 ng m^{-3} , corresponding to 2.8 - 16.9% of the total airborne Hg (Xiao et al., 1991).

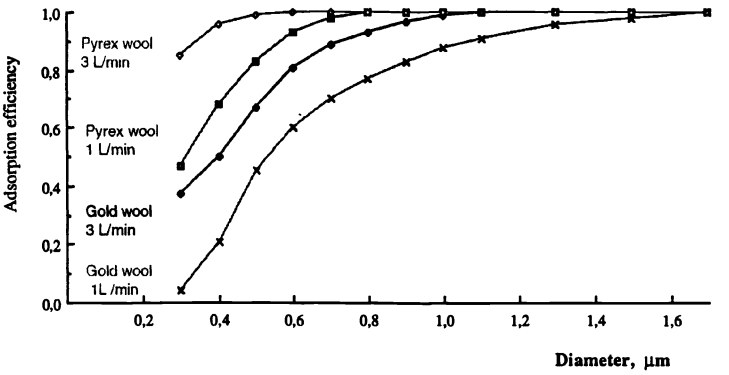

Fig. 1. Experimental collecting efficiency for particulate Hg using gold and pyrex wool traps at different flow rates.

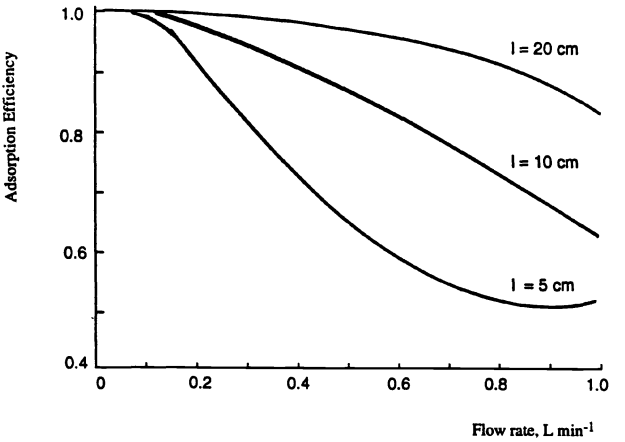

Fig. 2. Calculated collecting efficiencies for gaseous Hg using denuders with different lenghts at different flow rates.

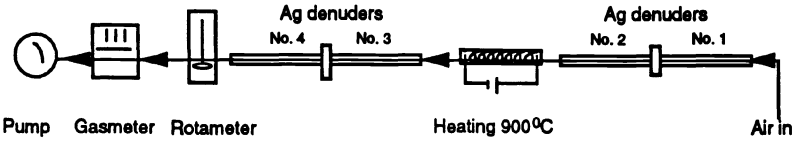

Fig. 3. Sampling system using silver denuder for separating gaseous and particulate Hg.

3.2. INTERCALIBRATION BETWEEN GOLD AND SILVER SAMPLING SET-UPS

Intercalibration was made between the silver and gold denuder sampling systems described above. The work was performed in October,1992 at the Department of Inorganic Chemistry, Chalmers University of Technology and University of Gothenburg. For the experimental set up of the gold denuder and other detailed information see Xiao et al., (1991).

Two sampling lines were arranged in a parallel way with the sampling inlets close to each other. The measuring results for the comparison are presented in Table III.

Table III. Measuring results for gaseous and particulate Hg, using different denuders.

No.	Sampling system	Hg Concentration, ng m^{-3}			Hg_p /Hg^o
		Hg^{o*}	Hg_p^{**}	Hg_T^{***}	(%)
1	Gold denuder	30.3	1.7	32.0	5.6
1.	Silver denuder	28.9	1.6	30.5	5.5
2.	Gold denuder	23.2	0.9	23.9	4.0
2.	Silver denuder	19.3	0.8	20.1	4.2

* Elemental Hg; ** Particulate Hg; *** Total Hg.

From Table III it can be seen that the results for the silver and gold denuders are comparable and that the two sampling set-ups give consistent results. Thus, both sampling combinations are suitable for sampling and separating gaseous and particulate Hg in the air.

4. Conclusions

Gold and silver denuders are both capable of removing gaseous Hg completely from air stream first and are suitable for partitioning this two forms of Hg in the atmosphere. Denuder-based sampling systems provide more accurate measurement results of particulate Hg than conventional quartz trap sampling method. Accurate determination of the concentration of particulate Hg is important, since this physical form of Hg is readily deposited back to the ground. The information thus obtained is useful for budget estimation and understanding the Hg transport and removal mechanism in the atmosphere.

Acknowledgements

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ON-LINE MEASUREMENT OF MERCURY IN SIMULATED FLUE GAS

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Abstract. Total and elemental mercury (Hg) in simulated flue gas was measured on-line by a commercial Semtech® Hg analyzer This instrument is based on Zeeman modulated Atomic Absorption Spectrometry . Both a wet chemical solution and a dry physical pyrolysis converter were applied to reduce the Hg(II) in the gas before leading it to the detector. Results show that the Semtech® analyzer is suitable for measuring elemental Hg even in the presence of 2500 ppm SO_2 and 500 ppm HCl. For the measurement of Hg(II), the wet method is suitable only at SO_2 concentrations <50 ppm. The dry thermal converter filled with crushed quartz chips together with a small amount of soda lime converts Hg(II) quantitatively at laboratory scale. This result is promising, since the trace gases delivered to the system, such as SO_2, and HCl are similar to those produced in coal burning and waste incineration processes. The limiting factor for such a converter is its comparatively short life time of performance, about 20 hours.

1. Introduction

High-temperature processes such as waste incineration and coal burning are major sources of mercury emission to the environment. The flue gases contain mercury (Hg) in different physical phases and chemical forms, most compounds being volatile. During recent years, several groups have tried to separate the oxidized Hg(II) species from the elemental form at both coal burning and waste incineration plants. Most of the samplings have been done in a batch mode by selective absorption of different forms of Hg in different media, e.g. liquid solution or solid absorbent (Bloom et al., 1993). In this way though, the analysis can only produce time averaged values corresponding to sampling periods which are typically at least 30 minutes. For complete process control, continuous measurements of different forms of Hg in the flue gas are necessary. Mercury (II) chloride, for example, differs from elemental Hg in that the former condenses rather easily and is highly soluble in water as opposed to the latter (Larjava, 1993 and references therein). Hence, while divalent Hg can be removed from flue gas using a wet scrubber, the recovery of elemental Hg is much more complicated. Hall et al. (1990) and Lindqvist and Schager (1990) tried to measure the Hg concentration on-line in flue gas by an Atomic Absorption Spectrometer (AAS). The concentrations of elemental and total Hg were measured separately, the difference between the two concentrations resulting from the presence of Hg(II). Elemental Hg was detected directly by AAS, while total Hg was measured by driving the flue gas through a tube, where an 20% $SnCl_2$ solution was delivered

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to meet the incoming gas. Thus, the divalent Hg was reduced upon contact with this reducing agent and the additionally formed elemental Hg was lead to the AAS detector.

In the present study a Semtech® analyzer, i.e., a portable commercial Zeeman modulated AAS, was employed on-line to monitor the concentration of Hg in a simulated flue gas. Initially, an improved version of Hall's method was applied to measure the total Hg content. Thus, the $SnCl_2$ solution was pumped to a sampling probe where the reducing solution and the flue gas met. The gas-liquid mixture was then carried concurrently by the gas through a teflon coil so as to increase the contact time and ensure the reduction of Hg(II). Below, this is often referred to as the "wet" method, since a chemical solution is used.

For on-line measurements, a physical "dry" method is usually preferred to a chemical wet one, due to the beneficial maintains properties of the former. Thus, according to a thermodynamic estimate (Larjava, 1993) $HgCl_2$ would be decomposed to its elemental form at temperatures greater than 800 °C in flue gas and combustion conditions. Based on this, a pyrolysis unit (thermal converter) was built in the present study. The converter consists of a quartz tube with different filling materials. Several materials such as molecular sieve, soda lime, boron carbide, boiling stones or quartz glass were tested as converter fillings. In particular, good results were obtained for a converter consisting of a quartz tube filled with smashed quartz glass chips (5-10 mesh) and some base-containing materials. The performance of such a converter for Hg(II) in the presence of HCl, SO_2, O_2 at different concentrations close to real industrial combustion levels was studied in the laboratory.

Below, results are presented for measurements of total and elemental Hg using both the dry thermal converter and the wet chemical solution in the laboratory and a combustion flue gas simulator, respectively. The advantages and practical limitations for both the wet and the dry methods will be discussed.

2. Experimental

2.1. ANALYTICAL INSTRUMENT

The commercial instrument Semtech® (Semtech metallurgy AB, Lund, Sweden) was chosen for this study. It is essentially a cold vapor atomic absorption spectrometer which uses a Hg lamp as a light source. By putting the lamp under a strong pulsed magnetic field, the wavelength is modulated by the Zeeman effect, which makes it possible to eliminate interfering absorptions that encompass the 253.7 nm line due to the presence of e.g. SO_2, hydrocarbons, particles etc (Bristow and Jonasson, 1972). This is the most outstanding feature of the instrument, since many combustion prosesses produce such pollutants. The lower detection limit so far is 2 $\mu g\ m^{-3}$ with an upper limit of 25 mg m^{-3}. These values depend on the length of the chosen absorption cell. The results of the measurements can be displayed directly in units of concentration on the digital screen of the instrument, and these data can also be collected by a personal computer through an RS232 interface for storage and further processing.

2.2. STANDARD $HgCl_2$ SOURCES

Mercury dichloride was chosen as the standard Hg source: it is an inorganic divalent Hg compound which has a relatively high vapor pressure; it is often a predominant Hg species formed in combustion processes. Gas phase $HgCl_2$ was generated by placing several grams of solid $HgCl_2$ in a temperature-regulated diffusion cell. Nitrogen gas was used to carry the Hg to the testing system. This system has been described in detail by Larjava (1993). Since $HgCl_2$ condenses on all available surfaces, a heating band is needed outside the themostated bath. A temperature of 90 °C was maintained by a thermostated oil bath and the flow rate of carrier gas was kept at 300 mL min^{-1} by using a mass flow regulator. It was necessary to purge the Hg-generating system with N_2 for at least one hour after the desired temperature was reached in order to obtain a stable Hg(II) concentration. The concentrations of Hg generated in this study were between 100 and 165 $\mu g\ m^{-3}$, controlled via the total flow rate of gases through the measuring system.

2.3. THERMAL CONVERTER

The thermal converters used for this investigation are similar to those described by Schroeder and Jackson (1985). Thus, quartz tubes with an inner diameter of 9 mm and a total length of 150 mm with 75 mm as the effective converter section were used initially. The efficiency of conversion at temperature > 650 °C was found to be around 100% when pure $HgCl_2$ was delivered to the converter. However, when other trace gases such as HCl and SO_2 were introduced into the testing system together with 6% O_2 in order to simulate a real combustion environment, the conversion efficiency dropped rapidly after 3-4 hours working time although it worked as good as in the pure $HgCl_2$ case at the first 2-3 hours. This would probably be due to the re-oxidation of Hg° by HCl and O_2, which would occur between the outlet of the converter and the analyzer, where the temperature drops from 900 °C to room temperature (Hall, 1992). In order to overcome this difficulty, a quartz tube of inner diameter of 18 mm was tried. In addition to the pure quartz chips, soda lime (Merck) was also filled into the tube at the outgoing end. The effective converter section length was still 75 mm but the total length was changed to 350 mm in order to make the system easier to handle (cf. Figure 1). $HgCl_2$ was now 100% converted to elemental Hg also in the presence of HCl and O_2. The reason for this is discussed below.

A furnace was built which can be heated to 1000°C by Nichrome wire. Insulating material was used to keep the temperature stable. The temperature was measured by a platinum thermocouple situated between the insulation layers.

2.4. THE EXPERIMENTAL SET-UP

Figure 1 illustrates the experimental set-up. The converter is located between the Hg source and the Semtech® instrument. It is necessary to have an ice bath between the converter and the analyzer in order to cool down the gas from several hundred degrees to room temperature and separate the moisture which might exist in the system.

To check the Hg concentration generated by the diffusion cell, so as to evaluate the efficiency of the converter and to calibrate the Semtech® instrument, the Swedish Standard (1992) method for flue gas Hg sampling was used. Thus, a wash bottle containing 100 ml solution of 6% $KMnO_4$ (w/v) and 1.8 M H_2SO_4 was connected to the gas generating system to sample the total concentration of Hg both before and after the converter. Mercury, thus collected in the $KMnO_4$ solution, was analysed by ordinary AAS equipment in the laboratory.

A gas distribution system was added to the testing line in order to deliver certain concentrations of trace gas similar to the concentrations produced in a real industrial combustion process. The total flow rate through the converter was around 1L min^{-1} in order to meet the requirement of the Semtech® instrument.

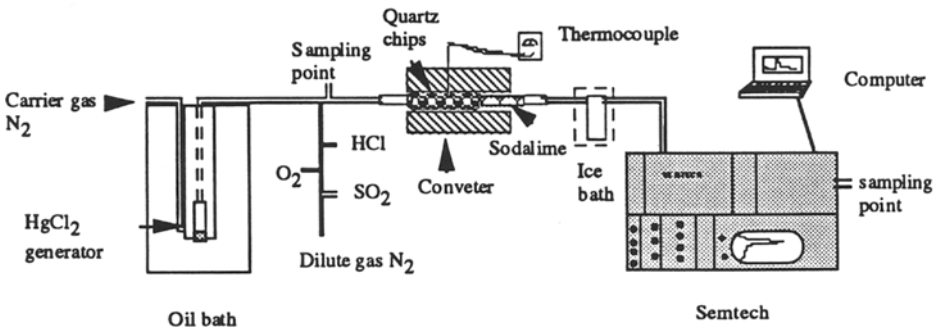

Fig. 1. The experimental set-up for on-line Hg measurements by the Semtech® instrument combined with a converter.

3. Results and Discussion

3.1. THE WET CHEMICAL METHOD

The wet chemical method was tested at a pilot scale flue gas generator with a maximum output of 17 kW and propane as fuel. Desired concentrations of Hg^0, O_2, SO_2 and HCl were supplied via the burner. The system has been described previously (Hall et. al., 1990). A Testo 33 Electrochemical Gas Analyser was connected to the system for measurement of the temperature inside and outside the duct, as well as the concentrations of O_2, SO_2, NO_x, CO and CO_2. These parameters can be read directly from the instrument and stored in a personal computer simultaneously.

All the samplings were done at the same location (having a temperature of about 280°C). The Hg concentration varied around 50-60 μg m^{-3} depending on the fuel/air ratio which was adjusted for other purposes. The results obtained with the wet chemical method are summarized in TABLE I.

Table I. Mercury concentrations (μg m^{-3}) measured with the Semtech® wet method and the standard Swedish $KMnO_4$ sampling method at different SO_2 and HCl concentrations.

Sampling occasion	Semtech® Hg°	Semtech® Hg_{tot}	$KMnO_4$ Hg_{tot}	SO_2 (ppm)	HCl (ppm)
930615-1	40.0	—*	51.6	0	0
930615-2	39.5	51.5	50.9	0	5
930615-4	46.0	58.0	60.9	0	10
930615-6	45.0	57.0	60.2	0	50
930610-4	57.0	74.5	—*	46	0
930610-6	70.0	63.5	—*	500	0
930611-1	48.9	23.8	—*	987	0
930609-2	47.0	37.5	—*	1081	50
930611-3	46.0	—*	—*	2500	0
930617-5	58.0	—*	—*	39	500

* No measurements were done.

In general, the Semtech® instrument is found to give quite stable and reliable results when elemental Hg is measured, even at quite high concentrations of SO_2 (2500 ppm) and HCl (500 ppm), as illustrated in Figure 2.

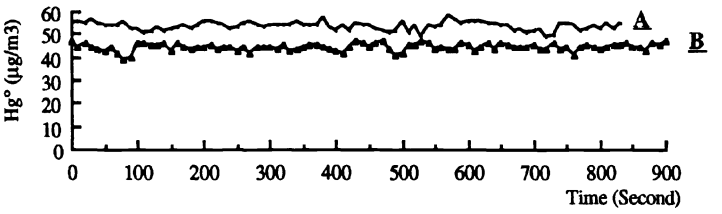

Fig. 2. Measurement of Hg° on the combustion flue gas simulator in the presence of A. 500 ppm HCl, B. 2500 ppm SO_2 (cf. 930611-3 and 930617-5 in Table I).

Some of the measurements of the Semtech® analyzer were confirmed by the standard Swedish $KMnO_4$ method for total Hg measurement, see Table I. As expected, no chemical interference by HCl on the Hg analyses is observed under these experimental conditions. Fairly good agreement was obtained between the Swedish standard and the Semtech for the measuring of total Hg when no SO_2 exists in the system. The results obtained in the presence of 46 ppm SO_2 are still reasonable, the elemental form making up about 80% of the total Hg content, which is similar to the no-SO_2 case.

At higher SO_2 concentrations though, unreasonable results were obtained as the total Hg concentrations were found to be lower than the concentration of elemental Hg, measured at the same

location and conditions(cf. Table I at SO2 concentration about 500-1000 ppm). A cause for this effect might be that $SnCl_2$ is consumed by reducing SO_2 to elemental sulphur or S^{2-}, since the reducing capacity of $SnCl_2$ is seen to drop rapidly with increase of SO_2. Still more important may be that Hg could be lost on the way to the measuring cell in the tubing and inside the cooler together with unknowm amount mingled in forms of HgS. Considering the relative low concentration of Hg measured, it can not be ruled out that Hg could also be lost in the exhausted reducing solution partly in the form of Hg^0, although the solubility of Hg^0 in water is low.

3.2. THE DRY METHOD

The dry converter method has until now only been tested in the laboratory. Gaseous $HgCl_2$ was generated as described in Section 2.2. Good converting efficiencies were achieved with quartz as the filling material for both the 8 and 18 mm inside diameter converters.

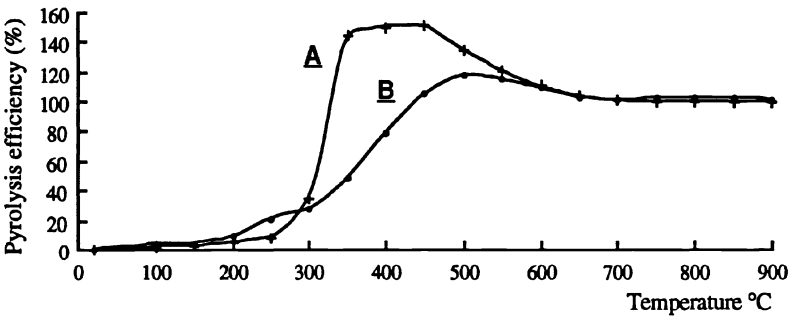

Fig. 3. Working efficiency of converters with quartz chips as filling material.. The internal diameter of the converter tube is 18 mm (A) and 8 mm (B)

From Figure 3 it can be seen that at temperatures above 600°C, both the 8 and 18 mm converters are capable of decomposing Hg(II) quantitatively, when pure $HgCl_2$ is driven through the converter. This is in agreement with the thermodynamic equilibrium calculations by Mojtahedi et al. (1987). The efficiency was also checked by the Swedish Standard (1992) method for sampling and measuring Hg in flue gas. Over 100% converting efficiency was observed at certain temperature ranges. This was due to the contribution of Hg(II) which had previously condensed inside the converter or on the tube surface at lower temperature. One half hour or one hour heating time was generally needed for the 8 mm and the 18 mm converter respectively, to reach a temperature over 600°C due to the different constructions of the ovens used and the different masses of quartz chips involved. However, all the experiments done during this study were conducted at 850 to 900 °C and the performance experiments were started at least one hour after the converter reached the 100% conversion level.

Other filling materials were also tested, such as molecular sieve, boiling stones, soda lime and boron carbide. In all cases the converting efficiencies decreased with performance time. This was probably

due to volume shrinkage and/or change of structure after baking at the elevated temperature resulting in poor packing in the quartz tube, thus allowing for some Hg(II) to pass. Since the quartz filling converter gave quite stable results still after about 1'oo hours of testing, no additional efforts have been made to improve on the efficiencies of the other materials. In what follows, the extensive testing was focused on the converter filled with quartz only.

During the processes of fossil fuel and municipal solid waste burning, raw materials with different chemical compositions are used, and a great variety of products are formed. Some of them react readily with Hg, as for example SO_2 , HCl and O_2. Typical concentrations of these gases in coal combustion are 4-10 % O_2, 100-1000 ppm SO_2 and 1-100 ppm HCl, while the corresponding concentrations in waste incineration are 6-15%, 100-300 ppm and 400-1000 ppm (Hall, 1992). In order to draw conclusions as to the applicability of a converter to real industrial processes, similar concentrations of these three gases were delivered to the converter. By misjudging the flow rate of the HCl to the system once, 12,000 ppm HCl was delivered to a converter, and the converting efficiency for Hg(II) was sustained for hours, which implies that no reaction between Hg° and HCl occurs, at least under the conditions selected for this study (Figure 4 A.). The test results for the relevant concentrations are shown in Figure 4 B.

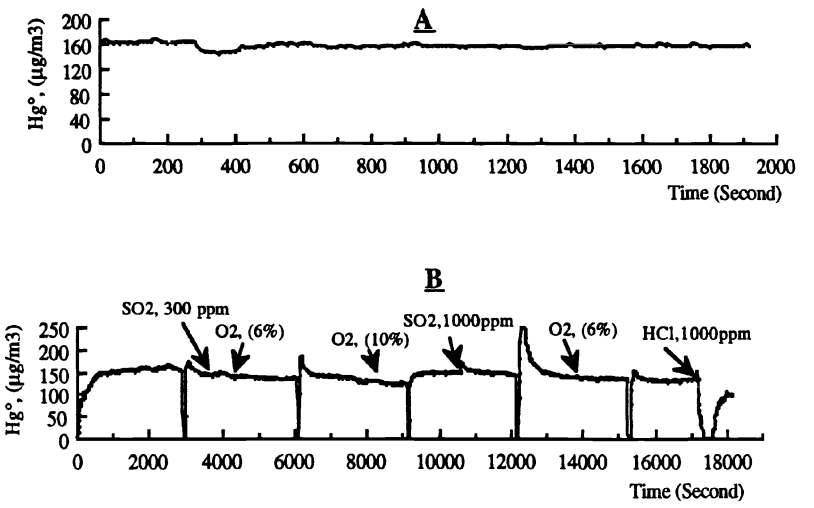

Fig. 4. The influence of HCl, SO_2, and O_2 on the performance of a thermal converter with pure quartz chips as filling material: A. HCl = 12,000 ppm; B. O_2= 6-10 %, SO_2= 300-1000 ppm, HCl= 1000 ppm. The sudden decreasing of the Hg concentration to zero in Fig. 4B. is caused by the hourly auto-zero function of the instrument (the same for Figure 5, below).

It is evident from Figure 4B that additions of O_2 and /or SO_2 to the $HgCl_2$ containing gas does not significantly change the converter efficiency. The 100% conversion efficiency was checked by the Swedish Standard (1992) method and the small variations that appear in Figure 4B are due to difficulties in keeping

the flow rate constant when the gas constituents were varied. However, addition of HCl kills the converter effect, which is discussed below.

SO_2 was reported to reduce Hg(II) under certain conditions both in gas and aqueous phases (Munthe et al., 1991). No increase of elemental Hg concentration was observed when 300 ppm SO_2 was introduced to the system, which indicates that the converter pyrolyses Hg(II) quantitatively in the testing system.

When 1000 ppm HCl was added to the system, the efficiency of the converter dropped rapidly. This is probably due to the re-oxidation of elemental mercury between the outlet of the converter and the Semtech® detector, where the temperature decreases from 900 °C to room temperature. The Equation (1) used by Hall (1992) to describe the re-oxidation reaction is very rapid at about 500 °C.

$$2Hg°(g) + 4HCl\ (g) + O_2\ (g) <=> 2HgCl_2\ (g, s) + 2H_2O\ (g) \qquad (1)$$

The converter efficiency started to recover after cutting off the HCl supply to the system, as can be seen from the last part of Figure 4B. A perfect filling material would therefore be one that not only can decompose the Hg(II) to Hg°, but can also be capable of eliminating HCl; therefore, base-containing material seems to be a suitable candidate.

On one occasion a converter was built with a filling of quartz chips treated by NaOH solution. It worked perfectly as expected. However, after using it for less than two days, the quartz tube was destroyed by the strong base at the high temperature. On another occasion, a small amount of soda lime (about 2 g) was put inside the quartz tube at the gas outlet end, the body being filled with ordinary quartz chips. The main composition of the commercial soda lime (Merck product) used for this study was $Ca(OH)_2$ (60-80%) and NaOH (5-20%) together with some additives and water (Cooper, 1994). Although the absorption efficiency of soda lime for HCl may not be efficient enough (Cooper, 1994), the converter built in this way gave a very good performance as illustrated in Figure 5.

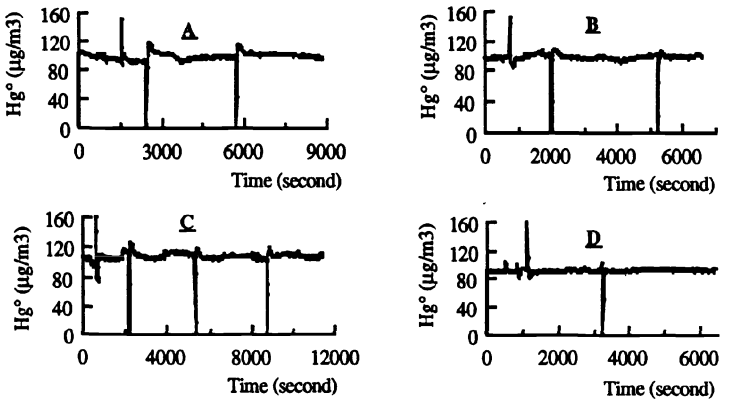

Figure 5. Working efficiency of a converter filled with quartz chips and about 2 g soda lime. A. O_2=6%, SO_2=300 ppm, HCl=100 ppm; B. O_2=10%, SO_2=300 ppm, HCl=100 ppm; C. O_2=10%, SO_2=100 ppm, HCl=500 ppm; D. O_2=10%, SO_2=1000 ppm, HCl=100 ppm. The sudden increasing of Hg concentration is caused by the flow rate variation when testing gases were delivered to the system.

The results are quite promising, since the concentration combinations chosen for the three gases are similar to those in flue gases emitted from real combustion processes.

When NaOH treated quartz chips or soda lime or Na_2CO_3 are involved in the converter, the following three overall reactions might occur, by which not only HCl but also SO_2 are eliminated from the system at the same time :

$$4NaOH(s)+2HCl(g)+SO_2(g)+1/2O_2(g)<=>Na_2SO_4(s)+2NaCl(s)+3H_2O(g) \quad (2)$$

$$2Ca(OH)_2(s)+2HCl(g)+SO_2(g)+1/2O_2(g)<=>CaSO_4(s)+CaCl_2(s)+3H_2O(g) \quad (3)$$

$$2Na_2CO_3(s)+2HCl(g)+SO_2(g)+1/2O_2(g)<=>Na_2SO_4(s)+2NaCl(s)+2CO_2(g)+H_2O(g) \quad (4)$$

According to Equation (1) all of these reactions should improve the overall conversion efficiency.

The influence of the converter diameter on the conversion efficiency of Hg(II) to Hg° was noticed by Cooper (1994). It was observed that the performance time increased when the 18 mm diameter converter was employed instead of the 8 mm one. This may be due to the greater amount of quartz chips in the former. Hence, only the 18 mm converter was employed in our investigations.

Freshly crushed quartz chips were found to perform much better than aged ones, both with respect to the ability to endure high concentration of HCl and to the working life time. Also, the efficiency and functional life-time dropped when the converter was used repeatedly. The cause for this is possibly the presence of irreversible surface reactions, which result in the decrease of the ability to eliminate HCl, SO_2 and O_2 from the system. The working efficiency can be partly recovered by removing the quartz chips from the tube and soaking them in strong nitric acid or aqua-regia solution overnight. After this, they are rinsed thoroughly with Milli-Q water, dried in oven and packed into the tube again. This was done daily during this investigation. However, the effective working hours of the converter decreased after each treatment, from ten or more hours down to 2-3 hours.

In some critical cases when both HCl and SO_2 was present at elevated concentrations, the effective working time of the converter dropped to two hours. The working time can be restored by mixing about 1 g Na_2CO_3 with the soda lime inside the converter. As in the case when the quartz filling was treated with NaOH, the base was found to damage the quartz tube at elevated temperatures, although not to the same extent. A limiting factor for such a converter is the performance time, which is approximately 30 hours.

Improved materials that can be used to build converters and can stand high temperatures at basic conditions are needed. Ceramic products based on Al_2O_3 or MgO are possible candidates. In the future we plan to investigate the properties of such materials for making converters and their possible usefulness in the measuring of Hg speciation in flue gases.

4. Conclusion

On-line measurement of elemental mercury in flue gas can be performed by the Semtech® instrument even under extreme conditions, e.g. with concentrations of SO_2 and HCl of up to 2500 ppm and 500 ppm, respectively. The typical concentration of SO_2 would be well below 1000 ppm for most fossil fuel burning processes.

A wet and a dry method to measure the amount of total Hg in the flue gas were tested. Both methods are based on the conversion of Hg(II) to Hg°. The wet method was found to be suitable only when the SO_2 concentration in flue gas is low, at 50 ppm for example. The dry converter works properly in the laboratory in the presence of SO_2, HCl and O_2 at concentrations close to those in industrial combustion flue gas. The working life-time of a quartz tube is a main limiting factor for its application under the conditions described.

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ATMOSPHERIC MERCURY MEASUREMENTS IN THE NORTHERN HEMISPHERE FROM 56° TO 82.5° N LATITUDE

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Abstract. Sampling of total gaseous mercury (TGM) in air was initiated at Alert, Northwest Territories, Canada (82.5°N;62.3°W) by Atmospheric Environment Service (AES) staff during August 1992 on an exploratory basis for a year. TGM was pre-concentrated onto traps (2 in series) containing Au-coated quartz sand for sampling periods of 1 (or more) week(s) at flow-rates of 30 - 50 mL/min. During the first winter cruise of the RV "POLARSTERN" from Germany (56°N) to the Nordic Seas, and at an ice-camp (81°N;5°E) in the Arctic, simultaneous samples of TGM and aerosol black carbon ("soot") were collected, from February to April 1993, by the GKSS group. The analytical methods for TGM determinations (2-stage gold amalgamation/thermal desorption, followed by cold-vapor atomic fluorescence spectroscopy) were essentially the same for both studies. Experimental details, results, and conclusions are presented and discussed.

1. Introduction

During the latter decades of the 20th Century, the perception of the importance of mercury (Hg) as an environmental contaminant has assumed increasingly broad dimensions. The scientific perspective has shifted from regarding Hg primarily as a local or regional problem (e.g., Minamata Bay and Niigata, Japan; Lake St. Clair, both on the Canadian and American sides; Lake Onondaga, New York State; the English-Wabigoon River system, Northwestern Ontario), to one of national significance (e.g., NAS,1978; NRCC,1979; SNV,1984), before arriving at the realization that Hg -- like a number of other persistent, volatile industrial chemicals -- displays all the characteristics of a global pollutant (Nriagu and Pacyna, 1988; Dick *et al.*, 1990; Fitzgerald, 1993; de Mora *et al.*, 1993; International Mercury Conference, 1994; Mackay *et al.*, this volume).

Scientific evidence now accumulating suggests that the concentration of Hg in the troposphere may be increasing (Nriagu and Pacyna, 1988; Slemr and Langer, 1992). Furthermore, rates of atmospheric Hg deposition have increased over large areas of Scandinavia and North America at least since the beginning of this century (Pheiffer-Madsen, 1981; Evans, 1986; Verta *et al.*, 1989; Jensen and Jensen, 1991; Swain *et al.*, 1992). Both lines of evidence point to the important role played by the atmosphere in the overall multi-media biogeochemical cycling of Hg in the environment (Lindqvist and Schroeder, 1989; Schroeder *et al.*, 1989). The residence time of gaseous mercury (predominantly Hg^0) in the lower atmosphere is thought to be about 1 year (Slemr *et al.*, 1985; Lindqvist and Rodhe, 1985). Thus, gaseous Hg should exhibit fairly uniform air concentrations at locations away from major anthropogenic or natural sources. A location such as Alert (NWT), the most northerly settlement in the world, should thus provide a good site for determining typical background concentrations for Hg in the lower troposphere (at least for the northern hemisphere). An international scientific study (Barrie, 1993) staged at Alert in 1992, presented an opportunity for the Canadian authors of this paper to initiate an exploratory set of atmospheric Hg measurements so as to determine, for the first time, representative values of TGM air concentrations in the Canadian Arctic environment.

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During the first winter cruise of the German research vessel "POLARSTERN" from Bremerhaven, Germany, to the northern Greenland Sea/Fram Strait and at an ice-camp ($81^{\circ}N;5^{\circ}E$), simultaneous samples of TGM and aerosol black carbon were collected by GKSS Research Centre personnel. The field campaign (February to April 1993), can be divided into the passage from 56° to $81^{\circ}N$ and the stationary phase at the ice-camp. Because soot particle and atmospheric ozone concentrations are important input parameters to a European long-range transport model for Hg developed by GKSS Research Centre scientists (Petersen *et al.*, 1994) they were measured, along with TGM, during the ship's cruise and at the ice-camp.

2. Methodology

2.1. SAMPLING

At Alert, sampling for airborne Hg was performed over a period of 1 year (Aug. 17, 1992 -Aug. 23, 1993). The equipment was located inside and on the roof of the 'Special Studies Laboratory' trailer situated about 6km south of the main base. A diagram of the essential components of the sampling train is given in Figure 1. At the front end are located 2 sequential quartz wool (QW) traps (Brooks-Rand Ltd.,Seattle,WA) housed inside PVC pipe for protection. This assembly was mounted on the roof of the trailer. It removed (under ambient conditions!) aerosols -- including particulate-phase mercury, PPM -- from the air stream. After entering the trailer, the incoming air was split into 2 streams (for replication/quality control of measurement results). Each stream passed through 2 vapor-phase Hg traps arranged in tandem. Each trap (Brooks-Rand Ltd., Seattle, WA) consists of a quartz tube containing a section of gold-coated quartz sand held in place by a fine quartz frit at one end and a QW plug at the other (upstream) end. The gaseous mercury species retained ("amalgamated") on these traps are operationally defined as constituting 'total gaseous mercury'. At flow-rates <0.5 L/min and sample volumes $< \sim 0.5\ m^3$, their collection efficiency is generally ~90% or more. Further downstream are two guard traps of similar construction (to prevent contamination of sample back-up traps in the event of failure of the sampling pump(s) or power outages). The flow-rate

Fig. 1. Components of sampling train used at Alert

of air in each stream is controlled by a needle valve and metered through a transducer coupled to a mass flow-meter with a built-in totalizer (Teledyne Hastings-Raydist; Hampton, VA) which provides the total volume of air sampled at standard conditions (0°C;1 atm). Figure 2 shows that, at least under the conditions prevailing at Alert, collection of samples with total volumes $> \sim 0.5$ m^3 may result in artificially low TGM air concentrations. Brosset and Iverfeldt (1989) reported a similar phenomenon for TGM sampling at a rural site on the west coast of Sweden. Reasons for this sampling artifact are not (yet) entirely clear.

