
1 Introduction

CONTENTS

1.1	The Incentive	2
1.2	Physical-Chemical Properties	3
1.2.1	The Key Physical-Chemical Properties	3
1.2.2	Partitioning Properties	3
1.2.3	Temperature Dependence	5
1.2.4	Treatment of Dissociating Compounds	7
1.2.5	Treatment of Water-Miscible Compounds	8
1.2.6	Treatment of Partially Miscible Substances	8
1.2.7	Treatment of Gases and Vapors	8
1.2.8	Solids, Liquids and the Fugacity Ratio	9
1.2.9	Chemical Reactivity and Half-Lives	10
1.3	Experimental Methods	11
1.3.1	Solubility in Water and pK_a	11
1.3.2	Vapor Pressure	12
1.3.3	Octanol-Water Partition Coefficient K_{OW}	13
1.3.4	Henry's Law Constant	13
1.3.5	Octanol-Air Partition Coefficient K_{OA}	14
1.4	Quantitative Structure-Property Relationships (QSPRs)	14
1.4.1	Objectives of QSPRs	14
1.4.2	Examples of QSARs and QSPRs	15
1.5	Mass Balance Models of Chemical Fate	18
1.5.1	Evaluative Environmental Calculations	18
1.5.2	Level I Fugacity Calculations	19
1.5.3	Level II Fugacity Calculations	22
1.5.4	Level III Fugacity Calculations	23
1.6	Data Sources and Presentation	28
1.6.1	Data Sources	28
1.6.2	Data Presentation	29
1.7	Illustrative QSPR Plots and Fate Calculations	29
1.7.1	QSPR Plots for Mononuclear Aromatic Hydrocarbons	29
1.7.2	Evaluative Calculations for Benzene	32
1.7.3	QSPR Plots for Chlorophenols and Alkylphenols	36
1.7.4	Evaluative Calculations for Pentachlorophenol	39
1.8	References	49

1.1 THE INCENTIVE

It is believed that there are some 50,000 to 100,000 chemicals currently being produced commercially in a range of quantities with approximately 1000 being added each year. Most are organic chemicals, and many are pesticides and biocides designed to modify the biotic environment. Of these, perhaps 1000 substances are of significant environmental concern because of their presence in detectable quantities in various components of the environment, their toxicity, their tendency to bioaccumulate, their persistence and their potential to be transported long distances. Some of these chemicals, including pesticides, are of such extreme environmental concern that international actions have been taken to ensure that all production and use should cease, i.e., as a global society we should elect not to synthesize or use these chemicals. They should be “sunsetting.” PCBs, “dioxins” and DDT are examples. A second group consists of less toxic and persistent chemicals which are of concern because they are used or discharged in large quantities. They are, however, of sufficient value to society that their continued use is justified, but only under conditions in which we fully understand and control their sources, fate and the associated risk of adverse effects. This understanding is essential if society is to be assured that there is negligible risk of adverse ecological or human health effects. Other groups of more benign chemicals can presumably be treated with less rigor.

A key feature of this “cradle-to-grave” approach to chemical management is that society must improve its skills in assessing chemical fate in the environment. We must better understand where chemicals originate, how they migrate in, and between, the various media of air, water, soils, sediments and their biota which comprise our biosphere. We must understand how these chemicals are transformed by chemical and biochemical processes and, thus, how long they will persist in the environment. We must seek a fuller understanding of the effects that they will have on the multitude of interacting organisms that occupy these media, including ourselves.

It is now clear that the fate of chemicals in the environment is controlled by a combination of three groups of factors. First are the prevailing environmental conditions such as temperatures, flows and accumulations of air, water and solid matter and the composition of these media. Second are the properties of the chemicals which influence partitioning and reaction tendencies, i.e., the extent to which the chemical evaporates or associates with sediments, and how fast the chemical is eventually destroyed by conversion to other chemical species. Third are the patterns of use, into which compartments the substance is introduced, whether introduction is episodic or continuous and in the case of pesticides how and with which additives the active ingredient is applied.

In recent decades there has emerged a discipline within environmental science concerned with increasing our understanding of how chemicals behave in our multimedia environment. It has been termed environmental chemistry or “chemodynamics.” Practitioners of this discipline include scientists and engineers, students and teachers who attempt to measure, assess and predict how this large number of chemicals will behave in laboratory, local, regional and global environments. These individuals need data on physical-chemical and reactivity properties, as well as information on how these properties translate into environmental fate. This handbook provides a compilation of such data and outlines how to use them to estimate the broad features of environmental fate. It does so for classes or groups of chemicals, instead of the usual approach of treating chemicals on an individual basis. This has the advantage that systematic variations in properties with molecular structure can be revealed and exploited to check reported values, interpolate and even extrapolate to other chemicals of similar structure.

With the advent of inexpensive and rapid computation there has been a remarkable growth of interest in this general area of quantitative structure-property relationships (QSPRs). The ultimate goal is to use information about chemical structure to deduce physical-chemical properties, environmental partitioning and reaction tendencies, and even uptake and effects on biota. The goal is far from being fully realized, but considerable progress has been made. In this series of handbooks we have adopted a simple and well-tried approach of using molecular structure to deduce a molar volume, which in turn is related to physical-chemical properties. In the case of pesticides, the application of QSPR approaches is complicated by the large number of chemical classes, the frequent complexity of molecules and the lack of experimental data. Where there is a sufficient number of substances in each class or homologous series QSPRs are presented, but in some cases there is a lack of data to justify them. QSPRs based on other more complex molecular descriptors are, of course, widely available, especially in the proceedings of the biennial QSAR conferences.

Regrettably, the scientific literature contains a great deal of conflicting data, with reported values often varying over several orders of magnitude. There are some good, but more not-so-good reasons for this lack of accuracy. Many of these properties are difficult to measure because they involve analyzing very low concentrations of 1 part in 10^9 or 10^{12} . For many purposes an approximate value is adequate. There may be a mistaken impression that if a vapor pressure is low, as is the case with DDT, it is not important. DDT evaporates appreciably from solution in water, despite its low vapor pressure, because of its low solubility in water. In some cases the units are reported incorrectly. There may be uncertainties about temperature or pH. In other cases the chemical is wrongly identified. Errors tend to be perpetuated

by repeated citation. The aim of this handbook is to assist the user to identify such problems, provide guidance when selecting appropriate values and where possible determine their temperature dependence.

The final aspect of chemical fate treated in this handbook is the depiction or illustration of likely chemical fate. This is done using multimedia “fugacity” models as described later in this chapter. The aim is to convey an impression of likely environmental partitioning and transformation characteristics, i.e., a “behavior profile.” A fascinating feature of chemodynamics is that chemicals differ so greatly in their behavior. Some, such as chloroform, evaporate rapidly and are dissipated in the atmosphere. Others, such as DDT, partition into the organic matter of soils and sediments and the lipids of fish, birds and mammals. Phenols and carboxylic acids tend to remain in water where they may be subject to fairly rapid transformation processes such as hydrolysis, biodegradation and photolysis. By entering the physical-chemical data into a model of chemical fate in a generic or evaluative environment, it is possible to estimate the likely general features of the chemical’s behavior and fate. The output of these calculations can be presented numerically and pictorially.

In summary, the aim of this series of handbooks is to provide a useful reference work for those concerned with the assessment of the fate of existing and new chemicals in the environment.

1.2 PHYSICAL-CHEMICAL PROPERTIES

1.2.1 THE KEY PHYSICAL-CHEMICAL PROPERTIES

In this section we describe the key physical-chemical properties and discuss how they may be used to calculate partition coefficients for inclusion in mass balance models. Situations in which data require careful evaluation and use are discussed.

The major differences between behavior profiles of organic chemicals in the environment are attributable to their physical-chemical properties. The key properties are recognized as solubility in water, vapor pressure, the three partition coefficients between air, water and octanol, dissociation constant in water (when relevant) and susceptibility to degradation or transformation reactions. Other essential molecular descriptors are molar mass and molar volume, with properties such as critical temperature and pressure and molecular area being occasionally useful for specific purposes. A useful source of information and estimation methods on these properties is the handbook by Boethling and Mackay (2000).

Chemical identity may appear to present a trivial problem, but most chemicals have several names, and subtle differences between isomers (e.g., cis and trans) may be ignored. The most commonly accepted identifiers are the IUPAC name and the Chemical Abstracts System (CAS) number. More recently, methods have been sought of expressing the structure in line notation form so that computer entry of a series of symbols can be used to define a three-dimensional structure. For environmental purposes the SMILES (Simplified Molecular Identification and Line Entry System, Anderson et al. 1987) is favored, but the Wisniewski Line Notation is also quite widely used.

Molar mass or molecular weight is readily obtained from structure. Also of interest for certain purposes are molecular volume and area, which may be estimated by a variety of methods.

When selecting physical-chemical properties or reactivity classes the authors have been guided by:

1. The acknowledgment of previous supporting or conflicting values,
2. The method of determination,
3. The perception of the objectives of the authors, not necessarily as an indication of competence, but often as an indication of the need of the authors to obtain accurate values, and
4. The reported values for structurally similar, or homologous compounds.

The literature contains a considerable volume of “calculated” data as distinct from experimental data. We have generally not included such data because they may be of questionable reliability. In some cases an exception has been made when no experimental data exist and the calculation is believed to provide a useful and reliable estimate.

1.2.2 PARTITIONING PROPERTIES

Solubility in water and vapor pressure are both “saturation” properties, i.e., they are measurements of the maximum capacity that a solvent phase has for dissolved chemical. Vapor pressure P (Pa) can be viewed as a “solubility in air,” the corresponding concentration C (mol/m³) being P/RT where R is the ideal gas constant (8.314 J/mol.K) and T is absolute temperature (K). Although most chemicals are present in the environment at concentrations well below saturation, these concentrations are useful for estimating air-water partition coefficients as ratios of saturation values. It is usually assumed

that the same partition coefficient applies at lower sub-saturation concentrations. Vapor pressure and solubility thus provide estimates of the air-water partition coefficient K_{AW} , the dimensionless ratio of concentration in air (mass/volume) to that in water. The related Henry's law constant H (Pa.m³/mol) is the ratio of partial pressure in air (Pa) to the concentration in water (mol/m³). Both express the relative air-water partitioning tendency.

When solubility and vapor pressure are both low in magnitude and thus difficult to measure, it is preferable to measure the air-water partition coefficient or Henry's law constant directly. It is noteworthy that atmospheric chemists frequently use K_{WA} , the ratio of water-to-air concentrations. This may also be referred to as the Henry's law constant.

The octanol-water partition coefficient K_{OW} provides a direct estimate of hydrophobicity or of partitioning tendency from water to organic media such as lipids, waxes and natural organic matter such as humin or humic acid. It is invaluable as a method of estimating K_{OC} , the organic carbon-water partition coefficient, the usual correlation invoked being that of Karickhoff (1981)

$$K_{OC} = 0.41 K_{OW}$$

Seth et al. (1999) have suggested that a better correlation is

$$K_{OC} = 0.35 K_{OW}$$

and that the error limits on K_{OC} resulting from differences in the nature of organic matter are a factor of 2.5 in both directions, i.e. the coefficient 0.35 may vary from 0.14 to 0.88.

K_{OC} is an important parameter which describes the potential for movement or mobility of pesticides in soil, sediment and groundwater. Because of the structural complexity of these agrochemical molecules, the above simple relationship which considers only the chemical's hydrophobicity may fail for polar and ionic compounds. The effects of pH, soil properties, mineral surfaces and other factors influencing sorption become important. Other quantities, K_D (sorption partition coefficient to the whole soil on a dry weight basis) and K_{OM} (organic matter-water partition coefficient) are also commonly used to describe the extent of sorption. K_{OM} is often estimated as $0.56 K_{OC}$, implying that organic matter is 56% carbon.

K_{OW} is also used to estimate equilibrium fish-water bioconcentration factors K_B , or BCF using a correlation similar to that of Mackay (1982)

$$K_B = 0.05 K_{OW}$$

where the term 0.05 corresponds to a lipid content of the fish of 5%. The basis for this correlation is that lipids and octanol display very similar solvent properties, i.e., K_{LW} (lipid-water) and K_{OW} are equal. If the rate of metabolism is appreciable, equilibrium will not apply and the effective K_B will be lower to an extent dictated by the relative rates of uptake and loss by metabolism and other clearance processes. If uptake is primarily from food, the corresponding bioaccumulation factor also depends on the concentration of the chemical in the food.

For dissociating chemicals it is essential to quantify the extent of dissociation as a function of pH using the dissociation constant pK_a . The parent and ionic forms behave and partition quite differently; thus pH and the presence of other ions may profoundly affect chemical fate. This is discussed later in more detail in Section 1.2.4.