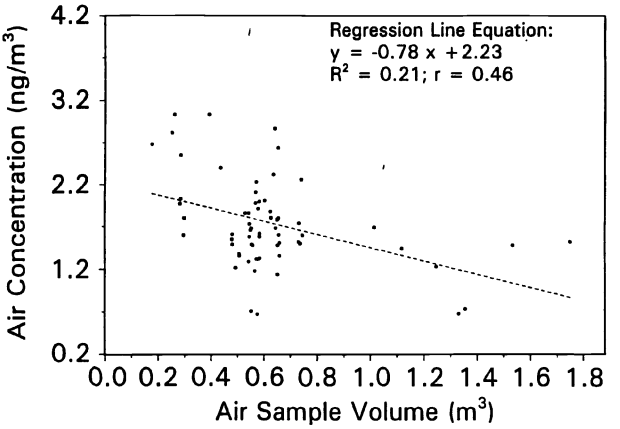

Fig. 2. Influence of air sample volume on [TGM] determined

During the "POLARSTERN" experiment, TGM was collected on gold-coated glass beads (see Figure 3). Ambient air was sucked through a 0.5 cm QW plug (to retain particle-bound Hg) before it entered the vapor-phase Hg traps. Approximately 400 L of air were collected at different flow-rates: during the passage to the ice-camp and back to Bremerhaven the flow-rate was about 5 L/min to enable short sampling periods (high spatial/temporal resolution), whereas at the ice-camp the air was collected at flow-rates of approximately 0.5 L/min because of the ship's stationary position.

2.2. ANALYSIS

For the Alert measurements, all samples and field/travel blanks were transported by air between CFB Trenton (near Belleville, Ontario) and Alert, and by passenger vehicle between CFB Trenton and the AES laboratories in Downsview where they were analyzed. The time between sampling and analysis was generally more than a week. TGM was determined by a procedure involving dual gold-amalgamation/thermal release, and detection by cold-vapor atomic fluorescence (CVAFS) similar to a method reported by Fitzgerald and Gill (1979). Our analytical train was automated by using Labtech Notebook software (Laboratory Technologies Corp.; Wilmington, MA) and importing the detector output into a 'Quattro-Pro' spreadsheet (Borland International,Inc.; Scotts Valley, CA). The instrument was calibrated several times each day by injecting saturated Hg^0 vapor standards using a gas-tight syringe. At each calibration point, injections were repeated until 3 successive results were within 3% of each other.

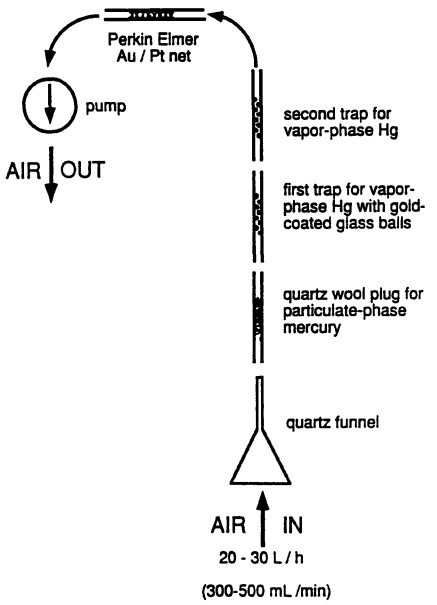

Fig. 3. Schematic of sampling train used on RV "POLARSTERN"

Analysis of the "POLARSTERN" samples was carried out at the GKSS Research Centre using CVAFS and a 2-step amalgamation technique wherein the Hg on the "field trap" (gold-coated glass beads) is transferred to an "analytical trap" (commercially available Au/Pt gauze). Calibration was performed in a manner similar to that described above. Soot was determined with an aethalometer (flow rate of ~17 L/min and a time base period of 30 min) based on the strong optically absorbing properties of soot particles. The PC-operated aethalometer measures the attenuation of a light beam transmitted through a quartz fiber filter, while aerosol samples are continuously collected. The attenuation is proportional to the mass of soot on the filter.

2.3. QUALITY ASSURANCE/CONTROL

All facets of the measurement program at Alert were designed with QA/QC in mind. Two traps (in series) were used for TGM collection to check on and take into account break-through from the first trap. Immediately after installation of a new set of traps, a leak check of the entire sampling system was performed by capping the inlet side of the first QW trap with a Teflon plug, starting the sampling pumps, and ensuring that a zero flow reading was registered by the mass flow-meters. This step is important because of the high resistance to air flow (large pressure drop) inherent in the Brooks-Rand Ltd. sample traps. After sampling, the traps were capped with tight-fitting Teflon plugs and kept inside sealed plastic tubes. Field blanks were treated exactly the same as sample traps except that no air was pulled through them. At least 1 out of every 10 traps was a field blank and each shipment of traps contained at least 2 blanks. Because it was not always possible to analyze samples immediately upon their arrival at the analytical laboratory, laboratory (storage) blanks were also determined (see TABLE I).

TABLE I. Statistical summary of operational blanks

BLANK TYPE	N[a]	MEAN VALUE (pg Hg)	STD. DEV. (pg Hg)	MEDIAN (pg Hg)	RANGE[b] (pg Hg)
Field	58	32	18	36	3 - 75
Lab.	121	45	49	29	4 - 270

a: number of determinations; b: values > 75 pg Hg indicate analytical problems or contamination in the laboratory

The CVAFS detector was calibrated (using the analytical trap) 4 times a day (twice in the morning; twice in the afternoon) and each sample or blank trap was desorbed twice. The volumes (microliter range) of gaseous Hg^0 standards injected into each trap for calibration purposes were adjusted to match the instrument response obtained for the sample, blank or spike. Recovery of analyte from sample and blank traps was checked regularly. Quality control check procedures were also routinely performed at all stages of field and laboratory data collection, handling, processing, and reporting.

Before departure of the German research vessel, sample volumes of 400 L and flow rates of 0.5 to 5 L/min were tested in the GKSS laboratories with respect to break-through and collection efficiency of Hg. Analysis of TGM on board the "POLARSTERN" was not possible. Thus, after sampling was finished, each trap was sealed with plastic caps and stored in a firmly closed glass container. To prevent contamination during storage, 10 g of silver wool were kept in the container (to bind gaseous Hg). In addition, "control samples" were obtained by using traps treated the same way as the samples, but not exposed to air. Analysis of these traps gave mean blank values of approximately 35 pg Hg (with n = 6). Consequently, contamination of samples/blanks during handling and storage was of minor importance.

3. Results and Discussion

Figure 4 depicts weekly-integrated TGM air concentrations during the 1-year time-series of our measurements at Alert. The frequency distribution of these data is shown in Figure 5. It has the characteristic shape of a log-normal rather than a Gaussian distribution. A statistical summary of the atmospheric Hg measurement results from this site is found in TABLE II. At Alert, the lowest TGM value (0.67 ng/m^3) was about one-half of the lowest value recorded for a series of atmospheric mercury measurements in the Great Lakes Basin near Lake Ontario during 1990 (Schroeder, 1994; Schroeder and Markes, 1994). Whereas the latter field measurement results spanned a 10-fold concentration range (1.3 - 13 ng/m^3), the Arctic data range is only about 4-fold (0.7 to 2.8 ng/m^3). At Egbert, Ontario (Schroeder, 1994) the median value and the geometric mean were 2.9 and 3.2 ng/m^3, respectively, but they were only 1.5 and 1.4 ng/m^3 at Alert.

Another noteworthy feature of the data set from Alert is evident from Figure 6 which shows the TGM concentration as a function of the average ambient air temperature during the various sampling periods. The regression line indicates a decrease in the TGM content of ambient air with decreasing temperature. This weak temperature dependence of atmospheric TGM concentrations is similar to the behavior found for hexachlorobenzene in the Arctic (T. Bidleman, Personal Communications, AES, Downsview, Ont., 1994). Possible explanations for this observed phenomenon include: a gradual shift in the gas/particle (or "frozen liquid") phase partitioning of Hg in ambient air (favoring the more condensed phase at lower temperatures);

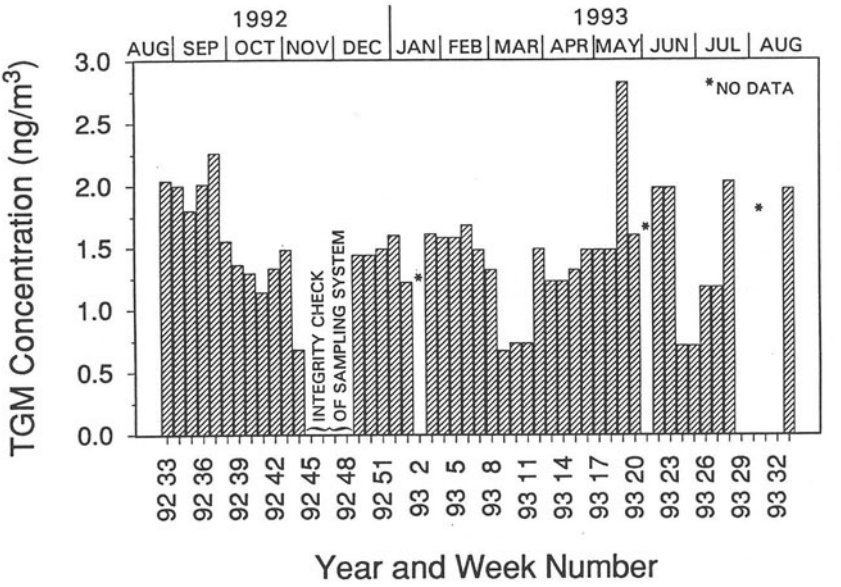

Fig. 4. Weekly average TGM concentrations at Alert (Aug. 1992 - Aug. 1993)

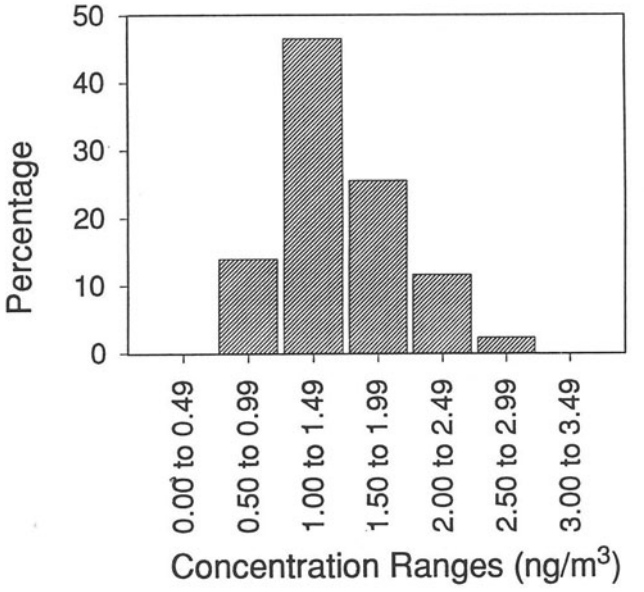

Fig. 5. Frequency distribution of TGM air concentrations at Alert

TABLE II. Statistical summary of measurement results

Ave.% of TGM collected on the front trap	89%
Ave.% difference in results from 2 streams	5.7%
Arithmetic mean ± std. dev. of TGM samples	1.47±0.46 ng/m^3
Geometric mean ± std. dev. of TGM samples	1.40±0.35 ng/m^3
Median value for TGM sample population	1.48 ng/m^3
Range of values for TGM measurements	0.67-2.82 ng/m^3

differences in the atmospheric transport/circulation patterns during warmer and colder seasons/times of the year; the influence of temperature on the rate of (re-)emission/ volatilization (source strength) of Hg from natural surfaces (e.g., snow/ice, water, vegetation, soil/tundra/permafrost) in the Arctic environment; increasing efficiency of removal (dry deposition) of Hg at ground level (to snow/ ice surfaces) as the temperature declines, thus resulting in progressive depletion of Hg in the atmospheric boundary layer. Further work is planned regarding this phenomenon. A similar observation was made during the "POLARSTERN" experiment at the ice-camp. The data are shown in Figure 7. Although the number of data points is smaller compared to the results from Alert, the same tendency is evident. An interesting observation made at the ice-camp was the positive correlation of soot with TGM (see Figure 8). Near anthropogenic emission sources (e.g., coal-burning power plants) this correlation might have been expected. However, at the ice-camp it was surprising and should be verified by future experiments.

During the passage from northern Germany to the ice-camp and back, a negative correlation of atmospheric mercury concentrations with degrees of latitude was observed (see Figure 9). This can be explained by: (i) the distance of the sampling location to source regions in central Europe and/or; (ii) the change in air temperature during the cruise. The lowest TGM concentration, namely 0.2 ng/m^3, was detected at the ice-camp at -40°C. The frequency distribution

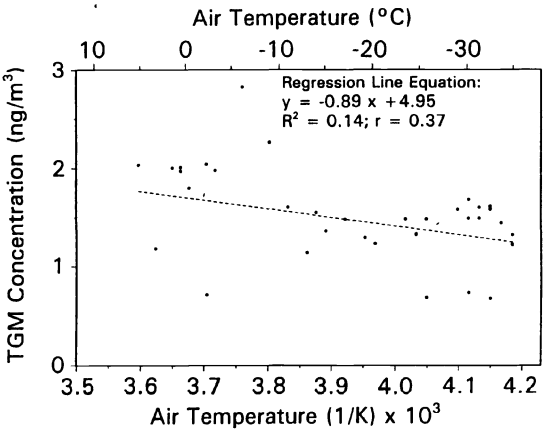

Fig. 6. Correlation of TGM concentration and air temperature at Alert

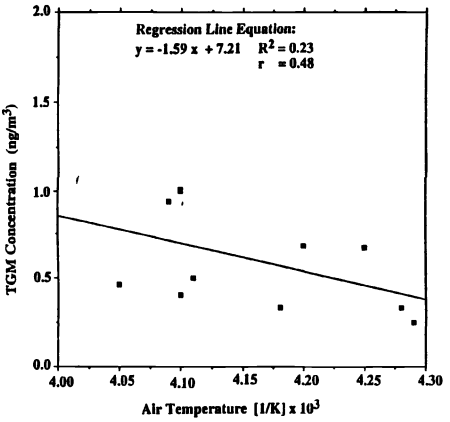

Fig. 7. Correlation of TGM concentration and air temperature during the "POLARSTERN" experiment

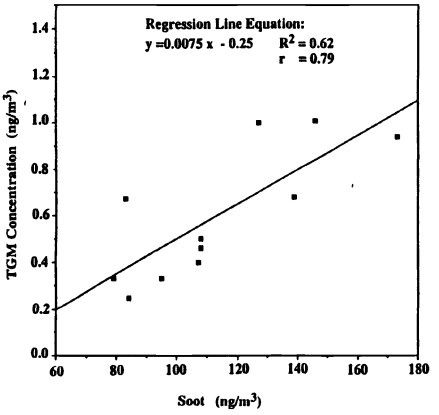

Fig. 8. Correlation of TGM concentration and soot during the "POLARSTERN" experiment

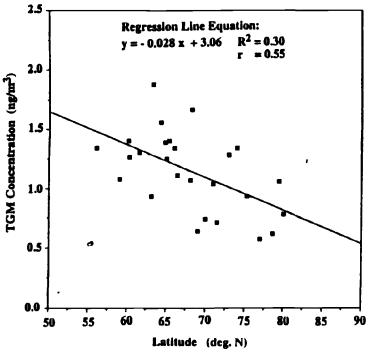

Fig. 9. (Anti-)correlation of TGM concentration and degree latitude (North)

of TGM measurements made at the ice-camp is log-normal and > 90% of the TGM concentrations were below 1 ng/m^3. However, the frequency distribution during passage to the camp has more of a normal ("Bell curve") distribution, with a maximum between 1.2 and 1.7 ng/m^3, which is comparable to values found by GKSS scientists during a North Sea cruise in 1991. The TGM frequency distributions during the "POLARSTERN" experiment are shown in Figure 10.

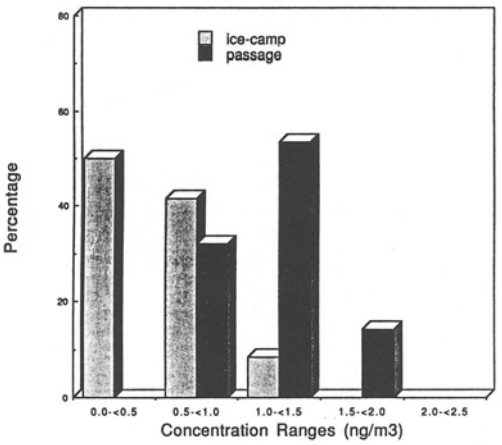

Fig 10 Frequency distributions of TGM concentration during the "POLARSTERN" experiment

4. Summary and Conclusions

Sampling of TGM in air at Alert, NWT, Canada was initiated by AES staff during August 1992 on an exploratory basis for one year. Collection of TGM, defined operationally as consisting of elemental mercury vapor as well as volatile organic and inorganic Hg species, involved preconcentration (at room temperature) onto gold-coated quartz sand traps (2 in series) for periods of one (or several) week(s). Major features of the time-series of TGM measurements in air at Alert include: a log-normal frequency distribution; an anti-correlation ("weak") of air concentrations with ambient temperatures; an arithmetic mean and standard deviation of 1.47 ± 0.46 ng/m^3 respectively; geometric mean = 1.40 and median = 1.48 ng/m^3; a range of values from 0.67 to 2.82 ng/m^3.

During the first winter cruise of the RV "POLARSTERN" from Germany to the Nordic Seas and at an ice-camp in the Arctic, simultaneous samples of TGM and soot were collected from February to April 1993. At the ice-camp, ~65% of the TGM concentrations were between 0.2 to 0.7 ng/m^3, with the lowest value detected at -40°C. During the voyage to the camp, the values showed a more "normal" distribution with a maximum between 1.0 and 1.5 ng/m^3. Statistical evaluation of these results indicate a positive correlation of TGM with soot concentration at the ice-camp and a negative correlation of atmospheric mercury concentration with the degree of latitude during the cruise.

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Hydride Generation ICP-MS (HG-ICP-MS) for the Ultra LowLevel Determination of Mercury in Biota

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Abstract. Inductively coupled plasma mass spectrometry (ICPMS) utilizing both hydride generation and conventional nebulization as methods for sample introduction, has been applied to the analysis of Hg in urine and biota at sub μg/g (solid) and sub ng/g (liquid) levels. Concentrations in certified reference materials were determined by standard addition, and isotope ratio measurements were performed to evaluate the potential for applying the methods of isotope dilution mass spectrometry (IDMS) in this area.

1. Introduction

The requirement for the determination of Hg in environmental samples and biological materials is constantly in evidence. The ultimate target is to determine its level of bioavailability and its influence on human health, this requires its determination in various matrices to establish source and pathways to its final point of deposition in biota.

The most widely used techniques for the determination of Hg at low concentration levels are cold vapor atomic absorption and the dithizone/spectrophotometry method (Chou and Naleway,1984; APHA,1989;Koirtyohamn and Khaill,1979). Both of these methods provide admirable levels of sensitivity and precision; however, questions always remain on absolute recovery of mercury during real sample preparation procedures and the ever present possibility of unexpected interferences. Normally these procedures require a series of chemical pretreatments, rendering them a lengthy and labor intensive exercise.

In order to provide other reference methods we have investigated ICP-Mass Spectrometry using two different types of sample input to the plasma of the mass spectrometer source; conventional liquid nebulization, and hydride generation. We will discuss and compare the relative merits of the two types of inlet, and the potential advantages of mass spectrometry as the analyzer/detector mechanism. It is noteworthy that an immediate benefit with this type of analysis is that the sample preparation for tissue specimens only requires a one step process of digestion in nitric acid.

2. Methods

We will provide only a brief description of the principle of ICP-Mass Spectrometry since this is now a well established technique used in environmental and biological materials analysis (Schmit *et al.*,1991; Gray,1986; Hutton and Eaton, 1986). The instruments used in our work were a Plasmaquad Type PQ2 PLUS manufactured by Fisons (VG)

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Elemental (UK) and a TS SOLA ICPMS manufactured by FINNIGAN MAT. Whilst the sample introduction and ion generation procedure are identical for both machines, the ion extraction and ion optics are of different design in that there is no photon stop in the TS SOLA, and the extraction lens has been replaced by an extraction cone in the latter. A consequence of this is that mass bias effects have been minimized (Turner,1993). To illustrate the operating principles of ICP-MS with conventional solutions nebulization, the source region schematic for the SOLA ICPMS is shown in Figure 1

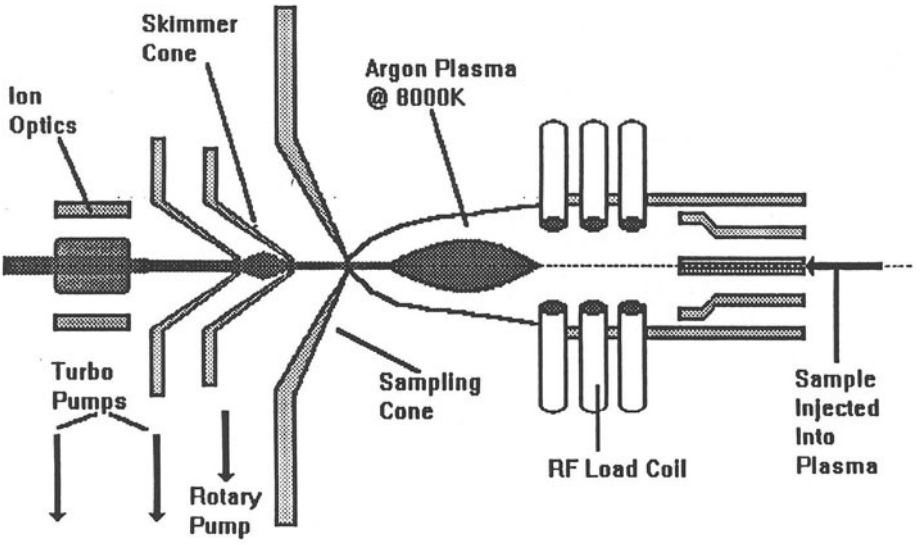

Fig. 1. Schematic diagram of an ICPMS ion source region.

2.1 Sample Handling and Introduction By Pneumatic Nebulization

Prior to analysis, samples were digested in precleaned teflon high pressure digestion vessels, using high purity nitric acid(Seastar). For ICPMS analysis, liquid samples are introduced through a peristaltic pump to a nebulizer, which produces a very fine "fog" within a spray chamber. The sample "fog" is carried into the central injector of a quartz plasma torch by a stream of argon gas to the high temperature plasma where the elements transported are desolvated and vaporized. Dissociation is virtually complete during transit through the plasma core and elements with a first ionization energy less than 10 eV are fully ionized.

2.2 Operating Principles

Ions are extracted from the central channel of the plasma at the sampling interface consisting of a 1 mm aperture in a water cooled cone. The ions are transmitted through the reduced pressure stage behind the sampling interface, through a second cone, referred to as a skimmer and into an ion lens region, which operates at further reduced pressure. The ion lens causes the focused and energy corrected ion beam to pass into the quadrupole mass filter where the ions are separated according to their mass to charge ratio, m/e.

All the separated ion species may be detected sequentially by a continuous dynode channeltron detector placed at the exit to the mass filter; this is accomplished by scanning the mass range from lithium at m/e 6 through uranium at m/e 238. The scan process is controlled by varying the radio frequency voltage applied to rods within the quadrupole mass filter. The pulses of ions are amplified and accumulated in a high capacity multi-channel analyzer/scaler then subsequently processed by a microcomputer. Alternatively a more rapid method of scanning involves "peak jumping", where the quadrupole voltage switches between selected masses in a stepwise fashion, allowing a set number of channels per peak. This allows very fast acquisition and minimizes contamination and carry over effects for high concentration samples.
In summary, ICPMS provides a most cost efficient means to establish the maximum amount of information, (even isotopic information) on a wide range of previously uncharacterized samples. At the same time providing the most sensitive means to determine the concentration of selected elements with the highest level of quantitation.

3. Results and Discussions

Conventional inlet ICPMS has intrinsic high sensitivity and provides limits of detection which equal or exceed those obtained by either Cold Vapour AA or Atomic Fluorescence. However, it is evident that memory problems occur when samples containing high concentrations of Hg are run in a sequence followed by low concentration samples. Sensitivity may also be compromised by the dilution factor involved when solid samples are digested.

On the positive side, mass spectrometry also provides isotopic information, which assists in two ways:
(a) Corroboration that the analyte spectra are not interfered, accomplished by isotopic abundance measurements.
(b)The ability to carry out isotopic analyses facilitates the use of isotopic dilution, a benchmark method used by NIST in certification of primary standards (Fasset and Paulsen,1989). This method has the advantage that total recovery of the analyte Hg is not mandatory as long as chemical/physical equilibration of the indigenous Hg, and the isotopic spike is achieved. The principle of the method is explained by the following equation,

$$C_x=(\frac{C_s.W_s}{W_x}).(\frac{A_s-R_m.B_s}{R_m.B_x-A_x}) \quad (1)$$

where C, W, A, B, and R are the elemental concentration, weight,atom fraction of isotope A, atom fraction of isotope B, and measured isotope ratio A/B respectively. The subscripts x, s refer to the sample and isotopically enriched spike. It is evident that the basis of the method relies upon the ability to measure isotopic ratios in an unspiked sample and an isotopically spiked sample to allow an accurate determination of the original concentration of the indigenous Hg.

3.1 Hydride Generation/Reduction and Sample Introduction

The potential problem of carry-over between samples is obviated to a great extent through the use of hydride reduction separation of Hg from the matrix for subsequent transfer and analysis of the separated gaseous phase Hg analyte. As a consequence, solutions with much higher dissolved solid content than that allowed by conventional nebulization may be analysed by this method. The modified spray chamber inlet used as a gas liquid separator is shown in Figure 2.

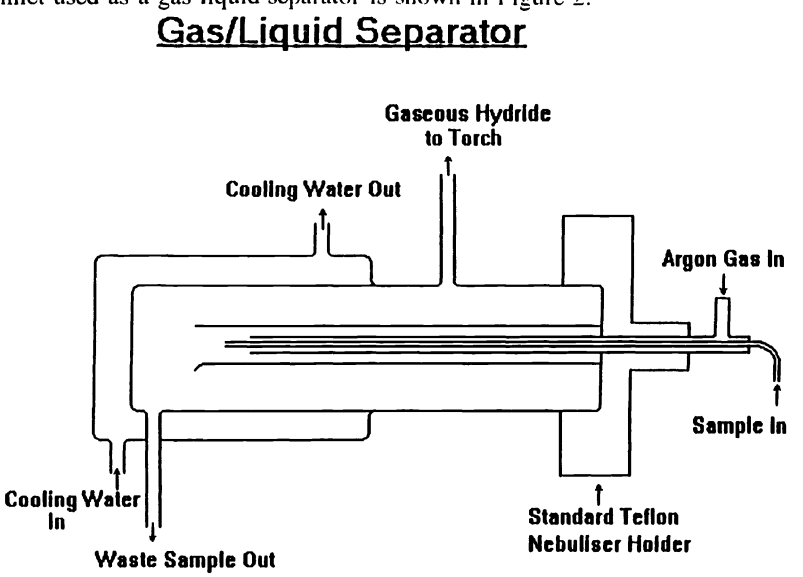

Fig. 2. Sample inlet system for hydride generation ICPMS.

It is important to carry out gas/liquid separation as close as possible to the high temperature plasma ionization source to minimize the potential for "plate out" of the Hg between separation and ionization. Consequently the chamber is mounted immediately before the torch using only a short gas transmission elbow connection. The nebulizer is

the conventional liquid analysis system has been replaced by a teflon capillary mounted in a glass support tube. The mixed solutions of sample and sodium borohydride reductant pass through the tube and the mixture drips from the capillary into the chamber wall where separation occurs. The Hg in the gaseous phase is swept on a stream of argon to the central injector of the plasma torch. The waste sodium borohydride and sample matrix are pumped out of the lower drain.

3.2 Applications

The hydride generation method has been applied to the analysis of digested urine from pregnant women to study the availability of Hg from dental fillings, and the potential influence on the fetus. Figure 3 and Table I provide information on regression analysis of standard additions of Hg to urine. The linear response for the analysis was good yielding an LOD for Hg in urine of 100 ng/L, and an LOQ near to 400 ng/L.

Internal standardization of the procedure was accomplished using bismuth which is readily converted to bismuthine BiH_3 by hydride reduction, and data were acquired in scanning mode. Great care

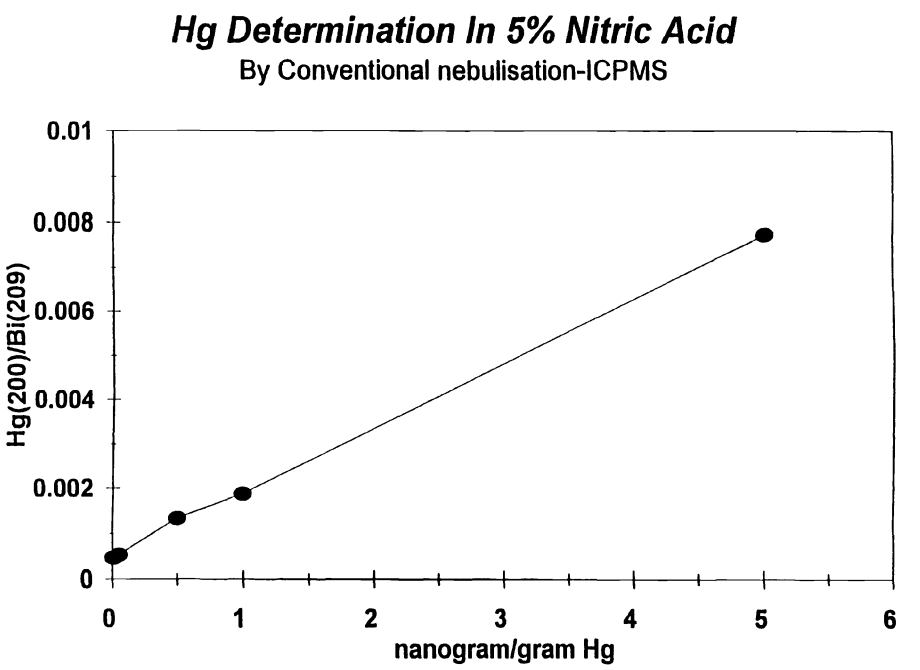

Fig. 3. Standard addition curve for urine spiked with Hg.

TABLE I

Linear regression analysis of a Hg standard addition curve in urine by HG-ICPMS. Nominal concentrations are in μg/L.

NOMINAL	Hg/Bi	%RECOVERY	Regression Output:	
			Constant	.082
			Std Err of Y Est	.0012
0.1	0.088	129.6	R Squared	.99997
0.2	0.092	107.0	No. of Observations	8
0.4	0.101	101.6	Degrees of Freedom	6
0.8	0.118	97.0		
1.6	0.154	97.1	X Coefficient(s)	.046
3.2	0.230	100.2	Std Err of Coef.	.0001
6.4	0.379	100.2		
12.8	0.674	100.0		

must be taken to assure stability of the generated bismuthine since both its dissociation temperature and boiling point are almost coincident around room temperature 20°C. Stability was maintained by chilling the sodium borohydride prior to the mixing T, minimizing path length after phase separation, and optimizing the relative reductant/sample flow rates to produce a uniform liquid-gas reaction.

Further work was carried out on the determination of Hg in primary NIST standards to evaluate the performance of HG-ICPMS to measure isotopic ratios; and determine an LOD for Hg in tissue samples. The SOLA ICPMS was used to determine the isotopic ratios because of this machine reportedly suffers from very little mass bias (Turner,1993). Prior to analysis, 0.5 g of each sample was weighed into precleaned teflon digestion vessels, digested in 2 ml nitric acid, and made up to a final volume of 25 ml with deionized water. Analysis was carried out immediately following this stage to ensure no loss of Hg from solution. It is anticipated that the Hg will be stabilised by indigenous chlorine in the sample matrix, and it is obvious from the data on urine that there are no interferences posed by this. Further, the samples were analysed using peak jumping data acquisition mode, to minimise the potential for carry over from sample to sample.

The measured isotopic ratios are shown in Table II, where the values given are the directly measured ratios and have not been corrected for mass bias. Table III shows the results for a linear regression analysis of the three standards studied. It is clear that a high level of precision and accuracy was achieved and the results also confirm the minimal mass bias in the SOLA instrument. The LOD for this method based on 3 times the standard deviation of a nitric acid blank, relative to the response of the NIST standards, was calculated to be 0.001 μg/g for the solid(20 ng/L for the liquid). As a comparison, a standard addition curve was made up in 5% nitric acid, and analysed by the conventional nebulization technique. The regression analysis for these data is shown

in Figure 4 and Table IV. The LOD in this case was 10 ng/L, slightly lower than the hydride technique, despite a lower relative ion yield. The source of this anomaly has been traced to impurities in the borohydride reagent, and has been reported elsewhere (Voellkopf *et al.*,1991).

TABLE II

Isotopic ratios determined by HG-ICPMS using peak jumping acquisition mode. Relative standard deviations are based on 4 seperate determinations.

ISOTOPES	198/202	199/202	200/202	201/202
NATURAL	0.34	0.57	0.78	0.44
TORT1				
AVG	0.33	0.57	0.78	0.44
%RSD	1.53	0.54	0.89	0.31
DORM1				
AVG	0.33	0.57	0.78	0.45
%rsd	1.05	1.69	1.26	1.27
DOLT2				
AVG	0.34	0.57	0.78	0.45
%rsd	1.21	1.63	0.83	1.02

TABLE III

Regression analysis of certified biological reference materials measured by HG-ICPMS.