The octanol-air partition coefficient K_{OA} was originally introduced by Paterson et al. (1991) for describing the partitioning of chemicals from the atmosphere to foliage. It has proved invaluable for this purpose and for describing partitioning to aerosol particles and to soils. It can be determined experimentally using the technique devised by Harner and Mackay (1995). Although there are fewer data for K_{OA} than for K_{OW} , its use is increasing and when available, data are included in this handbook. K_{OA} has been applied to several situations involving partitioning of organic substances from the atmosphere to solid or liquid phases. Finizio et al. (1997) have shown that K_{OA} is an excellent descriptor of partitioning to aerosol particles, while McLachlan et al. (1995) and Tolls and McLachlan (1994) have used it to describe partitioning to foliage, especially grasses. Hippelein and McLachlan (1998) have used K_{OA} to describe partitioning between air and soil.

An attractive feature of K_{OA} is that it can replace the liquid or supercooled liquid vapor pressure in a correlation. K_{OA} is an experimentally measurable or accessible quantity, whereas the supercooled liquid vapor pressure must be estimated from the solid vapor pressure, the melting point and the entropy of fusion. The use of K_{OA} thus avoids the potentially erroneous estimation of the fugacity ratio, i.e., the ratio of solid and liquid vapor pressures. This is especially important for solutes with high melting points and, thus, low fugacity ratios.

The availability of data on K_{AW} , K_{OW} and K_{OA} raises the possibility of a consistency test. At first sight it appears that K_{OA} should equal K_{OW}/K_{AW} , and indeed this is often approximately correct. The difficulty is that in the case of K_{AW} , the water phase is pure water, and for K_{OA} the octanol phase is pure “dry” octanol. For K_{OW} , the water phase inevitably contains dissolved octanol, and the octanol phase contains dissolved water and is thus not “dry.” Beyer et al. (2002) and Cole and Mackay (2000) have discussed this issue.

If the partition coefficients are regarded as ratios of solubilities S (mol/m³)

$$K_{AW} = S_A/S_W \text{ or } \log K_{AW} = \log S_A - \log S_W$$

$$K_{OA} = S_O/S_A \text{ or } \log K_{OA} = \log S_O - \log S_A$$

$$K_{OW} = S_{OW}/S_{WO} \text{ or } \log K_{OW} = \log S_{OW} - \log S_{WO}$$

where subscript A applies to the gas phase or air, W to pure water, O to dry octanol, OW to “wet” octanol and WO to water saturated with octanol. It follows that the assumption that K_{OA} is K_{OW}/K_{AW} is essentially that

$$(\log S_{OW} - \log S_O) - (\log S_{WO} - \log S_W) = 0$$

$$\text{or } S_{OW} S_W / (S_O \cdot S_{WO}) \text{ is } 1.0$$

This is obviously satisfied when S_{OW} equals S_O and S_{WO} equals S_W , but this is not necessarily valid, especially when K_{OW} is large.

There are apparently two sources of this effect. The molar volume of water changes relatively little as a result of the presence of a small quantity of dissolved octanol, however the quantity of dissolved water in the octanol is considerable, causing a reduction in molar volume of the octanol phase. The result is that even if activity coefficients are unaffected, $\log S_O/S_W$ will be about 0.1 units less than that of $\log K_{OW}$. Effectively, the octanol phase “swells” as a result of the presence of water, and the concentration is reduced. In addition, when $\log K_{OW}$ exceeds 4.0 there is an apparent effect on the activity coefficients which causes $\log (S_O/S_W)$ to increase. This increase can amount to about one log unit when $\log K_{OW}$ is about 8. A relatively simple correlation based on the analysis by Beyer et al. (2002) (but differing from their correlation) is that

$$\log K_{OA} = \log (K_{OW}/K_{AW}) - 0.10 + [0.30 \log K_{OW} - 1.20]$$

when $\log K_{OW}$ is 4 or less the term in square brackets is ignored

when $\log K_{OW}$ is 4 or greater that term is included

1.2.3 TEMPERATURE DEPENDENCE

All partitioning properties change with temperature. The partition coefficients, vapor pressure, K_{AW} and K_{OA} , are more sensitive to temperature variation because of the large enthalpy change associated with transfer to the vapor phase. The simplest general expression theoretically based temperature dependence correlation is derived from the integrated Clausius-Clapeyron equation, or van't Hoff form expressing the effect of temperature on an equilibrium constant K_p ,

$$R \cdot \ln K_p = A_o - B/T$$

which can be rewritten as

$$\ln (\text{Property}) = A - \Delta H/RT$$

where A_o , B and A are constants, ΔH is the enthalpy of the phase change, i.e., evaporation from pure state for vapor pressure, dissolution from pure state into water for solubility, and for air-water transition in the case of Henry's law constant.

The fit is improved by adding further coefficients in additional terms. The variation of these equilibrium constants with temperature can be expressed by (Clarke and Glew 1966),

$$R \cdot \ln K_p(T) = A + B/T + C \cdot \ln T + DT + ET^2 + FT^3 + \dots$$

where A, B, C, D, E, F are constants.

There have been numerous approaches to describing the temperature dependence of the properties. For aqueous solubility, the most common expression is the van't Hoff equation of the form (Hildebrand et al. 1970):

$$d(\ln x)/d(1/T) = -\Delta_{\text{sol}}H/R$$

where x is the mole fraction solubility, T is the temperature in K, R is the ideal gas constant, and $\Delta_{\text{sol}}H$ is the enthalpy of solution of the solute. The enthalpy of solution can be considered as the sum of various contributions such as cavity formation and interactions between solute-solute or solute-solvent as discussed by Bohon and Claussen (1951), Arnold et al. (1958), Owen et al. (1986) and many others. Assuming the enthalpy of solution is constant over a narrow temperature range, integrating gives,

$$\ln x = -\Delta_{\text{sol}}H/RT + C$$

where C is a constant.

The relation between aqueous solubility and temperature is complicated because of the nature of the interactions between the solute and water structure. The enthalpy of solution can vary greatly with temperature, e.g., some liquid aromatic hydrocarbons display a minimum solubility corresponding to zero enthalpy of solution between 285 and 320 K. For instance, benzene has a minimum solubility at 291 K (Bohon and Claussen 1951, Arnold et al. 1958, Shaw 1989a) and alkylbenzenes display similar behavior (Shaw 1989a,b, Owens 1986). As is illustrated later in [chapter 3](#), solid aromatic hydrocarbons show a slight curvature in plots of logarithm of mole fraction solubility versus reciprocal absolute temperature. For narrow ranges in environmental temperatures, the enthalpy of solution may be assumed to be constant, and the linear van't Hoff plot of $\ln x$ versus $1/T$ is often used (Dickhut et al. 1986). Other relationships such as quadratic or cubic equations have been reported (May et al. 1978), and polynomial series (Clarke and Glew 1966, May et al. 1983, Owens et al. 1986) have been used when the data justify such treatment.

Equations relating vapor pressure to temperature are usually based on the two-parameter Clausius-Clapeyron equation,

$$d(\ln P^S)/dT = \Delta_{\text{vap}}H/RT^2$$

where P^S is vapor pressure, $\Delta_{\text{vap}}H$ is the enthalpy of vaporization. Again assuming $\Delta_{\text{vap}}H$ is constant over a narrow range of temperature, this gives,

$$\ln P^S = -\Delta_{\text{vap}}H/RT + C$$

which can be rewritten as the Clapeyron equation

$$\log P^S = A - B/T$$

This can be empirically modified by introducing additional parameters to give the three-parameter Antoine equation by replacing T with $(T + C)$, where C is a constant, which is the most common vapor pressure correlation used to represent experimental data (Zwolinski and Wilhoit 1971, Boublik et al. 1984, Stephenson and Malanowski 1987, and other handbooks).

$$\log P^S = A - B/(t + C)$$

where A, B and C are constants and t often has units of °C.

Other forms of vapor pressure equations, such as Cox equation (Osborn and Douslin 1974, Chao et al. 1983), Chebyshev polynomial (Ambrose 1981), Wagner's equation (Ambrose 1986), have also been widely used. Although

the enthalpy of vaporization varies with temperature, for the narrow environmental temperature range considered in environmental conditions, it is often assumed to be constant, for example, for the more volatile monoaromatic hydrocarbons and the less volatile polynuclear aromatic hydrocarbons.

The van't Hoff equation also has been used to describe the temperature effect on Henry's law constant over a narrow range for volatile chlorinated organic chemicals (Ashworth et al. 1988) and chlorobenzenes, polychlorinated biphenyls, and polynuclear aromatic hydrocarbons (ten Hulscher et al. 1992, Alaei et al. 1996). Henry's law constant can be expressed as the ratio of vapor pressure to solubility, i.e., p/c or p/x for dilute solutions. Note that since H is expressed using a volumetric concentration, it is also affected by the effect of temperature on liquid density whereas k_H using mole fraction is unaffected by liquid density (Tucker and Christian 1979), thus

$$\ln (k_H/\text{Pa}) = \ln [(P^S/\text{Pa})/x];$$

or,
$$\ln (H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}) = \ln [(P^S/\text{Pa})/(C_w^S/\text{mol}\cdot\text{m}^{-3})];$$

where C_w^S is the aqueous solubility.

By substituting equations for vapor pressure and solubility, the temperature dependence equation for Henry's law constant can be obtained, as demonstrated by Glew and Robertson (1956), Tsonopoulos and Wilson (1983), Heiman et al. (1985), and ten Hulscher et al. (1991).

Care must be taken to ensure that the correlation equations are applied correctly, especially since the units of the property, the units of temperature and whether the logarithm is base e or base 10. The equations should not be used to extrapolate beyond the stated temperature range.

1.2.4 TREATMENT OF DISSOCIATING COMPOUNDS

In the case of dissociating or ionizing organic chemicals such as organic acids and bases, e.g., phenols, carboxylic acids and amines, it is desirable to calculate the concentrations of ionic and non-ionic species, and correct for this effect. A number of authors have discussed and reviewed the effect of pH and ionic strength on the distribution of these chemicals in the environment, including Westall et al. (1985), Schwarzenbach et al. (1988), Jafvert et al. (1990), Johnson and Westall (1990) and the text by Schwarzenbach, Gschwend and Imboden (1993).

A simple approach is suggested here for estimating the effect of pH on properties and environmental fate using the phenols as an example. A similar approach can be used for bases. The extent of dissociation is characterized by the acid dissociation constant, K_a , expressed as its negative logarithm, $\text{p}K_a$, which for most chloro-phenolic compounds range between 4.75 for pentachlorophenol and 10.2 to phenol, and between 10.0 and 10.6 for the alkylphenols. The dissolved concentration in water is thus the sum of the undissociated, parent or protonated compound and the dissociated phenolate ionic form. When the $\text{p}K_a$ exceeds pH by 2 or more units, dissociation is 1% or less and for most purposes is negligible. The ratio of ionic to non-ionic or dissociated to undissociated species concentrations is given by,

$$\text{ionic/non-ionic} = 10^{(\text{pH}-\text{p}K_a)} = I$$

The fraction ionic x_I is $I/(1 + I)$. The fraction non-ionic x_N is $1/(1 + I)$. For compounds such as pentachlorophenol in which pH generally exceeds $\text{p}K_a$, I and x_I can be appreciable, and there is an apparently enhanced solubility (Horvath and Getzen 1985, NRCC 1982, Yoshida et al. 1987, Arcand et al. 1995, Huang et al. 2000). There are other reports of pH effects on octanol-water partition coefficient (Kaiser and Valdmann 1982, Westall et al. 1985, Lee et al. 1990, Smejtek and Wang 1993), soil sorption behavior (Choi and Amoine 1974, Lee et al. 1990, Schellenberg et al. 1984, Yoshida et al. 1987, Lee et al. 1990), bioconcentration and uptake kinetics to goldfish (Stehly and Hayton 1990) and toxicity to algae (Smith et al. 1987, Shigeoka et al. 1988).