	CERTIFIED	DETERMINED	%RECOVERY
TORT	10.33	0.28	85
DORM1	0.8	0.87	109
DOLT2	1.99	1.97	99

REGRESSION:		
	Constant	4719
	Std Err of Y Est	29580
	R Squared	0.995
	No. of Observations	3
	Degrees Of Feedom	1
	X Coefficient(s)	337916
	Std Err Of Coef	.24438

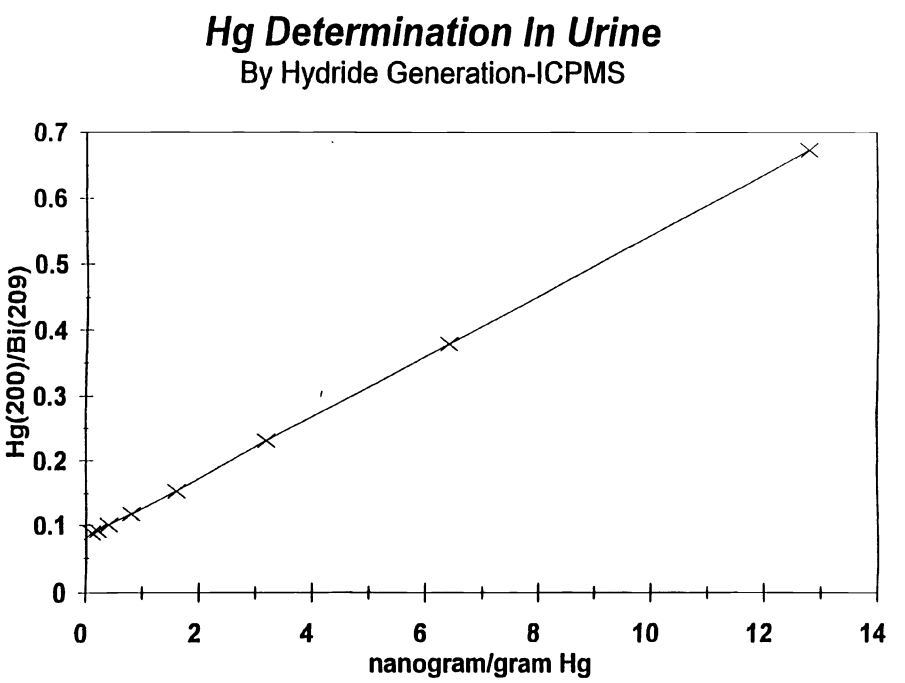

Fig. 4. Standard addition curve for HNO_3 spiked with Hg.

TABLE 4

Regression analysis of Hg in 5%HNO_3 by conventional inlet ICPMS.

NOMINAL(ng/g)	Hg202/In115	%RECOVERY
0.01	0.0005	58
0.05	0.0005	102
0.5	0.0013	119
1	0.1119	97
5	0.0077	100

REGRESSION:	
Constant	0.00046
Std Err of Y Est	8.326E-05
R Squared	0.999
No. of Observations	6
Degrees Of Feedom	4
X Coefficient(s)	0.0015
Std Err Of Coef.	1.906E-05

Both of these methods show distinct promise but the potential advantages of hydride generation are minimized by variation in the purity of the sodium borohydride supplies. This has necessitated selective purchases of borohydride with the lowest level of indigenous Hg or indeed any other analyte "hydride former" such as As, Ge, Se, Sb, Sn, Bi.

4. Conclusions

Future work will center upon the process of hydride reduction through enhancement of the efficiency of gas liquid separation. It is of significant importance that the method has intrinsically very high sensitivity, and in spite of the high ionization potential of Hg is not count rate limited but background/blank limited. Work on reducing this reagent blank is an avenue which must be followed to attain maximum benefit from this attractive method. Methods for pre-concentration of Hg by ion exchange procedures and post-reduction collection on gold followed by thermal desorption will be studied to lower detection limits further.Finally when the above questions have been settled the use of isotopic dilution, the benchmark method used by NIST for many elements will be pursued.

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FIELD SAMPLING AND ANALYTICAL INTERCOMPARISON FOR MERCURY AND METHYLMERCURY DETERMINATION IN NATURAL WATER

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Abstract. In fall 1993, two intercomparisons were conducted with laboratories performing mercury (Hg) and methylmercury (CH_3Hg) analysis in water. The first, conducted at the La Grande complex in northern Québec, involved two provincial universities and evaluated their respective sampling and analytical protocols. Some samples were spiked with a known amount of CH_3HgCl and $HgCl_2$ to evaluate the accuracy of the results. Samples preserved with HCl at pH<2 were analyzed up to 45 days after sampling without any change in the total Hg concentration. Filtration at the analytical lab of samples that had been previously frozen resulted in almost complete loss of Hg and CH_3Hg. It is recommended that filtration, if required, should be performed at the sampling point. The second intercomparison examined only analytical performances and included a total of seven laboratories which analyzed two samples from the Experimental Lake Area, in Northwestern Ontario. The standard deviation was 24 and 14% in total Hg for the first five labs and 31 and 21% in CH_3Hg for the first four labs. The average spike recovery in total Hg measured by three labs was 101± 9%, but the two labs that performed spike recoveries on CH_3Hg obtained variable results in one case and a constant negative bias in the other case. Standard addition on all samples is recommended to assure the accuracy of CH_3Hg analysis.

1. Introduction

For the last 30 years, traces of mercury (Hg) and methylmercury (CH_3Hg) in fresh water have been a concern throughout the world. The former concentration varies between 0.1 and 10 ng/L, while it is between 0.01 and 1.0 ng/L for the latter (Rudd *et al.*, 1983; Lee, 1987; Bloom, 1989, Parks *et al.*, 1989). Even if it represents less than 10% of the total Hg present in water, CH_3Hg accumulates through the trophic chain into fish where it represents 90 to 95% of the total Hg and can exceed the WHO health standards of 0.5 mg/kg of fish tissue.

It is generally observed that higher concentrations of CH_3Hg are associated with the decomposition of organic matter, which stimulates the activity of mercury-methylating microorganisms (Jackson, 1986). This is the case when a new hydroelectric reservoir is created, with the partial decomposition of flooded vegetation and organic soil the first few years after impoundment. The consequent increase of CH_3Hg in fish tissue, especially for piscivorous species, has been observed by many researchers (Abernathy and Cumbie, 1977; Bodaly and Hecky, 1979; Bodaly *et al.*, 1984; Environment Canada, 1979; Potter *et al.*, 1975) and by Hydro-Québec at its La Grande hydroelectric complex in northern Québec (Brouard *et al.*, 1990, Verdon *et al.*, 1991) where it was closely monitored for more than ten years.

The Hydro-Québec Environment Department continues to monitor Hg and CH_3Hg in the La Grande complex and is financing long-term research projects with two provincial universities to model the release and transport of Hg and to understand the complete phenomenon of methylation/demethylation and its transfer through the trophic chain. The two universities have different protocols in terms of sampling and analysis, however, and some of the 1992 data raised questions about the accuracy and comparability of the results.

The analytical chemistry team at Hydro-Québec's research institute, IREQ, was therefore asked to evaluate the protocols and establish a quality assurance program for Hg and CH_3Hg sampling and analysis in water. In the course of this project, two intercomparisons were conducted. The first involved the two Québec universities and compared their sampling techniques and analysis protocols; we also spiked some of the samples at the site with known amounts of inorganic Hg and CH_3Hg to establish the

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accuracy of the two analytical protocols. In the second intercomparison, we collaborated with Dr. Robert J. Flett from Flett Research Ltd. in Winnipeg, Canada, who initiated an analytical round including the two Québec universities as well as one American and four other Canadian laboratories which were asked to analyze two different water samples. In addition, the two Québec universities and one of the other labs received one demineralized-water and two natural-water samples spiked with different amounts of inorganic Hg and CH_3Hg. The results of these two intercomparison exercises are presented in this paper. Explanations are proposed for some of the differences observed in the results and recommendations for establishing the quality of the analytical results are given.

2. Experimental

2.1 SAMPLING SITES

The first intercomparison took place at the LA40 dike in the Laforge area forming part of the La Grande complex in northern Québec, on shallow recently flooded peatland. Previous studies had revealed that the water has a relatively high humic matter content, which is known to favor Hg methylation and form stable complex with Hg species, which causes problems for the analysis. For the second part of the work, the sites selected by Dr. Flett were chosen among those previously studied by the Freshwater Institute in the Experimental Lake Area (ELA) of northwestern Ontario (Rudd, J.W.M. *et al.*, 1992). The samples were taken at the outflow of a small stratified shield lake identified as #240 (referred to as lake A in the text) and #632, which is a pound of wetlands (referred to as lake B). The former has a low Hg, CH_3Hg and humic matter concentration while the latter has a moderately high level of these species.

2.2 MATERIALS

All the bottles used for sampling were made of Teflon, except in the second intercomparison where lab B supplied two borosilicate bottles because of a shortage of Teflon bottles. The bottles were acid-washed and sealed in two plastic bags. The volumetric flasks used for preparing the spike solutions were made of borosilicate and cleaned the same way. The solutions were carried to the sampling site, also in Teflon bottles sealed in two plastic bags, and kept separate from the sampling bottles. The volumetric dilution and spiking were done with automatic pipettes from Gilson (Villiers le Bel, France) Each pipette was calibrated at the volume used by weighing the exact pipetted amount of pure water 15 times on an analytical scale.

2.3 CHEMICALS

A 1000-ppm Hg standard solution of mercuric chloride ($HgCl_2$), from BDH (Montréal, Québec) was used as primary standard for the inorganic Hg spike solution. For the CH_3Hg spikes, a 1000-ppm Hg standard solution of methylmercury chloride (CH_3HgCl) from Alfa (Ward Hill, MA) was used in the first intercomparison round, while in the second round a fresher solution from the same company was used. Unfortunately, this last solution was found defective and a fresh 1-ppm Hg solution of CH_3HgCl was prepared and certified by Frontier Geosciences (Seattle, WA).

3. First intercomparison

3.1 METHODOLOGY

This round took place on September 24, 1993. Each laboratory took samples according to its own sampling protocol: lab A used a manually operated peristaltic pump and Teflon tubing to pump its samples through a 0.45-µm filter, while lab B filled its bottles by immersion in the water without filtering, using two persons following a "clean-hands dirty-hands" protocol similar to those described by Ahler *et al.* (1990) and Gill and Fitzgerald (1985), which are adapted from the earlier work of Patterson (Patterson and Settle, 1976). Both sampling teams took all the appropriate measures to avoid contamination. After collection, all the bottles were given to us and the samples were acidified at pH<2 with 4 mL of freshly distilled hydrochloric acid (HCl) 6M per litre of sample, which was analyzed for its Hg content. All the bottles were then separated into four groups and labeled A to D. Bottles labeled B received a known amount of inorganic Hg equivalent to an additional concentration of 8-9 ng/L Hg. Bottles labeled C received the same spike plus a known amount of CH_3Hg equivalent to an additional concentration of 0.6-0.7 ng/L Hg. For these samples, the exact volume of sample in each bottle was measured by weight, in order to accurately determine the concentration increase caused by the spike. Bottles A and D were left unspiked. One set of filtered samples (taken by lab A) and one set of unfiltered grab samples (taken by lab B) were given to each laboratory to be analyzed for CH_3Hg and total Hg by their own technique, without knowing the nature or the concentration of the spike. In addition, four additional sets of samples filtered at the sampling point were stored at 4°C and analyzed by lab A for total Hg at different intervals over a five-week period to verify the conservation time. Lab B received an additional set of unfiltered samples and was asked to filter them at its own lab on a 5-µm Teflon filter just before analysis. Lab A analyzed its samples for total Hg in its field laboratory without delay and shipped the rest of the sample to the university lab for CH_3Hg analysis. Samples analyzed by lab B, which were kept at 4°C during transport, were received three days after sampling, but the personnel were unfortunately unable to perform the analysis for two weeks and decided to freeze the samples.

3.2 ANALYTICAL PROTOCOLS

3.2.1 Total mercury

Lab A used the following protocol: 10 mL of sample is put in a quartz test tube. Potassium persulfate is added and the tube is subjected to UV light for 20 min to decompose the organic Hg into Hg^{2+}. An aliquot of 5 mL is taken and injected into a Teflon reactor containing stannous chloride ($SnCl_2$). An argon flow purges this volatile species to a custom-made fluorimeter consisting of a Hg lamp, a gas flow cell and a detector positioned at right angles to the light beam.

Lab B used the protocol developed by Bloom and Crecelius (1983) based on previous work by Fitzgerald and Gill (1979) and described by Brooks Rand Ltd. in the operational manual of the CVAFS model-2 Hg analyzer, with some modifications: a bromine chloride (BrCl) solution in HCl is added to 200 mL of sample and left for a minimum of 30 min to allow the degradation of organic Hg into Hg^{2+}. A hydroxylamine hydrochloride solution is then added to eliminate the traces of BrCl. A $SnCl_2$ solution is added to reduce the Hg^{2+} into Hg^0 which is purged with nitrogen and trapped on two gold foil traps. The two traps are heated and backflushed with nitrogen to liberate the Hg which is detected by atomic absorption in a LDC/Milton-Roy Hg monitor consisting of a Hg lamp, a 30-cm flow cell and a detector.

3.2.2 Methylmercury

Both laboratories use a two-step protocol based on that first proposed by Bloom (1989) and recently modified (Liang, *et al.*, 1994), where the CH_3Hg is first separated from most

of the other organic compounds and derivatized to the ethylmethylmercury ($CH_3HgC_2H_5$) form which is purged, trapped and analyzed by a gas chromatograph equipped with a fluorescence detector. However, each laboratory tackles the first step in a different way.

Lab A forms methylmercury bromide (CH_3HgBr) by adding a potassium bromide solution in sulfuric acid to 40 mL of the sample. Sub-boiling distillation with a flow of inert gas, as proposed by Horvat *et al.*(1988,1993), is performed until 80% of the sample has been transferred. Ethylation and detection follow, as described by Bloom, except that a Tenax trap is used instead of the carbotrap to collect the $CH_3HgC_2H_5$ and release it into the gas chromatograph.

Lab B protocol, based on the one first proposed by Bloom (1989), forms the CH_3HgCl by adding a potassium chloride solution in HCl to 60 mL of sample. The CH_3HgCl is extracted with 40 mL of methylene chloride and back-extracted into 10 mL of ultrapure water by solvent evaporation, after which 100 mL of ultrapure water is added to complete the volume.

3.3 RESULTS

Table 1 presents the results obtained by the two laboratories for the total Hg and CH_3Hg analysis. The spike recovery was calculated for samples B and C by subtracting the average concentration obtained for the two other samples. Looking first at the total Hg results obtained by lab B, we see that pre-analysis filtration of unfrozen samples removed most of the Hg from the solution. It should be noted that a precipitate was observed on

TABLE I

A) Analytical results of the first intercomparison round (expressed in ng/L Hg)

Sample	Filtration	Total Hg analysis				CH_3Hg analysis			
		Lab A		Lab B		Lab A		Lab B	
		Concentration	Standard deviation	Concentration	Standard deviation	Concentration	Standard deviation	Concentration	Standard deviation
A	none	5.00	1.04	1.91	0.07	0.23	0.04	0.46	0.07
	at sampling	3.68	0.08	2.09	0.15	0.19	0.06	0.51	0.15
	pre-analysis			0.95	0.03			0.12	0.02
D	none	5.61	1.02	1.50	0.03	0.16	0.16	0.23	0.01
	at sampling	3.72	0.17	1.12	0.06	0.23	0.12	0.21	0.01
	pre-analysis			0.48	0.09			0.05	0.02
B	none	13.61	0.62	6.07	0.24	0.39	0.03	0.47	0.02
	at sampling	12.73	0.04	7.10	0.06	0.17	0.10	0.56	0.12
	pre-analysis			1.03	0.05			0.14	0.03
C	none	14.17	0.28	6.54	0.41	0.46	0.21	0.50	0.13
	at sampling	12.46	0.09	6.58	0.29	0.52	0.21	0.51	0.04
	pre-analysis			1.01	0.05			0.12	0.02

B) Spike recovery

Sample	Filtration	Total Hg analysis				CH_3Hg analysis			
		Lab A		Lab B		Lab A		Lab B	
		Spike (ng/L Hg)	Percent recovery	Spike (ng/L Hg)	Percent recovery	Spike (ng/L Hg)	Percent recovery	Spike (ng/L Hg)	Percent recovery
B	none	8.6	97%	7.5	58%				
	at sampling	8.8	103%	8.2	67%				
	before analysis			7.5	4%				
C	none	9.1	97%	8.0	60%	0.68	39%	0.60	26%
	at sampling	8.8	99%	8.2	57%	0.68	46%	0.65	22%
	before analysis			8.0	4%			0.60	6%

most of the Hg from the solution. It should be noted that a precipitate was observed on the filter, even though no particulates were visible in the solution. It is possible that freezing the samples caused an irreversible microscopic precipitation of humic matter (and the Hg species bound to it) due to its high concentration and low pH. Secondly, lab B recovered only 60% of the spikes on average and its results are systematically lower than those of lab A, which obtained 100% spike recovery. It was thought initially that the precipitate that occurred after lab B thawed the samples trapped Hg in a form that was not totally released by BrCl oxidation. It was later found that the standard used in these analyses was contaminated, which resulted in an underestimation of the Hg content of the samples. After recalculation with the correct concentration of the standard, the average spike recovery increases to 84%. Also, lab B's results show no significant difference between unfiltered samples and samples filtered during sampling, whereas lab A's results for the unfiltered samples are on average 1.4 ng/L Hg higher. A possible explanation is that the 30-min BrCl oxidation used by lab B was not long enough to completely release the Hg adsorbed on particulates or bound to humic matter, while the UV-persulfate treatment used by lab A did.

As for the total Hg, the CH_3Hg results obtained by lab B on samples filtered in the laboratory before the analysis are significantly lower than the unfiltered samples or those filtered during sampling. This means that most of the CH_3Hg was also adsorbed on particulates and removed by filtration. Another observation is that except for one result, there is no difference in the two labs' results between samples filtered during sampling and unfiltered samples, which means that no significant CH_3Hg was originally adsorbed on particulates. For the rest of the results, the agreement between the two labs is somewhat less satisfactory. The same numbers should have been obtained for all samples except for C, which was spiked. This is the case for lab A, with the exception of the unfiltered B sample. The results for the spiked samples are significantly higher, even though the recoveries of the added CH_3Hg are only 39% and 46%. On the other hand, lab B obtained similar values to those of the other lab for sample D, but twice the concentration for the other three samples, without discriminating between spiked and unspiked samples. Because of the high value obtained for sample A, recovery of the spike is low even if the results are similar to those obtained by lab A. Since we could not double-check the spike solution, caution is recommended in interpreting the poor spike recoveries obtained by the two laboratories.

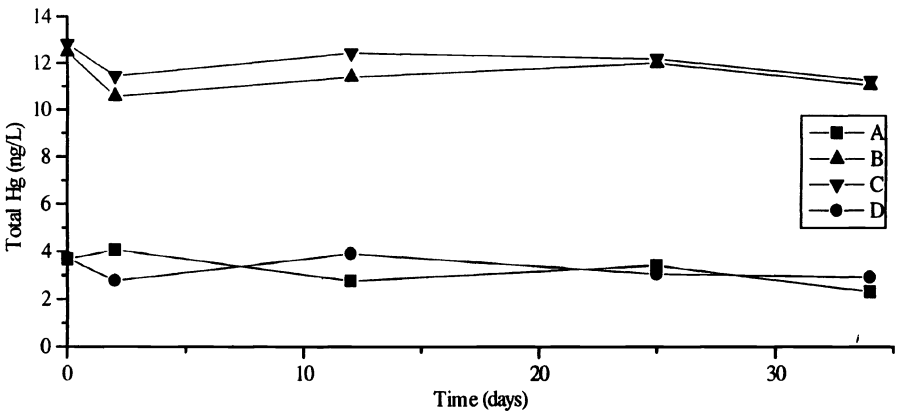

Fig. 1. Conservation of samples for total Hg analysis

noticing any variation greater than the instrumental error. Thus, the standard deviation, which ranges between 0.5 and 0.7 ng/L Hg for the five determinations of each sample, is associated with a variation between bottles rather than degradation with time. This means that preservation with HCl at pH<2 is adequate when samples are stored at 4°C.

4. Second intercomparison

4.1 METHODOLOGY

A second round, considering strictly the analytical performances of the two laboratories, was scheduled for late fall 1993. In the mean time, another intercomparison was initiated by Dr. Robert J. Flett from Flett Research Ltd. in Winnipeg, Canada, who invited six Canadian (including the two Québec universities) and one American laboratory to analyze two unfiltered lake water samples for total Hg and CH_3Hg (except for labs F and G which only perform total-mercury analysis). We decided to pool our efforts and participated in the collection of the samples on December 6, 1993 at the ELA site. Each laboratory was responsible for cleaning and sending separate bottles for the total Hg and CH_3Hg determination. The samples were taken in duplicate bottles, according to the "clean-hands dirty-hands" protocol. For total mercury, pre-analyzed HCl containing 7 ng/L Hg was used to acidify the samples to pH<2 within 6 h of sampling, except for the bottles from lab G which already had the preservative in them. They were all kept at 4°C during transport. For methylmercury, the samples were frozen within 6 h of sampling without any preservative and packed with dry ice for transport, except for lab E which asked us to refrigerate its samples without freezing.

Additional samples of Lake A were taken and spiked with different amounts of CH_3Hg and inorganic Hg. They were then sent to the two Québec universities (labs A and B) and one other participating laboratory (lab C) along with two duplicate samples (one spiked and one unspiked) of laboratory water, with no indication as to the exact amount of Hg and CH_3Hg added. The CH_3Hg spike solution was added at the camp before freezing the samples, while the inorganic Hg solution (for total Hg analysis) was added at each participating laboratory upon delivery of the samples. Each of the two spike solutions was poured into two separate bottles, one of which stayed at 4°C in our lab and the other was taken to the field and used to spike all the samples. After delivering the samples to all participants, we sent the spike solutions and the duplicate that had remained at our lab to Frontier Geosciences (Seattle, WA) for analysis. The participating laboratories also received a duplicate sample of the two spike solutions.

4.2 ANALYTICAL PROTOCOLS

4.2.1 Total mercury

Labs A and B used the methods already described in section 3.2 with some minor modifications. This time, lab A used a trap composed of gold-coated glass beads to concentrate the Hg after the $SnCl_2$ reduction before thermally releasing it to the fluorimeter.

Lab C uses a protocol similar to that used by lab B. A bromine chloride (BrCl) solution in HCl is added to 125 mL of sample and left for a minimum of 60 min to allow the degradation of organic Hg into Hg^{2+}. A hydroxylamine hydrochloride solution is then added to eliminate the traces of BrCl. A 70-mL aliquot is transferred to a bubbler and a $SnCl_2$ solution is added to reduce the Hg^{2+} to Hg^0, which is purged with nitrogen and trapped on a gold-coated sand trap. The trap is heated and backflushed with nitrogen to liberate the mercury, which is detected by atomic fluorescence. The four other labs, which did not analyze spiked samples, were not asked to supply their protocol.

4.2.2 Methylmercury

Labs A and B used the same protocols as in the first round. Lab C uses a protocol where the isolation (step 1) is similar to lab A, except that CH_3HgCl is first formed (as in the original reference by Bloom, 1989) by adding KCl in H_2SO_4 to a 45-mL sample. The CH_3HgCl is distilled until 35 mL is collected, to which sodium tetraethylborate is added to obtain the $CH_3HgC_2H_5$. The rest is identical to lab B's protocol. The two other labs, which performed CH_3Hg analysis on unspiked samples only, were not asked to supply their protocol.

4.3 Results

4.3.1 Spike solution analysis

The triplicate analysis of the $HgCl_2$ solution used to spike the samples and the duplicate kept at our lab gave 6.35 ± 0.05 and 6.33 ± 0.07 µg/L Hg respectively, which means that no degradation or contamination of the spike solution occurred during the field trip. This value was also confirmed by lab A, which analyzed its duplicate of the spike solution.

Analysis of the CH_3Hg spike solution gave 4.8 ± 1.1 ng/L Hg while the duplicate solution kept at our lab gave 38.2 ± 3.8 ng/L Hg, which clearly indicates that degradation had unfortunately occurred during the field campaign. Also, the duplicate solution was 20 times less concentrated than it should have been. After verification, the commercial primary standard solution used for this round was found to be the source of the problem. For this reason, even if degradation did occur after the spikes were performed, the amount added was negligible in comparison to the expected concentration in the natural sample and it was decided to obtain a fresh certified CH_3Hg standard and use it to respike one of the two bottles for each set of samples just before the analysis. This was done for labs A and B, but not for lab C, which had already analyzed all the samples.

4.3.2 Total mercury

The results are shown in Tables II and III. The first five labs have similar results for the lake A and lake B samples, with a relative deviation of 24 and 14% respectively, while lab F is approximately 2.5 times higher. Lab A has higher results than labs B, C and D as was the case in the first round for unfiltered samples. This again may indicate that the UV-persulfate oxidation used by this laboratory is more efficient to release all the Hg linked to organic matter than the BrCl treatment used by the other laboratories. To verify this hypothesis, Lab A conducted a comparative test using tap water to which 10 mg/L of humic acid was added plus 5.5 ng/L Hg in CH_3HgCl form. Duplicate analyses were performed with a 30-min (Lab B protocol) and 60-min (Lab C protocol) BrCl treatment and its UV-persulfate treatment. While the initial total Hg content was identical, the recuperation of CH_3Hg was 87% for the first protocol, 95% for the second and 100% for the third. The same test will be performed this summer on field samples to see if this difference in treatment could be more pronounced with more organic matter present. The three labs obtained very good results in the blind analysis performed on spiked samples, with an average recovery of $101 \pm 9\%$ for the added concentration.

4.3.3 Methylmercury

The results of the CH_3Hg analysis are presented in Tables IV and V. Except for Lab E, which is 2 to 3 times higher than the other participants, there is a certain agreement in the results for the two natural samples. The relative standard deviation for the first four labs is 31 and 21% for Lakes A and B respectively. This is satisfactory for the former because the concentration is near the quantification limit but the variation is a little high for the more concentrated Lake B, with a 60% difference between the highest and lowest results.

Table II

Total Hg analysis of unspiked samples (ng/L Hg)

Lab	Lake A			Lake B			Lab water		
	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean
A	5	0.16	1.34	3	0.07	3.48	4	0.18	0.58
	3	0.07	1.52	3	0.02	3.12	3	0.26	0.52
B	3	0.04	1.02	3	0.10	2.82	3	0.06	0.51
	3	0.04	1.09	3	0.08	2.76	3	0.05	2.24*
C	2	0.02	0.97	2	0.01	2.29	2	0.02	1.55
	2	0.01	0.88	2	0.03	2.19	2	0.79	4.66
D	1		0.87	1		2.66			
	1		0.71	1		2.49			
E	3	0.09	1.31	5	0.50	2.78			
F	3	0.09	2.77	4	0.44	7.33			
	3	0.03	2.89	5	0.77	7.48			
G	conc. too low			conc. too low					
First 5 labs		0.26	1.08		0.39	2.73			

* Borosilicate bottle used due to shortage of Teflon bottles and probably not rigorously cleaned.

Table III

A) Total Hg analysis of spiked samples (ng/L Hg)

Lab	Lake A - spike A			Lake A - spike B			Lab water - spike C		
	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean
A	3	0.12	4.89	3	0.41	8.18	3	0.14	3.98
	3	0.06	5.05	3	0.47	7.65	2	0.25	4.54
B	3	0.20	5.14	3	0.21	7.74	3	0.30	3.33
	3	0.21	5.01	3	0.41	7.26	3	0.40	3.56
C	2	0.04	4.67	2	0.01	6.86	2	1.04	4.48
	2	0.14	4.50	2	0.23	6.30	2	0.09	5.06

B) Spike recovery

Lab	Lake A - spike A		Lake A - spike B		Lab water - spike C	
	Spike (ng/L)	Percent recovery	Spike (ng/L)	Percent recovery	Spike (ng/L)	Percent recovery
A	3.81	91%	6.26	108%	3.24	106%
	3.93	92%	5.89	106%	3.29	121%
B	3.89	105%	5.94	113%	3.09	91%
	3.84	103%	5.97	104%	2.98	102%
C	3.81	99%	6.17	96%	3.14	93%
	3.94	91%	5.83	92%	3.24	108%

The results obtained by labs A and B on samples freshly spiked just before analysis revealed some differences in the accuracy of the methods used. Lab A's recovery of the added CH_3Hg is consistent but only around 50%. This systematic bias could have been corrected if standard additions had been used, which was not considered necessary at the time the analyses were performed. The personnel have investigated the possibility of a loss of CH_3HgBr at the beginning of distillation when no water has yet condensed in the collector, but have ruled out this hypothesis. One explanation proposed for the low spike recovery and the slightly lower results in Lake B samples is that traces of dissolved oxygen might oxidize some of the CH_3HgBr, which is easier to oxidize than the CH_3HgCl formed by the other laboratories. They are now exploring this possibility and considering returning to the formation of CH_3HgCl in the first step of the protocol, especially when the sample has a low content of easily oxidizable organic matter. Lab B spike recoveries

Table IV
CH_3Hg analysis of unspiked samples (ng/L Hg)

Lab	Lake A			Lake B			Lab water		
	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean
A	3	0.01	0.08	3	0.06	0.31	4	0.01	0.03
	3	0.01	0.07	2	0.01	0.27	4	0.01	0.04
B	3	0.01	0.10	3	0.02	0.39	3	0.02	0.00
	3	0.01	0.11	3	0.02	0.36	3	0.01	0.00
C	1		0.06	1		0.43	3	0.01	0.03
	2	0.02	0.08	2	0.03	0.45	3	0.02	0.03
D	1		0.06	1		0.28			
	1		0.04	1		0.28			
E	3	0.03	0.24	3	0.12	0.72			
First 4 labs		0.02	0.07		0.07	0.35			

Note: Labs F and G do not perform CH_3Hg analysis.

Table V
A) CH_3Hg analysis of spiked samples (ng/L Hg)

Lab	Lake A - spike A			Lake A - spike B			Lab water - spike C		
	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean	No. of analyses	Standard deviation	Mean
A	5	0.08	0.36	4	0.01	0.50	4	0.04	0.20
B	3	0.04	0.62	3	0.05	0.64	3	0.03	0.36

B) Spike recovery

Lab	Lake A - spike A		Lake A - spike B		Lab water - spike C	
	Spike (ng/L)	Percent recovery	Spike (ng/L)	Percent recovery	Spike (ng/L)	Percent recovery
A	0.54	52%	0.79	52%	0.38	46%
B	0.54	98%	0.81	68%	0.40	79%

are higher but quite variable, which means that the source of this error is random and not easy to find or correct. Loss during evaporation of the CH_2Cl_2 might be a cause for the less than 100% and variable CH_3Hg recoveries.

5. Conclusions

The question whether to use filtered or unfiltered samples depends on the type of study a person wants to conduct. The results of the first intercomparison showed that filtration, if required, can and should be performed during sampling, with a manually or battery-operated all-Teflon pump. Conservation with HCl at pH<2 at 4°C is adequate for at least 45 days for total Hg determination but the samples should not be frozen, as this could initiate irreversible precipitation. For methylmercury, this work cannot tell whether the same conservation technique can be applied or a separate treatment (such as freezing the sample without any preservative) should be used.

Five out of six labs gave comparable total Hg results. The slightly higher results obtained by one laboratory using UV-persulfate instead of BrCl oxidation seem to indicate that the latter treatment is less effective and might leave some of the Hg undetected if the reaction time is not long enough. This question should be investigated in a more systematic study. The spike recoveries showed good accuracy of the

techniques. The problem of contaminated standard solution experienced by one lab in the first round stressed the need to frequently verify the accuracy of the primary and secondary standard solutions, which can be done by analyzing certified material or by standard exchange with other labs.

The agreement obtained by four out of the five labs which performed CH_3Hg analysis was not as good as for the total Hg, with a 60% difference between the lowest and highest values for the more concentrated sample. Also, the recovery of added CH_3Hg on spiked samples raised a few questions about the accuracy of the techniques. One lab obtained good albeit variable recoveries (between 68 and 98%), while the other had a consistent but systematic negative bias. We recommend that analysis with and without standard additions should be performed on all samples, which would correct the bias and provide an idea of the accuracy of the results for each sample.

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RESULTS OF THE INTERNATIONAL AQUEOUS MERCURY SPECIATION INTERCOMPARISON EXERCISE

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Abstract. Twenty-seven laboratories from around the world agreed to participate in an intercomparison exercise for total Hg (Hg_t) and methyl Hg (MMHg) in pristine lake water. Unfiltered samples from a remote brown water lake in northern Wisconsin (USA) were collected into acid cleaned Teflon® bottles using ultra-clean sample handling techniques. The samples were acidified in the field with 0.4% by volume of pre-analyzed HCl (12N; <5 pg Hg/mL), and sent to the primary reference laboratory (PRL) by overnight mail. Within one week of receipt, the samples were randomized, and 10% analyzed for Hg_t and MMHg at the PRL to verify the homogeneity of the set. Each participating laboratory was then sent 3 randomly selected 1 L bottles, while the PRL retained 30, and the secondary reference laboratory (SRL) retained 12 samples. The participating laboratories were asked to analyze each bottle in triplicate for both Hg_t and MMHg , reporting all QA data including blanks, spike recoveries, and detection limits. The PRL analyzed samples in triplicate at both the beginning and the end of the analytical window, to provide a controlled estimate of any changes in concentration or speciation over that time. Of the 23 laboratories that returned results, 18 utilized BrCl oxidation, gold trapping, and cold vapor atomic fluorescence (CVAFS) detection for Hg_t. Four laboratories reported similar techniques, varying either in detector (cold vapor atomic absorption), or wet chemistry. Only 16 laboratories reported MMHg results, with 15 using a variation of the aqueous phase ethylation, GC separation, and CVAFS detection technique. The results show good convergence between the participating labs for both Hg_t and MMHg. For Hg_t 18 of 23 labs reported means within 20% of the consensus value and PRL results (1.27 ± 0.18 ng/L and 1.27 ± 0.14 ng/L respectively). For MMHg, 13 of the 16 labs reported results within 20% of either the consensus value (0.420 ± 0.055 ng/L) or the PRL value (0.446 ± 0.041 ng/L).

1. Introduction

The advent of specific, ultra-low-level methods for determining of MMHg has contributed to a recent spate of environmental Hg research around the world (Horvat et al., 1993; Bloom, 1989; Bloom and Fitzgerald, 1988; Lee, 1987). Because of the numerous independent projects involving ambient level Hg speciation, the International Mercury Speciation Intercomparison Exercise Organizing Committee was formed in July, 1992 to design a study to help assess the compatibility of the various datasets. As a result, a 3-step process was developed involving, first, an analytical-only intercomparison for total Hg (Hg_t) and MMHg in ambient lake water (in 1993), second, an intercomparison of sampling methodologies for surface water (in 1994), and finally, a workshop to

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discuss results and technological developments (in 1995). In this paper we discuss the results from the first phase.