The following treatment has been suggested by Shiu et al. (1994) and is reproduced briefly below. The simplest, "first-order" approach is to take into account the effect of dissociation by deducing the ratio of ionic to non-ionic species I , the fraction ionic x_I and the fraction non-ionic x_N for the chemical at both the pH and temperature of experimental data determination (I_D , x_{ID} , x_{ND}) and at the pH and temperature of the desired environmental simulation (I_E , x_{IE} , x_{NE}). It is assumed that dissociation takes place only in aqueous solution, not in air, organic carbon, octanol or lipid phases. Some ions and ion pairs are known to exist in the latter two phases, but there are insufficient data to justify a general procedure for estimating the quantities. No correction is made for the effect of cations other than H^+ . This approach must be regarded as merely a first correction for the dissociation effect. An accurate evaluation should preferably be based on experimental

determinations. The reported solubility C mol/m³ and K_{OW} presumably refer to the total of ionic and non-ionic forms, i.e., C_T and $K_{OW,T}$, at the pH of experimental determination, i.e.,

$$C_T = C_N + C_I$$

The solubility and K_{OW} of the non-ionic forms can be estimated as

$$C_N = C_T \cdot x_{ND}; \quad K_{OW,N} = K_{OW,T} / x_{ND}$$

Vapor pressure P^S is not affected, but the apparent Henry's law constant H_T , must also be adjusted to H_T/x_N , being P^S/C_N or $P^S/(C_T \cdot x_N)$.

C_N and $K_{OW,N}$ can be applied to environmental conditions with a temperature adjustment if necessary. Values of I_E , x_{Ix} and x_{NE} can be deduced from the environmental pH and the solubility and K_{OW} of the total ionic and non-ionic forms calculated.

In the tabulated data presented in this handbook the aqueous solubilities selected are generally those estimated to be of the non-ionic form unless otherwise stated.

1.2.5 TREATMENT OF WATER-MISCIBLE COMPOUNDS

In the multimedia models used in this series of volumes, an air-water partition coefficient K_{AW} or Henry's law constant (H) is required and is calculated from the ratio of the pure substance vapor pressure and aqueous solubility. This method is widely used for hydrophobic chemicals but is inappropriate for water-miscible chemicals for which no solubility can be measured. Examples are the lower alcohols, acids, amines and ketones. There are reported "calculated" or "pseudo-solubilities" that have been derived from QSPR correlations with molecular descriptors for alcohols, aldehydes and amines (by Leahy 1986; Kamlet et al. 1987, 1988 and Nirmalakhandan and Speece 1988a,b). The obvious option is to input the H or K_{AW} directly. If the chemical's activity coefficient γ in water is known, then H can be estimated as $v_w \gamma P_L^S$, where v_w is the molar volume of water and P_L^S is the liquid vapor pressure. Since H can be regarded as P_L^S/C_L^S , where C_L^S is the solubility, it is apparent that $(1/v_w \gamma)$ is a "pseudo-solubility." Correlations and measurements of γ are available in the physical-chemical literature. For example, if γ is 5.0, the pseudo-solubility is 11100 mol/m³ since the molar volume of water v_w is 18×10^{-6} m³/mol or 18 cm³/mol. Chemicals with γ less than about 20 are usually miscible in water. If the liquid vapor pressure in this case is 1000 Pa, H will be 1000/11100 or 0.090 Pa·m³/mol and K_{AW} will be H/RT or 3.6×10^{-5} at 25°C. Alternatively, if H or K_{AW} is known, C_L^S can be calculated. It is possible to apply existing models to hydrophilic chemicals if this pseudo-solubility is calculated from the activity coefficient or from a known H (i.e., C_L^S , P_L^S/H or P_L^S or $K_{AW} \cdot RT$). This approach is used here. In the fugacity model illustrations all pseudo-solubilities are so designated and should not be regarded as real, experimentally accessible quantities.

1.2.6 TREATMENT OF PARTIALLY MISCIBLE SUBSTANCES

Most hydrophobic substances have low solubilities in water, and in the case of liquids, water is also sparingly soluble in the pure substance. Some substances such as butanols and chlorophenols display relatively high mutual solubilities. As temperature increases, these mutual solubilities increase until a point of total miscibility is reached at a critical solution temperature. Above this temperature, no mutual solubilities exist. A simple plot of solubility versus temperature thus ends at this critical point. At low temperatures near freezing, the phase diagram also become complex. Example of such systems have been reported for *sec*-butyl alcohol (2-butanol) by Ochi et al. (1996) and for chlorophenols by Jaoui et al. (1999).

1.2.7 TREATMENT OF GASES AND VAPORS

A volatile substance may exist in one of three broad classes that can be loosely termed gases, vapors and liquids.

A *gaseous* substance such as oxygen at normal environmental conditions exists at a temperature exceeding its critical temperature of 155 K. No vapor pressure can be defined or measured under this super-critical condition, thus no Henry's law constant can be calculated. Empirical data are required.

A substance such as propane with a critical temperature of 370 K has a measurable vapor pressure of 998000 Pa, or approximately 10 atm at 27°C, which exceeds atmospheric pressure of 101325 Pa, the boiling point being -42°C or 231 K. It is thus a *vapor* at normal temperatures and pressures. A Henry's law constant can be calculated from this vapor pressure and a solubility as described earlier.

Most substances treated in this handbook are liquids or solids at environmental conditions; thus their boiling points exceed 25°C. Benzene, for example, has a critical temperature of 562 K, a boiling point of 80°C and a vapor pressure of 12700 Pa at 25°C.

When a solubility in water is measured and reported for gases and vapors an ambiguity is possible. For gases the solubility and the corresponding partial or total pressure in the gas phase must be reported since the solubility is dependent on this pressure as dictated by Henry's Law. For liquids and solids the solubility is presumably measured under conditions when the partial pressure equals the vapor pressure. For vapors such as propane the solubility can be measured either at a specified pressure (usually 1 atmosphere) or under high-pressure conditions (e.g., 10 atm) when the substance is a liquid. When calculating H or K_{AW} it is essential to use the correct pressure corresponding to the solubility measurement. Care must be exercised when treating substances with boiling points at or below environmental temperatures to ensure that the solubility is interpreted and used correctly.

1.2.8 SOLIDS, LIQUIDS AND THE FUGACITY RATIO

Saturation properties such as solubility in water and vapor pressure can be measured directly for solids and liquids. For certain purposes it is useful to estimate the solubility that a solid substance would have if it were liquid at a temperature below the melting point. For example, naphthalene melts at 80°C and at 25°C the solid has a solubility in water of 33 g/m³ and a vapor pressure of 10.9 Pa. If naphthalene was a liquid at 25°C it is estimated that its solubility would be 115 g/m³ and its vapor pressure 38.1 Pa, both a factor of 3.5 greater. This ratio of solid to liquid solubilities or vapor pressures is referred to as the fugacity ratio. It is 1.0 at the melting point and falls, in this case at lower temperatures to 0.286 at 25°C.

Solubilities and vapor pressures of a solid substance in the liquid state are often reported for the following four reasons.

Measurements of gas chromatographic retention time are often used as a fast and easy method of estimating vapor pressure. These estimated pressures are related to the gas/substrate partition coefficient, which can be regarded as a ratio of solubility of the substance in the gas to that in the substrate, both solubilities being of the substance in the liquid state. As a result the estimated vapor pressures are of the liquid state. To obtain the solid vapor pressure requires multiplication by the fugacity ratio. It is important to establish if the estimated and reported property is of the vapor or liquid.

QSPRs in which solubilities and vapor pressures are correlated against molecular structure are done exclusively using the liquid state property. This avoids the complication introduced by the effect of fugacity ratio or melting point on the solid state property.

When a solid is in liquid solution it behaves according to its liquid state properties because it is in a liquid mixture. When applying Raoult's Law or similar expressions, the pure substance property is that of the liquid. Liquids such as crude oils and PCB mixtures consist largely of solid substances, but they are in the liquid state and generally unable to precipitate as solid crystals because of their low individual concentrations.

When estimating air-aerosol partitioning of gas phase substances such as PAHs, most of which are solids, it is usual to use the liquid state vapor pressure as the correlating parameter. This is because the PAH is effectively in a liquid-like state on or in the aerosol particle. It does not exist in crystalline form.

When calculating partition coefficients such as K_{AW} , K_{OW} or K_{OA} from solubilities it is immaterial if the values used are of solids or liquids, but it is erroneous to mix the two states, e.g., a solid solubility and a liquid vapor pressure.

The fugacity ratio F can be estimated at temperature T (K) from the expression

$$\ln F = -\Delta S (T_M - T)/RT$$

where ΔS is the entropy of fusion, T_M is the melting point, and R is the gas constant. ΔS is related to the measurable enthalpy of fusion ΔH at the melting point as $\Delta H/T_M$. The reader should use experimental data for ΔH , ΔS and melting point whenever possible. The most reliable method is to measure ΔH calorimetrically, calculate ΔS and use this value to estimate F . Only in the absence of ΔH data should a QSPR be used or Walden's Rule applied that ΔS is approximately 56.5 J/mol K. This assumption leads to the equations

$$F = \exp(-6.79(T_M/T - 1))$$

$$\log F = -0.01(T_M - 298)$$

F is thus 1.0 at the melting point, with lower values at lower temperatures. It is not applied at temperatures exceeding T_M . This issue is discussed by Mackay (2001), Tesconi and Yalkowsky (2000), Yalkowsky and Banerjee (1992) and Chickos et al. (1999).

1.2.9 CHEMICAL REACTIVITY AND HALF-LIVES

Characterization of chemical reactivity presents a challenging problem in environmental science in general and especially in handbooks. Whereas radioisotopes have fixed half-lives, the half-life of a chemical in the environment depends not only on the intrinsic properties of the chemical, but also on the nature of the environmental compartments. Factors such as sunlight intensity, hydroxyl radical concentration and the nature of the microbial community, as well as temperature, affect the chemical's half-life so it is impossible (and misleading) to document a single reliable half-life. We suggest that the best approach is to suggest a semi-quantitative classification of half-lives into groups or ranges, assuming average environmental conditions to apply. Obviously, a different class will generally apply between compartments such as in air and bottom sediment. In this compilation we use the following class ranges for chemical reactivity in a single medium such as water.

These times are divided logarithmically with a factor of approximately 3 between adjacent classes. With the present state of knowledge it is probably misleading to divide the classes into finer groupings; indeed, a single chemical is likely to experience half-lives ranging over three classes, depending on season. These half-lives apply to the reaction of the parent substance. Often a degradation product or metabolite is formed that is of environmental concern. Since it has different properties it requires separate assessment. The ultimate degradation to inorganic species may require a much longer time than is indicated by the initial half-life.

class	mean half-life (hours)	range (hours)
1	5 < 10	
2	17 (~ 1 day)	10–30
3	55 (~ 2 days)	30–100
4	170 (~ 1 week)	100–300
5	550 (~ 3 weeks)	300–1,000
6	1700 (~ 2 months)	1,000–3,000
7	5500 (~ 8 months)	3,000–10,000
8	17000 (~ 2 years)	10,000–30,000
9	55000 (~ 6 years)	30,000–100,000
10	> 11 years	> 100,000

When compiling the suggested reactivity classes, the authors have examined the available information on reaction rates of the chemical in each medium by all relevant processes. These were expressed as an overall half-life for transformation. The product of the half-life and the corresponding rate constant is $\ln 2$ or 0.693. For example, a chemical may be subject to biodegradation with a half-life of 20 days or 480 hours (rate constant 0.0014 h^{-1}) and simultaneous photolysis with a rate constant of 0.0011 h^{-1} (half-life 630 hours). The overall rate constant is thus 0.0025 h^{-1} and the half-life is 277 hours or 12 days. Data for homologous chemicals have also been compiled, and insights into the reactivity of various functional groups considered. In most cases a single reaction class is assigned to the series; in the above case, class 4 with a mean half-life of 170 hours would be chosen. These half-lives must be used with caution, and it is wise to test the implications of selecting longer and shorter half-lives.

The most reliable kinetic data are for atmospheric oxidation by hydroxyl radicals. These data are usually reported as second-order rate constants applied to the concentration of the chemical and the concentration of hydroxyl radicals (usually of the order of 10^6 radicals per cm^3). The product of the assumed hydroxyl radical concentration and the second-order rate constant is a first-order rate constant from which a half-life can be deduced.

Extensive research has been conducted into the atmospheric chemistry of organic chemicals because of air quality concerns. Recently, Atkinson and coworkers (1984, 1985, 1987, 1988, 1989, 1990, 1991), Altshuller (1980, 1991) and Sabljic and Güsten (1990) have reviewed the photochemistry of many organic chemicals of environmental interest for their gas phase reactions with hydroxyl radicals (OH), ozone (O_3) and nitrate radicals (NO_3) and have provided detailed information on reaction rate constants and experimental conditions, which allowed the estimation of atmospheric lifetimes. Klöpffer (1991) has estimated the atmospheric lifetimes for the reaction with OH radicals to range from 1 hour to 130 years, based on these reaction rate constants and an assumed constant concentration of OH

radicals in air. As Atkinson (1985) has pointed out, the gas phase reactions with OH radicals are the major tropospheric loss process for the alkanes, haloalkanes, the lower alkenes, the aromatic hydrocarbons, and a majority of the oxygen-containing organics. In addition, photooxidation reactions with O_3 and NO_3 radicals can result in transformation of these compounds. The night-time reaction with NO_3 radicals may also be important (Atkinson and Carter 1984, Sabljic and Güsten 1990).