A total of 27 laboratories around the world participated, with 23 returning results for Hg_t (3 labs used one set of samples) and 16 for MMHg. In Table I the participating laboratories, and the methods they used, are in alphabetical order by the prime researcher's name. The data discussed are listed according to randomly assigned identification numbers, to protect the anonymity of the participants. The results from the primary and secondary reference laboratories (PRL and SRL) are identified. The sample set was subjected to intense QA scrutiny by the reference laboratories to insure that the entire set was homogeneous and randomly distributed for both species, and that no changes in speciation or concentration were encountered over the 4 month exercise period.

TABLE I

Laboratories submitting intercomparison results. DLs are 3 σ of the reported blanks (ng/L).

	Total Hg		Methyl Hg	
Principle Investigator	Method	DL	Method	DL
J. Benoit U. of Wisconsin, .(USA)	BrCl	0.08	Distill	0.03
N. Bloom Frontier Geosciences (USA) **PRL**	BrCl	0.05	Dist/Extract	0.04
T.M. Chandrasekhar Florida DEP (USA)	BrCl-dir.	1.2	---	---
D. Cossa IFREMER (FRANCE)	Hydride	0.06	Labile	0.03
R. Flett Flett Research (CANADA)	BrCl	0.06	Distill	0.02
C. Gilmore Benedict Estaurine Lab.(USA)	BrCl	0.03	Distill	0.07
G. Gill Texas A & M U.(USA)	Hydride	0.25	----	---
G. Glass USEPA Archeometry (USA)	EPA	0.3	----	---
M. Hempel GKSS (GERMANY)	BrCl	0.12	HPLC	1.6
H. Hintelmann Trent University (CANADA)	BrCl	0.33	Distill	0.12
M. Horvat IAEA-MEL (MONACO) **SRL**	BrCl	0.12	Distill	0.20
J. Keeler U. Michigan (USA)	BrCl	0.07	----	---
J. Kim NIWAR (NEW ZEALAND)	BrCl	0.04	Extract	0.03
J. Guentzel Florida State U.(USA)	Hydride	0.04	----	---
B. Lasorsa Battelle Northwest MRL (USA)	BrCl	0.05	Extract	0.04
S. Lindberg Oak Ridge National Lab. (USA)	BrCl	0.15	----	---
L. Liang Brooks Rand Ltd. (USA)	BrCl	0.06	Dist/Extract	.003
C. Meulemann Free U. Brussels (BELGIUM)	BrCl	0.1	Extract	0.03
J. Munthe IVL (SWEDEN)	BrCl	0.09	Dist/Extract	0.06
E. Saouter USEPA (USA)	BrCl	0.06	Extract	0.09
W. Stratton Earlham College (USA)	BrCl	0.3	----	---
G. Vandal U. Connecticut , Dept. Marine Sci. (USA)	BrCl	0.07	Distill	0.06
C. Watras Wisconsin DNR (USA)	BrCl	0.09	Distill	0.09

BrCl = BrCl oxidation, $SnCl_2$, reduction, Au trapping, CVAFS (-direct = direct CVAFS)
Hydride = $NaBH_4$ reduction, Au trapping, CVAFS
EPA = $KMnO_4$ + $K_2S_2O_8$ oxidation, direct (recirculating) CVAAS
Distill = Distillation, ethylation, gas chromatography, CVAFS
Extract = Methylene chloride extraction, ethylation, gas chromatography, CVAFS
Labile = Direct ethylation, gas chromatography, CVAFS
HPLC = High pressure liquid chromatography separation + CVAFS detection

2. Materials and Methods

2.1 SAMPLE BOTTLES

Samples were collected in rigorously cleaned and tested 1 L Teflon® bottles. The new bottles were first heated to 75°C for 48 hours in 4N HCl, followed by rinsing with low Hg (<1 ng·L^{-1}) deionized water (DW). The bottles were then filled with the same DW, and 10 mL of low Hg (<5 pg·mL^{-1}) HCl added. The lids were replaced, and the bottles were heated in a stainless steel oven at 70°C for 48 hours. Finally, they were thoroughly rinsed inside and out with DW using clean sample handling protocols (Bloom, 1995; Fitzgerald and Watras, 1989), filled with DW, and acidified with 4 mL low Hg HCl in a class 100 laminar flow hood. The lids were tightened with a clean stainless steel wrench, and the bottles were randomized. An additional five Teflon® bottles, frequently used for low-level Hg research, and known to be clean, were prepared in exactly the same way (as controls). The bottles were double-enclosed in new polyethylene bags, packed into new polyethylene foam shipping boxes, and stored in a low Hg atmosphere (8 to 10 ng·m^{-3}) for 60 days. After the storage period, twenty randomly selected bottles from the intercomparison set, as well as the five control bottles, were analyzed for Hg_t. No differences were found between the test bottles (0.43 ± 0.27 ng·L^{-1}, n=20) and the control bottles (0.46 ± 0.31 ng·L^{-1}, n=5), indicating that they were cleaned adequately for low-level Hg work.

2.2 SAMPLE COLLECTION

The intercomparison samples were collected on November 7, 1993 from Mud Lake, a small moderately colored (DOC = 5.8 mg·L^{-1}; pH = 6.0) lake located in North Central Wisconsin, USA, using ultra-clean sampling protocols. Sample collection occurred after fall turnover to ensure a well-mixed water column. Samples of unfiltered water were collected from a depth of 1 m, using a plastic submersible pump and acid-cleaned vinyl tubing. This technique has been well tested and intercompared with the earlier Teflon® tubing/peristaltic pump method, and found to be non-contaminating (Watras and Bloom, 1994). Samples were collected sequentially over a 10 hour period, and their order recorded to allow an accounting for any observed temporal trends in concentration.

2.3 ANALYTICAL METHODS

A brief description of the analytical methods used by each laboratory is given in Table I. Although we will not attempt to describe each technique in detail, some

general comments will follow. Both reference laboratories used near identical techniques for all analyses. The majority of participating laboratories also used the same methods, somewhat limiting the ability of the survey to establish absolute accuracy.

For Hg_t, 18 out of 23 reporting laboratories utilized BrCl wet digestion, $SnCl_2$ reduction, purging onto gold, and cold vapor atomic fluorescence (CVAFS) detection (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988). The PRL also conducted a limited number of comparisons using UV photo-oxidation (75 watts at 254 nm for 4 hours) as a pre-treatment step, while the SRL used BrCl plus photo oxidation on all samples. Three of the laboratories used direct reduction with $NaBH_4$, gold trapping and CVAFS (Gill and Bruland, 1990). Both of these methods have detection limits in the range of 0.1-0.05 $ng \cdot L^{-1}$ Hg, which is determined by the variability in the reagent blank. One laboratory utilized a modified USEPA method 245.1, which uses pre-oxidation $KMnO_4/K_2S_2O_8$, followed by $SnCl_2$ reduction, and purging directly into a cold vapor atomic absorption spectrometer (CVAAS) (Glass et al., 1990). This technique has an EPA defined detection limit of 0.9 $ng \cdot L^{-1}$, although using the 3 σ definition in this paper, the DL was approximately 0.3 ng/L.

To determine MMHg, 15 laboratories utilized some variation of aqueous phase ethylation, GC separation, and CVAFS detection (Rapsomanakis, et al., 1985; Bloom, 1989). The major differences between laboratories were that 10 used distillation (Horvat et al., 1993), while 7 utilized methylene chloride extraction (Bloom, 1989) as the preconcentration method. Three laboratories reported results using both extraction techniques. One group determined only the labile MMHg by direct ethylation of the sample. Five laboratories utilized isothermal GC separation of the alkyl Hg species (Liang et al., 1995), while 10 laboratories utilized cryogenic GC separation (Bloom, 1989). Carbotrap® (Bloom, 1989) was the favored precollection media for alkyl Hg species (14 labs), while only 1 group utilized Tenax® (Liang et al., 1994) as the sorbant. One group used an HPLC/CVAFS technique, (Hintelmann and Wilken, 1993) but the DL was too high to quantify the MMHg present.

2.4 QUALITY CONTROL

All laboratories reported blank and replicate determinations, allowing verification of the mean results and detection limit claims. In Table I, method detection limits have been reported as 3 σ of the actual within-day method blanks. Less than half of the laboratories reported spike recoveries. Of those reporting, mean Hg_t recoveries ranged from 88 to 106% (97.2 $\pm$ 5.0%, n=11), while mean MMHg recoveries ranged from 73 to 100% (88.1 $\pm$ 10.2%, n=14). Prior to analysis of the field samples, the PRL and SRL intercompared standard solutions, finding no measurable bias. The PRL conducted all analyses in

triplicate. If a point in the triplicate was lost, or deviated from the other two by more than 20%, a fourth determination was made, and the best three points retained. At the PRL, one blank and one spike recovery was analyzed for every triplicate of samples. Mean values of the blanks, and spike recovery corrections (MMHg only) were calculated for each batch of samples processed (typically 4 samples) in a single day. At intervals during the investigation, digestions of certified fish tissue (NRCC DORM-1) were analyzed to verify the stability of the standards. Hg_t standards were prepared by serial dilution of NIST NBS-3133 (certified 10,000 $mg \cdot L^{-1}$ Hg standard), while MMHg was periodically calibrated against this standard as Hg_t (using BrCl oxidation) minus labile Hg. Six samples were tested for Hg_t by adding BrCl directly to the bottle, thereby allowing an assessment of the potential loss of Hg to the bottle walls (Bloom, 1994).

3. Results and Discussion

3.1 PRIMARY REFERENCE LAB QC.

Shortly after sample collection and preservation, the PRL conducted a random survey of Hg concentrations in 18 of the samples as a benchmark comparison of the true between-bottle variability. Each bottle was analyzed for each species in triplicate to help assess the relative contribution of analytical and sampling variability to the total observed variability. These results, together with an additional 12 samples analyzed at the end of the study (Figure 1 and Table II) indicate no bias in concentration for either Hg_t or MMHg as a function of sampling time. The mean precision (relative standard deviation, RSD) for triplicate analyses of the same sample was 4.8% for Hg_t and 6.7% for MMHg. This gives an estimated PRL analytical variability, for the triplicate analyses of a given bottle (mean/$\sqrt{3}$), of 2.8% for Hg_t and 3.9% for MMHg. The PRL observed a between-bottle RSD of 11.0% for Hg_t (n=30 bottle means) and 9.2% for MMHg (n=20 bottle means). Thus, we estimate that the approximate true (1 RSD) between-bottle variability for this exercise is 8.2% ($\pm$ 0.10 $ng \cdot L^{-1}$) for Hg_t and 5.3% (0.023 $ng \cdot L^{-1}$) for MMHg.

To verify that the methods used by the PRL were quantitative, checks were undertaken. Six previously unopened sample bottles were selected, and BrCl added directly to each. They were left overnight to allow an estimation of Hg losses to the bottle walls. Aliquots of the same samples were then UV photo oxidized with BrCl to verify that all Hg had been recovered by the normal BrCl digestion. These results, shown in Table II may indicate a small (c.a. 5%), statistically insignificant additional recovery of Hg.

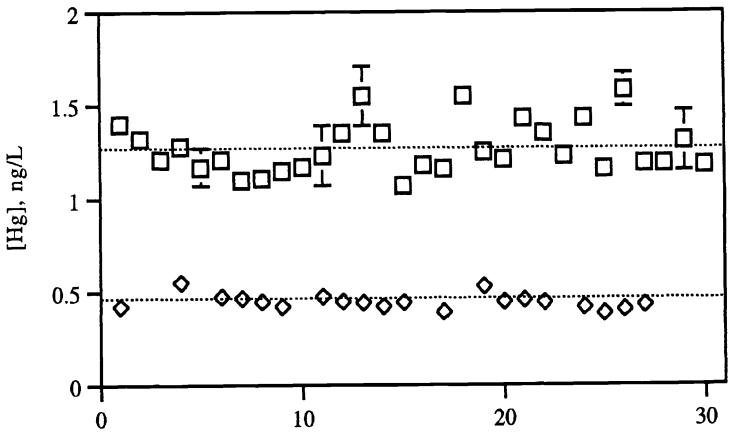

Fig. 1. PRL results for randomly selected bottles, as a function of field sampling order (see Fig. 2 also). Squares are Hg_t, diamonds are MMHg. Dash lines indicate grand means. All results are the mean of 3 analyses per bottle (1 σ error bars shown).

Many groups, including the PRL, reported the presence of settled matter (coagulated humics) in the samples which could result in within-bottle inhomogeneity. Most labs, including the PRL, homogenized the samples by vigorous shaking prior to analysis, which appears to minimize the effect of this inhomogeneity. Since Hg is known to adsorb to coagulated humics in acidified solution, (Bloom, 1994b) insufficient homogenization could result in significant within-bottle variability, causing variability between bottles as well.

In the case of MMHg, samples analyzed in triplicate using the distillation procedure were also analyzed by the CH_2Cl_2 extraction procedure. The latter recovered approximately 90% of the MMHg as the former (Table II). This is in keeping with past comparisons of the two methods (Horvat et al., 1993), which indicate a small fraction of particulate-bound MMHg is inaccessible to the solvent extraction procedure.

3.2 STABILITY OF THE Hg SPECIATION IN THE SAMPLES

A total of 18 samples retained at the PRL were analyzed prior to shipment of samples to the participating laboratories. Three months later, a set of 8 Teflon® and 4 borosilicate glass bottles (all previously unopened) were analyzed using the same protocols, to assess stability over the QA period (Table II). The results indicate no detectable changes in either Hg_t or MMHg for samples stored in Teflon® bottles with 0.4% HCl, in darkness. This assures that all labs analyzed samples of the same composition during the course of the intercomparison.

Table II

Primary Reference Laboratory QA/QC Results.

Species	Parameter	Mean	SD	N
Hg(tot)	all results (ng/L)	1.27	0.14	30
	analyzed week 1 (ng/L)	1.25	0.14	19
	analyzed week 13 (ng/L)	1.31	0.15	11
	BrCl in original bottle (ng/L)	1.21	0.07	6
	photo-oxidized + BrCl (ng/L)	1.33	0.12	6
	spike (5.0 ng/L) recoveries (%)	100.0	8.8	22
	all blanks (ng/L)	0.28	0.03	12
	NRCC DORM-1 (ng/g)	792	18	12
	certified value (ng/g)	798	69	--
MMHg	all distilled samples (ng/L)	0.446	0.041	20
	distilled week 1 (ng/L)	0.449	0.033	12
	distilled week 13 (ng/L)	0.441	0.052	8
	dist. spike (4.7 ng/L) rec. (%)	90.5	8.0	26
	all distillation blanks (ng/L)	0.048	0.018	23
	extracted samples (ng/L week 1)	0.420	0.055	12
	extract. spike (3.5 ng/L) rec.(%)	78.7	6.5	4
	extraction blanks	0.065	0.005	2
	NRCC DORM-1 (ng/g)	738	58	6
	certified value (ng/g)	732	60	--

Interestingly, although Hg_t was found to be stable in glass bottles over three months, a mean 12.2% decrease in MMHg was observed. Also, when some of the samples in Teflon® bottles (n=3) were stored an additional 46 days at room temperature and under normal lighting, a 9.9% decrease in MMHg was observed. More complete storage experiments are currently underway and will be the subject of a future paper.

3.3 BETWEEN-LAB COMPARISON

The convergence of results by all laboratories was good, with almost all reported values for both MMHg and Hg_t coming within a factor of two of the grand mean (Table III). The consensus mean value was calculated by excluding those laboratory means that were more than one standard deviation from the grand laboratory mean. Several laboratories reported mean results from less than three bottles, either because one bottle clearly and repeatedly deviated significantly from the other two (n=1 case), because sample was lost (n=3 cases), or because only one bottle was purchased for the intercomparison (n=1 case). For MMHg, only those data reported using distillation were used to create the consensus value, as this procedure has been shown to recover MMHg

TABLE III

Summary results from all ICE participating laboratories (values in italics excluded from summary statistics).

	Total Hg ($ng \cdot L^{-1}$)			Methyl Hg ($ng \cdot L^{-1}$)		
Lab ID	Mean	SD	N[a]	Mean	SD	N[a]
1 (PRL)	1.27	0.14	30	0.446	0.041	20
2 (SRL)	1.20	0.18	12	0.418	0.078	9
3	1.12	0.05	3	*0.210*	*0.011*	2
4	1.29	0.16	2	0.342	0.018	3
5	1.07	0.11	3	0.431	0.011	3
6	*2.74*	*0.30*	*3*	*0.63*	*0.12*	*3*
7	1.15	0.10	3	0.372	0.064	3
8	1.35	0.03	3	0.360	0.062	3
9	1.3	0.3	3	---	---	---
10	1.39	0.08	3	0.336	0.020	3
11	1.00	0.18	3	---	---	---
12	*1.91*	*0.81*	*3*	0.402	0.134	3
13	1.24	0.03	3	---	---	---
14	*0.79*	*0.09*	*3*	0.487	0.067	3
15	1.42	0.09	3	0.44	0.06	3
16	1.39	0.06	2	---	---	---
17	1.19	0.09	3	0.436	0.045[b]	1
18	1.20	0.10	3	---	---	---
19	1.17	0.16	3	0.495	0.134	2
20	1.32	0.02	2	0.352	0.062	3
21	1.14	0.10	3	---	---	---
22	1.26	0.26[b]	1	---	---	---
23	*3.47*	*1.59*	*3*	*<1.6*	---	*3*
grand mean	1.31	0.38	22	0.410	0.088	17[c]
consensus value[d]	1.27	0.18	19	0.420	0.055	8

[a]N equals the number of bottles for labs, number of lab means for grand statistics.

[b]SD is calculated from relpicates on only one bottle.

[c]N includes both distillation and extraction results from three laboratories (Table IV).

[d]Excludes outlying laboratory means (italics), and only uses MMHg results by distillation.

quantitatively, while the extraction procedure does not (see below, and Horvat, et. al, 1993). For Hg_t, 18 of 23 laboratories reported results within 20% of the consensus or PRL values, while for MMHg, 13 of 15 laboratories did so.

The bottle means for all individual bottles are presented as a function of sampling order (labs not reporting ICE bottle numbers (n=6) are all located at the end of the graph) in Figure 2, while the lab means and group statistics are presented in Table III and Figure 3. There was no general bias observed as a function of sample order, or how long after receipt the samples were analyzed, further substantiating the overall homogeneity and stability of the samples. These results indicate a significant convergence over a recent intercomparison (Cossa and Courau, 1990) in the ability of research laboratories to obtain

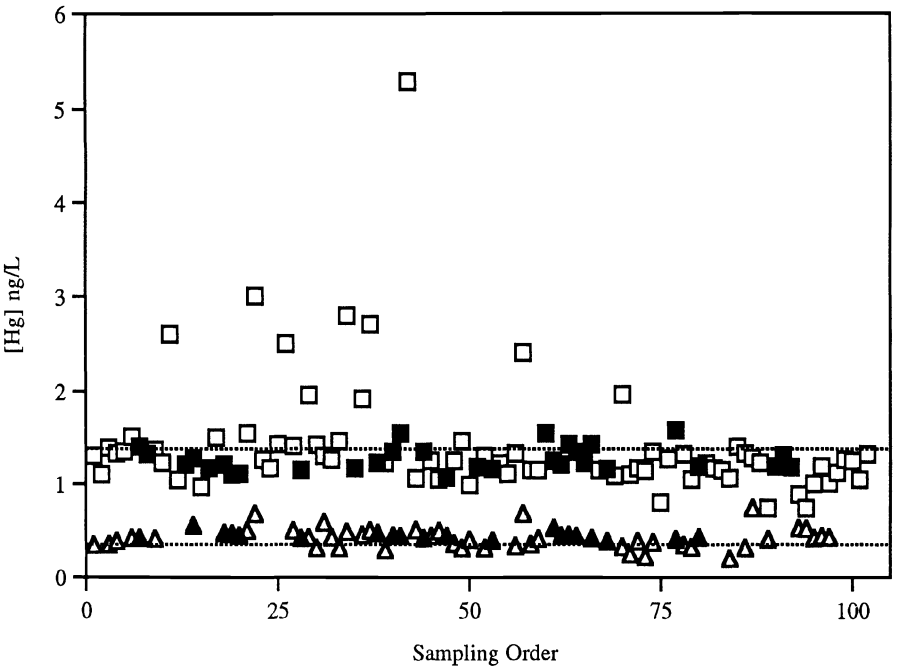

Fig. 2. Bottle means for all reported results, as a function of field sampling order. Squares are Hgt, triangles are MMHg. Dark symbols are the PRL data shown in Fig. 1. Dashed lines indicate the consensus values.

comparable results on aqueous samples for Hg_t, as well as the first published comparison for MMHg. quantitatively, while the extraction procedure does not (see below, and Horvat, et. al, 1993). For Hg_t, 18 of 23 laboratories reported results within 20% of the

Although the participating labs relied on similar methods, there were several significant differences in technique. Unfortunately, the one laboratory reporting a clearly different technique for MMHg (HPLC separation/CVAFS detection) was unable to obtain a sufficiently low detection limit. Amongst the laboratories utilizing aqueous phase ethylation, the participants were evenly split between those utilizing CH_2Cl_2 and those using distillation in the extraction step. The distillation procedure was developed to overcome low recoveries on complex media, such as brown waters (Horvat et al., 1993), and its efficacy in this respect is demonstrated here. Overall, the consensus mean for distillation was 0.420 ± 0.055 ng·L^{-1} (n=9 labs), while for extraction the mean was 0.396 ± 0.043 ng·L^{-1} (n=7 labs), resulting in a mean extraction to distillation recovery ratio of 0.942. This bias, although not statistically significant, is also evident in a direct comparison provided by three laboratories that provided MMHg results using both extraction procedures (Table IV).

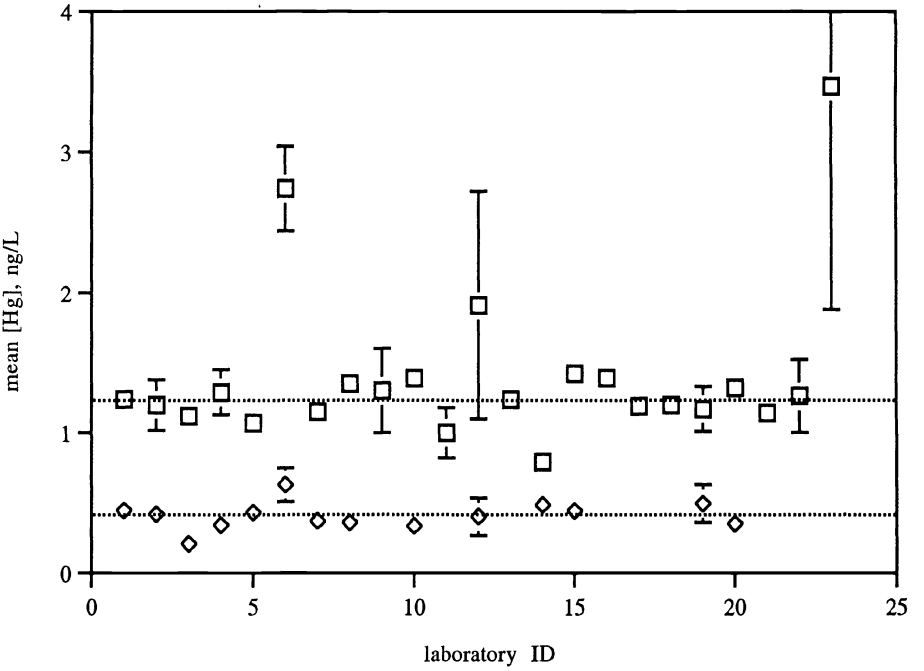

Fig. 3. Mean results (typically n = 3 bottles) as a function of submitting laboratory. Squares are Hgt, diamonds are MMHg. Error bars represent 1 s of the reported mean bottle values. Dashed lines indicate the consensus values.

For Hg_t, the only significant methodological difference was that three laboratories utilized direct $NaBH_4$ reduction rather than the wet oxidation followed by $SnCl_2$ reduction. The $NaBH_4$ method appears to give slightly lower results (1.17 ± 0.20 ng·L^{-1}, n=3 laboratories) than the consensus value, although the number of laboratories is too small to make the difference significant. In another noteworthy comparison, two different modifications of EPA method 245.1, involving direct purging of the $SnCl_2$ reduced sample into the detector (CVAAS or CVAFS), gave equivalent results to the more sensitive methods based upon pre-trapping with gold, albeit with significantly poorer detection limits.

TABLE IV

Comparison of methylene chloride extraction and distillation for MMHg recovery

	Methyl Hg (ng.L-1)		
Lab ID	Extraction	Distillation	E/D
1	0.420 ± 0.055	0.446 ± 0.041	0.941
5	0.390 ± 0.006	0.431 ± 0.011	0.905
14	0.443 ± 0.042	0.487 ± 0.067	0.910
lab mean	0.418 ± 0.026	0.454 ± 0.029	0.921

4. Conclusion

The results of this intercomparison exercise are very encouraging, with greater than 80% of the participating laboratories obtaining results for both total and methyl Hg within 20% of the consensus value on very low level, natural lake water. This demonstrates the compatability of the data sets being generated by diverse groups from around the world. The exercise design also demonstrates the soundness of utilizing sequentially pumped natural lake waters as a constant trace-metal concentration intercomparison source at ambient levels. We believe that it is important for the on-going quality assurance of these globally-linked research projects for similar intercomparison exercises to be conducted with a frequency of once every two years. Finally, it is unfortunate that no fundamentally different methods of Hg analysis were available for the intercomparison, as the narrowly defined consensus result still remains unverified as to a true value. An important goal for the near future must be the development of a fundamentally different method for low-level Hg speciation to stringently test the methods in common use today.

Acknowledgments

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USE OF A REFLUXING MIST CHAMBER FOR MEASUREMENT OF GAS-PHASE MERCURY(II) SPECIES IN THE ATMOSPHERE

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Abstract. As part of current efforts to understand the cycling of mercury (Hg) in the atmosphere, information is needed on its atmospheric speciation. Almost no data exists on water-soluble Hg(II) species in ambient air. A new technique for measuring gas phase water-soluble Hg(II) species has been developed, utilizing a high-flow refluxing mist chamber. Extensive testing has been carried out, including attempts to rule out production of artifact Hg(II). Measurements at two locations (East-Central Tennessee and the Ohio-Indiana border) found approximately 0.05-0.15 ng/m^3 of reactive Hg(II), representing ca. 3 to 5 % of the total gaseous Hg. Limited tests of artifact Hg(II) production in the mist chamber by ozone oxidation and co-sampled aerosol Hg(II) suggest that the majority of the collected Hg(II) exists in ambient air in the gas phase.

1. Introduction

Mercury (Hg) is accumulating in fish tissue at harmful levels in lakes in North America and Europe which receive no direct industrial discharges (Watras, 1990; Wiener *et al.*,1990; Lindqvist *et al.*, 1991). This Hg is thought to originate from long-range transport of atmospheric emissions of Hg in the vapor phase. Considerable progress has been made over the past 15 years in understanding the cycling of Hg in aquatic ecosystems (e.g. Rada *et al.*,1989; Verta, 1990; Lindqvist *et al.*, 1991), but very little is known about the air/surface exchange of Hg, especially deposition to ecosystems. Although new data are becoming available on the behavior of elemental Hg vapor (Hg^0), the role of water-soluble Hg compounds in the atmosphere is unknown. New data suggests that a significant fraction of the Hg emitted from combustion sources exists in this form, termed Hg(II) and assumed to be Hg^{2+}, perhaps as gas-phase $HgCl_2$ or $Hg(OH)_2$ (Prestbo and Bloom, 1995) but some workers doubt its existence in ambient air (Brosset and Lord, 1991). A consensus reached at two recent workshops emphasized the need to develop and apply methods to quantify vapor-phase Hg(II) in ambient air (Lindqvist *et al.*, 1991; Osa, ed., 1994) since this form will deposit much more rapidly than Hg^0 (Lindberg *et al.*, 1992). Models of Hg transport and deposition are highly sensitive to assumptions of the fraction of mercury present as Hg(II) (Petersen *et al.*, 1989).

Various gas scrubbing devices have been employed for extraction and concentration of reactive or soluble atmospheric trace gases. These have most commonly involved bubblers or impingers in which air is passed through a strongly-absorbing liquid in which accumulation of the analyte occurs. The advantages and disadvantages of these methods have been summarized (Cofer *et al.*, 1985). In particular these sampling methods suffer from the limitations of low gas flow and the necessity for long sampling times.

Water, Air, and Soil Pollution **80**: 1269–1278, 1995.

An alternate approach is to use solid-phase denuders, such as those used for HNO_3 (Ferm, 1986) or HCl (Keene, 1993), however none have been developed to separate Hg(II) from Hg^0. The use of solid sorbents for Hg(II) is limited to use in highly-concentrated stack gases unless the detection limit can be reduced. (Prestbo and Bloom, 1995).

Another approach to the problem of collecting trace atmospheric gases makes use of a refluxing mist chamber. This technique was developed by Cofer, Talbot, Harriss and co-workers at the NASA Langley Research Center (Cofer *et al.*, 1985; Cofer and Edahl, 1986) and has been used for various studies of trace gases in the atmosphere, including formaldehyde (Cofer and Edahl 1986), carboxylic acids (Talbot *et al.*, 1988), HNO_3 (Talbot *et al.*, 1990), SO_2 (Klemm and Talbot, 1991), HCl and Cl_2 (Keene *et al.*, 1993). In this device, air, at flows of 10 to 30 L/min, is aspirated through the chamber and water soluble gases are efficiently absorbed by the nebulized mist. Water droplets (estimated at 3 to 10 μm diameter) containing scrubbed gases collect and coalesce on the surface of a hydrophobic membrane, then drain back into the chamber. An intercomparison of measurement systems for atmospheric carboxylic acid gases (Keene, *et al* 1989) found the mist chamber to be superior.

We describe here the testing and first use of a refluxing mist chamber of the type described above for measurement of water-soluble Hg(II) species in ambient air. Because of the possibility that artifact-Hg(II) could be formed within the mist chamber or leached from co-sampled aerosols, leading to biased results for ambient Hg(II) , we also describe results of some tests of possible artifact formation.

2. Experimental

2.1. MIST CHAMBER.

Measurements were made using a mist chamber on loan from R. Talbot at the University of New Hampshire. This chamber (Figure 1) had four nebulizing nozzles. Refluxing was achieved by means of a hydrophobic Teflon filter (Zefluor™, 2 μm pore size, 50 mm diameter) mounted in a custom-fabricated all-Teflon conical top. The assembled unit had a working flow range of 12 to 25 L/min. It required a minimum of 8 mL of liquid for nebulization to occur. The combined volume of the chamber and refluxing top was 75 mL. The mist chamber was filled and emptied by means of a plastic syringe attached via a Mininert™ valve to a 1/6 inch TFE tube leading to the bottom of the chamber.

The mist chamber was connected to a Gast 1 cfm carbon vane pump. The flow was monitored either by a Gilmont flowmeter attached momentarily to the inlet or (more accurately) by a Rockwell gas meter, model CL-175, connected to the pump outlet. (Tests showed no contamination resulting from the Gilmont flowmeter attached briefly to the inlet.) Calibration was checked with a Gilibrator flowmeter (Gilian Instrument Co.).

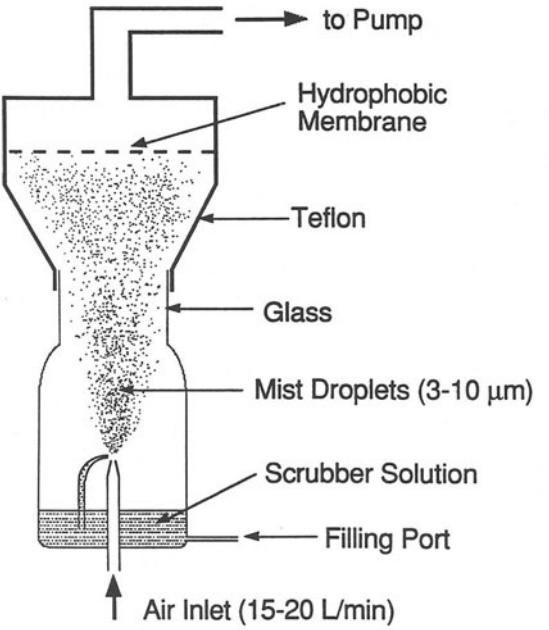

Fig. 1. Design of the mist chamber.

2.2. SAMPLING PROCEDURES.

2.2.1. *Sampling for Hg(II).* The scrubbing solution for most measurements was 0.5% HCl (0.046 *M*, pH 1.42) prepared by dilution of high-purity HCl (EM Science "Suprapur") in high quality deionized water. Fresh supplies of diluted HCl were made just prior to each sampling event. The Hg blank for this diluted HCl was negligibly small

Samples and blanks were collected and transported in 40 mL vials with TFE-lined caps. For most measurements these vials had been acid washed and treated with 1% BrCl solution, then rinsed and baked at 500°C. The TFE-coated cap liners were acid washed and dried at 60°C. All items were stored and transported in Ziplok™ plastic bags.

In a typical run, the mist chamber was filled with 15 to 20 mL of the 0.5% HCl and the sampling time was *ca.* 1 hour, resulting in *ca.* 1 m^3 of air sampled. (Runs were occasionally as short as 30 min or as long 2 hours.) Evaporation occurred at a rate of *ca.* 4 to 6 mL per hour, depending on ambient temperature and relative humidity. Thus, larger volumes were needed for long runs on hot days or when the humidity was very low. Occasionally more HCl solution was added midway through a run. At the end of each sampling period, the remaining liquid was transferred to a clean vial. The chamber was then filled with one 10 mL portion of the scrubbing liquid, aspirated for ca. 15 s (to rinse all surfaces) and the rinse combined with the sample. Studies of rinsing efficiency

demonstrated that ~ 10% of the analyte was left in the mist chamber each time it was emptied; thus inclusion of one rinse should recover 99% of the Hg. An additional 10 mL rinse was discarded before filling the chamber for the next sample.

Field sample blanks were obtained before and after each sample or set of samples. The mist chamber was filled in the usual way, then the liquid was aspirated for *ca.* 15 s (to rinse all surfaces) and transferred to a vial. The rinse was repeated and combined with the first rinse. Upon analysis by CVAFS these blanks represented the sum of contributions from the acid solution, syringe, mist chamber, and sample vial. Field sample blanks were sometimes variable and unpredictable, but were generally in the range of 20 to 50 pg Hg. During the first sampling campaign (Autumn, 1992) most samples were stored overnight in a refrigerator and analyzed the following day. In subsequent studies, nearly all samples were analyzed within 6 hours of the sampling time. All samples were corrected for the mean field blank determined on the same day.

A few measurements were made to investigate possible photochemical effects. For these, the mist chamber and sample containers were covered by aluminum foil to exclude light. Field blanks were treated in the same manner as the samples.