There are fewer studies on direct or indirect photochemical degradation in the water phase; however, Klöpffer (1991) had pointed out that the rate constant or lifetimes derived from these studies “is valid only for the top layer or surface waters.” Mill (1982, 1989, 1993) and Mill and Mabey (1985) have estimated half-lives of various chemicals in aqueous solutions from their reaction rate constants with singlet oxygen, as well as photooxidation with hydroxyl and peroxy radicals. Buxton et al. (1988) gave a critical review of rate constants for reactions with hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solutions. Mabey and Mill (1978) also reviewed the hydrolysis of organic chemicals in water under environmental conditions. Recently, Ellington and coworkers (1987a,b, 1988, 1989) also reported the hydrolysis rate constants in aqueous solutions for a variety of organic chemicals.

In most cases, a review of the literature suggested that reaction rates in water by chemical processes are 1 to 2 orders of magnitude slower than in air, but with biodegradation often being significant, especially for hydrocarbons and oxygen-containing chemicals. Generally, the water half-life class is three more than that in air, i.e., a factor of about 30 slower. Chemicals in soils tend to be shielded from photolytic processes, and they are less bioavailable, thus the authors have frequently assigned a reactivity class to soil of one more than that for water. Bottom sediments are assigned an additional class to that of soils largely on the basis that there is little or no photolysis, there may be lack of oxygen, and the intimate sorption to sediments renders the chemicals less bioavailable.

Because of the requirements of regulations for certain chemicals such as pesticides, extensive data usually exist on partitioning properties and reactivity or half-lives of active ingredients. In some cases these data have been peer-reviewed and published in the scientific literature, but often they are not generally available. A reader with interest in a specific pesticide can often obtain additional data from manufacturers or from registration literature, including accounts of chemical fate under field application conditions. Frequently these data are used as input to pesticide fate models, and the results of these modeling exercises may be available or published in the scientific literature.

The chemical reactivity of these substances is a topic which continues to be the subject of extensive research; thus there is often detailed, more recent information about the fate of chemical species which are of particular relevance to air or water quality. The reader is thus urged to consult the original and recent references because when considering the entire multimedia picture, it is impossible in a volume such as this to treat this subject in the detail it deserves.

1.3 EXPERIMENTAL METHODS

1.3.1 SOLUBILITY IN WATER AND pK_a

Most conventional organic contaminants are fairly hydrophobic and thus exhibit a low but measurable solubility in water. Solubility is often used to estimate the air-water partition coefficient or Henry's law constant, but this is not possible for miscible chemicals; indeed the method is suspect for chemicals of appreciable solubility in water, i.e., exceeding 1 g/100 g. Direct measurement of the Henry's law constant is thus required.

The conventional method of preparing saturated solutions for the determination of solubility is batch equilibration. An excess amount of solute chemical is added to water and equilibrium is achieved by shaking gently (generally referred as the “shake flask method”) or slow stirring with a magnetic stirrer. The aim is to prevent formation of emulsions or suspensions and thus avoid extra experimental procedures such as filtration or centrifuging which may be required to ensure that a true solution is obtained. Experimental difficulties can still occur with sparingly soluble chemicals such as longer chain alkanes and polycyclic aromatic hydrocarbons (PAHs) because of the formation of emulsion or micro-crystal suspensions. An alternative approach is to coat a thin layer of the chemical on the surface of the equilibration flask before water is added. An accurate “generator column” method is also used (Weil et al. 1974, May et al. 1978a,b) in which a column is packed with an inert solid support, such as glass beads and then coated with the solute chemical. Water is pumped through the column at a controlled, known flow rate to achieve saturation.

The method of concentration measurement of the saturated solution depends on the solute solubility and its chemical properties. Some common methods used for solubility measurement are listed below.

1. Gravimetric or volumetric methods (Booth and Everson 1948)

An excess amount of solid compound is added to a flask containing water to achieve saturation solution by shaking, stirring, centrifuging until the water is saturated with solute and undissolved solid or liquid

residue appears, often as a cloudy phase. For liquids, successive known amounts of solute may be added to water and allowed to reach equilibrium, and the volume of excess undissolved solute is measured.

2. Instrumental methods

- a. UV spectrometry (Andrews and Keefer 1950, Bohon and Claussen 1951, Yalkowsky and Valvani 1976);
- b. Gas chromatographic analysis with FID, ECD or other detectors (McAuliffe 1966, Mackay et al. 1975, Chiou et al. 1982, Bowman and Sans 1983);
- c. Fluorescence spectrophotometry (Mackay and Shiu 1977);
- d. Interferometry (Gross and Saylor 1931);
- e. High-pressure liquid chromatography (HPLC) with I.R., UV or fluorescence detection (May et al. 1978a,b, Wasik et al. 1983, Shiu et al. 1988, Doucette and Andren 1988a);
- f. Liquid phase elution chromatography (Schwarz 1980, Schwarz and Miller 1980);
- g. Nephelometric methods (Davis and Parke 1942, Davis et al. 1942, Hollifield 1979);
- h. Radiotracer or liquid scintillation counting (LSC) method (Banerjee et al. 1980, Lo et al. 1986).

For most organic chemicals the solubility is reported at a defined temperature in distilled water. For substances which dissociate (e.g., phenols, carboxylic acids and amines) it is essential to report the pH of the determination because the extent of dissociation affects the solubility. It is common to maintain the desired pH by buffering with an appropriate electrolyte mixture. This raises the complication that the presence of electrolytes modifies the water structure and changes the solubility. The effect is usually "salting-out." For example, many hydrocarbons have solubilities in seawater about 75% of their solubilities in distilled water. Care must thus be taken to interpret and use reported data properly when electrolytes are present.

The dissociation constant K_a or its commonly reported negative logarithmic form pK_a is determined in principle by simultaneous measurement or deduction of the ionic and non-ionic concentrations and the pH of the solution.

The most common problem encountered with reported data is inaccuracy associated with very low solubilities, i.e., those less than 1.0 mg/L. Such solutions are difficult to prepare, handle and analyze, and reported data often contain appreciable errors.

As was discussed earlier, care must be taken when interpreting solubility data for gases, i.e., substances for which the temperature exceeds the boiling point. Solubility then depends on the pressure which may be atmospheric or the higher vapor pressure.

1.3.2 VAPOR PRESSURE

In principle, the determination of vapor pressure involves the measurement of the saturation concentration or pressure of the solute in a gas phase. The most reliable methods involve direct determination of these concentrations, but convenient indirect methods are also available based on evaporation rate measurements or chromatographic retention times. Some methods and approaches are listed below.

- a. Static method, the equilibrium pressure in a thermostatic vessel is directly measured by use of pressure gauges: diaphragm gauge (Ambrose et al. 1975), Rodebush gauge (Sears and Hopke 1947), inclined-piston gauge (Osborn and Douslin 1975);
- b. Dynamic method (or boiling point) for measuring relatively high vapor pressure, eg., comparative ebulliometry (Ambrose 1981);
- c. Effusion methods, torsion and weight-loss (Balson 1947, Bradley and Cleasby 1953, Hamaker and Kerlinger 1969, De Kruif 1980);
- d. Gas saturation or transpiration methods (Spencer and Cliath 1970, 1972, Sinke 1974, Macknick and Prausnitz 1979, Westcott et al. 1981, Rordorf 1985a,b, 1986);
- e. Dynamic coupled-column liquid chromatographic method- a gas saturation method (Sonnefeld et al. 1983);
- f. Calculation from evaporation rates and vapor pressures of a reference compound (Gückel et al. 1974, 1982, Dobbs and Grant 1980, Dobbs and Cull 1982);
- g. Calculation from GC retention time data (Hamilton 1980, Westcott and Bidleman 1982, Bidleman 1984, Kim et al. 1984, Foreman and Bidleman 1985, Burkhard et al. 1985a, Hinckley et al. 1990).

The greatest difficulty and uncertainty arises when determining the vapor pressure of chemicals of low volatility, i.e., those with vapor pressures below 1.0 Pa. Vapor pressures are strongly dependent on temperature, thus accurate temperature control is essential. Data are often regressed against temperature and reported as Antoine or Clapeyron constants. Care

must be taken if the Antoine or other equations are used to extrapolate data beyond the temperature range specified. It must be clear if the data apply to the solid or liquid phase of the chemical.

1.3.3 OCTANOL-WATER PARTITION COEFFICIENT K_{OW}

The experimental approaches are similar to those for solubility, i.e., employing shake flask or generator-column techniques. Concentrations in both the water and octanol phases may be determined after equilibration. Both phases can then be analyzed by the instrumental methods discussed above and the partition coefficient is calculated from the concentration ratio C_O/C_W . This is actually the ratio of solute concentration in octanol saturated with water to that in water saturated with octanol.

As with solubility, K_{OW} is a function of the presence of electrolytes and for dissociating chemicals it is a function of pH. Accurate values can generally be measured up to about 10^7 , but accurate measurement beyond this requires meticulous technique. A common problem is the presence of small quantities of emulsified octanol in the water phase. The high concentration of chemical in that emulsion causes an erroneously high apparent water phase concentration.

Considerable success has been achieved by calculating K_{OW} from molecular structure; thus, there has been a tendency to calculate K_{OW} rather than measure it, especially for “difficult” hydrophobic chemicals. These calculations are, in some cases, extrapolations and can be in serious error. Any calculated log K_{OW} value above 7 should be regarded as suspect, and any experimental or calculated value above 8 should be treated with extreme caution.

For many hydrophilic compounds such as the alcohols, K_{OW} is low and can be less than 1.0, resulting in negative values of log K_{OW} . In such cases, care should be taken when using correlations developed for more hydrophobic chemicals since partitioning into biota or organic carbon phases may be primarily into aqueous rather than organic media.

Details of experimental methods are described by Fujita et al. (1964), Leo et al. (1971), Hansch and Leo (1979), Rekker (1977), Chiou et al. (1977), Miller et al. (1984, 1985), Bowman and Sans (1983), Woodburn et al. (1984), Doucette and Andren (1987), and De Bruijn et al. (1989).

1.3.4 HENRY'S LAW CONSTANT

The Henry's law constant is essentially an air-water partition coefficient which can be determined by measurement of solute concentrations in both phases. This raises the difficulty of accurate analytical determination in two very different media which usually requires different techniques. Accordingly, effort has been devoted to devising techniques in which concentrations are measured in only one phase and the other concentration is deduced from a mass balance. These methods are generally more accurate. The principal difficulty arises with hydrophobic, low-volatility chemicals which can establish only very small concentrations in both phases.

Henry's law constant can be regarded as a ratio of vapor pressure to solubility, thus it is subject to the same effects that electrolytes have on solubility. Temperature affects both properties. Some methods are as follows:

- a. Volatility measurement of dilute aqueous solutions (Butler et al. 1935, Burnett 1963, Buttery et al. 1969);
- b. Multiple equilibration method (McAuliffe 1971, Munz and Roberts 1987);
- c. Equilibrium batch stripping (Mackay et al. 1979, Dunnivant et al. 1988, Betterton and Hoffmann 1988, Zhou and Mopper 1990);
- d. GC-determined distribution coefficients (Leighton and Calo 1981);
- e. GC analysis of both air/water phases (Vejrosta et al. 1982, Jönsson et al. 1982);
- f. EPICS (Equilibrium Partitioning In Closed Systems) method (Lincoff and Gossett 1984, Gossett 1987, Ashworth et al. 1988);
- g. Wetted-wall column (Fendinger and Glotfelty 1988, 1989, 1990);
- h. Headspace analyses (Hussam and Carr 1985);
- i. Calculation from vapor pressure and solubility (Mackay and Shiu 1981);
- j. GC retention volume/time determined activity coefficient at infinite dilution γ^∞ (Karger et al. 1971a,b, Sugiyama et al. 1975, Tse et al. 1992).

When using vapor pressure and solubility data, it is essential to ensure that both properties apply to the same chemical phase, i.e., both are of the liquid, or of the solid. Occasionally, a solubility is of a solid while a vapor pressure is extrapolated from higher temperature liquid phase data.

As was discussed earlier under solubility, for miscible chemicals it is necessary to determine the Henry's law constant directly, since solubilities are not measurable.