2.2.2. *Sampling for Total Gaseous Hg.* For all but the first sampling period, simultaneous measurements of Hg^0 were carried out using gold-coated sand traps. A small 6 volt air sampling pump was operated at a flow of ca. 0.5 L/min, monitored with a Tylan General mass flow meter connected to a voltmeter or data logger. The mass flow meter was calibrated against a Gilibrator bubble flow meter.

2.3. ANALYSIS.

Hg was determined by cold vapor atomic fluorescence (CVAFS) and dual gold-sand trap amalgamation (Bloom.and Fitzgerald, 1987). Quantitation was by peak area rather than peak height, using a Spectra Physics chromatographic integrator. The analyzer was calibrated either by a vapor injection method using 20 µL of Hg-saturated nitrogen at slightly sub-ambient temperature or by $SnCl_2$-reduction & purging of aqueous 0.5 to 1 ng standards. The two methods generally agreed within 5%, with the aqueous method typically lower. Analyses were carried out at two laboratories, located in Tennessee and Indiana, with satisfactory intercalibration results between them.

It should be noted that throughout this paper, "Hg(II)" refers to reactive, water-soluble Hg^{2+} species. It is defined analytically as the fraction of Hg which is easily reduced to Hg^0 by stannous chloride ($SnCl_2$). In the Swedish speciation scheme (Lindqvist *et al.*, 1991) this fraction is denoted as Hg(IIa) and is called "reactive" or "acid-labile" Hg. In an alternative speciation scheme (Bloom, 1992) this fraction is called "ionic Hg", distinguished (by analytical method) from both "strongly complexed" and "inert" (i.e. particle-bound) Hg

All mist chamber samples and blanks were analyzed for easily-reducible Hg by reduction with $SnCl_2$ and purging to a gold-coated sand trap. A small 30 mL bubbler with a fritted inlet was used with purge flows of 100 to 200 mL/min and purge times of 6

minutes. Total gaseous Hg (from field collection on gold-sand traps) was determined by direct thermal desorption to the second gold trap.

A few mist chamber samples were analyzed for Hg^0 and/or for Hg(total). Hg^0 was determined by purging the solution directly to a gold trap, using a small (30 mL) bubbler which had never been in contact with $SnCl_2$. Hg(total) was determined by treatment of the samples with BrCl, followed by reduction with hydroxylamine and stannous chloride. In both cases, field blanks were analyzed in an identical manner.

The analytical detection limit (bubbler, dual gold trap amalgamation and CVAFS detection) was *ca.* 5 pg Hg (3x std. dev. of bubbler blanks). For samples collected in the mist chamber, the detection limit was estimated to be *ca.* 10 pg Hg (based on precision of the field blanks) corresponding to an atmospheric concentration of *ca.* 0.01 ng/m^3.

To estimate the analytical precision for the mist chamber samples, a few samples were split and analyzed in two portions, generally agreeing with 5%. Comparison of successive field samples frequently showed similar agreement. With only one mist chamber it was not possible to determine accurately the precision of the samples because of the necessity of using sequential samples (with possible short-term changes in atmospheric concentrations); nevertheless Figure 2 shows good agreement between many pairs of sequential samples.

2.4. DESCRIPTION OF SAMPLING SITES.

Two sites were used for most of the studies reported here. A large body of data was collected at the Walker Branch Watershed in east-central Tennessee, near Oak Ridge National Laboratory. This is an upland forested site, elevation *ca.* 330 m, located approximately 20 km from two large (1,000 megawatt) coal-fired power plants. Sampling was done in a grassy clearing of 1.5 ha. Extensive meterological monitoring equipment at this site, operated by NOAA (Hicks, 1991) provided 15 minute averages of O_3, SO_2, NO_2, temperature, solar radiation, wind direction/wind speed, and other parameters. Most sampling for Hg(II) was done on a platform in the middle of the clearing, *ca.* 2 m above the ground.

The other primary sampling site was in Richmond, Indiana, a small Midwestern city at the Ohio/Indiana border. A small (60 megawatt) coal-fired power plant is located 3 km downwind (by prevailing wind direction). The nearest large cities are 60 to 120 km away and numerous large coal-fired power plants are located along the Ohio River Valley to the south and west. Most sampling was done in open grassy locations, approximately 1.5 m above the ground. Limited sampling was also done on the roof of a building at a height of 12 m with only a few large trees in the vicinity.

3. Results

Five sampling campaigns have been carried out to date, as summarized in Table I. Although there was substantial variability, the Hg(II) concentrations averaged *ca* 0.06 ng/m^3 at the Tennessee location and 0.10 ng/m^3 at the Indiana location.

Table I. Summary of Mist Chamber Sampling Campaigns and Results

Place[a]	Time	Days	Samples	Hg(II) found, ng/m^3 Mean (± S.D.)	Range	Ratio Hg(II)/Hg
TN	Fall 1992	7	15	0.045 ± 0.03	(0 01 - 0.10)	0.021 ± 0.015
TN	Summer 1993	11	38	0.065 ± 0.03	(0.02 - 0.17)	0.029 ± 0.013
IN	Spring 1993	6	7	0.27 ± 0.09	(0.15 - 0.36)	0.081 ± 0.048
IN	Fall 1993	8	11	0.12 ± 0.05	(0.04 - 0.21)	0.040 ± 0.033
IN	Spring 1994	20	57	0.073 ± 0.03	(0.02 - 0.14)	0.022 ± 0.015

a. TN = Walker Branch near Oak Ridge, Tennessee. IN = Richmond, Indiana

The Hg(II) results may be compared with Hg^0 concentrations that were measured simultaneously. Hg^0 was generally in the range of 2-3 ng/m^3 at the Tennessee site and 3-8 ng/m^3 at the Indiana site. The last column in Table I summarizes the *ratios* of Hg(II) to Hg^0. A representative set of data for one sampling campaign is shown graphically in Figure 2. This illustrates the day-to-day variation and the variation between sequential samples within one sampling day.

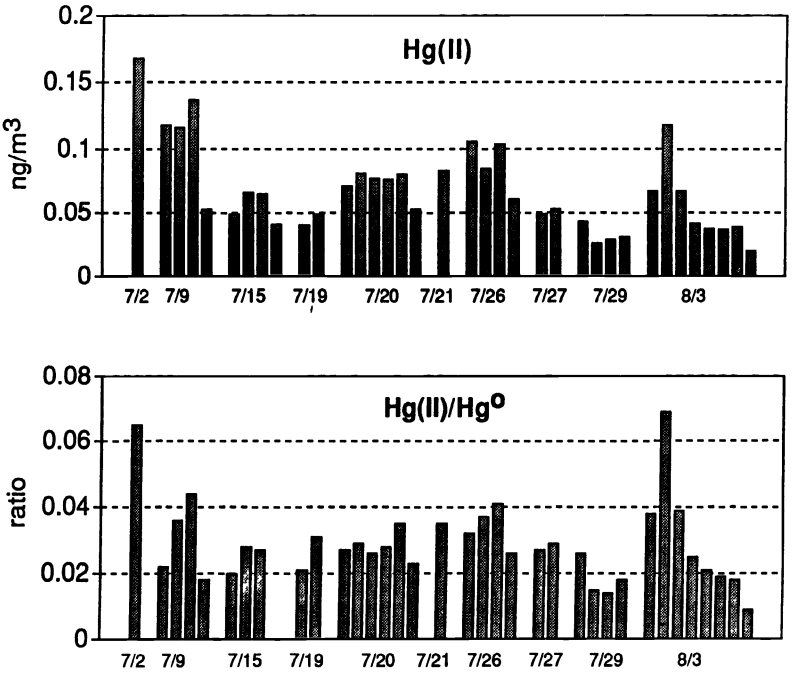

Fig. 2. Atmospheric Hg(II) concentrations (top) and Hg(II)/Hg^0 ratios (bottom), Walker Branch, TN, July-Aug 1993.

4. Discussion

4.1 TESTS OF THE VALIDITY OF THE MEASUREMENTS.

Before discussing the results, we need to address several questions regarding the validity of the experimental data. We first ask whether we were measuring Hg(II) or simply a portion of the atmospheric Hg^0 that dissolved in the aspirated air samples. The Henry's Law constant for Hg^0 in water is *ca.* 0.3 (Sanemasa, 1975); from this we calculate that the equilibrium solubility of Hg^0 in the *ca.* 20 mL. of mist chamber liquid should be <1 pg or less than 1% of the observed amounts of Hg (*ca.* 100 pg) in the mist chamber samples. (Here we assume that the solubility of Hg^0 in 0.046 *M* HCl will not be substantially different from that in pure water.) A few measurements of Hg^0 in mist chamber solutions confirmed that Hg^0 was very low (< 2% of the measured Hg) and thus it could be ignored.

Second, we are aware of the potential for artifact Hg(II) to be produced in the mist chamber solution during sampling. For example, Brosset and Lord (1991) concluded from bubbler studies that Hg(II) was most probably formed in the bubbler solution by ozone oxidation of Hg^0. It must be emphasized that their studies employed bubblers operating at a much slower flow (0.7 L/min), with much longer sampling times, longer residence times, higher solution/gas ratios and, therefore, greater likelihood of artifact formation. We identify two possible sources of artifact Hg(II): (1) oxidation of atmospheric Hg^0 within the mist chamber, with the most likely oxidant being ozone and (2) dissolution of Hg(II) from co-sampled particles. We therefore designed several studies to test these possibilities.

4.1.1. *Tests of artifact formation of Hg(II): Co-sampled particulate-Hg.* Addition of a particle filter in the mist chamber inlet stream adds a new uncertainty because such filters may also remove a portion of the gaseous Hg(II). Nevertheless, several tests were carried out in which a 3 μm Zefluor™ filter was mounted on the mist chamber inlet. Sequential measurements, with and without the filter, showed no statistically-significant difference in Hg(II). (Mean difference of 13 pairs = 1.5%.) In addition, several independent studies of particulate Hg were carried out at the Walker Branch sampling site, using glass fiber or Teflon filters and one-week sampling periods during Oct-Nov 1992 and May-June 1993 The filters were extracted and analyzed for both Hg(II) and Hg(total) The results showed total particulate Hg concentrations of 0.012±0.008 ng/m^3 (with Hg(II) accounting for 80-90% of the total). Based on this indirect evidence, aerosol Hg could contribute, at most, 10 to 25% of the measured Hg(II) in the mist chamber solutions if it were efficiently collected by the mist droplets.

4.1.2. *Tests of artifact formation: Oxidation of Hg^0.* Oxidation of Hg^0 in aqueous solutions by ozone (O_3) has been studied extensively (Iverfeldt and Lindqvist, 1986; Munthe, 1992). We considered several ways to test for oxidation reactions within the mist chamber, such as use of denuders to remove either O_3, Hg^0 or Hg(II), but all were

either impossible or could, at the same time, remove some unknown portion of Hg(II). We also considered using a controlled atmosphere chamber to sample zero air, air with Hg^0 and with or without O_3, etc, but the requisite flow rate for the mist chamber was too high for the available chamber.

We were left, therefore, with the necessity to use field tests of possible artifact formation, such as comparison of Hg(II) with simultaneous O_3 measurements. Our data from the Oak Ridge site in July 1993 showed essentially no correlation between Hg(II) and ambient O_3 concentrations ($r = 0.19$) or between the Hg(II)/Hg^0 ratio and O_3 ($r = 0.16$). Although this is an indirect test, it strongly supports the absence of significant reaction with ozone within the mist chamber to produced the measured Hg(II).

Because of the location of the Walker Branch site near Oak Ridge Tennessee, we were able to do one very interesting and revealing test. Samples were collected within the Oak Ridge Y-12 industrial site, *ca* 4 km from the Walker Branch site and near a point source heavily contaminated with elemental Hg. Measurements were made on 7/30/93 at two locations where atmospheric Hg^0 concentrations were ~ 5 and 70 ng/m^3, or 2.5-fold and 40-fold above the then-current background level of Hg^0 at the nearby Walker Branch site. At the first location, the Hg(II) concentration was 0.060 ng/m^3, indistinguishable from Hg(II) measurements at Walker Branch on the preceding and following days. At the more contaminated site, Hg(II) was 0.160 ng/m^3, representing less than a 3-fold increase in Hg(II) despite a 40-fold increase in Hg^0 -- and in fact Hg(II) was within the experimental range of Hg(II) at Walker Branch. We assume that ambient O_3 at this location was similar to that at Walker Branch, i.e. 50 ppbv for this sampling period.

Using a published model for oxidation of Hg^0 by O_3 in acid solution (Munthe, 1992), it is possible to estimate the amount/concentration of Hg^{2+} which could be formed in the mist chamber during sampling. Assuming an ozone concentration of 60 ppbv and typical experimental conditions for our samples, the model predicts formation of *ca* 15 pg of Hg^{2+} in 1 hour (Munthe, private communication). At a sampling flow rate of 18 L/min, this corresponds to 0.014 ng Hg^{2+} per m^3 of air sampled or less than 1/4 of the measured Hg(II) (cf Table 1). We interpret these results to show that relatively little Hg^0 oxidation has taken place within the mist chamber

4.1.3. *Photochemical effects.* To test whether any photochemical process is occurring within the chamber, several tests were carried out in which the chamber was covered with aluminum foil during sampling. Paired sequential samples, with & without foil, showed no statistically-significant difference in concentrations of Hg(II).

4.2 SUMMARY OBSERVATIONS ABOUT ATMOSPHERIC Hg SPECIES.

Having tentatively concluded that we are measuring Hg(II) in excess of either artifact Hg(II) created within the mist chamber or particulate-Hg(II) extracted in the chamber, we now turn to a brief discussion of the assembled data. At our study sites, the total gaseous Hg (designated as Hg^0) was generally in the range of 2 to 6 ng/m^3, with a tendency for

higher values in Indiana than in Tennessee. These values are consistent with those reported by many other workers for atmospheric Hg^0.

The following generalizations about atmospheric Hg(II) may be made from our data. (1) Measured concentrations were in the general range of 0.05 to 0.2 ng/m^3. It is interesting to note that these are consistent with results reported by Brosset (1987), despite later postulation of artifact formation (Brosset and Lord, 1991). (2) There is very little correlation between measured Hg(II) and ambient ozone concentrations, which argues against both in-air and in-chamber oxidation of Hg^0 to Hg(II). (3) There does appear to be a moderate correlation between Hg(II) and Hg^0 ($r = 0.57$, $n = 38$, $P<0.01$). (4) We frequently observed a slight tendency for Hg(II) to peak in mid-day.

Finally, we can use these results combined with other data for particulate-Hg to estimate the atmospheric speciation of Hg at the Tennessee site. We estimate mean summer concentrations to be as follows: $Hg^0 = 2.4\pm0.5$ ng/m^3, Hg(II) = 0.07 ± 0.03 ng/m^3 and particulate Hg = 0.012 ± 0.008 ng/m^3.

5. Conclusion

Use of a high-flow refluxing mist chamber has been demonstrated to provide a useful approach to measurements of reactive Hg species in the atmosphere. Hg(II) is a small but measurable fraction (ca. 2-8%) of total atmospheric Hg. Several experimental difficulties are not yet fully resolved and are still under investigation.

Acknowledgements

We thank Robert Talbot for the loan of the mist chamber and Barry Lefer for many helpful conversations concerning mist chambers and their use. WS wishes to thank Ralph Turner for introducing him to Hg studies and for gracious hospitality during a sabbatical year at ORNL. Jim Owens was unstinting in providing technical support for many aspects of these studies. Finally WS wishes to acknowledge the important contributions of several undergraduate students at Earlham College: Elizabeth Malcolm, Amanda Salanitro, Maria Verbrugge and Eric Dudas. This study was sponsored, in part, by the Electric Power Research Institute under contract RP322218-02 with ORNL (managed by Martin Marietta Energy Systems, Inc., under contract DE-AC05-88840R-21,400). This is Environmental Sciences Division publication number 4358.

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AUTOMATED MERCURY DETERMINATION IN WATERS

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stract. A rapid technique for dissolved Hg determination in water at ultra-trace level is described. It sists of the automatisation of the cold-vapor/gold amalgamation/atomic fluorescence technique, which ows the determination of 8 samples per hour with an analytical precision of 5 % and a 0.1 $ng.l^{-1}$ tection limit for a 45 ml sample. It is suitable for Hg determination in most of the natural waters.

1. Introduction

ver the last decade investigations to determine Hg in natural waters have established that the pical dissolved Hg concentration are at the nanogram per liter level (e.g. Bloom and ecelius, 1983 ; Gill and Bruland, 1990 ; Mason and Fitzgerald, 1990).

Despite these major advances, the behavior of this metal in the environment is still orly understood. High resolution vertical distributions of Hg concentrations in the oceans, as and coastal zones, and temporal variations in freshwater systems are needed for a better derstanding of its geochemical pathways and for building realistic mass balance budgets. In ldition to these scientific needs, there is a tendency, within the regulatory agencies, towards quirements of better detection limits for dissolved Hg determinations in monitoring ogrammes. Therefore a sensitive and automatic technique for dissolved Hg determination in ater would be very helpful. Here we propose the optimization of a commercially available tomated system (PS Analytical Ltd) which allow the determination of sub-nanogram per re Hg concentrations in waters.

2. Material and method

strumentation (Figure.1). Recently Stockwell *et al.* (1989) proposed a fully automated stem for the determination of Hg at very low levels in environmental samples. This system nsists of a random access auto sampler (PSA 20.099), a continuous flow vapor generator SA 10.003) which converts the dissolved Hg (II) into elemental Hg using a reducing agent. ercury vapor is then stripped from the liquid through a phase separator using an argon rrier gas and collected on a gold trap (PSA 10.501 Galahad) ; on heating the gold trap the g is re-vaporised into an atomic fluorimeter (PSA 10.023 Merlin) by means of an argon gas ream. The different analytical steps are controlled by a computer using the PSA TouchStone 1023T150) software package which also processes analogue data. The combination of the e-concentration step on a gold trap and the utilization of the atomic fluorescence detection

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maximalizes the sensitivity of the Hg determination. However, until now, reagent blanks and blanks originating from the carrier gas streams have constantly been introduced to the gold trap and therefore the limit of detection was limited to the nanogram per litre range.

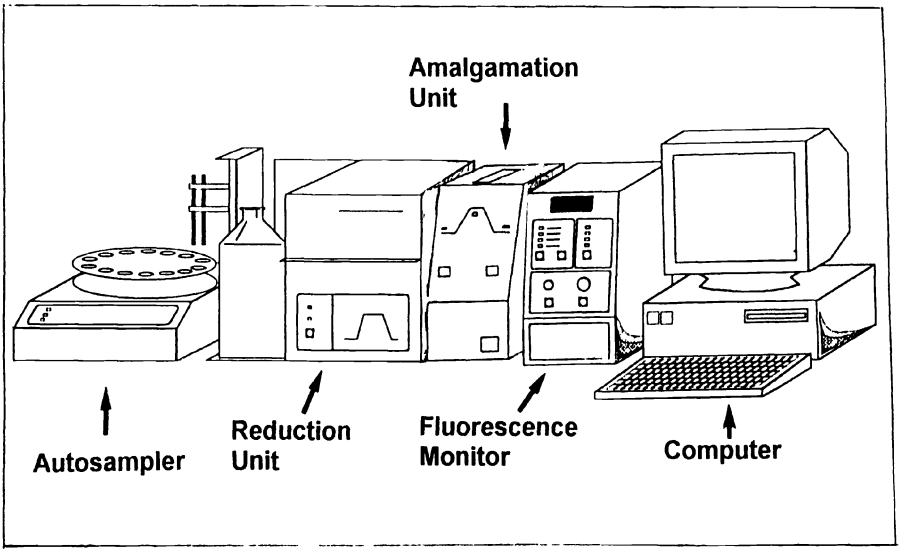


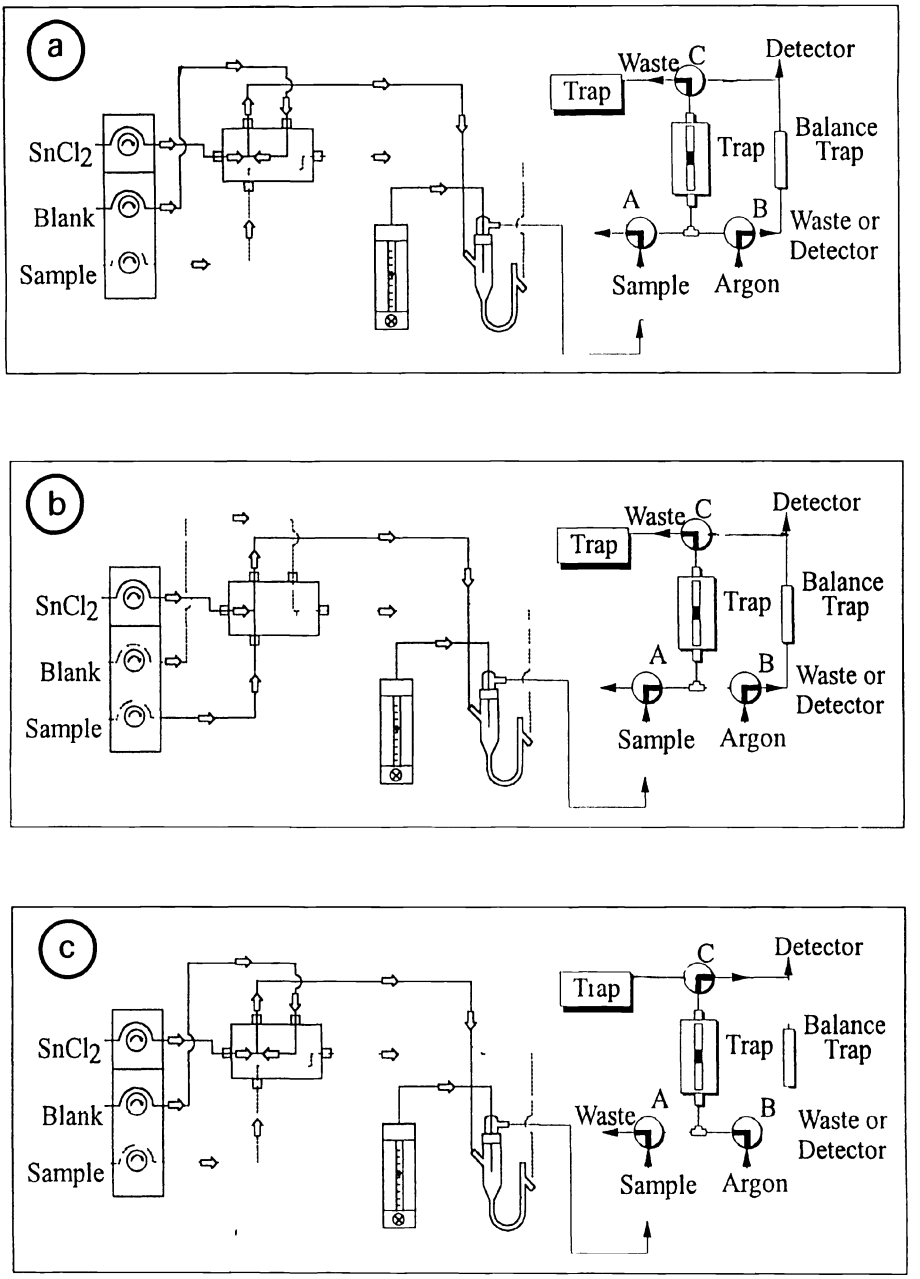
Fig. 1. Instrumentation.

Consequently, we developed a new Hg vapor generator, which has a complete flexibility in terms of valve time sequencing. Previously the valve sequence was operated by the control panel on the vapor generator, which only allowed a pre designated selection of the times. The new system is computer controlled allowing the introduction of sample volumes between several ml and several liters. This flexibility allows discrete samples to be introduced in a flow injection type manner. To increase the flexibility and accuracy of the flow rate the standard pump was replaced by a 4 channels Labcraft peristaltic pump.

The vapor generator activates the valve sequence for the amalgamation unit. This effectively diverts the Hg carrier gas over the gold trap only during the sample introduction period. The sequence of events during the analysis of a sample is outlined in figure 2. In order to minimize the procedural blank, these modifications were combined with the addition of gold coated sand traps on the gas lines to produce Hg free carrier gases and with the sheltering of the auto sampler under a plastic bell-jar. A nitrogen flow (50 $ml.min^{-1}$), free of Hg by passing the gas on a gold coated sand cartridge, was introduced in the jar during the analysis in order to avoid atmospheric contamination. In addition, all the plastic tubing, except those of the peristaltic pump of the vapor generator unit, and the vials were of Teflon and acid washed. The tubing for the pump of consists of acid washed C-Flex silicone rubber.

Reducing solution. The reductant solution used was tin (II) chloride (10 % (m/v) in 20 % HCl (Suprapur®, Merck)). This solution was continuously purged with Hg free nitrogen (100

ıl mın^{-1}) durıng the runnıng of the operatıon to maıntaın low Hg contamınatıon The ɛductant solutıon was prepared daily



ıg 2 Schematıc dıagram of the automated Hg system (a) non samplıng perıod , durıng thıs stage the gold trap ıs ısolated to mınımıze blank levels (b) pre-concentratıon stage , (c) measurement perıod

Sequences for the pre-concentration and analysis. All the sequences are driven by the microcomputer using the TouchStone software. This allows totally automated pre-concentration and analysis. A summary of the total procedure is out-lined below:

(i) When no sample is being introduced the reductant and the blank are continuously mixed in the gas liquid separator where the background level is established. During this stage the gold trap is isolated to minimize blank levels.
The orientation of the valve manifold is shown in Figure 2a. A flow of argon gas is continuously introduced to the fluorescence detector.

(ii) The sample is collected from the auto sampler via Teflon probe and flows through the vapor generator for 35 s to ensure complete flush out of any residuals from the previous sample.

(iii) When the valve of the vapor generator is activated to introduce the sample, this triggers the valve manifold to the orientation shown in Figure 2b. The Hg generated during this stage is pre-concentrated on the gold trap. A continuous flow of argon is introduced to the detector at all the times.

(iv) After pre-concentration the vapor generator valve switches back to the reagent blank solution. This process activates the auto sampler to stop collecting the sample and switches the valve manifold to that shown in Figure 2c.

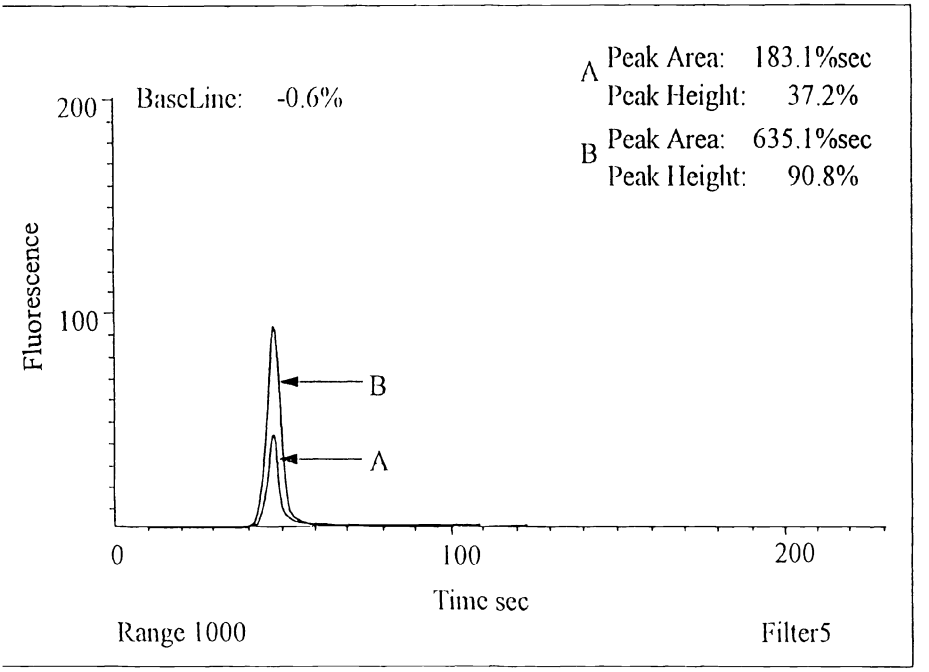
(v) The analysis cycle now starts and TouchStone software begins to acquire data. Residual sample gases are flushed through the system, the gold is heated to release Hg and the trap is cooled rapidly in the chamber. After the coolant cycle has finished the system is ready to collect the next sample.

3. Results

Quality of the signal. Typical peak shape are shown in Figure 3. These represent a reagent blank (A) and tap water (B) respectively. The tap water was found to contain 0.6 ng l^{-1} Hg. The profiles illustrate a rapid rise in the signal and excellent symmetry; Results indicate that both peak height and peak area provide equivalent good measurements of the quantity of Hg which passed through the detector.

Linearity. The linearity of the detector spans over 5 orders of magnitude. All calibration curves obtained during the study were found to be linear over the analytical range tested (0-10 ng.l^{-1}).

Sensitivity. The absolute sensitivity obtained with the operating conditions used in this study was 0.5 pg of Hg per unit of fluorescence. For a 45 ml water sample and if one takes into account only the instrument noise of the detector, the theoretical detection capacity would be 0.06 ng.l^{-1}. However, because of the blank level and reproducibility the actual limit of detection was slightly higher.



ig. 3. Typical peak profile for the analysis of reagent blank (A) and tap water (B) using amalgamation.

lank. The total blank was quantified to be 17.8 ± 0.8 pg as the average (± sd) of eight plicated runs of the reagent blank. The argon used as carrier gas was tested and was 5.3 pg hich is 30% of the total blank.

imit of detection. In order to take into account the errors of type I and II at a confidence limit f 95% and assuming a standard deviation of the sample near the blank is the same as the tandard deviation of the blank (sd_{blk}), the detection limit is defined as $4.65sd_{blk}$ (Hewitt, 1989) e., 4 pg of Hg. On the basis of results on table I and owing to the volume of sample, the etection limit of the current method is 0.1 $ng.l^{-1}$.

epeatability. On the basis of the results on the blank assessment, the coefficient of variation d.100/average) is 5 %.

4. Conclusion

The automatic system for ultra-trace Hg determination in natural water described here consists of a autosampler, a continuous flow vapor generation, a pre-concentration unit and an atomic fluorescence spectrometer controlled by a computer. The method proposed achieves a limit of detection of 0.1 $ng.l^{-1}$ with a sample size of 45 ml. Approximately eight samples per hours can be analyzed with a precision of 5%. It is more sensitive that a recent automated technique proposed by McIntosh (1993). The instrumentation is very reliable but strict control measures are required to ensure a Hg free environment around the instrumentation.

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Method Development and Sample Processing of Water, Soil, and Tissue for the Analysis of Total and Organic Mercury by Cold Vapor Atomic Fluorescence Spectrometry

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Abstract. Atomic Fluorescence-based methods have been developed for measuring ultratrace levels of mercury (Hg) in environmental (water, soil) and biological (fish tissue) samples. In addition, methods for preparation of water, soil, and tissue samples have been developed. For the analysis of total Hg in soil, sediment and fish the samples are digested with concentrated nitric acid in sealed glass ampules, and subsequently autoclaved. Water samples are digested using standard brominating procedures. A Merlin Plus, PS Analytical atomic fluorescence spectrometer (AFS) system equipped with an autosampler, vapor generator, fluorescence detector and a PC based integrator package is used in the determination of total Hg. The determination of Hg mercury species in water, without pre-derivatization, involves adsorbent pre-concentration of the organomercurials onto sulfydryl-cotton fibers. The organic Hg compounds are eluted with a small volume of acidic KBr and $CuSO_4$ and extracted into dichloromethane. Sediment, soil and tissue samples are homogenized and the organomercurials first released from the sample by the combined action of acidic KBr and $CuSO_4$ and extracted into dichloromethane. The initial extracts are subjected to thiosulfate clean-up and the organomercury species are isolated as their chloride derivatives by cupric chloride addition and subsequent extraction into a small volume of dichloromethane. Analysis of organic Hg compounds is accomplished by capillary column chromatography coupled with atomic fluorescence detection.

1. Introduction

Mercury is a widely distributed pollutant in the environment and has gained considerable toxicological concern in recent years. In some cases, the desired quantitation levels of this metal challenge the detection limits of the instrumentation and methods in current use (Swift and Campbell, 1993; Kammin and Knox, 1992). This has certainly encouraged the development of sensitive, reliable and precise methods for the analysis of Hg. Further, the organic forms of Hg, particularly methylmercury (CH_3Hg^+), are far more toxic than the inorganic forms (Hg^{2+}, Hg^0) of the pollutant (Rubi *et al.*, 1992; Bryan and Langston, 1992). In efforts to project long-term health risks and the ecological impact associated with trace amounts of Hg in the environment, reliable quantitation and accurate speciation at increasing lower levels are necessary.

The open-vessel digestion procedures and detection methods for total Hg analysis in water samples that are commonly used are based on acid leaching and permanganate/persulfate oxidation followed by cold vapor atomic absorption (CVAAS), (Szakács *et al.*, 1980; Van Delft and Vos, 1988). One of the most commonly used analytical technique for the determination of organomercurials is gas chromatography with electron capture detection (GC-ECD), (Rubi *et al.*, 1992; O'Reilly, 1982) with or without pre-derivatization of the organic mercury compounds. The instrumentation and sample preparation

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of the existing methods strongly limit the ultimate sensitivity and efforts to lower the detection limits have not been entirely successful (Swift and Campbell, 1993). In addition, the ECD is an unselective detector and the column has to be tediously conditioned with large injections of Hg (II) chloride to alleviate poor chromatographic response to organomercurials (Hight and Capar, 1984; Rubi *et al.*, 1992; Uthe *et al.*, 1972; Bryan and Langston, 1992; Bulska *et al.*, 1992). These disadvantages demonstrate the need for the development of new methods in this field.

This paper describes atomic fluorescence-based methods for analyzing total Hg and organic Hg compounds at low part-per-trillion levels in environmental and biological samples. The atomic fluorescence (AFS) method (Bloom, 1989; Alli *et al.*, 1994) has become increasingly important compared to CVAAS, since the instrumental detection limit of this method is about 1 picogram or less and at least one order of magnitude better than for CVAAS (Lindqvist, 1993). Total Hg analysis involves three stages: sample digestion, cold vapor generation and atomic fluorescence detection.

In water samples, the difficulty in measuring MeHg and other organomercurials lies in concentrating these compounds from solution. This work employs a sulfydryl cotton fibre medium (Lee and Mowrer, 1989) which effectively adsorbs and preconcentrates trace levels of organomercurials. The organic Hg compounds are eluted with acidic potassium bromide and extracted into dichloromethane and subjected to GC analysis with AFS detection. Soil, sediment and tissue samples are treated with acidic potassium bromide and copper sulfate, and extracted with dichloromethane. The initial extracts are subjected to sodium thiosulfate clean-up subsequent to capillary gas chromatography with atomic fluorescence detection (Alli *et al.*, 1994).

2. Materials and Methods

2.1 SAMPLE COLLECTION AND PREPARATION

Surface water samples are collected in 2 L Teflon (Nalgene) bottles using a vacuum system. Samples are screened (105 μm Nytex netting) to prevent the collection of large particles with the water samples. All tubings and fittings used in the sampling system are constructed of teflon (SERP, internal SOP, 1994). The samples are collected by a "clean person" using double gloves (short vinyl gloves under shoulder length polyethylene gloves, OakTech) and a double bagging technique. All samples are placed in zip-lock polyethylene bags (Fisher Scientific), then in an additional plastic sample bag and placed in an icechest/cooler. In the clean room, concentrated hydrochloric acid, (trace metal grade, Fisher Scientific) is added to the water samples for preservation.

Surface, soil and sediment samples are collected using either a stainless steel spade, trowel or Eckman dredge. These samples are placed into wide mouth polyethylene specimen cups (125 ml, Fisher Scientific). Subsurface soil or sediment samples are collected in polycarbonate core tubes. Upon arrival to the laboratory the samples are immediately frozen to preserve their chemical integrity.

Fish samples are collected using a dip net, with the sampler wearing two pairs of gloves. The fish are placed in zip-lock sample bags, labelled, and stored in a cooler with ice for transport to the laboratory. Fish samples remain frozen until ready for analysis.

2.2 SAMPLE DIGESTION FOR TOTAL MERCURY DETERMINATION

Water Samples. Water samples are digested in a 125 mL teflon bottle with 1 mL HCl and 2.5 mL potassium bromate ($KBrO_3$)/potassium bromide (KBrO) mixture overnight (Szakács *et. al.*, 1980; Bloom and Fitzgerald, 1988). These

samples are prepared and remain (in capped bottles) in the Hg-clean room. Prior to analysis, 500 μL hydroxylamine hydrochloride is added to destroy excess bromine and the samples thoroughly shaken.

Soil and Sediment Samples. Soils (such as peat, marls and marly peat) are first homogenized by adding 30 to 50 mL of deionized water and blended for 3 minutes to a uniform consistency with a blender (Osterizer). From the homogenized slurry 5 mL is diluted into 45 mL of 0.6N HCl to neutralize any carbonates, in a clean specimen cup. Of this mixture 1 mL is placed in a 10 mL ampule with 2 mL of concentrated nitric acid (HNO_3), (trace metal grade, Fisher Scientific). Digested soil and sediment samples are left to stand under a fume hood for 20 minutes. The ampules are subsequently sealed and autoclaved for 1 h at 151°C. Before analysis the digestates are diluted with 0.12N HCl solution in a 20 mL polyethylene vial.

Fish Samples. To quantify total Hg in small fish (< 0.4 g, < 30 mm in length) the entire fish is weighed and placed in 10 mL ampules and digested using 1 mL deionized water and 2 mL concentrated HNO_3. After standing 20 minutes under a fume hood, the ampules are sealed and autoclaved as described above. For the analysis of larger fish (approximately 30 cm or longer), 3 tissue plugs (stainless steel core tube, 4 mm in diameter) are taken from the left side (using only muscle tissue), and combined to obtain a representative sample (approximately 0.4 g). The samples are then processed as indicated above for soil and sediment.

These digestion procedures result in the conversion of organic forms of Hg to inorganic mercury (Hg^{2+}). The digested samples are introduced to the cold vapor generator, at which point tin (II) chloride is used to effectively reduce inorganic mercury (Hg^{2+}) to its elemental gaseous form (Hg^0), prior to detection by atomic fluorescence.

2.3 INSTRUMENTATION AND ANALYSIS

A PS Analytical Merlin Mercury Fluorescence Detector System used in this study was supplied by P.S. Analytical Ltd. (UK). This system incorporates an Autosampler, Vapor Generator, Fluorescence Monitor and an IBM compatible Computer System. Instrument operating conditions for ultratrace and high levels of Hg concentrations are given in Table I.

Table I. Optimized operating conditions of the AFS System for total-Hg concentrations.

Ultratrace levels		*High levels*	
Carrier gas mL/min	125	Carrier gas mL/min	200
Sheath gas mL/min	150	Sheath gas mL/min	350
Calibration range	1000	Calibration range	100
Fine grain	4.0	Fine grain	2.5
Damping Switch	On	Damping Switch	On

Cold Vapor Generation. In the continuous flow vapor generator system, Hg(II) is reduced to Hg^0 following the addition of tin(II) chloride. The volatile Hg is stripped from the solution (in the gas liquid separator) by a carrier gas (argon). The rate of argon flow depends on whether the analysis is for ultratrace or high levels of Hg determination (P.S. Analytical, 1991).

Atomic Fluorescence Detection. A sheath gas (also argon) is used to channel the Hg vapor through a chimney past a light source and a photomultiplier tube that are at right angles to each other. With a specific high intensity Hg lamp source (Cathodeon Ltd., Cambridge) and a fixed 254 nm filter, efficient isolation of the required excitation and emission wavelengths is achieved (P.S. Analytical, 1992).

Reagents. All reagents used in total Hg analysis are of certified ACS grade and obtained commercially from Fisher Scientific, unless otherwise stated. A Barnstead B-pure system (located in the Hg-clean room) produces all deionized water used in making up reagents, sample digestates, calibration solutions, stock solution and quality control standards. This water is first filtered through a Culligan system consisting of activated charcoal and two mixed bed ion exchange cartridges before being piped to the Hg-clean room. 0.1 N $KBrO_3$, 0.2 N KBrO and 1.7 M hydroxylamine hydrochloride solutions are made up by dissolving the appropriate amounts of the salts in deionized water. The $KBrO_3$ and KBrO salts are heated overnight in a glass vial at 250°C to remove adsorbed Hg. The digesting solution is made up daily by mixing equal volumes (100 mL) of 0.1N $KBrO_3$ and 0.2N KBrO solutions. All solutions are prepared weekly and stored in borosilicate bottles with teflon lined caps.

Standards. Working standards are prepared daily from a Hg stock solution (100 ng/mL) and diluted to the desired concentration. The stock solution is also made up daily from a commercially available mercury standard (1000 μg/mL, SPEX Industries, Edison, NJ). Calibration solutions are made up in 500 mL teflon bottles and stabilized by adding 5 mL concentrated HCl. No certified material exists for quality control of Hg in water near ultratrace levels. Soil (NIST sediment nominal value 60 ng/g, 8406) and tissue (NBS 1566a Oyster Tissue, 64 ng/g) quality control standards are obtained from the National Institute of Standards and Technology (Gaithersburg, MD).

2.4 ORGANIC MERCURY DETERMINATION

Sediment, Soil and Tissue Samples. A 1.0-5.0 g portion of the homogenized sample (as prepared above) is placed in a 20 mL borosilicate glass scintillation vial (Kimble, #74511). To the vial 5 mL distilled water, 3.0 mL of 1.0 M copper sulfate and 3.0 mL of acidic potassium bromide solution are added. The mixture is shaken for 1 hr at 330 rpm (Gyrotory Shaker Model G2). Dichloromethane (5 mL) is added and the mixture is shaken for 24 h at 330 rpm and then centrifuged for 10 min at 5000 x g in a Sorvall Model RC-5 refrigerated centrifuge (Dupont). An exactly known volume of the dichloromethane layer (3.5-4.0 mL) is transferred to a 7.0 mL borosilicate glass scintillation vial (Kimble, #0333726) and 1.0 mL of 0.01 M sodium thiosulfate is added. The mixture is shaken for 20 min at 330 rpm and centrifuged at high speed in a IEC clinical centrifuge. The aqueous layer (0.9 mL) is placed in a 2.0 mL microcentrifuge tube (Fisherbrand, Fisher Scientific), and 0.3 mL of 0.5 M copper chloride and 0.3 mL dichloromethane are added. The contents are mixed for 1 min on a Vortex Genie mixer and centrifuged for 2 min at high speed (16,749 x g) in a Hermle centrifuge. The dichloromethane is transferred to a 2.0 mL glass sampling vial containing a few crystals of anhydrous sodium sulphate and subjected to GC analysis. Injections of 5.0 μL are used. Samples spiked with known concentrations of methyl - and ethlymercury chloride are

extracted to evaluate the recovery factor used for quantification.

Water Samples. The sulfydryl-cotton (SFC) fibre columns are made of 1 mL disposable pipette tips containing 0.1 g of SFC fibre, packed loosely and as evenly as possible. Two SFC columns are connected in series and the water sample is passed through these by vacuum. One mL of acidic potassium bromide and 0.5 mL of 1.0 M copper sulfate are then pipetted on the surface of the adsorbent and the eluate is collected in a 2 mL micro-centrifuge tube (Fisher Scientific). This is extracted with 0.2 mL dichloromethane on a Vortex Genie mixer for 1.5 min and centrifuged as described above. The dichloromethane layer is then transferred to a 2 mL glass sampling vial containing a few crystals of anhydrous sodium sulfate and subjected to GC analysis.

2.5 INSTRUMENTATION AND ANALYSIS

A schematic diagram of the GC-AFS system used in this work is shown in Figure I and the optimum operating conditions are summarized in Table II. A

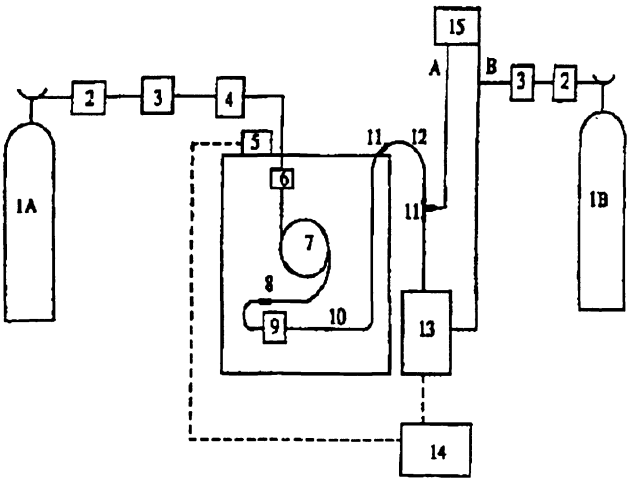

Figure I. Gas Chromatographic-Atomic Fluorescence Spectrometric System. 1A: Helium, 1B: Argon, 2: Oxygen trap, 3: Mercury trap, 4: Moisture trap, 5: Automatic sampler, 6: Injector, 7: Column, 8: Press-fit union, 9: Pyrolyser, 10: Deactivated fused-silica 0.53mm i.d., 11: Teflon unions, 12: Teflon transfer line 0.5mm i.d., 13: Atomic Fluorescence detector, 14: E-Lab chromatographic control and data acquisition system, 15: Mass flow controller-Channel A make-up, Channel B sheath gas.

Hewlett-Packard (Model 5890 Series II) gas chromatograph coupled with an HP (Model 7673) automatic sampler is used. A fused-silica, bonded phase megabore column (15 m x 0.53 mm i.d., 1 μm non-polar DB-1 coating, J & W Scientific) and the splitless injection mode is employed. The effluent from the

column is led through a pyrolyser (P.S. Analytical Ltd., UK), positioned inside the GC oven via a piece of 65 cm length of deactivated fused-silica (0.53 mm i.d., J & W Scientific), which is connected to the column with a glass "press fit" union (J & W Scientific). The Hg atoms formed in the pyrolysis unit are transferred from the outlet end of the deactivated fused-silica tubing to the fluorescence detector (teflon transfer line, 0.5 mm i.d., Alltech Associates). The transfer line is passed through a small hole on the top of the GC oven to a Merlin Mercury Fluorescence Detector, and the connections are made *via* teflon unions.

Table II. Optimized operating conditions of GC-AFS.

Gas chromatograph.	
Injector temperature	250°C
Temperature program	1 min at 40°C, 60°C/min to 140°C, 3 min at 140°C, 50°C/min to 200°C, 10 min at 200°C.
Pyrolyser temperature	800°C
Column flow	4.0 mL/min
Make-up flow	60 mL/min
Atomic fluorescence system	
Sheath gas flow	300 mL/min
Integrate time	0.25s
Calibration range	1000 (most sensitive)
Fine gain	10 (maximum)
Recorder output voltage	1V
Damping switch (for signal smoothing)	On

A real time chromatographic control and data acquisition system (E-Lab, Version 4.10R, OMS TECH, INC.) is interfaced with the GC and AFS detector system. In this work, the detection limit is defined as the amount of Hg necessary to give a peak area equal to three times the standard deviation of the background signal.

Gases. All gases are supplied by Liquid Carbonic Speciality Gases and are of zero grade quality. Helium (99.995%) is used as the carrier gas (GC), passed first through an oxygen trap, then through a Hg trap (gold-activated carbon) and a moisture trap prior to the GC. Argon (99.998%) is employed as the make-up gas and the sheath gas for the GC-AFS system and is also passed through moisture and Hg traps before use. Its flow is regulated by a mass flow controller (Omega) equipped with two channels, channel A (make-up flow) and channel B (sheath gas flow, see Figure I).

Reagents. Double deionized water produced by a Barnstead B-Pure system is used in all solutions. Certified ACS grade potassium bromide, copper(II) sulfate, copper(II) chloride and sodium thiosulfate (Fisher Scientific) are used throughout this work. The acidic potassium bromide solution is prepared by dissolving 180 g in 200 mL water. Trace metal grade concentrated sulphuric acid (50 mL, Fisher Scientific) is added to 100 mL of water. After cooling to room temperature the solutions are mixed and made up to 1 L with water. Copper sulfate (1.0 M), copper chloride (0.5 M) and sodium thiosulfate (0.01 M) solutions are prepared by dissolving appropriate amounts of the salts in water. All solutions are extracted with dichloromethane prior to use.

Standards. All Hg standards are purchased from Ultra Scientific. Stock standard solutions of methyl- and ethylmercury chloride are prepared by dissolving appropriate amounts of the standards in optima grade methanol (Fisher

Scientific). These solutions are stored in dark brown bottles and diluted with dichloromethane to give working standards of the desired concentrations when required.

Synthesis of Sulfydryl-cotton (SHC) fiber adsorbent. This synthesis follows the procedure used by Lee and Mowrer (1989). A mixture is first prepared by adding the following reagents in sequence to round bottom flask: 100 mL thioglycolic acid, 60 mL acetic anhydride, 40 mL acetic acid (36%) and 0.30 mL concentrated sulfuric acid. The mixture is allowed to cool to 45°C, then 30 g of cotton wool are added and allowed to soak thoroughly in the mixture. The reaction bottle is placed in an oven for 3 to 4 days at 40°C, then the product is placed in a filter-funnel with suction filtration and washed thoroughly with deionized water to remove traces of thioglycolic acid. The SHC fiber obtained is dried at 40°C for 24 h and stored in the refrigerator.

3. Results and Discussion

Internal standard operating procedures (SERP, Internal SOP, 1994) for quality assurance purposes have been developed for ultratrace levels of Hg determination. The method detection limit (MDL, ppt), accuracy (%R) and precision (%RSD) for the various matrices and analytes considered in this study are shown in Table III. An MDL of 0.3 ng/L is achieved which is based on the US EPA method used for the calculation of this parameter. This number can also be viewed as the instrument detection limit, since the matrix of determination is a spiked blank that did not undergo the standard Hg digestion procedure. The method detection limit obtained is based on the analysis of seven replicate samples of spiked reagent blank water stabilized with concentrated HCl conducted on 3 nonconsecutive days. The standard deviation for each set of analyses is multiplied by the students' t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom is, $t = 3.14$ for seven replicates (US EPA, 1993). As shown in Table III, the MDL for water samples has a precision of about 5% relative standard deviation (%RSD) and recovery between 90 and 110%. The concentrations of Hg in sediment and tissue samples are significantly higher than water samples and can be determined at better precision (<5 %RSD) and accuracy (95 to 105 %R). The MDL is reevaluated every 6 months (SERP, Internal SOP, 1994).

In total-Hg determination, samples are prepared and analyzed according to the internal SOP established. The optimized operating conditions of the AFS System are listed in Table I, and as indicated, these parameters vary markedly depending on whether ultratrace levels or high levels of Hg are to be measured. In addition, the calibration levels used in the generation of daily calibration curves also depend on the level of Hg to be monitored in the sample. For ultratrace levels of Hg determination, calibration levels are 0, 10, 20 and 30 ng/L. Calibration levels for soil, sediment and fish samples are 0, 100, 250 and 500 ng/L. The linear correlation coefficient met EPA Contract Laboratory Program requirements of $\leq$ 0.995 (Inorganic USEPA CLP SOW 3/90).

Quality control checks are performed on NIST soil and tissue standards that are digested and autoclaved. Subsequent analysis of the digestates (1:20 dilution) yielded recovery values of 90 to 110% (58 to 70 ng/g) for the tissue standard and 95 to 105 % (57 to 63 ng/g) for soil standard. These values are within the acceptance criteria window for soil and tissue standards of $\pm$10%.

Table III. Precision, recovery and method detection limits for inorganic, total and organic Hg.

Analyte	Matrix	Precision (%RSD)	Recovery (%)R	MDL
Inorganic Hg	Water	~5	90 - 110	0.3 ng/L
Total Hg	Water	~5	90 - 110	0.3 ng/L
Total Hg	Tissue (NBS oyster tissue 1566a 64 ng/g)	<5	90 - 110	—
Total Hg	Soils, sediments (NIST sediment 8406 60 ng/g)	<5	95 - 105	—
Organic Hg ($MeHg^+$, $EtHg^+$)	Water	<5	98 - 110	0.02 ng/L
Organic Hg ($MeHg^+$, $EtHg^+$)	Soils, sediments, tissue	<5	67 - 80	0.2 pg

In the analysis of organomercurials, the mercuric chloride conditioning of the GC column is associated with many drawbacks (Rubi *et al.*, 1992) and this procedure is a major limitation of the analytical technique. The aqueous phase ethylation technique derivatizes both inorganic mercury (Hg^{2+}) and ethylmercury ($C_2H_5Hg^+$) to diethylmercury [$(C_2H_5)_2Hg$] and thus the quantification of these species inherent in the sample can become difficult. These disadvantages indicate the need for the development of more straightforward methods in the analysis of organic Hg compounds.

This work employed a capillary column for higher efficiency separation and a mercury fluorescence detector which affords better selectivity and sensitivity compared to the ECD. The configuration of the GC-AFS System is outlined in Figure I and the optimized operating conditions is shown in Table II. The extraction of soil, sediment and tissue samples involve a thiosulfate clean-up step and with this procedure, no mercuric chloride conditioning is necessary (Alli *et al.*, 1994). In addition, the thiosulfate back-extraction step effectively removes sample matrix interferences (high-molecular-weight compounds, possibly containing sulfur), which cause rapid stationary phase deterioration (Alli *et al.*, 1994; Lansens *et al.*, 1991; O'Reilly, 1982). A typical chromatogram of a sediment sample is shown in Figure II. Note that both methyl- and ethylmercury are efficiently separated.

In natural waters, organomercurials are present in very low concentrations and this is one of the major limitations in analyzing these compounds. The SHC fiber lends efficiently to solid phase extraction (SPE) and

allows for the analysis of trace levels of organomercurials. Further, since the SHC fiber has a high selectivity for organic mercury compounds, it avoids the extraction of extraneous compounds which causes severe column problems.

Quantitative data are obtained using the calibration curves generated daily. The chlorides of methyl- and ethylmercury are used to create the standard calibration curves expressed in terms of peak area *vs* organomercury chloride concentration (pg Hg/5 μL injection). The relative standard deviation of the signal for a 2 pg Hg/5 μL standard was 1.5% for peak area measurements (n = 3). The linear range used for the generation of calibration

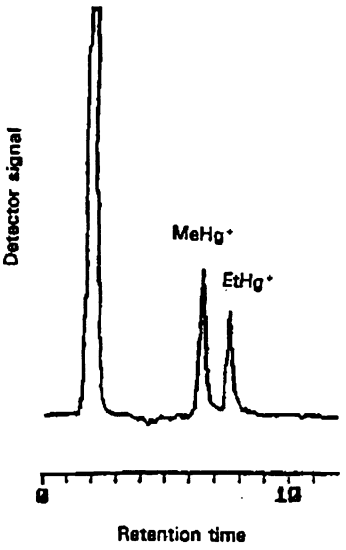

Figure II. Chromatogram of sediment sample after thiosulfate clean-up (MM: 1945 pg Hg/g, EM: 1236 pg Hg/g)

curves is 0 and 4 pg Hg/μL and the linear correlation coefficients are typically 0.998 and 0.999 for methylmercury chloride and ethylmercury chloride respectively.

Quality control is maintained by determination of % recoveries for each sample. The recovery factor (%R) varies between 67 and 80% for soil, sediment and tissue samples, compared to 98 and 110% for water samples (Table III). This establishes the importance for determining a recovery factor for each sample since this value is influenced by differences in sample matrices which affect the partitioning of organic Hg compounds. Further support for this determination (%R) is not possible due to the lack of official standard materials (for organic Hg analysis) and also demonstrates the current need for internal standard(s).

4. Conclusion

Sealed ampule digestion of environmental and biological samples for total Hg determination described in this article is a relatively new method which provides accuracy of 95 - 105% recovery of Hg^0. Digestion of soil, sediment and fish samples in sealed 10 mL ampules is a clean and straightforward method for Hg determination. When these samples are autoclaved they liquify which makes it very easy to dilute samples suitable for AFS detection. Closed vessel digestion followed by cold vapor generation and atomic fluorescence detection has yielded detection limits that allow the quantification of ultratrace levels of Hg in water samples. The preparation techniques and use of an Hg-clean room have made it possible to reduce significantly contamination of samples.

In the speciation of organic Hg by GC, sample matrix interferences become adsorbed or bound to the stationary phase of the column after various injections, exerting a negative effect on the efficiency of the analysis. With a thiosulfate back-extraction step, these interferences can be effectively removed, allowing efficient analysis of the organomercurials. In water samples, the organic Hg compounds can be efficiently preconcentrated onto the SHC fiber, which also provide a sample clean-up. The column life becomes considerably longer with the clean-up step and can be used routinely for the analysis of organomercurials with no apparent loss in efficiency.

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FIELD ANALYSIS OF MERCURY IN WATER, SEDIMENT AND SOIL USING STATIC HEADSPACE ANALYSIS

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Abstract. We developed a field screening method for the rapid analysis of mercury (Hg) in water, soil and sediment which can be applied cost-effectively at Hg-contaminated sites . The samples are chemically pretreated in ordinary containers, followed by analysis of the sample headspace Hg vapor using a portable commercially-available analyzer. Mercury in water samples is reduced directly by the addition of stannous chloride, while solids are first digested with aqua regia or piranha solution to liberate the Hg from the solids. Aided by vigorous agitation after addition of the reductant, the elemental Hg partitions between the solution and headspace according to Henry's Law. The method requires about 2 and 15 minutes to complete for water and solids, respectively. The method provides very useful detection limits for water (0.1 μg/L) and solids ($\leq$ 2 μg/g). Intercomparisons with laboratory-analyzed environmental samples have shown reasonable agreement.

1. Introduction

Techniques for the rapid field analysis of mercury (Hg) in water, sediment and soil samples are needed to permit immediate screening of these environmental media at Hg-contaminated sites. Such capability can provide cost efficient guidance for locating sampling sites for laboratory analysis, and help direct cleanup activities. Mercury analytical technology is generally limited to laboratory applications, and existing field technologies (e.g., X-ray fluorescence, immunoassay) often suffer from poor detection limits, matrix restrictions, or extraction difficulties encountered when analyzing solids.

We describe here a field method which employs static headspace measurements on samples pretreated to convert Hg to the elemental form. Aided by vigorous agitation, elemental Hg will partition between a solution and any headspace according to Henry's Law. The headspace can be sampled using a portable Hg vapor analyzer. The theory supporting static headspace measurement is governed by the solubility of elemental Hg vapor in water (Sanemasa, 1975). Stannous chloride is used in our method to reduce Hg to the element in water samples which have not been pre-oxidized (as in standard laboratory methods), and in strong acid extractions of soil or sediment.

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2. Materials and methods

2.1. INSTRUMENTATION

The Hg vapor analyzer (Jerome Model 411 or 431-X, Arizona Instruments, Phoenix, Arizona) is small (15 cm x 33 cm x 10 cm), lightweight (2.3 kg) and analysis is rapid (single measurement obtained in 10 to 13 seconds). It is battery operated, and includes an internal air pump, which operates at a rate of 750 cm^3/min. The air flows through a protective column packed with sodalime, to remove moisture and acid gases. The dry vapor is then deposited onto a thin gold film which forms an amalgam selectively with Hg. The Hg/Au amalgam increases the electrical resistance of the gold film, which is measured using a Wheatstone bridge. The increase in resistance is proportional to the mass of the Hg incorporated by the film (McNerney et al., 1972; Murphy, 1979; McNerney, 1983).

A probe (Teflon tubing) and external sodalime trap (Figure 1) were added to the instrument's sample path. Because the instrument was not designed for measuring samples with high moisture and acid content, the additional trap provides extra protection against the inadvertent aspiration of water or chemicals into the instrument. This modification does not affect the sample flow rate, and greatly reduces the chance of destroying the internal gold foil. It does, however, create additional dead volume, necessitating purging of the instrument between measurements until zero signal is obtained.

According to the manufacturer, and our experience, the Model 431-X is inherently more sensitive than the Model 411 and includes a pre-sampling purge that can affect some results in our application. We disabled this purge cycle but believe acceptable results can be obtained with the as-built Model 431-X provided the highest of three successive measurements is used to calculate Hg concentrations in water or solid extraction solutions.

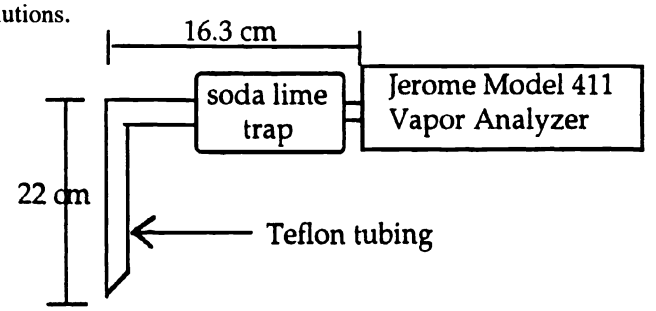

Fig. 1. Schematic of probe tip and external sodalime trap.

2.2. ANALYSIS OF WATER

The initial water studies were done with Hg-spiked water samples. One hundred milliliters of deionized distilled water was first added to 1-L high density polyethylene bottles (I-CHEM IRE13-1000). A stock solution containing 10 mg Hg^{2+}/L in 1.0 N HNO_3, or a diluted working solution of this standard, were used to produce water samples

at the desired Hg concentrations (0.2 - 30 μg/L). Stannous chloride solutions were prepared by dissolving 200.0 g $SnCl_2$ dihydrate (J. T. Baker, analytical grade) in 100 mL of 30% hydrochloric acid (EM Science, Suprapur), and diluting to 1.0 L with deionized distilled water. The solution was stirred for 24 hours at room temperature while bubbling with "Hg-free" air. A reagent blank was then measured using the portable Hg vapor analyzer to verify that no signal was produced by the solution alone.

To the 100 mL of Hg-spiked water in the 1-L bottle, 10.0 mL of $SnCl_2$ solution was added after which a small square (7.5 cm x 7.5 cm) of parafilm was rapidly secured atop the bottle. The cap was then pressed gently over the parafilm and the bottle vigorously shaken (manually) for one minute. Next, the cap was removed and the parafilm seal was punctured using the probe tip illustrated in Figure 1. The highest of three successive air samples was recorded as the headspace concentration. The parafilm seal reduces the possibility of variable amounts of unequilibrated air entering the bottle while sampling and thus increased precision of replicate measurements.

To identify the time interval necessary for establishment of equilibrium between the aqueous phase and the headspace vapor, seven 1-L bottles containing 100.0 mL of deionized water were spiked with 100.0 μL of a 5.0 x 10^{-5} M $Hg(NO_3)_2$ solution. $SnCl_2$ solution was added to each bottle, followed by vigorous manual agitation for 30 s for one sample, and 1.0 min for the other six samples. The headspace vapor in the bottle equilibrated for 30 s, and the vapor in one of the bottles agitated for 1.0 min, were analyzed immediately following agitation. The five remaining bottles were placed on the benchtop following the one minute agitation, until the headspace was analyzed using the field analyzer technique at intervals of 5 min, 2 hr, 5 hr, and 22 hr. Results from the kinetic study showed that equilibrium between the aqueous phase and the headspace vapor is reached between 30 seconds (0.354 mg/m^3) and a one minute (0.398 mg/m^3) reaction time. Readings beyond one minute (0.395 to 0.408 mg/m^3) were not appreciably different from the reading taken after the one minute equilibration interval.

Environmental water samples were collected from surface water outfalls, storm sewers and sumps in several buildings at the U.S. Department of Energy's Y-12 Plant in Oak Ridge, Tennessee. Additional samples were collected from the East Fork Poplar Creek (EFPC), which originates at the Y-12 Plant. The 100-mL aliquots were transferred to 1-L polyethylene bottles for field analysis. Laboratory analyses were performed using EPA method 245.1 (EPA, 1982).

A signal of $\leq$ 0.003 mg/m^3 in air (corresponding to $\leq$ 0.09 μg/L in water) is believed from experience to be spurious and therefore this value is reported as the approximate detection limit. The upper limit for an undiluted water sample is determined by the maximum instrument reading (1.99 and 0.99 mg/m^3 for the Jerome Model 411 and 431, respectively) and varies from about 10 to 45 μg/L depending on the model being used. A typical relative standard deviation for replicate measurements is about 10%. The formula converting signal to aqueous mercury concentration follows:

$$\text{Signal (mg Hg/m}^3\text{ air) x Constant} = \mu\text{g Hg/L water.}$$

The constant, which should be determined using one or more aqueous standards, converts mg/m^3 of air to μg/L of water, accounts for the aqueous and vapor volumes in the system, and adjusts for partitioning between phases according to Henry's Law. This

constant varies among, and with the condition of, each instrument (Jerome Model 411 or 431-X). We prefer not to use the instrument reading and Henry's constant directly to calculate aqueous concentration, although such calculations typically agreed with known (spiked) aqueous concentrations. If such direct calculations are desired then the operator should regularly verify the calibration of the instrument using an Hg vapor standard.

2.3. SOIL/SEDIMENT METHOD

Two procedures were developed for soil/sediment analysis. For both methods, 0.050 g of homogenized soil or sediment was weighed into 125-mL glass bottles with Teflon-lined silicone septum caps and chemically treated using aqua regia (three parts concentrated HCl to one part concentrated HNO_3) or piranha solution (four parts concentrated H_2SO_4 to one part 30 % H_2O_2). For soil method 1, the extracted Hg was reduced by addition of $SnCl_2$ (saturated solution) directly in the 125-mL bottle, followed by agitation for about a minute. A 1.0-mL sample of the headspace gas was collected in a gas-tight syringe, and injected into the vapor analyzer using the septum arrangement provided by the instrument manufacturer for calibration checking. The gas sample transfer was necessary because in most cases, Hg-contaminated soils would yield headspace vapor values too high to measure by direct headspace analysis with the portable analyzer.

The piranha solution evolves oxygen when the reagents behave properly. It is important to note this evolution since aqueous solutions of hydrogen peroxide spontaneously disproportionate to water and oxygen. Soil/sediment samples were allowed to react with the aqua regia or piranha solutions for 15 minutes prior to the addition of 20 mL of a saturated $SnCl_2$ solution. This addition produces an exothermic reaction. As this step involves addition of a strong reductant to a strong oxidant, appropriate safety measures should be taken. The bottles should be cooled in a refrigerator or ice bath for about 10 minutes and then allowed to return to ambient temperature prior to analysis. The sample was manually shaken for one minute, then the headspace vapor was sampled as described above.

Using aqua regia, it was necessary to remove the acid gases from the bottle prior to addition of $SnCl_2$ solution (headspace was changed with Hg-free air for two minutes in benchtop studies). In the field, bottles can be left uncapped and the acid gases allowed to diffuse out of the vessel or a battery-powered air pump may be used to ventilate the samples. After addition of $SnCl_2$, the bottles were cooled to room temperature, followed by manual shaking for one minute. The headspace vapor was sampled (1.0 cm^3) using a gas-tight syringe and measured using the vapor analyzer.

The calculation for soil measured using soil method 1 involves a correction for sample dilution (1.0 mL of headspace vapor is injected and the instrument collects 125 mL of air) followed by application of Henry's constant to find the aqueous Hg concentration (C_{aq}). The following relationship may then be used to find the total mass of mercury in the system:

$$C_{aq}V_{aq} + C_{vap}V_{vap} = \text{total Hg}.$$

Where V_{aq}, C_{vap} and V_{vap} are aqueous volume, vapor concentration and vapor volume,

respectively. Dividing the total Hg value by sample weight yields μg Hg/g soil.

An alternative soil method (soil method 2) involved extracting the soil in 5.0 mL of aqua regia or piranha solution either directly in a 1-L polyethylene bottle, or in a small glass container (e.g., 40-mL septum vial) followed by transferring a 0.1 to 1.0-mL aliquot of the extract to a 1-L polyethylene bottle and diluting to a final volume of 100 mL with deionized water. A 10-mL aliquot of $SnCl_2$ solution is then added and the headspace measured directly (as in the water method).

2.4. EXTRACTION EFFICIENCY

Two replicates of NIST Standard Reference Material 2710 (Montana soil, 0.05 g each) containing 32.6 ± 1.8 μg Hg/g, NIST Research Material 8407 (soil) 50 μg/g and a soil from the EFPC floodplain containing 2500 μg Hg/g (as measured by EPA method 245.5), were weighed into clean Erlenmeyer flasks. A 5.0 mL aliquot of piranha solution or a 3.5 mL aliquot of aqua regia was added to each flask. The flasks were swirled and then placed on the benchtop for exactly 15 minutes. Next, the slurries were poured and rinsed quantitatively through 25 mm glass fiber filters (Gelman Sciences, Ann Arbor, MI), and the filtrate was collected in 250-mL polypropylene bottles and about 175 mL distilled deionized water. The extraction filtrates were submitted for laboratory analysis using EPA method 245.1.

Data in Table I indicate that both aqua regia and piranha solution are good extraction reagents for Hg in soil. Perhaps at very high Hg concentrations, the aqua regia is slightly more effective in the 15-minute reaction interval used in this procedure. The interval is sufficient to expect nearly complete metal ion extraction by piranha solution and complete extraction by aqua regia. The EFPC soil (2500 μg/g) and NIST RM 8407 were extracted with high efficiency, in spite of the observation that sediment from this location has been characterized (Revis et al., 1989) as containing about 85 % of the total Hg present in the highly insoluble sulfide form.