1.3.5 OCTANOL-AIR PARTITION COEFFICIENT K_{OA}

As was discussed earlier the octanol-air partition coefficient is increasingly used as a descriptor of partitioning between the atmosphere and organic phases in soils and vegetation. A generator column technique is generally used in which an inert gas is flowed through a column containing a substance dissolved in octanol. The concentration in the equilibrated gas leaving the column is then measured (Harner and Mackay 1995). More recent methods have been described by Harner and Bidleman (1996) and Shoeib and Harner (2002). Su et al (2002) have described a GC retention time method.

1.4 QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS (QSPRs)

1.4.1 OBJECTIVES OF QSPRs

Because of the large number of chemicals of actual and potential concern, the difficulties and cost of experimental determinations, and scientific interest in elucidating the fundamental molecular determinants of physical-chemical properties, considerable effort has been devoted to generating quantitative structure-property relationships (QSPRs). This concept of structure-property relationships or structure-activity relationships (QSARs) is based on observations of linear free-energy relationships, and usually takes the form of a plot or regression of the property of interest as a function of an appropriate molecular descriptor which can be calculated using only a knowledge of molecular structure or a readily accessible molecular property.

Such relationships have been applied to solubility, vapor pressure, K_{OW} , K_{AW} , K_{OA} , Henry's law constant, reactivities, bioconcentration data and several other environmentally relevant partition coefficients. Of particular value are relationships involving various manifestations of toxicity, but these are beyond the scope of this handbook. These relationships are valuable because they permit values to be checked for "reasonableness" and (with some caution) interpolation is possible to estimate undetermined values. They may be used (with extreme caution!) for extrapolation.

A large number of descriptors have been, and are being, proposed and tested. Dearden (1990) and the compilations by Karcher and Devillers (1990) and Hermens and Opperhuizen (1991) give comprehensive accounts of descriptors and their applications.

A valuable source of up-to-date information is the proceedings of the biennial QSAR conferences. The QSAR 2002 conference proceedings have been edited by Breton et al. (2003). A set of critical reviews has been edited by Walker (2003). Of particular note is the collection of estimation methods developed by the Syracuse Research Corporation with US EPA support and available on the internet at www.syrres.com under "estimation methods."

Among the most commonly used molecular descriptors are molecular weight and volume, the number of specific atoms (e.g., carbon or chlorine), surface areas (which may be defined in various ways), refractivity, parachor, steric parameters, connectivities and various topological parameters. Several quantum chemical parameters can be calculated from molecular orbital calculations including charge, electron density and superdelocalizability. It is likely that existing and new descriptors will continue to be tested, and that eventually a generally preferred set of readily accessible parameters will be adopted for routine use for correlating purposes.

From the viewpoint of developing quantitative correlations it is desirable to seek a linear relationship between descriptor and property, but a nonlinear or curvilinear relationship is adequate for illustrating relationships and interpolating purposes. In this handbook we have elected to use the simple descriptor of molar volume at the normal boiling point as estimated by the Le Bas method (Reid et al. 1987). This parameter is very easily calculated and proves to be adequate for the present purposes of plotting property versus relationship without seeking linearity.

The Le Bas method is based on a summation of atomic volumes with adjustment for the volume decrease arising from ring formation. The full method is described by Reid et al. (1987), but for the purposes of this compilation, the volumes and rules as listed in Table 1.3.1 are used.

Example: The experimental molar volume of chlorobenzene 115 cm³/mol (Reid et al. 1987). From the above rules, the Le Bas molar volume for chlorobenzene (C₆H₅Cl) is:

$$V = 6 \times 14.8 + 5 \times 3.7 + 24.6 - 15 = 117 \text{ cm}^3/\text{mol}$$

Accordingly, plots are presented at the end of each chapter for solubility, vapor pressure, K_{OW} , and Henry's law constant versus Le Bas molar volume.

TABLE 1.3.1
Le Bas molar volume

	increment, cm ³ /mol
Carbon	14.8
Hydrogen	3.7
Oxygen	7.4
In methyl esters and ethers	9.1
In ethyl esters and ethers	9.9
Join to S, P, or N	8.3
Nitrogen	
Doubly bonded	15.6
In primary amines	10.5
In secondary amines	12.0
Bromine	27.0
Chlorine	24.6
Fluorine	8.7
Iodine	37.0
Sulfur	25.6
Rings	
Three-membered	−6.0
Four-membered	−8.5
Five-membered	−11.5
Six-membered	−15.0
Naphthalene	−30.0
Anthracene	−47.5

As was discussed earlier in Section 1.2.8 a complication arises in that two of these properties (solubility and vapor pressure) are dependent on whether the solute is in the liquid or solid state. Solid solutes have lower solubilities and vapor pressures than they would have if they had been liquids. The ratio of the (actual) solid to the (hypothetical supercooled) liquid solubility or vapor pressure is termed the fugacity ratio F and can be estimated from the melting point and the entropy of fusion. This “correction” eliminates the effect of melting point, which depends on the stability of the solid crystalline phase, which in turn is a function of molecular symmetry and other factors. For solid solutes, the correct property to plot is the calculated or extrapolated supercooled liquid solubility. This is calculated in this handbook using where possible a measured entropy of fusion, or in the absence of such data the Walden’s Rule relationship suggested by Yalkowsky (1979) which implies an entropy of fusion of 56 J/mol·K or 13.5 cal/mol·K (e.u.)

$$F = C_S^S/C_L^S = P_S^S/P_L^S = \exp\{6.79(1 - T_M/T)\}$$

where C^S is solubility, P^S is vapor pressure, subscripts S and L refer to solid and liquid phases, T_M is melting point and T is the system temperature, both in absolute (K) units. The fugacity ratio is given in the data tables at 25°C, the usual temperature at which physical-chemical property data are reported. For liquids, the fugacity ratio is 1.0.

The usual approach is to compile data for the property in question for a series of structurally similar molecules and plot the logarithm of this property versus molecular descriptors, on a trial-and-error basis seeking the descriptor which best characterizes the variation in the property. It may be appropriate to use a training set to obtain a relationship and test this relationship on another set. Generally a set of at least ten data points is necessary before a reliable QSPR can be developed.

1.4.2 EXAMPLES OF QSARs AND QSPRs

There is a continuing effort to extend the long-established concept of quantitative-structure-activity-relationships (QSARs) to quantitative-structure-property relationships (QSPRs) to compute all relevant environmental physical-chemical properties (such as aqueous solubility, vapor pressure, octanol-water partition coefficient, Henry’s law constant, bioconcentration factor (BCF), sorption coefficient and environmental reaction rate constants from molecular structure).

Examples are Burkhard (1984) and Burkhard et al. (1985a), who calculated solubility, vapor pressure, Henry's law constant, K_{OW} and K_{OC} for all PCB congeners. Hawker and Connell (1988) also calculated $\log K_{OW}$; Abramowitz and Yalkowsky (1990) calculated melting point and solubility for all PCB congeners based on the correlation with total surface area (planar TSAs). Doucette and Andren (1988b) used six molecular descriptors to compute the K_{OW} of some chlorobenzenes, PCBs and PCDDs. Mailhot and Peters (1988) employed seven molecular descriptors to compute physical-chemical properties of some 300 compounds. Isnard and Lambert (1988, 1989) correlated solubility, K_{OW} and BCF for a large number of organic chemicals. Nirmalakhandan and Speece (1988a,b, 1989) used molecular connectivity indices to predict aqueous solubility and Henry's law constants for 300 compounds over 12 logarithmic units in solubility. Kamlet and co-workers (1986, 1987, 1988) have developed the "solvatochromic" parameters with the intrinsic molar volume to predict solubility, $\log K_{OW}$ and toxicity of organic chemicals. Warne et al. (1990) correlated solubility and K_{OW} for lipophilic organic compounds with 39 molecular descriptors and physical-chemical properties. Atkinson (1987, 1988) has used the structure-activity relationship (SAR) to estimate gas-phase reaction rate constants of hydroxyl radicals for organic chemicals. Mabey et al. (1984) have reviewed the estimation methods from SAR correlation for reaction rate constants and physical-chemical properties in environmental fate assessment. Other correlations are reviewed by Lyman et al. (1982) and Yalkowsky and Banerjee (1992). As Dearden (1990) has pointed out, "new parameters are continually being devised and tested, although the necessity of that may be questioned, given the vast number already available." It must be emphasized, however, that regardless of how accurate these predicted or estimated properties are claimed to be, ultimately they have to be confirmed or verified by experimental measurement.

A fundamental problem encountered in these correlations is the mismatch between the accuracy of experimental data and the molecular descriptors which can be calculated with relatively high precision, usually within a few percent. The accuracy may not always be high, but for correlation purposes precision is more important than accuracy. The precision and accuracy of the experimental data are often poor, frequently ranging over a factor of two or more. Certain isomers may yield identical descriptors, but have different properties. There is thus an inherent limit to the applicability of QSPRs imposed by the quality of the experimental data, and further efforts to improve descriptors, while interesting and potentially useful, may be unlikely to yield demonstrably improved QSPRs.

One of the most useful and accessible set of QSARs is that developed primarily by Howard and Meylan at the Syracuse Research Corporation, NY. These estimation methods are available as the EPISuite set from their website at www.syrres.com.

For correlation of solubility, the correct thermodynamic quantities for correlation are the activity coefficient γ , or the excess Gibbs free energy ΔG , as discussed by Pierotti et al. (1959) and Tsonopoulos and Prausnitz (1971). Examples of such correlations are given below.

1. Carbon number or carbon plus chlorine number (Tsonopoulos and Prausnitz 1971, Mackay and Shiu 1977);
2. Molar volume cm^3/mol
 - a. Liquid molar volume - from density (McAuliffe 1966, Lande and Banerjee 1981, Chiou et al. 1982, Abernethy et al. 1988, Wang et al. 1992);
 - b. Molar volume by additive group contribution method, e.g., Le Bas method, Schroeder method (Reid et al. 1987, Miller et al. 1985);
 - c. Intrinsic molar volume, V_i , cm^3/mol - from van der Waals radius with solvatochromic parameters α and β (Leahy 1986, Kamlet et al. 1987, 1988);
 - d. Characteristic molecular volume, m^3/mol (McGowan and Mellors 1986);
3. Group contribution method (Irmann 1965, Korenman et al. 1971, Polak and Lu 1973, Klopman et al. 1992);
4. Molecular volume - $\text{\AA}^3/\text{molecule}$ (cubic Angstrom per molecule)
 - a. van der Waals volume (Bondi 1964);
 - b. Total molecular volume (TMV) (Pearlman et al. 1984, Pearlman 1986);
5. Total surface area (TSA) - $\text{\AA}^2/\text{molecule}$ (Hermann 1971, Amidon et al. 1975, Yalkowsky and Valvani 1976, Yalkowsky et al. 1979, Iwase et al. 1985, Pearlman 1986, Andren et al. 1987, Hawker and Connell 1988, Dunnivant et al. 1992);
6. Molecular connectivity indices (MCI) or χ (Kier and Hall 1976, Andren et al. 1987, Nirmalakhandan and Speece 1988b, 1989);
7. Boiling point (Almgren et al. 1979);
8. Melting point (Amidon and Williams 1982);
9. Melting point and TSA (Abramowitz and Yalkowsky 1990);
10. High-pressure liquid chromatography (HPLC) - retention data (Locke 1974, Whitehouse and Cooke 1982, Brodsky and Ballschmiter 1988);

11. Adsorbability index (AI) (Okouchi et al. 1992);
12. Fragment solubility constants (Wakita et al. 1986).

Several workers have explored the linear relationship between octanol-water partition coefficient and solubility as a means of estimating solubility.

Hansch et al. (1968) established the linear free-energy relationship between aqueous and octanol-water partition of organic liquid. Others, such as Tulp and Hutzinger (1978), Yalkowsky et al. (1979), Mackay et al. (1980), Banerjee et al. (1980), Chiou et al. (1982), Bowman and Sans (1983), Miller et al. (1985), Andren et al. (1987) and Doucette and Andren (1988b) have all presented similar but modified relationships.

The UNIFAC (UNIQUAC Functional Group Activity Coefficient) group contribution (Fredenslund et al. 1975, Kikic et al. 1980, Magnussen et al. 1981, Gmehling et al. 1982 and Hansen et al. 1991) is widely used for predicting the activity coefficient in nonelectrolyte liquid mixtures by using group-interaction parameters. This method has been used by Kabadi and Danner (1979), Banerjee (1985), Arbuckle (1983, 1986), Banerjee and Howard (1988) and Al-Sahhaf (1989) for predicting solubility (as a function of the infinite dilution activity coefficient, γ^∞) in aqueous systems. Its performance is reviewed by Yalkowsky and Banerjee (1992).