TABLE I
Extraction efficiency results

Sample	Reference Value (μg/g)	Extractant	Observed Value (μg/g)[1]	Average % Extracted
NIST RM 8407	50	piranha	49 (11)[2]	98
NIST RM 8407	50	aqua regia	50 (14)	100
NIST SRM 2710	32.6 ± 1.8	piranha	24 (5.7)	75
NIST SRM 2710	32.6 ± 1.8	aqua regia	31 (7.8)	96
EFPC soil	2500	piranha	2300	92
EFPC soil	2500	aqua regia	2600	103

[1] Average of duplicate (except EPPC soil) extracts analyzed using EPA Method 245.1 (EPA 1982).

[2] Values in ( ) are relative percent differences in duplicates

Although the field use of either aqua regia or piranha solution presents safety concerns, less hazardous extractants were ineffective for short interval extraction or caused interferences in the reduction or analysis steps. Alternate extractants and reductants are currently being sought.

3. Results and Discussion

3.1. WATER RESULTS

Figure 2 illustrates the reasonable agreement between field and laboratory values and suggests that the method is useful as screening tool for measuring Hg in water. The average relative percent difference (RPD) between field and laboratory values obtained during the development and testing of this method was 37%. Although agreement between

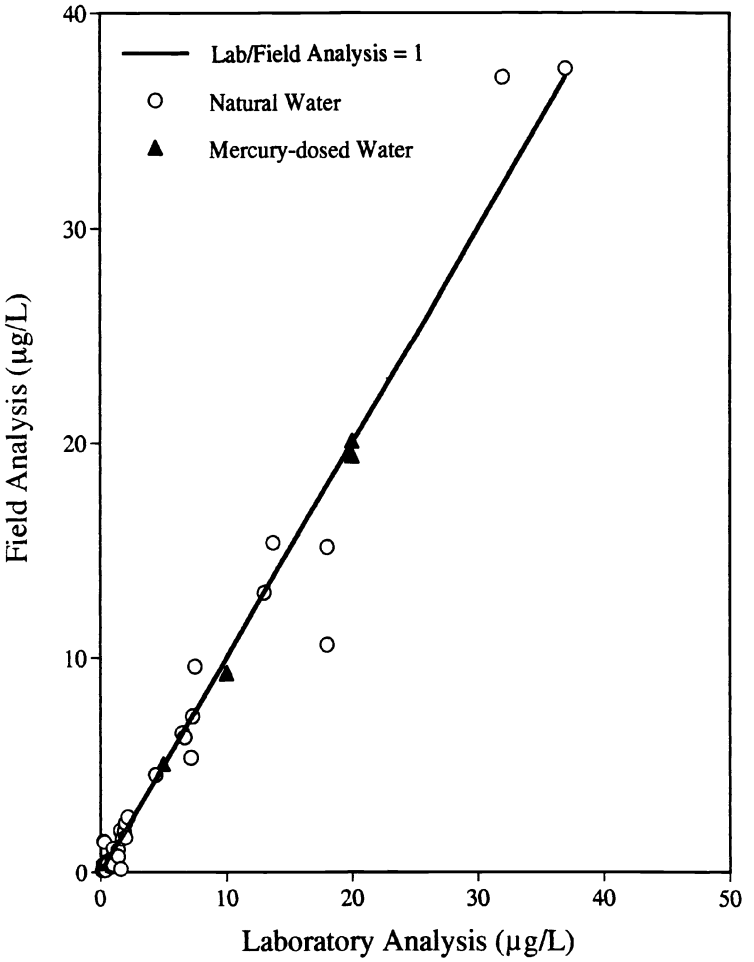

Fig. 2. Field analyzer performance for natural and Hg-dosed water samples.

laboratory and field results was not achieved in all cases, the field results are close enough to provide an indication of Hg concentrations with reasonable confidence. In a very few instances, the field method produced a false positive result; that is, the result suggested there was a small amount of Hg present when the laboratory value was given as less than the detection limit (0.2 μg/L). More importantly, however, in no case did the field technique indicate that Hg was not detectable when laboratory results indicated it should have been detected (false negative). In those cases (about 50% of results shown) where the field method results were lower than the laboratory results, a possible explanation is the absence of an oxidation step in the field method prior to reduction. Industrial outfalls and shallow groundwater samples seemed to yield more comparable results than Hg-contaminated stream water (EFPC) downstream of the outfalls, suggesting some conversion of Hg in stream water to forms requiring oxidation prior to reduction with $SnCl_2$. To maintain simplicity we did not include a preoxidation step but such a modification would be feasible if better comparability with laboratory results is desired.

A much higher concentration of Hg was also accurately measured in shallow groundwater collected at the U.S. Department of Energy's Oak Ridge Y-12 Plant. Laboratory analysis indicated the Hg concentration was 400 μg/L, while the value obtained (required 10-fold dilution) using the field method was 460 μg/L.

3.2. SOIL/SEDIMENT

Soil method 1 was used to analyze a series of surface soil samples and one soil core collected in the Hg-contaminated EFPC floodplain (Oak Ridge, Tennessee). These samples were also submitted for laboratory analysis. Figure 3 illustrates the linear relationship between laboratory and field data up to about 60 μg/g, at which point a plateau in the field data is observed. Complete saturation of the headspace volume will occur at 24 °C ($Hg°_{sat}$ = 18 ng/mL; Weast, 1980) for soil samples having concentrations which are $\geq$ 66 μg/g. The leveling in the plot of experimental data is in very good agreement with the calculated point where this phenomenon should occur. While employing a smaller sample size could extend the upper useful range for this method, 0.05 g is about the smallest sample size practical for either laboratory or field analysis. The measured values above about 20 μg/g also fell a little short of the actual soil concentrations (the average RPD for samples $\leq$60 μg/g was 54%). This effect could be due to assuming Henry's constant is 0.3 even when the aqueous phase is a strong acid mixture.

To further investigate the accuracy and precision of the field method, several NIST soil standards were measured using soil method 1. Figure 3 shows that reasonable accuracy was obtained at low Hg concentrations, while the most contaminated soils were less accurately measured. This is consistent with the saturation effect noted earlier for soil containing $\geq$ 66 μg/g. Additionally, using soil method 1 the partitioning between the extractants and the headspace may be unlike that in water. Therefore, the use of Henry's constant for water in the calculation converting the instrument's signal to soil concentration may cause the measured values to deviate from the ideal line.

Extension of this technique to include soil concentrations above 66 μg/g required the development of soil method 2. Data from the analysis of NIST standards appearing in Figure 4 were measured using soil method 2, which involved extracting the sediment

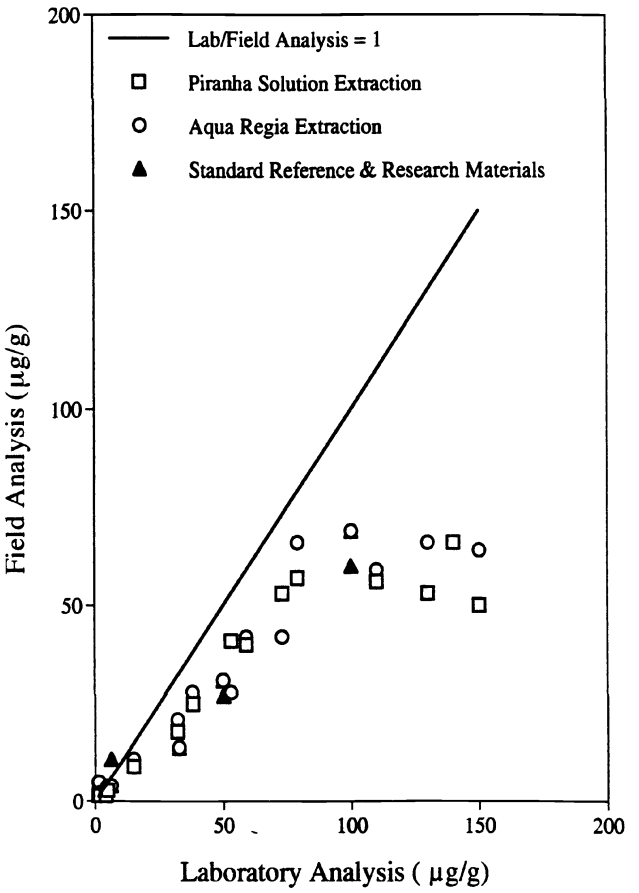

Fig. 3. Field analyzer performance for soils using method 1.

in glass bottles into 5.0 mL of piranha solution, then transferring a small aliquot to a 1-L bottle where the extract was diluted to 100 mL with water. The procedure for water samples was then followed. The standards were measured accurately (RPDs $<1\%$). Since the dilution (soil method 2) involves addition of a large volume of water relative to the volume of acid, use of Henry's constant for water appears more reasonable. Thus, this method permits accurate Hg measurements in soils exceeding the 66 μg/g upper limit established for method 1 and avoids some of the problems (e.g., acid gases and exothermic reaction during reduction). Figure 4 also illustrates the accurate (average RPD = 18%) measurement of mercury in dry finely sieved sediment obtained from the Clinch River near Oak Ridge, Tennessee. These sediment samples were extracted into 5 mL of aqua regia directly in a 1.0 L polyethylene bottle, diluted to 100 mL with distilled water and analyzed by direct headspace analysis (water technique).

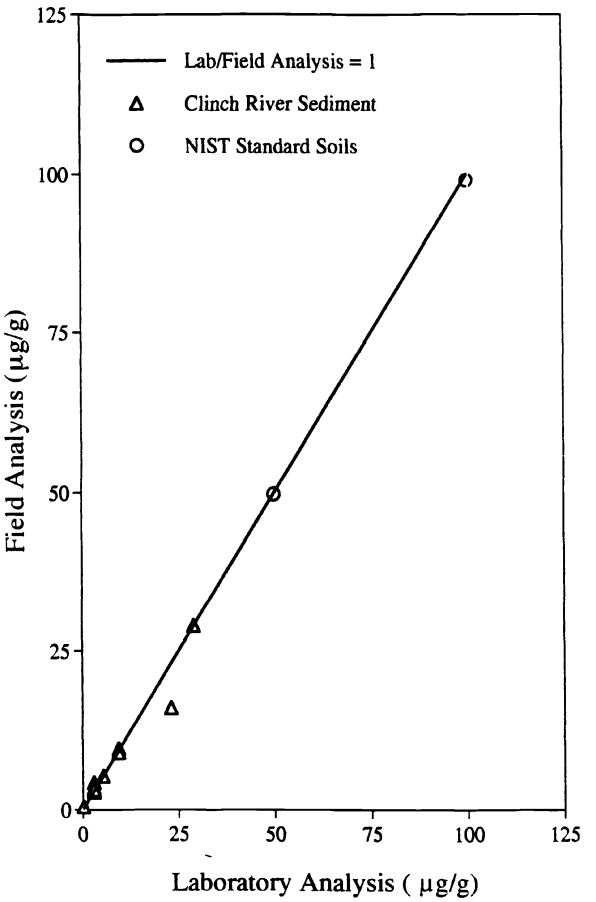

Fig. 4. Field analyzer performance for soil and sediment using water method (Clinch River sediment) and soil method 2 (NIST standard soils)

4. Conclusions

The field method described here provides a new screening tool for the analysis of Hg in water, sediment and soil. Over the tested range of concentrations in water (0.1 - 400 µg/L), precision and accuracy were quite acceptable for a field screening method. The method is sufficiently simple and easily implemented for field studies. However, this method is not intended to replace submission of samples for laboratory analysis, but rather to guide sampling and to identify samples which should be submitted for confirmatory laboratory analysis.

For Hg extraction from soil and sediment, both aqua regia and piranha solution are effective for short interval ambient temperature extraction. The aqua regia may work a little better under these experimental conditions; however, using the piranha solution

does eliminate one step because removal of acid gases before reduction is not necessary. For general soil surveys, method 2 is recommended for its improved accuracy over an unlimited upper range of soil concentrations and the advantage that multiple aliquots of one extraction can be analyzed to stay within the calibration range. The limit of detection using this technique depends largely on weight of soil extracted and the volume which is transferred for reduction, but is at least 2 μg/g. The linear dynamic range depends on whether a Model 411 or 431-X is employed. Linearity can be maintained at even high concentrations as long as the quantity of mercury transferred and reduced is kept below the air saturation value. Application of method 1 extends only to soils containing up to 66 μg/g at which point the headspace vapor in this system becomes saturated (24 °C). Reasonable precision is obtained by method 1, but results become progressively less accurate with increasing Hg concentration. This may be due to the assumption that Henry's constant is 0.3 in the formula converting signal to soil Hg concentration since partitioning from a strong acid mixture is likely different than when water is the sole solvent. Method 2 seems to avoid this problem and offers other advantages.

Practical applications for this field screening technique include defining the boundaries of shallow groundwater Hg plumes (e.g., using push screen sampling), tracking surface water sources of Hg in an industrial complex, preliminary site mapping of soil/sediment contamination, selecting soil/sediment samples for laboratory analysis, field monitoring of the progress of soil remedial action, and detecting initial breakthrough in sorbent column studies or full-scale treatment systems. Using our method, the number of samples collected for laboratory analysis may be greatly reduced as a rapid field method exists to direct the collection.

Acknowledgments

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A NEW SENSITIVE AND PORTABLE MERCURY VAPOR ANALYZER GARDIS-1A

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Abstract. A possibility to build a mercury (Hg) analyzer based on the cold vapor atomic absorption spectrometry (CVAAS) with a sub-picogram detection limit was investigated Construction of the gold traps and the optical cell, carrier gas flow rate and gold traps heating power were chosen in order to effectively concentrate sampled Hg vapor and to obtain highest possible response in the optical and electronic system The newly created analyzer is able to detect 0 5 pg of elemental Hg vapor Optimization of construction resulted in stable performance and good selectivity for gaseous Hg of the analyzer The instrument is commercially available

1. Introduction

Various methods suitable for Hg determination at a picogram level can be mentioned the cold vapor atomic absorption spectrometry (CVAAS), cold vapor atomic fluorescence spectrometry (CVAFS), plasma atomic emission (plasma-AES), photoacoustic, and inductively coupled plasma-mass spectrometry (ICP/MS) The most widely used of these methods is the CVAAS During the last decade importance of the CVAFS and plasma-AES has increased as the detection limit of the instruments based on these methods, about 1 pg and less, was at least one order of magnitude better than that obtained with instruments based on the CVAAS (Lindqvist *et al*, 1991, Bloom, 1992, Brooks Rand Ltd, 1991) The CVAAS method has, however, the important advantage that air instead of noble gases may be used as a carrier gas The instruments therefore are portable and, in most cases, less expensive The aim of our investigations was to find out ways to increase sensitivity of the CVAAS method

According to the Bouguer-Lambert law of analytical chemistry, the change in intensity of light transmitted through an absorbing substance is approximately proportional to the concentration of absorbing substance if this change is small (e g due to low concentration of the substance)

$$\Delta I/I_0 \cong k \times l \times c,$$

Here

ΔI - change in intensity of light,

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I_0 - initial intensity of light;
k - light absorption coefficient of the substance;
l - length of the optical cell;
c - concentration of the substance, averaged along the cell.

We assume that the optical cell has a shape of a thin and long cylinder and substance concentration can be considered constant across the cell.

Assume that some amount of Hg vapor, m, has been collected onto a gold (or other) trap, then Hg is released, and all this amount appears in the optical cell simultaneously. Taking into account that $c = m/(l \times S)$, where S is cross-section of the cell, we arrive at the equation:

$$\Delta I/I_0 \cong k \times l \times m/(l \times S) = k \times m/S.$$

It is evident from the last equation that the same amount of Hg vapor, m, causes the more noticeable light absorption, $\Delta I/I_0$, if the optical cell cross-section S is less. The experimental task is to evaporate the sampled Hg vapor so that it all appears in the optical cell simultaneously. It is possible to increase the volume of the optical cell as far as necessary by increasing its length but this results in a dramatic fall in the light intensity, I_0, and in worse signal-to-noise ratio.

Finally, the aim of our investigations was to find out optimal conditions of the analysis and to build a sensitive CVAAS Hg vapor analyzer.

2. Materials and Methods

2.1. OPTICAL AND ELECTRONIC SYSTEM

A low pressure electrodeless discharge Hg lamp (EDL), diameter 2 cm, was used as a light source with $\lambda = 254$ nm, and a phototube sensitive to the spectral region from 220 nm to 330 nm was used as a detector. The two-beam optical system with the light modulation was built. The mechanical chopper enabled the light to pass through the sample and reference cells alternatively, with a frequency of 15 Hz. The reference cell had the same dimensions as the sample cell and was filled with argon to avoid generation of ozone (O_3) by the UV light, and closed hermetically. No measures to condense or collimate the light were taken. The signal generated by the phototube was detected using a synchronic detection circuit. The gain was controlled automatically according to the light intensity in the reference beam. Output of the synchronic detector was connected both to the recorder and to the microprocessor system (MPS). Light absorption peak heights were calculated by the MPS, eliminating thermal drift of the system. Necessary corrections were made taking into account non-linearity of the Bouguer-Lambert law. The intermediate results were multiplied by the calibrating constant, and the final results, in picograms, were presented on the LED display.

2.2. GAS TRAIN

The gas train consisted of the concentrating trap (CT), the analytical trap (AT), the sample optical cell and the gas pumping system, connected in series with the short Teflon tubings. Both the CT and AT were made of the gold wool (99.99% pure gold, fiber diameter 20 μm). The gold wool was placed in the Quartz tube (5 mm o.d., 3 mm i.d. and 52 mm length) and packed so that it filled about 1cm along the tube. It was fixed with the quartz wool plugs at both ends. The Nichrome wire (diameter 0.3 mm) was wrapped around the tube. Length of the wrapped part of the tube was 3 cm.

The gas pumping system provided the two flow rates: 1 l/min for ambient air sampling and about 10 ml/min for the analysis. During analysis, the CT and AT were consequently heated performing the "dual amalgamation" procedure. When the CT was heated while the AT was still cold, the recorder sometimes registered peaks the shape and appearance time of which showed them not to be caused by Hg vapor but by some other unknown substances. On the contrary, the false peaks were never noticed after a later heating of the AT, even if sampling in noticeably smoky areas was performed. Thus the method seemed to be particularly selective for the gaseous Hg. It turned out to be important, however, not to use too dense gold wool plugs when producing the traps. Amounts of the gold wool just enough to ensure effectiveness of 98 to 99%, at the appropriate flow rate, were used. It was about 30 mg for the CT and 1 mg for the AT. The construction of the traps proved to be quite stable. After several hundreds of measurements no decrease in the effectiveness was observed.

3. Results and Discussion

3.1. OPTIMIZATION OF PARAMETERS

The dimensions of the optical cell, the gas flow rate used for the analysis and the gold trap heating power were varied to achieve the highest response of the optical and electronic system to Hg vapor. The final choice was as follows: the inner diameter of the optical cell 0.3 cm, its length 15 cm, trap heating power 30 W and air flow rate 10 ml/min. Under these conditions about 80% of released Hg vapor appeared in the optical cell simultaneously. Dependencies of the light absorption peak height on the gas flow rate and on the trap heating power proved to have extended plateau regions (Figure 1.) which released the researcher from the necessity to keep the two parameters precisely constant and to often calibrate the system. This is contrary to the strong dependencies of sensitivity on the gas flow rate reported for other Hg analyzers (Brooks Rand Ltd., 1991; Stuart, 1979).

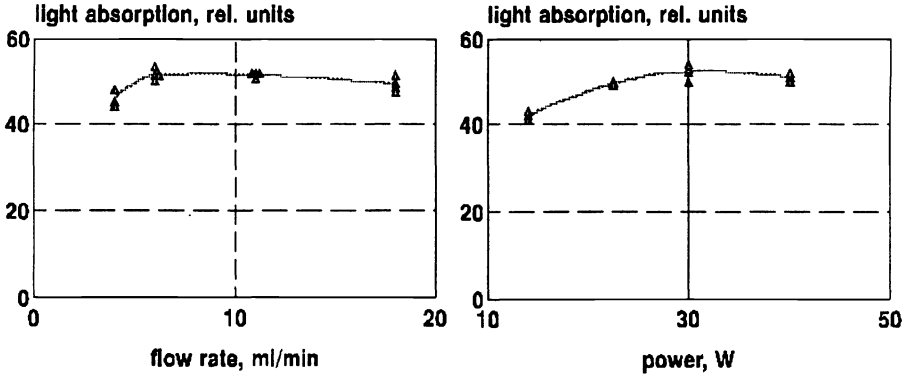

Figure 1. Dependencies of light absorption peak heights on the gas flow rate and the trap heating power.

3.2. TESTING RESULTS

A compact and self-contained Hg analyzer was constructed following the above mentioned observations. The instrument was tested with different experiments:

Dosing saturated Hg vapor with syringe injections within a range 0.1 to 1.0 ng. Number of experiments was n = 20, the correlation coefficient was r = 0.996;

Determination of mercury vapor concentration in premises. The ventilation was switched off and the air was let to equilibrate during a few days. The sampling time was 30 s. The concentration calculated was c = 65 ng/m^3 and the coefficient of variation was CV = 3.5%;

Determination of Hg vapor concentration in premises with two instruments simultaneously. The samples were taken from the same inlet by using a three-way valve. The experiment was done for 5 days, n = 100. Sampling time was 1, 2 and 4 minutes. Average concentration was c = 20 ng/m^3, and the correlation coefficient was r = 0.9985;

Determination of Hg vapor concentration in the open air at a border of Vilnius city (the capital of Lithuania, 600.000 inhabitants) on September 10, 1993, 17.30-21.00. The sampling time was 1 minute and 5 minutes; n = 15, c= 3.2 ng/m^3, and the coefficient of variation CV = 12 %;

Determination of Hg vapor concentration in the open air at a border of Vilnius city in windy and rainy weather in June 22, 1994, 14.00-17.30. Number of measurements was n = 15, sampling time was 2 min and 20 min. Temperature varied within a range 15.5 to 18.0^0 C, and the humidity varied within a range 75 to 90%. Average concentration was 4.3 ng/m^3 and dispersion was σ = 0.5 ng/m^3. No correlation was found between calculated concentration and sampling time (r = -0.27), humidity (r = 0.25), or temperature (r = -0.3), respectively.

4. Conclusion

A highly sensitive, portable and automated Hg vapor analyzer based on the CVAAS method was designed. The detection limit of the instrument, 0.5 pg, is at least 40 times lower than other CVAAS Hg analyzers previously reported (Bloom, 1992). The detection limit is comparable to (Brooks Rand. Ltd., 1991) or even better than (Tekran Inc., 1994) the detection limit achieved with the CVAFS Hg analyzers.

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INTERCOMPARISON OF STACK GAS MERCURY MEASUREMENT METHODS

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Abstract. The Electric Power Research Institute (EPRI) and the United States Environmental Protection Agency (EPA) have carried out joint tests for validation of EPA (Draft) Method 29 ("multi-metals method") for measurement of mercury (Hg) and other selected metals in the stack gas of a coal-fired electric utility. The tests were performed according to the "analyte spiking" procedure of EPA Method 301 protocol for the field validation of stationary source emission measurements. Several other Hg measurement methods were also employed during the tests to provide a comparison to the Method 29 measurements; these included EPA Method 101A, the Hazardous Element Sampling Train (HEST), and two solid sorbent methods, one using activated charcoal and the other using iodated carbon traps in series with soda lime traps. Results indicate reasonably good agreement between the total Hg measurements by the different methods.

1. Introduction

The Electric Power Research Institute (EPRI) initiated the PISCES (Power Plant Integrated Systems - Chemical Emissions Study) project in 1990, to better understand emissions of trace substances from power plants. As part of PISCES, a field testing program was undertaken to obtain information regarding the concentrations of selected Hazardous Air Pollutants (HAPs), including Hg in power plant streams. There was significant variability in the measured Hg concentrations (using EPA (Draft) Method 29) in various power plant streams in early field tests which made it difficult to achieve Hg mass balance closures. While the EPA (draft) Method 29 and EPA Method 101A were formally validated, as defined by EPA Method 301 protocol (EPA, 1991), for measurement of Hg in combustion flue gas of hazardous waste incinerators, the methods had not been validated in utility combustion flue gas where the Hg concentrations are much lower.

This paper presents selected results from the tests sponsored jointly by EPRI and US. EPA for formal evaluation of EPA (Draft) Method 29 and for comparison of several methods for measurement of Hg in a coal-fired utility stack gas. A more detailed account of the test program can be found elsewhere (NOTT *et al.*, 1994).

2. Test Program Description

2.1. METHODS TESTED

EPA (Draft) Method 29. A detailed description of Method 29 can be found elsewhere (EPA, 1992). In this method, sample gas is isokinetically pulled through a heated quartz fiber filter and a series of chilled impingers. Particulates present in the gas stream are retained by the filter and vapor phase components pass through the filter to the impinger solutions. The vapor-phase component of Hg in gas streams is collected in a series of liquid impingers consisting of two nitric acid/ hydrogen peroxide (HNO_3/H_2O_2) impingers followed by two potassium permanganate / sulfuric acid ($KMnO_4/H_2SO_4$) impingers. The resulting impinger solutions are then analyzed by cold-vapor atomic absorption spectrophotometry.

Frontier Geosciences Mercury Speciation Method. In this method, flue gas is first drawn through heated quartz tubing containing a quartz wool plug to remove particulate matter. Immediately following the quartz tubing is a set of two KCl/soda lime traps and two

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iodated carbon traps through which the flue gas passes. Oxidized Hg is captured by the KCl/ soda lime traps while elemental Hg passes through and is collected by the iodated carbon. Temperature of the sorbent traps is maintained (90-100 ^{o}C). Quantification of Hg is made using cold vapor atomic fluorescence spectrometry (CVAFS), following appropriate sample pre-treatment. Further details of the method can be found elsewhere (Prestbo *et al.,* 1994)

MIT's Solid Sorbent Method. In this method, flue gas is passed through two activated charcoal sorbent traps connected in series. The sorbent traps are maintained at 100 to 120 ^{o}C to prevent moisture condensation. The traps capture oxidized as well as elemental Hg. The sorbent is analyzed by instrumental neutron activation analysis (INAA) to determine the total Hg collected. More details of the method can be found elsewhere (Olmez., 1992).

HEST Method. The Hazardous Element Sampling Train (HEST), developed by Chester Environmental. uses an in-stack filter probe to draw an isokinetic sample through a filter pack of three filters arranged in series. The first filter is made of quartz or Teflon and is used for particulate collection. The second and third filters are carbon impregnated filters that adsorb gas phase elements, including Hg. After the sample collection, the filters are analyzed by non-destructive energy dispersive x-ray fluorescence (XRF) analysis for total Hg determination. More details of the method can be found elsewhere (Cooper, 1993).

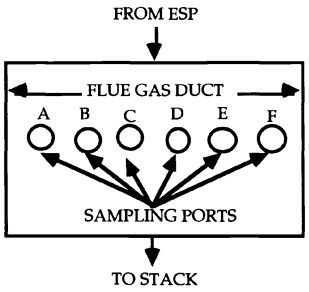
EPA Method 101A. This method is described in 40 CFR, Part 61, Appendix B (EPA, 1982). The Method 101A sampling train is similar to the Method 29 train. In contrast with Method 29, the Method 101A train does not use HNO_3/H_2O_2 impingers, but instead uses only $KMnO_4/H_2SO_4$ impingers.

2.2 EPA Method 301 Protocol for Evaluation of EPA (Draft) Method 29

EPA Method 301, which is used to assess the acceptability of proposed reference and alternative sampling and analytical procedures, calls for collecting at least six runs with a quadruplicate sampling device (quad train). This device uses two spiked and two unspiked sampling trains to sample flue gas (generating two paired data sets per run). Subsequent determination of metals concentrations were used to calculate recovery of spiked material, as well as the precision of the measurements. These results were then used to determine whether the required criteria for precision (less than or equal to 50% relative standard deviation), and bias (if significant bias occurs, bias correction factor should be in the range of 0.7 to 1.3) were met.

2.3. Test Setup and Experiments

The tests were conducted at a coal-fired utility that employs an electrostatic precipitator (ESP) for particulate collection. The flue gas was sampled in a vertical run of duct between the ESP outlet and the stack using the six sample ports at this location. The cross-sectional duct dimensions were 10 ft. x 10 ft. Figure 1 shows a schematic of the sampling arrangement. Two quad trains were used for Method 29. One was operated by Radian Corporation, EPRI's contractor; the other Method 29 train was operated by EPA's contractor Pacific Environmental Systems / Deeco, Inc. A total of eight runs were performed over 8 consecutive days. The flue gas was sampled for 4 hours during each run. During the test period, coal samples were collected and analyzed for Hg content to provide a comparison with the flue gas Hg measurements.



Port C - Method 29 EPRI Quad Train; Port D - Method 29 EPA Quad
Port F - Quad Train with Frontier Geosciences Trains + MIT Train
Port A - Quad with 1 HEST Train + 2 Meth 101A Trains, Port B- 1 HEST Train

Figure 1. Stack Gas Sampling Arrangement

3. Results and Discussion

Table I shows the precision and bias of the stack gas Hg measurements from data collected by the EPRI contractor. From this data, the average bias is calculated as -0.57. The 95% confidence interval for the bias indicates a negative bias significantly different from zero and the bias correction factor was calculated to be 1.16. The RSD for the spiked trains was calculated to be 2.3% and that for the unspiked train was 4.2%. The Method 301 evaluation of Hg data obtained from the Method 29 train indicates that, using the eight sets of Hg data obtained by the EPRI team, the precision and bias met the criteria of Method 301.

Table I. Precision and Bias of Stack Gas Hg Measurements
EPA (draft) Method 29 - EPRI Quad Train

Precision (RSD[a])			Bias				
Unspiked	Spiked	301 Criterion	Mean	LCI[b] 95%	UCI[c] 95%	Correction Factor	301 Criterion
4.2	2.3	50.0	-0.57	-0.63	-0.49	1.16	0.7-1.3

a RSD = Relative Standard Deviation; b LCI = Lower Confidence Interval; c UCI = Upper Confidence Interval

Table II compares the results of the (unspiked) flue gas Hg concentrations measured by the different methods. Note that the table shows total Hg data for the Frontier Geosciences method. The table shows good agreement between the EPA and EPRI contractors' measurements using Method 29, and generally good agreement among the various methods. The mean concentration of Hg in the flue gas was approximately $1.5\mu g/m^3$. This concentration was consistent with the coal Hg concentration, as measured by perchloric acid digestion followed by CVAFS analysis. Measurement of Hg at these low concentrations resulted in some analytical results very near detection limit. As concentrations approach the detection limit, the relative error for the measurement becomes larger. Note that these measurements were made on very low concentrations; the bias and precision estimates could be different at higher concentration gas streams.

Table II. Stack Gas Mean Hg Concentration
Measured by Various Methods ($\mu g/m^3$)

Run #	Meth 29 (EPRI)	Meth 29 (EPA)	Frontier Geosciences	MIT	HEST	Meth 101A
1	1.42	1.60	1.46	1.77	1.17	-
2	1.04	-	1.28	1.08	0.73	1.19
3	1.77	1.98	1.98	1.80	1.70	2.26
4	1.62	2.11	1.78	2.07	-	2.06
5	2.28	1.62	2.46	3.08	2.23	2.87
6	0.65	0.58	0.75	0.30	0.68	0.96
7	1.68	1.96	1.94	1.74	1.46	2.28
8	1.88	2.40	2.35	2.09	1.91	2.39

4. Conclusions

EPA (Draft) Method 29 met the precision and bias criteria requirements of EPA Method 301 (analyte spiking) protocol, based on Hg measurements by the EPRI contractor in a coal-fired utility stack gas. There was reasonably good agreement among the different methods tested in total Hg stack gas measurement at this site.

Acknowledgment

The following individuals played key roles in the conduct of the intercomparison exercise: Mr. Eugene Youngerman, and Dr. Krystina Huyck, of Radian Corporation, Mr. William DeWees, of DEECO, Inc., Dr. Eric Prestbo of Frontier Geosciences, Dr. Ilhan Olmez of MIT, and Mr. Christopher Tawney of TRC Environmental Corporation.

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DETERMINATION OF ATMOSPHERIC Hg BY COLLECTION ON IODATED CARBON, ACID DIGESTION AND CVAFS DETECTION

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Abstract. An established industrial monitoring technique has been refined to allow the accurate determination of total gaseous Hg in air at background levels (1-3 ng m^{-3}) Samples are collected under vacuum through a commercially available iodide-impregnated carbon trap For analysis, the trap is digested in a 7 3 (v/v) mixture of HNO_3 + H_2SO_4, and an aliquot of the digest analyzed by $SnCl_2$ reduction, dual gold amalgamation, and cold vapor atomic fluorescence spectrometric (CVAFS) detection The traps exhibit little breakthrough (<5%) under flow rates of up to 1 0 l·min^{-1} for periods up to 10 days The mean value for the blank on the half traps was found to be 0 40 ± 0 16 ng (n=20), resulting in a 3 σ detection limit of 0 07 ng m^3 (1 week sample at 1 0 L m^{-3}). Replicate field collections show a between-trap RSD of ± 6 4%, while field intercomparison with gold trapping resulted in 104 ± 20% recovery in the 1-4 ng/m^3 concentration range

1. Introduction

Since the advent of the amalgamation/atomic spectroscopy technique for the determination of total gaseous Hg (Fitzgerald and Gill, 1979), virtually all published atmospheric Hg determinations at non-contaminated sites have used this technique. Although the method appears near ideal from the standpoint of sensitivity and ease of use, field researchers (Gill, personal communication, 1994; Brosset and Iverfeldt, 1989) have noted that inexplicable losses in trapping efficiency can sometimes occur, especially in air masses of terrestrial origin. Iodide impregnated carbon traps have long been used for industrial monitoring applications (Turner and Bogel, 1993; Lindberg, 1980; Lindberg 1981; Lindberg and Turner, 1977; Moffit and Kupel, 1974), but because the blanks related to the wet chemistry of sorbent digestion are much higher than those related to gold trapping, they have not been applied to ambient air monitoring. Our flue gas application of iodide-impregnated carbon, however, has suggested that the blanks are low enough to be applied to ambient air monitoring (Bloom, 1993). In this report, we will detail analytical measures taken to extend the application of this media to ambient air.

2. Materials and Methods

Samples were collected onto iodide-impregnated carbon traps (MSA, Pittsburgh) under vacuum, with flow and total volume quantified using an integrating mass flowmeter. For analysis, the trap is opened by scoring with a glass cutter just above the glass cloth plug (input side), and then gently breaking. Using a hook-shaped stainless steel needle, the contents of the front ("A") and back ("B") halves of the trap are emptied into separate 25.6 mL Teflon™ digestion vials. 10 mL of 7:3 HNO_3 + H_2SO_4 mixture is added to each vial and the lids are screwed on tightly. The vials are placed on a Teflon™-coated hot plate,

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and heated to approximately 125°C for two hours (the samples should reflux, with acid condensing on the inside of the vial lids). After cooling thoroughly, the vials are opened in a fume hood and diluted to volume, using 5% (v/v) BrCl solution.