HPLC retention time data have been used as a pseudo-molecular descriptor by Whitehouse and Cooke (1982), Hafkenscheid and Tomlinson (1981), Tomlinson and Hafkenscheid (1986) and Swann et al. (1983).

The octanol-water partition coefficient K_{OW} is widely used as a descriptor of hydrophobicity. Variation in K_{OW} is primarily attributable to variation in activity coefficient in the aqueous phase (Miller et al. 1985); thus, the same correlations used for solubility in water are applicable to K_{OW} . Most widely used is the Hansch-Leo compilation of data (Leo et al. 1971, Hansch and Leo 1979) and related predictive methods. Examples of K_{OW} correlations are:

1. Molecular descriptors
 - a. Molar volumes: Le Bas method; from density; intrinsic molar volume; characteristic molecular volume (Abernethy et al. 1988, Chiou 1985, Kamlet et al. 1988, McGowan and Mellors 1986);
 - b. TMV (De Bruijn and Hermens 1990);
 - c. TSA (Yalkowsky et al. 1979, 1983, Pearlman 1980, 1986, Pearlman et al. 1984, Hawker and Connell 1988);
 - d. Molecular connectivity indices (Doucette and Andren 1988b);
 - e. Molecular weight (Doucette and Andren 1988b).
2. Group contribution methods
 - a. π -constant or hydrophobic substituent method (Hansch et al. 1968, Hansch and Leo 1979, Doucette and Andren 1988b);
 - b. Fragment constants or f-constant (Rekker 1977, Yalkowsky et al. 1983);
 - c. Hansch and Leo's f-constant (Hansch and Leo 1979; Doucette and Andren 1988b).
3. From solubility - K_{OW} relationship
4. HPLC retention data
 - a. HPLC- k' capacity factor (Könemann et al. 1979, McDuffie 1981);
 - b. HPLC-RT retention time (Veith et al. 1979, Rapaport and Eisenreich 1984, Doucette and Andren 1988b);
 - c. HPLC-RV retention volume (Garst 1984);
 - d. HPLC-RT/MS HPLC retention time with mass spectrometry (Burkhard et al. 1985c).
5. Reversed-phase thin-layer chromatography (TLC) (Ellgehausen et al. 1981, Bruggeman et al. 1982).
6. Molar refractivity (Yoshida et al. 1983).
7. Combination of HPLC retention data and molecular connectivity indices (Finizio et al. 1994).
8. Molecular orbital methods (Reddy and Locke 1994).

As with solubility and octanol-water partition coefficient, vapor pressure can be estimated with a variety of correlations as discussed in detail by Burkhard et al. (1985a) and summarized as follows:

1. Interpolation or extrapolation from equation for correlating temperature relationships, e.g., the Clausius-Clapeyron, Antoine equations (Burkhard et al. 1985a);
2. Carbon or chlorine numbers (Mackay et al. 1980, Shiu and Mackay 1986);
3. Le Bas molar volume (Shiu et al. 1987, 1988);
4. Boiling point T_b and heat of vaporization ΔH_v (Mackay et al. 1982);
5. Group contribution method (Macknick and Prausnitz 1979);

6. UNIFAC group contribution method (Jensen et al. 1981, Yair and Fredenslund 1983, Burkhard et al. 1985a, Banerjee et al. 1990);
7. Molecular weight and Gibbs' free energy of vaporization ΔG_v (Burkhard et al. 1985a);
8. TSA and ΔG_v (Amidon and Anik 1981, Burkhard et al. 1985a, Hawker 1989);
9. Molecular connectivity indices (Kier and Hall 1976, 1986, Burkhard et al. 1985a);
10. Melting point T_M and GC retention index (Bidleman 1984, Burkhard et al. 1985a);
11. Solvatochromic parameters and intrinsic molar volume (Banerjee et al. 1990).

As described earlier, Henry's law constants can be calculated from the ratio of vapor pressure and aqueous solubility. Henry's law constants do not show a simple linear pattern as solubility, K_{OW} or vapor pressure when plotted against simple molecular descriptors, such as numbers of chlorine or Le Bas molar volume, e.g., PCBs (Burkhard et al. 1985b), pesticides (Suntio et al. 1988), and chlorinated dioxins (Shiu et al. 1988). Henry's law constants can be estimated from:

1. UNIFAC-derived infinite dilution activity coefficients (Arbuckle 1983);
2. Group contribution and bond contribution methods (Hine and Mookerjee 1975, Meylan and Howard 1991);
3. Molecular connectivity indices (Nirmalakhandan and Speece 1988b, Sabljic and Güsten 1989, Dunnivant et al. 1992);
4. Total surface area - planar TSA (Hawker 1989);
5. Critical reviews by Mackay and Shiu 1981, Shiu and Mackay 1986 and Suntio et al. 1988.

For water-miscible compounds the use of aqueous solubility data is obviously impossible.

Bioconcentration Factors:

1. Correlation with K_{OW} (Neely et al. 1974, Könemann and van Leeuwen 1980, Veith et al. 1980, Chiou et al. 1977, Mackay 1982, Briggs 1981, Garten and Trabalka 1983, Davies and Dobbs 1984, Zaroogian et al. 1985, Oliver and Niimi 1988, Isnard and Lambert 1988);
2. Correlation with solubility (Kenaga 1980, Kenaga and Goring 1980, Briggs 1981, Garten and Trabalka 1983, Davies and Dobbs 1984, Isnard and Lambert 1988);
3. Correlation with K_{OC} (Kenaga 1980, Kenaga and Goring 1980, Briggs 1981);
4. Calculation with HPLC retention data (Swann et al. 1983);
5. Calculation with solvatochromic parameters (Hawker 1989, 1990b).

Sorption Coefficients:

1. Correlation with K_{OW} (Karickhoff et al. 1979, Schwarzenbach and Westall 1981, Mackay 1982, Oliver 1984);
2. Correlation with solubility (Karickhoff et al. 1979);
3. Molecular connectivity indices (Gerstl and Helling 1984; Sabljic 1984, 1987, Bahnick and Doucette 1988, Sabljic et al. 1989, Meylan et al. 1992);
4. Estimation from molecular connectivity index/fragment contribution method (Meylan et al. 1992, Lohninger 1994);
5. From HPLC retention data (Swann et al. 1983, Szabo et al. 1990).
6. Molecular orbital method (Reddy and Locke 1994).

Octanol-Air Partition coefficient.

The molecular descriptors used for K_{OW} , solubility in water and vapor pressure can potentially be applied to K_{OA} .

1.5 MASS BALANCE MODELS OF CHEMICAL FATE

1.5.1 EVALUATIVE ENVIRONMENTAL CALCULATIONS

When conducting assessments of how a chemical is likely to behave in the environment and especially how different chemicals behave in the same environment, there is incentive to standardize the evaluations using "evaluative" environmental models. The nature of these calculations has been described in a series of papers, notably Mackay (1979),

Paterson and Mackay (1985), Mackay and Paterson (1990, 1991), and a recent text (Mackay 2001). Only the salient features are presented here. Three evaluations are completed for each chemical, namely the Level I, II and III fugacity calculations. These calculations can also be done in concentration format instead of fugacity, but for this type of evaluation the fugacity approach is simpler and more instructive. The mass balance models of the types described below can be downloaded for the web site www.trentu.ca/cemc

1.5.2 LEVEL I FUGACITY CALCULATIONS

The Level I calculation describes how a given amount of chemical partitions at equilibrium between six media: air, water, soil, bottom sediment, suspended sediment and fish. No account is taken of reactivity. Whereas most early evaluative environments have treated a one square kilometre region with about 70% water surface (simulating the global proportion of ocean surface), it has become apparent that a more useful approach is to treat a larger, principally terrestrial area similar to a jurisdictional region such as a US state. The area selected is 100,000 km² or 10¹¹ m², which is about the area of Ohio, Greece or England. This environment was used in previous editions of this Handbook and is identical to the EQC or Equilibrium Criterion model described by Mackay et al. (1996).

The atmospheric height is selected as an arbitrary 1000 m reflecting that region of the troposphere which is most affected by local air emissions. A water surface area of 10% or 10,000 km² is used, with a water depth of 20 m. The water volume is thus 2×10^{11} m³. The soil is viewed as being well mixed to a depth of 10 cm and is considered to be 2% organic carbon. It has a volume of 9×10^9 m³. The bottom sediment has the same area as the water, a depth of 1 cm and an organic carbon content of 4%. It thus has a volume of 10⁸ m³.

For the Level I calculation both the soil and sediment are treated as simple solid phases with the above volumes, i.e., the presence of air or water in the pores of these phases is ignored.

Two other phases are included for interest. Suspended matter in water is often an important medium when compared in sorbing capacity to that of water. It is treated as having 20% organic carbon and being present at a volume fraction in the water of 5×10^{-6} , i.e., it is about 5 to 10 mg/L. The volume is thus 10⁶ m³. Fish is also included at an entirely arbitrary volume fraction of 10^{-6} and are assumed to contain 5% lipid, equivalent in sorbing capacity to octanol. The volume is thus 2×10^5 m³. These two phases are small in volume and rarely contain an appreciable fraction of the chemical present, but it is in these phases that the highest concentration of chemical often exists.

Another phase which is introduced later in the Level III model is aerosol particles with a volume fraction in air of 2×10^{-11} , i.e., approximately 30 µg/m³. Although negligible in volume, an appreciable fraction of the chemical present in the air phase may be associated with aerosols. Aerosols are not treated in Level I or II calculations because their capacity for the chemical at equilibrium is usually negligible when compared with soil.

These dimensions and properties are summarized in Tables 1.5.1 and 1.5.2. The user is encouraged to modify these dimensions to reflect conditions in a specific area of interest.

The amount of chemical introduced in the Level I calculation is an arbitrary 100,000 kg or 100 tonnes. If dispersed entirely in the air, this amount yields a concentration of 1 µg/m³ which is not unusual for ubiquitous contaminants such as hydrocarbons. If dispersed entirely in the water, the concentration is a higher 500 µg/m³ or 500 ng/L, which again is reasonable for a well-used chemical of commerce. The corresponding value in soil is about 0.0046 µg/g. Clearly for restricted chemicals such as PCBs, this amount is too large, but it is preferable to adopt a common evaluative amount

TABLE 1.5.1
Compartment dimensions and properties for Levels I and II calculations

Compartment	Air	Water	Soil	Sediment	Suspended sediment	Fish
Volume, V (m ³)	10 ¹⁴	2×10^{11}	9×10^9	10 ⁸	10 ⁶	2×10^5
Depth, h (m)	1000	20	0.1	0.01	—	—
Area, A (m ²)	100×10^9	10×10^9	90×10^9	10×10^9	—	—
Fraction OC	—	—	0.02	0.04	0.2	—
Density, ρ (kg/m ³)	1.2	1000	2400	2400	1500	1000
Adv. Residence	100	1000	—	50,000	—	—
Time, t (hours)						
Adv. flow, G (m ³ /h)	10 ¹²	2×10^8	—	2000	—	—

TABLE 1.5.2**Bulk compartment dimensions and volume fractions (v) for Level III calculations**

Compartment		Volume
Air	Total volume	10^{14} m^3 (as above)
	Air phase	10^{14} m^3
	Aerosol phase	2000 m^3 ($v = 2 \times 10^{-11}$)
Water	Total volume	$2 \times 10^{11} \text{ m}^3$
	Water phase	$2 \times 10^{11} \text{ m}^3$ (as above)
	Suspended sediment phase	10^6 m^3 ($v = 5 \times 10^{-6}$)
	Fish phase	$2 \times 10^5 \text{ m}^3$ ($v = 1 \times 10^{-6}$)
Soil	Total volume	$18 \times 10^9 \text{ m}^3$
	Air phase	$3.6 \times 10^9 \text{ m}^3$ ($v = 0.2$)
	Water phase	$5.4 \times 10^9 \text{ m}^3$ ($v = 0.3$)
	Solid phase	$9.0 \times 10^9 \text{ m}^3$ ($v = 0.5$) (as above)
Sediment	Total volume	$500 \times 10^6 \text{ m}^3$
	Water phase	$400 \times 10^6 \text{ m}^3$ ($v = 0.8$)
	Solid phase	$100 \times 10^6 \text{ m}^3$ ($v = 0.2$) (as above)

TABLE 1.5.3**Equations for phase Z values used in Levels I, II and bulk phase values used in Level III**

Compartment	Z values
Air	$Z_1 = 1/RT$
Water	$Z_2 = 1/H = C^S/P^S$
Soil	$Z_3 = Z_2 \cdot \rho_3 \cdot \phi_3 \cdot K_{OC}/1000$
Sediment	$Z_4 = Z_2 \cdot \rho_4 \cdot \phi_4 \cdot K_{OC}/1000$
Suspended Sediment	$Z_5 = Z_2 \cdot \rho_5 \cdot \phi_5 \cdot K_{OC}/1000$
Fish	$Z_6 = Z_2 \cdot \rho_6 \cdot L \cdot K_{OW}/1000$
Aerosol	$Z_7 = Z_1 \cdot 6 \times 10^6 / P_L^S$ or $0.1 Z_1 K_{OA}$
where	
R = gas constant (8.314 J/mol·K)	
T = absolute temperature (K)	
C^S = solubility in water (mol/m ³)	
P^S = vapor pressure (Pa)	
H = Henry's law constant (Pa·m ³ /mol)	
P_L^S = liquid vapor pressure (Pa)	
K_{OA} = octanol-air partition coefficient	
K_{OW} = octanol-water partition coefficient	
ρ_i = density of phase i (kg/m ³)	
ϕ_i = mass fraction organic-carbon in phase i (g/g)	
L = lipid content of fish	

Note for solids $P_L^S = P^S / \exp\{6.79(1 - T_M/T)\}$, where T_M is melting point (K) of the solute and T is 298 K. An experimental entropy of fusion should be used if available.

for all substances. No significance should, of course, be attached to the absolute values of the concentrations which are deduced from this arbitrary amount. Only the relative values have significance.

The Level I calculation proceeds by deducing the fugacity capacities or Z values for each medium (see Table 1.5.3), following the procedures described by Mackay (2001). These working equations show the necessity of having data on molecular mass, water solubility, vapor pressure, and octanol-water partition coefficient. The fugacity f (Pa) common to all media is deduced as

$$f = M / \sum V_i Z_i$$

where M is the total amount of chemical (mol), V_i is the medium volume (m^3) and Z_i is the corresponding fugacity capacity for the chemical in each medium. It is noteworthy that Z values contain all the necessary partition information. The partition coefficient K_{12} is simply the ratio of Z values, i.e., Z_1/Z_2 . Definition of the Z values starts in the air compartment then proceeds to other compartments using the appropriate partition coefficients.

The molar concentration C (mol/m^3) can then be deduced as Zf mol/m^3 or as WZf g/m^3 or $1000 WZf/\rho$ $\mu\text{g}/\text{g}$, where ρ is the phase density (kg/m^3) and W is the molecular mass (g/mol). The amount m_i in each medium is $C_i V_i$ mol, and the total in all media is M mol. The information obtained from this calculation includes the concentrations, amounts and distribution.

Note that this simple treatment assumes that the soil and sediment phases are entirely solid, i.e., there are no air or water phases present to “dilute” the solids. Later in the Level III calculation these phases and aerosols are included (see Table 1.5.4).

Correction for Dissociation

As discussed earlier in Section 1.2.4, for dissociating or ionizing organic chemicals in aqueous solution, it is necessary to consider the effect of pH and thus the degree of dissociation, and to calculate the concentrations of both ionic and non-ionic species. The EQC model does not address dissociation.

The Z values are calculated using the conventional equations at the pH of the experimental data (i.e., the system pH). The total Z value in water is then separated into its ionic and non-ionic contributions, i.e., fractions of $I/(I+1)$ and $1/(I+1)$. The Z value for the non-ionic form in water is assumed to apply at all pHs i.e., including the environmental pH, but an additional and possibly different ionic Z value in water is deduced at the environmental pH using I calculated at that pH. The total Z values in water are then calculated. Z values in other media are unaffected.

The calculation is illustrated in Table 1.5.5 for pentachlorophenol. The experimental aqueous solubility is $14.0 \text{ g}/\text{m}^3$ at a pH of 5.1. The environmental pH is 7. Higher environmental pH increases the extent of dissociation, thus increasing the Z value in water, increasing the apparent solubility, decreasing the apparent K_{OW} and Henry's law constant and the air-water partition coefficient, and decreasing the soil-water partition coefficient.

Note: At pH of 5.1, K_{OW} is 112200 and is the ratio of concentration in octanol to total concentration in water comprising fractions $1/(1+I)$ or $1/(1+2.29)$ or 0.304 of neutral and 0.696 of ionic species. K_{OW} is thus $112200/0.304$ or 369000 for the neutral species and zero for the ionic species. For the neutral species K_{OC} is assumed to be $0.41 \cdot K_{\text{OW}}$ or 151300, thus K_p is $151300 \times 0.02 \text{ L}/\text{kg}$, i.e., 3027 for a soil of 2% organic carbon. K_{SW} is thus 3027×2.4 where 2.4 is the solid density (kg/L) or 7265. Z_s for the neutral species is thus $7265 \times Z_w$ or 27970. At pH of 7, the neutral species Z values are unaffected, but the Z value for water increases to 704 because of the greater extent of dissociation. K_{SW} thus decreases to $27970/704$ or 39.72.

TABLE 1.5.4

Bulk phase Z values, Z_{Bi} deduced as $\sum v_i Z_i$, in which the coefficients, e.g., 2×10^{-11} , are the volume fractions v_i of each pure phase as specified in Table 1.5.2

Compartment	Bulk Z values		
Air	$Z_{\text{B1}} = Z_1 + 2 \times 10^{-11} Z_7$	(approximately $30 \mu\text{g}/\text{m}^3$ aerosols)	
Water	$Z_{\text{B2}} = Z_2 + 5 \times 10^{-6} Z_5 + 1 \times 10^{-6} Z_6$	(5 ppm solids, 1 ppm fish by volume)	
Soil	$Z_{\text{B3}} = 0.2 Z_1 + 0.3 Z_2 + 0.5 Z_3$	(20% air, 30% water, 50% solids)	
Sediment	$Z_{\text{B4}} = 0.8 Z_2 + 0.2 Z_4$	(80% water, 20% solids)	

TABLE 1.5.5

Calculated Z values at different experimental and environmental pHs of pentachlorophenol. Z values at 25°C , $\log K_{\text{OW}}$ is 5.05, $\text{p}K_a$ 4.74, at data pH of 5.1 and environmental pH of 7.0 for air, water and soil of fraction organic carbon 0.02 and density of soil 2.4 kg/L

	At data pH of 5.1 ($I = 2.29$)			At environ. pH of 7 ($I = 182$)		
	Neutral	Ionic	Total	Neutral	Ionic	Total
Air	4.03×10^{-4}	0	4.03×10^{-4}	4.03×10^{-4}	0	4.03×10^{-4}
Water	3.85	8.82	12.67	3.85	700.4	704.2
Soil solids	27970	0	27970	27970	0	27970

TABLE 1.5.6

Calculated Z_w values and some partition coefficients at different environmental pHs for pentachlorophenol (PCP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and *p*-cresol at 25°C. K_{AW} is the air-water partition coefficient and K_{SW} is the soil-water partition coefficient

At pH	Z values in water				Partitioning properties			
	Neutral	Ionic	Total Z_w	Fraction x_N	S_T g/m ³	H_T Pa·m ³ /mol	K_{AW}	K_{SW}
<i>PCP</i>								
4	3.849	0.7004	4.549	0.846	16.55	0.224	8.9×10^{-5}	6147
6	3.849	70.04	73.89	0.052	268.8	0.0135	5.46×10^{-6}	378.5
7	3.849	700.4	704.2	0.0055	2562	0.00142	5.73×10^{-7}	39.7
<i>2,4,6-TCP</i>								
4	1.7677	0.0140	1.7817	0.992	434	0.5612	2.26×10^{-4}	105.2
6	1.7677	1.4041	3.1718	0.557	772	0.315	1.272×10^{-4}	59.09
7	1.7677	14.041	15.8088	0.118	3644	0.172	6.945×10^{-5}	11.86
<i>2,4-DCP</i>								
4	3.063	0.000386	3.063	1.0	6000	0.326	0.000132	31.24
6	3.063	0.0386	3.101	0.988	6073	0.322	0.000130	30.85
7	3.063	0.386	3.448	0.888	6760	0.290	0.000117	27.75
<i>p</i> -Cresol								
4	11.97	0	11.948	1.0	22000	0.0836	3.37×10^{-5}	1.968
7	11.97	0.0066	11.975	1.0	22000	0.0836	3.35×10^{-5}	1.968

This is further demonstrated in Table 1.5.6 which shows the effects of environmental pH on the partitioning behavior of 2,4-dichlorophenol ($pK_a = 7.90$, solubility of 6000 g/m³ at pH of 5.1 and $\log K_{OW} = 3.20$), 2,4,6-trichlorophenol ($pK_a = 6.10$, solubility of 430 g/m³ at pH of 5.1 and $\log K_{OW} = 3.69$), pentachlorophenol ($pK_a = 4.74$, solubility of 14.0 g/m³ at pH of 5.1 and $\log K_{OW} = 5.05$) and *p*-cresol ($pK_a = 10.26$, a solubility of 22000 g/m³ and $\log K_{OW} = 2.0$) in the multimedia environment at 25°C. For environmental pH from 4 to 7, there is no significant effect for *p*-cresol (or for chemicals for which $pK_a \gg pH$), very little effect for 2,4-dichlorophenol (and chemicals with pK_a ranging between 7–10). There is some effect on 2,4,6-trichlorophenol (and chemicals with pK_a of 6–7) and a large effect for pentachlorophenol.

A similar treatment can be applied to other dissociating compounds such as the carboxylic acids, nitrophenols. For bases such as amines the pK_a is defined as (14 - pK_b), and the extent of dissociation is estimated as above.

1.5.3 LEVEL II FUGACITY CALCULATIONS

The Level II calculation simulates a situation in which a chemical is continuously discharged into the multimedia environment and achieves a steady-state and equilibrium condition, at which input and output rates are equal. The task is to deduce the rates of loss by reaction and advection and the prevailing concentrations and masses.

The reaction rate data developed for each chemical in the tables are used to select a reactivity class as described earlier, and hence a first-order rate constant for each medium. Often these rates are in considerable doubt; thus the quantities selected should be used with extreme caution because they may not be widely applicable. The rate constants k_i h⁻¹ are used to calculate reaction D values for each medium D_{Ri} as $V_i Z_i k_i$. The rate of reactive loss is then $D_{Ri} f$ mol/h.

For advection, it is necessary to select flow rates. This is conveniently done in the form of advective residence times, t in hour (h); thus the advection rate G_i is V_i/t m³/h for each medium. For air, a residence time of 100 hours is used (approximately 4 days), which is probably too long for the geographic area considered, but shorter residence times tend to cause air advective loss to be a dominant mechanism. For water, a figure of 1000 hours (42 days) is used, reflecting a mixture of rivers and lakes. For sediment burial (which is treated as an advective loss), a time of 50,000 hours or 5.7 years is used. Only for very persistent, hydrophobic chemicals is this process important. No advective loss from soil is included. The D value for loss by advection D_{Ai} is $G_i Z_i$, and the rates are $D_{Ai} f$ mol/h.

There may thus be losses caused by both reaction and advection D values for the four primary media. These loss processes are not included for fish or suspended matter. At steady-state and equilibrium conditions, the input rate E mol/h can be equated to the sum of the output rates, from which the common fugacity can be calculated as follows

$$E = f \cdot \Sigma D_{Ai} + f \cdot \Sigma D_{Ri}$$

thus,

$$f = E / (\Sigma D_{Ai} + \Sigma D_{Ri})$$

The common assumed emission rate is 1000 kg/h or 1 tonne/h. To achieve an amount equivalent to the 100 tonnes in the Level I calculation requires an overall residence time of 100 hours. Again, the concentrations and amounts m_i and Σm_i or M can be deduced, as well as the reaction and advection rates. These rates obviously total to give the input rate E . Of particular interest are the relative rates of these loss processes, and the overall persistence or residence time, which is calculated as

$$t_o = M/E$$

where M is the total amount present. It is also useful to calculate a reaction and an advection persistence t_R and t_A as

$$t_R = M / \Sigma D_{Ri} f \quad t_A = M / \Sigma D_{Ai} f$$

Obviously,

$$1/t_o = 1/t_R + 1/t_A$$

These persistences indicate the likelihood of the chemical being lost by reaction as distinct from advection. The percentage distribution of chemical between phases is identical to that in Level I. A pie chart depicting the distribution of losses can be drawn.

1.5.4 LEVEL III FUGACITY CALCULATIONS

Whereas the Levels I and II calculations assume equilibrium to prevail between all media, this is recognized as being excessively simplistic and even misleading. In the interests of algebraic simplicity, only the four primary media are treated for this level. The task is to develop expressions for intermedia transport rates by the various diffusive and non-diffusive processes as described by Mackay (2001). This is done by selecting values for 12 intermedia transport velocity parameters which have dimensions of velocity (m/h or m/year), are designated as U_i m/h and are applied to all chemicals. These parameters are used to calculate seven intermedia transport D values.