Samples were analyzed by first adding 0.25 mL $SnCl_2$ and then an aliquot (typically 2.0 mL) of the sample digest to a pre-purged bubbler, followed by purging for 20 minutes onto a gold/sand trap using N_2 (Bloom and Crecelius, 1983). The gold trap is then placed into the analyzer train of the dual amalgamation system, and heated to a temperature of approximately 450°C, with Ar passing through to the "analytical" gold trap, and then on to the CVAFS detector (Bloom and Fitzgerald, 1989). The analytical trap is then similarly heated, allowing the desorbed Hg^0 to pass into the CVAFS detection cell. The instrumental detection limit of the system is approximately 0.2 pg Hg.

3. Results and Discussion

As a check for matrix interferences, aliquot volumes from 0.2 to 10 mL of the same digest were analyzed. The results were linear over the entire range, indicating no significant interferences due to the digestion matrix. Using an aliquot volume of 2.0 mL, virtually all of the observed variability was due to actual between-trap differences in Hg (rather than within-digest analytical differences), meaning that no further reduction in the detection limit can be made by further increasing aliquot size. Digest storage experiments showed that to avoid losses of Hg back to the carbon granules, the diluted carbon digests must contain at least 40% (v/v) mineral acids.

Twenty blank traps were analyzed to assess variability, as summarized in Table I. The traps are narrowly constrained in Hg, with the half-traps showing a mean of 0.40 ± 0.16 ng, and no differences observed between the front and back halves. Analysis of similar sets of traps from two other lots of MSA iodated carbon traps (lot #21 in 1991, and lot #22 in 1992), gave similar results, indicating good long-term reproducibility in the manufacturing process. A one month storage test was conducted with ends open to room air, closed with Teflon™ plugs, or closed with polyethylene end caps provided by MSA. The results of this test (Table II) indicate the need to keep the ends covered after breaking the glass, and that the use of Teflon™ end plugs results in no measurable contamination.

TABLE I

Mean blank results. Whole traps are the front plus back sections, excluding copper screen (except where noted)

	Hg Level, ng/Trap		
Description	Mean	SD	N
lot #23 front halves	0.40	0.17	10
lot #23 back halves	0.40	0.16	10
lot #23 whole traps	0.69	0.22	10
lot #22 whole traps (1992)	0.74	0.35	9
lot #22 whole traps + Cu screen (1992)	1.29	0.25	4
lot #21 whole traps (1991)	0.85	0.57	10
10-13 ng Hg digestion spike rec. (%)	101.4	5.22	7

TABLE II

Effect of one month storage on the iodated carbon blank, comparing a number of different trap-end coverings.

	Net Hg on Whole Trap (Nanograms)			
Sample	Sealed Glass	Teflon	Polyprop.	Open ends
#1	0.53	0.67	2.22	15.10
#2	0.79	0.65	1.56	13.88
#3	0.55	nd	1.33	18.86
#4	0.69	nd	3.49	29.33
mean	0.62	0.66	2.15	19.29
SD	0.12	0.01	0.96	7.0
% increase	---	6.4%	246.7%	3011%

To determine the maximum atmospheric sampling rate and volume, a matrix of conditions ranging from 0.2 $L \cdot min^{-1}$ to 2 $L \cdot min^{-1}$ and from 1 day to 10 days was tested. The breakthrough measured was from the first (A) to the second (B) section in the same trap. The results of all such experiments are summarized in Figure 1. Greater breakthrough is observed as sampling rate or time period increases. Breakthrough is negligible (<5%, indicating >99% recovery on the sum of A + B traps) under all conditions with the exception of high flow (>1.5 $L \cdot min^{-1}$) combined with long sampling periods (> 5 days).

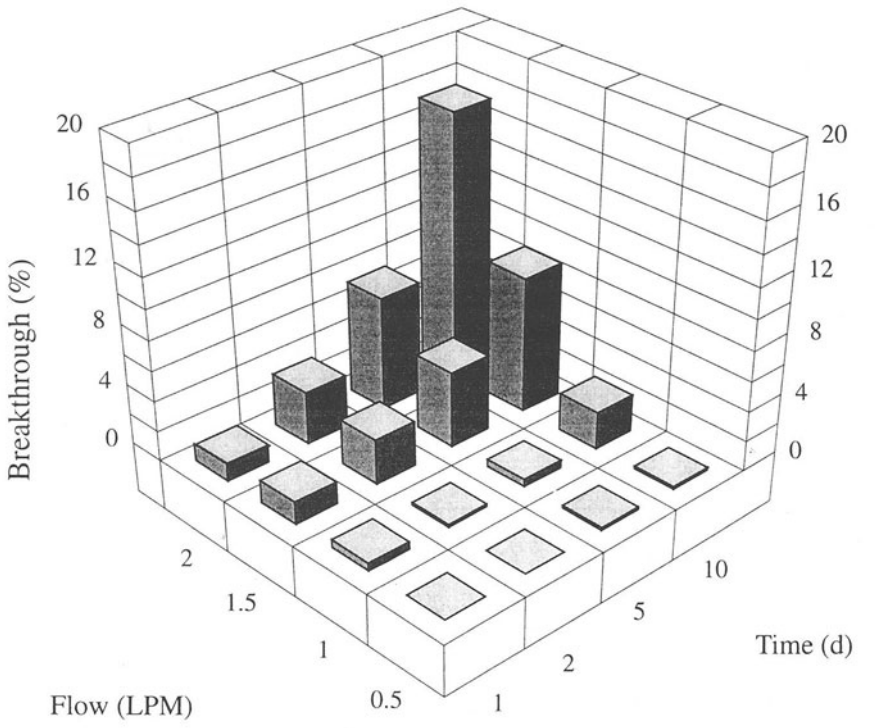

Fig. 1. Effect of sampling time and flow rate on trap breakthrough of Hg (2-3 reps).

TABLE III

Field comparison of iodated carbon (IC) with gold sand (Au) collection of atmospheric Hg

Location	Sample Mid-Date	Total [Hg] $ng \cdot m^3$ IC	Au	IC/Au
Seattle, WA	1/27/94	4.31	4.31	1.00
Seattle, WA	1/30/94	3.15	3.70	0.85
Seattle, WA	2/7/94	3.69	3.79	0.97
Lake Barco, FL	5/29/94	1.49	1.12	1.33
Lake Barco, FL	6/5/94	1.19	1.29	0.92
Lake Barco, FL	6/12/94	1.14	0.91	1.25
Lake Barco, FL	6/19/94	1.28	0.98	1.31
Fakahatchee Strand, FL	5/29/84	1.39	1.11	1.25
Fakahatchee Strand, FL	6/5/94	1.07	1.13	0.95
Fakahatchee Strand, FL	6/12/94	1.37	1.66	0.83
Fakahatchee Strand, FL	6/19/94	1.08	1.33	0.81
Mean				**1.04**
SD				**0.20**

In early 1994, a series of atmospheric collections were taken in downtown Seattle Washington and Southern Florida using both the iodated carbon and gold coated sand (Gill, 1995) collectors. The intercomparisin was most stringent, as gold traps from the Florida sites were analysed at a different institution (Texas A & M University), using a different calibration procedure (gaseous injection). In these tests, the trapping efficiency of the iodated carbon traps under more natural conditions of temperature (-5°C to 30°C) and humidity (70 to 100%) were investigated using a variety of flow rates and sampling periods (0.2-1.1 LPM and 1-8 days). In all cases, breakthrough from the front to the back section of a single trap was under the target value of 5%, with a mean of 2.6 ± 1.1% (n=28). The relative standard deviations for six triplicate collections with iodated carbon traps ranged from 1.0 to 13.4%, with a mean of 6.5%. The mean of 11 comparisons of Hg collection on iodated carbon with collection on gold traps was 104 ± 20%, with no apparent bias.

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MATRIX MODIFICATION TO IMPROVE THE RECOVERY OF MMHg FROM CLEAR WATER USING DISTILLATION

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Abstract. The use of distillation from aqueous solution dramatically improves the recovery of methyl mercury (MMHg) from complex water samples, as compared to solvent extraction techniques. However, low and irreproducible spike recoveries are often observed when distillation is applied to very clear water samples (i.e., precipitation, double deionized water (DDW), etc.) or those containing high chloride concentrations. Based upon the observation that recoveries and reproducibility are higher for waters containing strong complexing compounds, such as humic matter, we investigated the potential of matrix modification to improve the reproducibility of MMHg by distillation from more difficult matrices. At sample acid concentrations of less than 0.1M hydrochloric acid (HCl), we found that the addition of complexers such as ammonium pyrrolidine dithiocarbamate (APDC), and aqueous humic substances improved distillation spike recoveries and reproducibility. The use of complexers was also found to suppress the co-distillation of divalent mercury (Hg(II), which, in highly contaminated samples can be an interferant with the MMHg determination. At higher HCl concentrations, irreproducibility was dominated by the interference caused by chloride co-distilled with the water. In these cases, neither the addition of complexing agents, or buffers to bind the free hydrogen ions (H^+) in solution were effective in improving results.

1. Introduction

Due to very low ambient concentrations, the analysis of methyl mercury (MMHg) in most media requires an extraction step prior to analysis. A dramatic improvement in reliability has been achieved through the application of distillation from aqueous media (Horvat et al., 1993). In applying this method, the MMHg chloride is distilled from an acidic aqueous solution of the sample amended with chloride. MMHg is found to co-distill approximately azeotropically with water, resulting in a solution very easily and reproducibly analyzed by the ethylation/gas chromatography (GC) method (Bloom, 1989). Distillation has been found to eliminate all interferences caused by sulfide and organic carbon components. Unfortunately, poorer reproducibility and spike recoveries have been reported when applying the method to very clean samples, such as precipitation and deionized water. The problem is compounded by using too high a concentration of HCl (>0.05 N) to preserve the samples. Based on our observation that samples containing high dissolved organic carbon (DOC) give better recoveries and reproducibility than low DOC samples, we investigated matrix modification to help insure more accurate results and uniform recoveries across a range of sample types.

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2. Materials and Methods

Water samples (40 or 45 mL) were distilled from 55 mL Teflon® vials, as described elsewhere (Horvat et al., 1993). Except where noted, the volume distilled was 5 mL less than the initial volume, and the samples were acidified to 0.5% (0.06N) with HCl. Chemical modifiers were added directly to the vial prior to the distillation step. All common reagents, gases, and DW were high purity and pre-analyzed for mercury (Hg). Ammonium pyrrolidine dithiocarbamate (APDC), was added as a 1% solution. Humic extract was the residue from the previous distillation of brown water samples. After distillation, samples were analyzed by aqueous phase ethylation, purging onto Carbotrap, isothermal GC separation, and cold vapor atomic fluorescence detection (Liang et al., 1994; Bloom, 1989; Bloom et al., 1988).

3. Results and Discussion

Spike recoveries and blanks were first measured in DW, with and without adding 1% (v/v) of the lake humics extract. Results of this experiment (Table I) indicated that recovery could be improved by adding natural lake water humic materials. Horvat et al., (1993) showed conclusively that recovery of MMHg by distillation improves by using sulfuric acid (H_2SO_4) plus potassium chloride (KCl), rather than HCl, due to reduction in HCl co-distilling with the water. We investigated four schemes to reduce the HCl co-distilled. These were (a) adding potassium sulfate (K_2SO_4) to provide a similar ionic mix as with H_2SO_4 and KCl; (b) adding potassium acetate to the distillation vial to force the preferential distillation of acetic acid instead of HCl; (c) reducing from 88% to 77% the fraction of the sample distilled; and (d) reducing the HCl added as a preservative from 0.12 N to 0.06 N. Results of these experiments (Table II) indicate that, with the exception of reducing the concentration of HCl to less than 0.5% (0.06 N), modifying the acid matrix has little effect upon recovery of MMHg. The use of H_2SO_4, with the addition of 0.01 N KCl at the time of distillation also results in consistent high MMHg recoveries (Horvat et al., 1993).

Figure 1 shows the effect of the APDC addition (0.1 mL) on the recovery of Hg from aqueous matrices. It is clear that APDC generally results in substantial improvement in both the yield and precision of the MMHg distillation. The effect is more pronounced on samples in the following order: DDW > clear natural waters > brown natural waters. The effect of APDC on the distillation efficiency was assessed by distilling over various fractions of a spiked sample and observing the recovery of MMHg (Figure 2). When the sample contained no APDC the recovery of MMHg was approximately proportional to the recovery of water. With APDC however, the MMHg was observed to distill over more rapidly than the water.

Table I

Recovery of MMHg from deionized water (DW) with and without humic matter (n=3 reps)

Sample	Parameter	DW	DW + Humics
4.44 ng/L MMHg	mean	2.72	4.28
	SD	0.43	0.31
	% recovery	61.7	96.9
1.11 ng/L MMHg	mean	0.74	1.05
	SD	0.09	0.14
	% recovery	68.0	94.2

Table II

Effect on MMHg recovery of modifiers to reduce HCl volatility (n=4 reps)

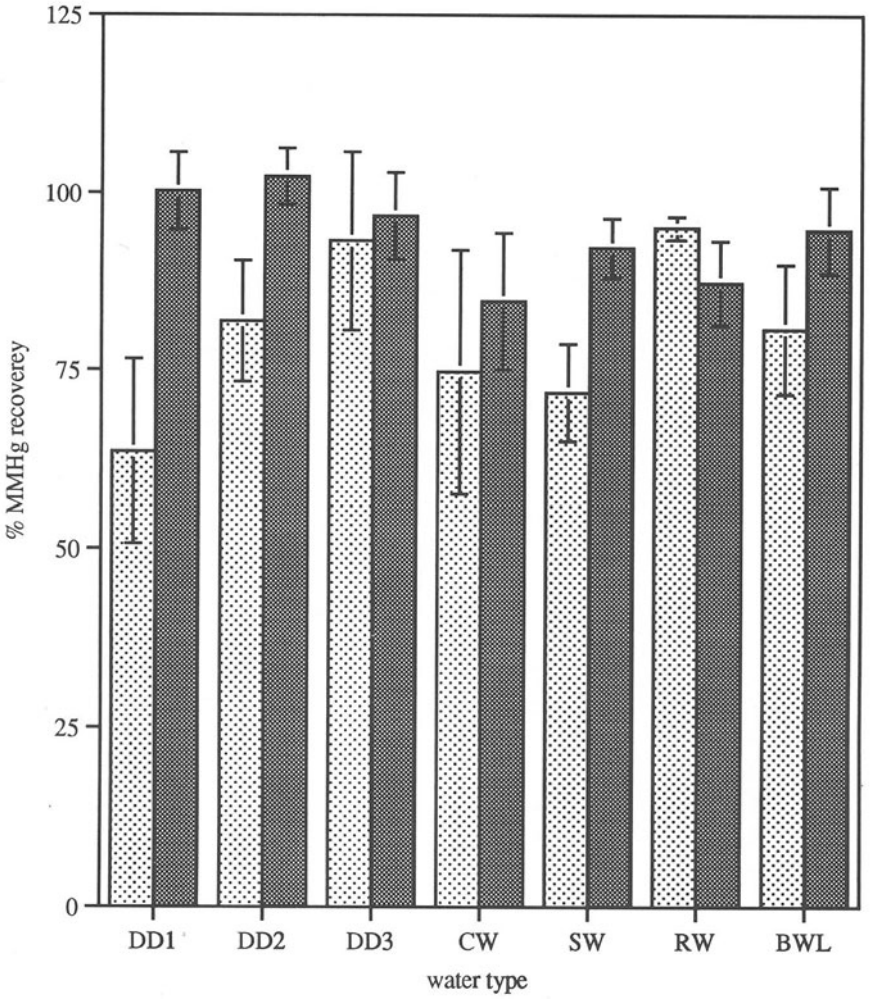
	% MMHg (4.44 ng/L) Recovered	
Distillation Matrix	77% Distilled	88% Distilled
0.12 N HCl	65.1 ± 18.4	63.6 ± 12.9
0.12 N HCl + 0.003-0.1 N H_2SO_4	—	63.4 ± 11.3
0.12 N HCl + 0.005-0.15 N KOAc	—	78.3 ± 12.7
0.06 N HCl	87.1 ± 7.0	81.9 ± 8.5
0.18 N H_2SO_4 + 0.01 N KCl	85.5 ± 11.3	93.2 ± 12.0

Another benefit of adding APDC prior to distillation is that it strongly complexes Hg(II), thus diminishing the volatility of this species during distillation. In cases where highly Hg(II) contaminated waters are analyzed, the Hg(II) that is co-distilled, although only a small fraction of the total can interfere with the analyses of MMHg by peak overlap. The use of APDC has resulted in an approximate 10-fold reduction in the level of Hg(II) in the distillate. This amount is generally sufficient to eliminate potential errors in quantifying the MMHg in the presence of high Hg(II) concentrations.

4. Conclusion

In addition to the beneficial effect of APDC on the recovery of MMHg from aqueous samples by distillation, this work confirms that of Horvat, et al., (1993), which suggests that samples should be preserved if possible with H_2SO_4, rather than HCl, to reduce the degree of HCl co-distillation. Work in progress at our laboratory suggests that the use of 0.1 N H_2SO_4 is an acceptable preservative for both total and MMHg in natural waters, although more

comprehensive studies on a wide variety of waters is still needed. If HCl is used as a preservative, much more satisfactory results for MMHg are obtained when the concentration is kept to less than 0.06 N (0.5% v/v).



DD1-3 are DIW 0.12 N HCl, 0.06 N HCl, and 0.18 N H_2SO_4 added, respectively. CW are clear lake water; SW is sea water; RW is rain; and BW is brown water.

Figure 1. Recovery of MMHg with (dark bars) and without (light bars) APDC (n=3-16 reps)

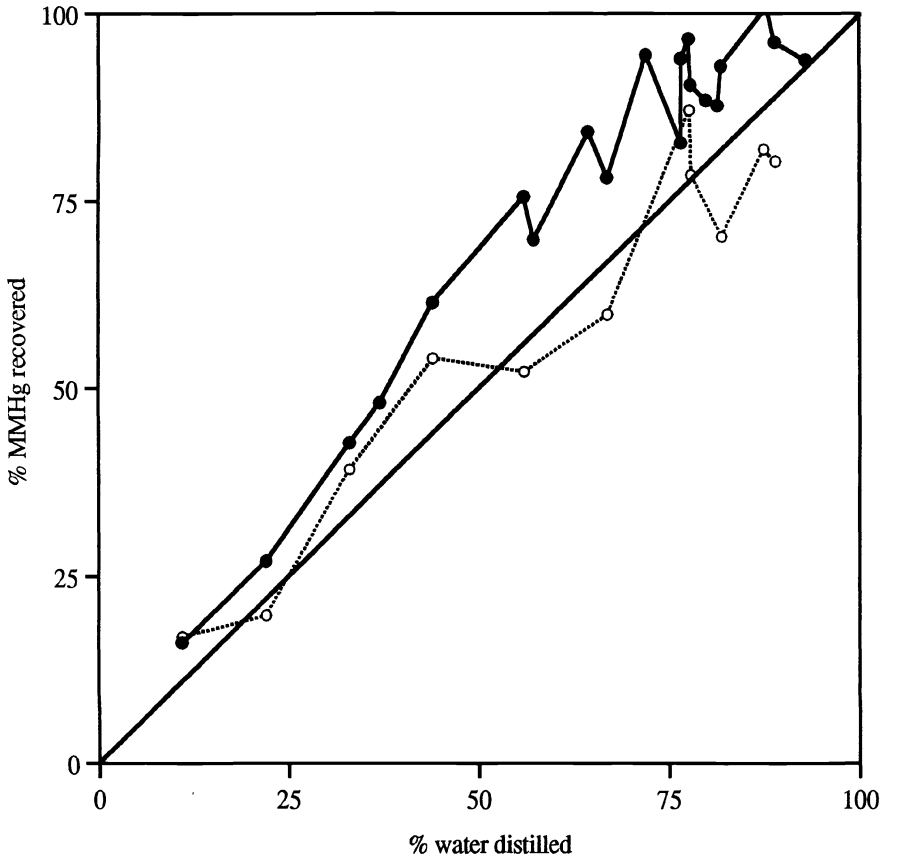


Figure 2. Distillation efficiency for MMHg chloride in (open circle) 0.06 N HCl, (dark circle) 0.06 N HCl plus APDC.

Acknowledgments

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VOLATILIZATION OF DIMETHYLMERCURY AND ELEMENTAL MERCURY FROM RIVER ELBE FLOODPLAIN SOILS

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Abstract. It has been shown that an untreated mercury-polluted floodplain soil (containing 10 μg/g per dry weight (d.w.) total Hg and 12 ng/g (d.w.) monomethylmercury compounds (MMM)) of the river Elbe in Northern Germany contains both dimethylmercury (DMM) and elemental mercury (Hg^0). This is the first time ever that DMM has been detected in unmodified soils. A novel purge-and-trap-technique involving a sequential thermodesorption-separation of the two species after trapping on a carbon molecular sieve (CMS) has been developed that allows the determination of the two species DMM and Hg^0 from aqueous solutions or soil samples by GC-CVAFS. The compounds' identities as Hg-species were confirmed by GC-ICP/MS. A DMM-concentration of 740 pg/g (d.w.) was determined in the soil; the Hg^0-concentration was found to be at least four times larger, but could not yet be quantified. Since no precautions against losses via evapoartion were taken during sampling and storage, the original concentrations were probably much higher. Both DMM and Hg^0 are easily purged with N_2 from soils as well as from soil suspensions, indicating that the two species may readily evaporate from those soils under natural conditions. The amount of DMM determined in the soil suspension was significantly lower (80 pg/g (d.w.)) compared to that in the original soil sample, suggesting that DMM might not be stable under these conditions. Also, it was shown that in natural samples, MMM can be converted into DMM in the presence of sulfide, at S^{2-}-levels as low as 100 μg/g.

1. Introduction

Ever since research on organomercurials in the environment began, the focus has been on monomethylmercury compounds (MMM). Even though dimethylmercury (DMM) might play an important role in the biogeochemical cycling as well, to date, there is little information available on this compound in the environment. It is still unclear whether the biotic and abiotic processes that methylate Hg^{2+} produce MMM only, or form DMM as well. While most authors claim that DMM is only a sideproduct of the reaction, others found that both compounds are formed in comparable amounts (Filippelli and Baldi, 1993), and others again hold the opinion that DMM is the primary methylation product, and MMM is only formed as its breakdown product (Imura *et al.*, 1971). In addition, it has been shown that MMM can be converted to DMM in the presence of sulfide (Craig and Bartlett, 1978; Craig and Moreton, 1984). The results obtained from natural samples are as ambiguous as the methylation theories: whereas most studies find only MMM , DMM was reported to be found in tropical deep-sea waters (Mason and Fitzgerald, 1990), and Quevauviller *et al.* (1992) even reported that they found only DMM, but no MMM, in mangrove sediment cores. The question remains: is DMM really formed in natural environments, and if so, is it stable enough to be measured there? Since the answer to this question is fundamental to the understanding of biogeochemical Hg-cycling, and may reveal enormous impacts on contaminated ecosystems, this study was undertaken to see if DMM could be detected in unmodified floodplain soils from the river Elbe in Germany. These samples have already been shown to be highly contaminated with total Hg and MMM species (Hintelmann and Wilken, 1994).

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2. Material and Methods

2.1. ANALYTICAL PROCEDURE

Separation of Hg-species is performed by thermodesorption-GC-CVAFS (Figure 1a) (see e.g. Bloom and Fitzgerald, 1988). Water samples and soil suspensions are purged from a bubbler bottle with N_2 for 5 min at 600 ml/min; soils are purged from a U-tube for 30 min at 50 ml/min. The analytes are collected on a carbon molecular sieve (CMS) adsorber, which is adsorbing so strongly that direct thermodesorption onto the GC-column in compatible time can only be achieved at temperatures that cause the DMM's thermal breakdown. In order to overcome this problem, both analytes have to be transferred onto a weaker adsorbent prior to analysis. Therefore, DMM is thermodesorbed onto Tenax TA (35-60 mesh) at 100 °C. During this process, no Hg^0 is released from the CMS, due to its much stronger adsorption (Figure 1b); it can be desorbed afterwards at 400 °C onto a second Tenax trap. Both Tenax adsorbers are subsequently analyzed separately (Figure 1b+c). GC-ICP/MS was used to confirm, that the signals obtained from natural samples did indeed result fom Hg species (Figure 1e+f). Calibration for DMM is made by spiking distilled water with diluted solutions of DMM in acetone (Figure 1d). The calibration curve is linear within the examined range between 7.68 pg and 768 pg DMM (Figure 2). Reproducibility is better than 5 % and there is no substantial blank, so we estimated a detection limit of ≈ 1 pg DMM absolute. Recovery of DMM-spikes from soil suspensions is quantitative. The analytical procedure was not optimized and calibrated for Hg^0 for all steps (especially for the purging); thus it is not possible to quantify the analyzed amounts correctly. The presented Hg^0-values are therefore only minimal amounts. It was proven, though, that all trapped Hg^0 is quantitatively transferred to the GC-CVAFS via the second Tenax trap exclusively. Since no calibration was performed, Hg^0-values can only be shown as relative signals in fluorescence units (thus, the curves for both species are not directly comparable!); they can be converted into Hg-amounts, if one assumes that the AFS has equal sensitivity for different Hg-species; this approximation was used for further quantitative estimations of Hg^0 in the results part.

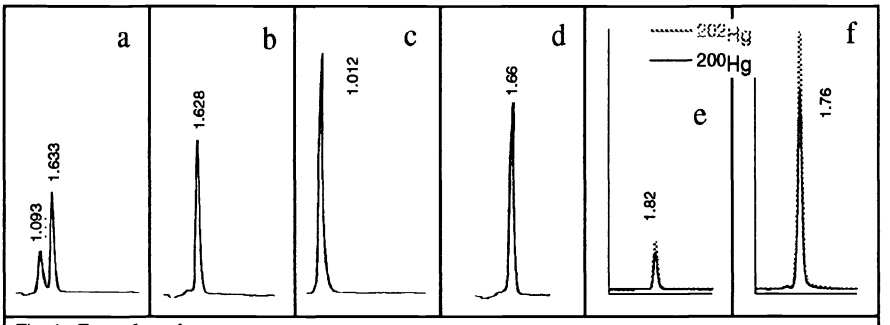

Fig. 1: Exemplary chromatograms

separation Hg^0 / DMM	DMM, soil samp (GC-CVAFS)	Hg^0, soil sample (GC-CVAFS)	DMM, standard (GC-CVAFS)	DMM, soil samp. (GC-ICP/MS)	DMM, standard (GC-ICP/MS)

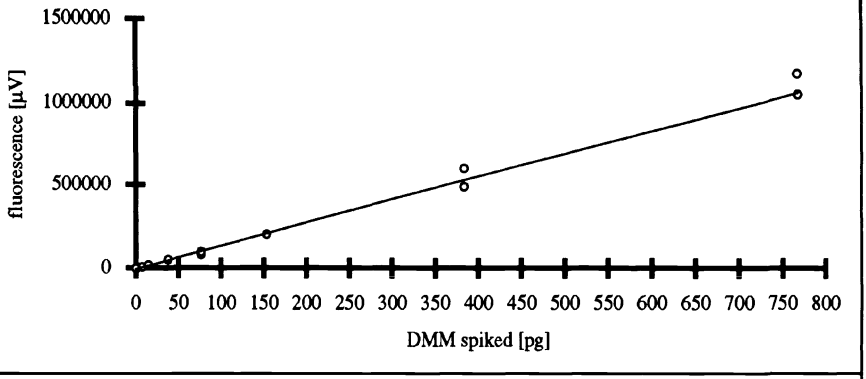

Fig. 2: Calibration curve for the determination of dimethylmercury from spiked aqueous solutions by purge-and-trap-thermodesorption-GC-CVAFS

2.2. SAMPLE CHARACTERIZATION

The floodplain soil sample was collected in November 1993 as a grab sample from the surface (0-15 cm) of an Elbe river floodplain soil and stored in the dark at 4 °C, but occasionally used for other analyses. No precautions against loss of compounds by evaporation or against changes in redox conditions were taken. The sample is high in organic content, contains 50 % water, 10 µg/g (d.w.) total Hg and 12 ng/g (d.w.) MeHg.

3. Results and Discussion

3.1. HG-SPECIES IN SOILS AND SOIL SUSPENSIONS

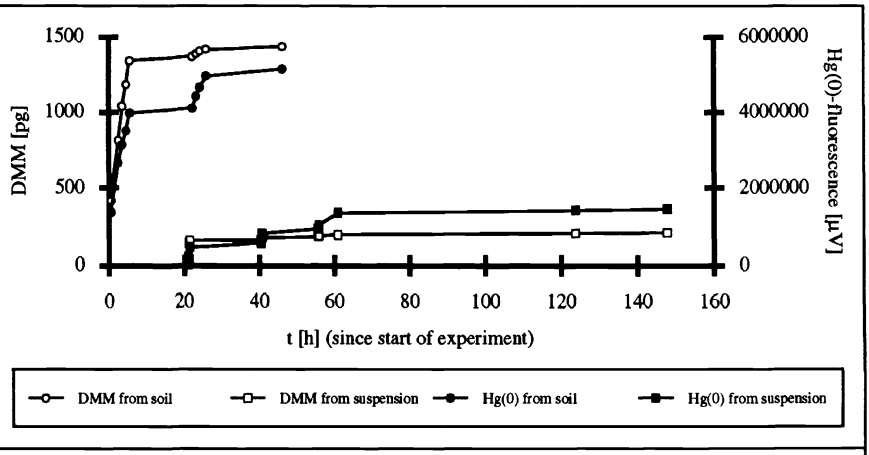

Fig. 3: Volatilization of dimethylmercury and elemental Hg from an Elbe river floodplain soil and its aqueous suspension (cumulative plot)

3.75 g of the described Elbe river floodplain soil sample and a suspension of 5 g of that soil in 100 ml water were purged with N_2 at room temperature without any further treatment whatsoever (Figure 3). Both DMM and Hg^0 are found in these soils. We are not aware that anyone before this report has positively identified Hg^0 in soils by proper chromatographic separation coupled with element specific detection. Even more surprising is the finding of DMM in an unaltered natural soil sample. Again, we are not aware of any other comparable reports; Quevauviller *et al.* (1992) have found DMM in mangrove sediments, but during their procedure, the sample is treated with $NaBH_4$-solution. Both species are easily released from the soils, indicating that they are weakly bound by the matrix. This means that evaporation can probably occur under natural circumstances to a large extent. If the DMM-data in Figure 3 are reconverted into fluorescence units, it becomes visible that there is more Hg^0 volatilized than DMM.; the factor between the total volatilized amounts (comparing the relative signals) is approximately 2 to 4. Given the sample's history, it seems reasonable to assume that the original contents, especially that of DMM, were much higher. The cumulated DMM curve approaches a plateau around 1.4 ng total volatilized DMM, which would be equivalent to 370 pg/g (w.w.) or 740 pg/g (d.w.); from this we estimate the total volatilization potential for Hg^0 to be several ng/g, although no replicates were performed. From the soil suspension, too, more Hg^0 is volatilized than DMM, only this time the factor is about 10. The total amounts of both Hg^0 and DMM are significantly lower, suggesting that these species are either not soluble or not stable in soil suspensions. In total, approximately 200 pg of DMM are released from the soil suspension, equalling 40 pg/g (w.w.) or 80 pg/g (d.w.). It also seems that both processes are terminated over the observed period of time. Generally, the situation of a "dry" soil should be more relevant to floodplains than that of a suspension; therefore we assume a large mobilization potential for both species.

3.2. ADDITION OF SULFIDE TO THE SOIL SUSPENSION

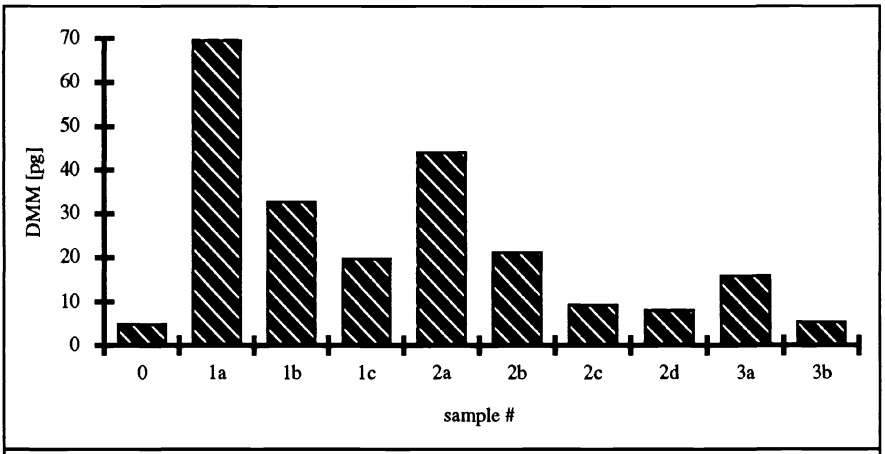

Fig. 4: Evolution of dimethylmercury upon addition of sulfide to a suspension of an Elbe river floodplain soil (1 & 2 = 100µg/g S^{2-} added, 3 = 1 mg/g S^{2-} added; a, b, c, d: subsequent 30 min-purgings)

After the release of volatile Hg-species from the soil solution had ceased, we tried to reproduce the findings of Craig and Moreton (1984) that sulfide addition increases the DMM-production, possibly via intermediate formation of $(CH_3Hg)_2S$ (Craig and Bartlett, 1978). The results (Figure 4) show that sulfide addition clearly and rapidly produces new DMM, already at S^{2-}-levels below 1.5 mg/g, for which Craig and Moreton (1984) found no DMM-evolution, but this is probably due to our much lower detection limit. We suspect that it is likewise formed from the large MMM-amount found in the sample.

4. Conclusion and Perspectives

For the first time ever, both DMM and Hg^0 were positively identified in unaltered natural soil samples. The two species can readily be purged from both the investigated soils and their suspensions with N_2, indicating a high evaporation potential and low binding strength by the soil matrix. Since the released amounts of both species are comparably high, these reactions may well be an important factor in the biogeochemical cycling of Hg in the investigated polluted river ecosystem. Especially the Hg evaporation as DMM needs further investigation, considering the compound's extreme volatility and toxicity. In addition, other polluted ecosystems must be checked for the occurrence of DMM to assess its role in the global Hg-cycling processes. The factors that lead to DMM occurrence have to be elucidated in order to predict ecosystem development, and the fate of DMM after the release from soils has to be studied.

Acknowledgements

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