It is desirable to calculate new “bulk phase” Z values for the four primary media which include the contribution of dispersed phases within each medium as described by Mackay and Paterson (1991) and as listed earlier. The air is now treated as an air-aerosol mixture, water as water plus suspended particles and fish, soil as solids, air and water, and sediment as solids and porewater. The Z values thus differ from the Level I and Level II “pure phase” values. The necessity of introducing this complication arises from the fact that much of the intermedia transport of the chemicals occurs in association with the movement of chemical in these dispersed phases. To accommodate this change the same volumes of the soil solids and sediment solids are retained, but the total phase volumes are increased. These Level III volumes are also given in Table 1.5.2. The reaction and advection D values employ the generally smaller bulk phase Z values but the same residence times; thus the G values are increased and the D values are generally larger.

Intermedia D Values

The justification for each intermedia D value follows. It is noteworthy that, for example, air-to-water and water-to-air values differ because of the presence of one-way non-diffusive processes. A fuller description of the background to these calculations is given by Mackay (2001).

1. Air to Water (D_{12})

Four processes are considered: diffusion (absorption), dissolution in rain of gaseous chemical, and wet and dry deposition of particle-associated chemical.

For diffusion, the conventional two-film approach is taken with water-side (k_w) and air-side (k_A) mass transfer coefficients (m/h) being defined. Values of 0.05 m/h for k_w and 5 m/h for k_A are used. The absorption D value is then

$$D_{vw} = 1/[1/(k_A A_w Z_1) + 1/(k_w A_w Z_2)]$$

where A_w is the air-water area (m^2) and Z_1 and Z_2 are the pure air and water Z values. The velocities k_A and k_w are designated as U_1 and U_2 .

For rain dissolution, a rainfall rate of 0.876 m/year is used, i.e., U_R or U_3 is 10^{-4} m/h. The D value for rain dissolution D_{RW} is then

$$D_{RW} = U_R A_w Z_2 = U_3 A_w Z_2$$

For wet deposition, it is assumed that the rain scavenges Q (the scavenging ratio) or about 200,000 times its volume of air. Using a particle concentration (volume fraction) v_Q of 2×10^{-11} , this corresponds to the removal of Qv_Q or 4×10^{-6} volumes of aerosol per volume of rain. The total rate of particle removal by wet deposition is then $Qv_Q U_R A_w$ m^3/h , thus the wet "transport velocity" $Qv_Q U_R$ is 4×10^{-10} m/h.

For dry deposition, a typical deposition velocity U_Q of 10 m/h is selected yielding a rate of particle removal of $U_Q v_Q A_w$ or $2 \times 10^{-10} A_w$ m^3/h corresponding to a transport velocity of 2×10^{-10} m/h. Thus,

$$U_4 = Qv_Q U_R + U_Q v_Q = v_Q (QU_R + U_Q)$$

The total particle transport velocity U_4 for wet and dry deposition is thus 6×10^{-10} m/h (67% wet and 33% dry) and the total D value D_{QW} is

$$D_{QW} = U_4 A_w Z_7$$

where Z_7 is the aerosol Z value.

The overall D value is given by

$$D_{12} = D_{vw} + D_{RW} + D_{QW}$$

2. Water to Air (D_{21})

Evaporation is treated as the reverse of absorption; thus D_{21} is simply D_{vw} as before.

3. Air to Soil (D_{13})

A similar approach is adopted as for air-to-water transfer. Four processes are considered with rain dissolution (D_{RS}) and wet and dry deposition (D_{QS}) being treated identically except that the area term is now the air-soil area A_s .

For diffusion, the approach of Jury et al. (1983, 1984a,b,c) is used as described by Mackay and Stiver (1991) and Mackay (1991) in which three diffusive processes are treated. The air boundary layer is characterized by a mass transfer coefficient k_s or U_7 of 5 m/h, equal to that of the air-water mass transfer coefficient k_A used in D_{12} .

For diffusion in the soil air-pores, a molecular diffusivity of 0.02 m^2/h is reduced to an effective diffusivity using a Millington-Quirk type of relationship by a factor of about 20 to 10^{-3} m^2/h . Combining this with a path length of 0.05 m gives an effective air-to-soil mass transfer coefficient k_{SA} of 0.02 m/h, which is designated as U_5 .

Similarly, for diffusion in water a molecular diffusivity of 2×10^{-6} m^2/h is reduced by a factor of 20 to an effective diffusivity of 10^{-7} m^2/h , which is combined with a path length of 0.05 m to give an effective soil-to-water mass transfer coefficient of k_{SW} 2×10^{-6} m/h.

It is probable that capillary flow of water contributes to transport in the soil. For example, a rate of 7 cm/year would yield an equivalent water velocity of 8×10^{-6} m/h, which exceeds the water diffusion rate by a factor of four. For illustrative purposes we thus select a water transport velocity or coefficient U_6 in the soil of 10×10^{-6} m/h, recognizing that this will vary with rainfall characteristics and soil type. These soil processes are in parallel with boundary layer diffusion in series, so the final equations are

$$D_{VS} = 1/[1/D_s + 1/(D_{SW} + D_{SA})]$$

where

$$D_S = U_7 A_S Z_1 \quad (U_7 = 5 \text{ m/h})$$

$$D_{SW} = U_6 A_S Z_2 \quad (U_6 = 10 \times 10^{-6} \text{ m/h})$$

$$D_{SA} = U_5 A_S Z_1 \quad (U_5 = 0.02 \text{ m/h})$$

where A_S is the soil horizontal area.

Air-soil diffusion thus appears to be much slower than air-water diffusion because of the slow migration in the soil matrix. In practice, the result will be a nonuniform composition in the soil with the surface soil (which is much more accessible to the air than the deeper soil) being closer in fugacity to the atmosphere.

The overall D value is given as

$$D_{13} = D_{VS} + D_{QS} + D_{RS}$$

4. Soil to Air (D_{31})

Evaporation is treated as the reverse of absorption, thus the D value is simply D_{VS} .

5. Water to Sediment (D_{24})

Two processes are treated, diffusion and deposition.

Diffusion is characterized by a mass transfer coefficient U_8 of 10^{-4} m/h, which can be regarded as a molecular diffusivity of 2×10^{-6} m²/h divided by a path length of 0.02 m. In practice, bioturbation may contribute substantially to this exchange process, and in shallow water current-induced turbulence may also increase the rate of transport. Diffusion in association with organic colloids is not included. The D value is thus given as $U_8 A_W Z_2$.

Deposition is assumed to occur at a rate of 5000 m³/h, which corresponds to the addition of a depth of solids of 0.438 cm/year; thus 43.8% of the solids resident in the accessible bottom sediment is added each year. This rate is about 12 cm³/m²-day, which is high compared to values observed in large lakes. The velocity U_9 , corresponding to the addition of 5000 m³/h over the area of 10^{10} m², is thus 5×10^{-7} m/h.

It is assumed that of this 5000 m³/h deposited, 2000 m³/h or 40% is buried (yielding the advective flow rate in [Table 1.5.1](#)), 2000 m³/h or 40% is resuspended (as discussed later) and the remaining 20% is mineralized organic matter. The organic carbon balance is thus only approximate.

The transport velocities are thus:

deposition U_9	5.0×10^{-7} m/h or 0.438 cm/y
resuspension U_{10}	2.0×10^{-7} m/h or 0.175 cm/y
burial U_B	2.0×10^{-7} m/h or 0.175 cm/y
(included as an advective residence time of 50,000 h)	

The water-to-sediment D value is thus

$$D_{24} = U_8 A_W Z_2 + U_9 A_W Z_5$$

where Z_5 is the Z value of the particles in the water column.

6. Sediment to Water (D_{42})

This is treated similarly to D_{24} giving:

$$D_{42} = U_8 A_W Z_2 + U_{10} A_W Z_4$$

where U_{10} is the sediment resuspension velocity of 2.0×10^{-7} m/h and Z_4 is the Z value of the sediment solids.

7. Sediment Advection or Burial (D_{A4})

This D value is $U_B A_W Z_4$, where U_B , the sediment burial rate, is 2.0×10^{-7} m/h. It can be viewed as $G_B Z_{B4}$, where G_B is the total burial rate specified as V_S/t_B where t_B (residence time) is 50,000 h, and V_S (the sediment volume) is the product of sediment depth (0.01 cm) and area A_W . Z_4 , Z_{B4} are the Z values of the sediment solids and of the bulk sediment, respectively. Since there are 20% solids, Z_{B4} is about 0.2 Z_4 . There is a slight difference between these approaches because in the advection approach (which is used here) there is burial of water as well as solids.

8. Soil to Water Run-Off (D_{32})

It is assumed that there is run-off of water at a rate of 50% of the rain rate, i.e., the D value is

$$D = 0.5 U_3 A_S Z_2 = U_{11} A_S Z_2$$

thus the transport velocity term U_{11} is $0.5U_3$ or 5×10^{-5} m/h.

For solids run-off it is assumed that this run-off water contains 200 parts per million by volume of solids; thus the corresponding velocity term U_{12} is $200 \times 10^{-6}U_{11}$, i.e., 10^{-8} m/h. This corresponds to the loss of soil at a rate of about 0.1 mm per year. If these solids were completely deposited in the aquatic environment (which is about 1/10th the soil area), they would accumulate at about 0.1 cm per year, which is about a factor of four less than the deposition rate to sediments. The implication is that most of this deposition is of naturally generated organic carbon and from sources such as bank erosion.

Summary

The twelve intermedia transport parameters are listed in Table 1.5.7 and the equations are summarized in Table 1.5.8.

Algebraic Solution

Four mass balance equations can be written, one for each medium, resulting in a total of four unknown fugacities, enabling simple algebraic solution as shown in Table 1.5.9. From the four fugacities, the concentration, amounts and rates of all transport and transformation processes can be deduced, yielding a complete mass balance.

The new information from the Level III calculations are the intermedia transport data, i.e., the extent to which chemical discharged into one medium tends to migrate into another. This migration pattern depends strongly on the proportions of the chemical discharged into each medium; indeed, the relative amounts in each medium are largely a reflection of the locations of discharge. It is difficult to interpret these mass balance diagrams because, for example, chemical depositing from air to water may have been discharged to air, or to soil from which it evaporated, or even to water from which it is cycling to and from air.

To simplify this interpretation, it is best to conduct three separate Level III calculations in which unit amounts (1000 kg/h) are introduced individually into air, soil and water. Direct discharges to sediment are unlikely and are not

TABLE 1.5.7
Intermedia transport parameters

U		m/h	m/year
1	Air side, air-water MTC*, k_A	5	43,800
2	Water side, air-water MTC, k_W	0.05	438
3	Rain rate, U_R	10^{-4}	0.876
4	Aerosol deposition	6×10^{-10}	5.256×10^{-6}
5	Soil-air phase diffusion MTC, k_{SA}	0.02	175.2
6	Soil-water phase diffusion MTC, k_{SW}	10×10^{-6}	0.0876
7	Soil-air boundary layer MTC, k_S	5	43,800
8	Sediment-water MTC	10^{-4}	0.876
9	Sediment deposition	5.0×10^{-7}	0.00438
10	Sediment resuspension	2.0×10^{-7}	0.00175
11	Soil-water run-off	5.0×10^{-5}	0.438
12	Soil-solids run-off	10^{-8}	8.76×10^{-5}

*MTC is mass transfer coefficient. Scavenging ratio Q is 2×10^5 , dry deposition velocity U_Q is 10 m/h and sediment burial rate U_B is 2.0×10^{-7} m/h

TABLE 1.5.8
Intermedia transport D value equations

Air-Water	$D_{12} = D_{vw} + D_{rw} + D_{qw}$ $D_{vw} = A_w / (1/U_1 Z_1 + 1/U_2 Z_2)$ $D_{rw} = U_3 A_w Z_2$ $D_{qw} = U_4 A_w Z_7$
Water-Air	$D_{21} = D_{vw}$
Air-Soil	$D_{13} = D_{vs} + D_{rs} + D_{qs}$ $D_{vs} = 1 / (1/D_s + 1/(D_{sw} + D_{sa}))$ $D_s = U_7 A_s Z_1$ $D_{sa} = U_5 A_s Z_1$ $D_{sw} = U_6 A_s Z_2$ $D_{rs} = U_3 A_s Z_2$ $D_{qs} = U_4 A_s Z_7$
Soil-Air	$D_{31} = D_{vs}$
Water-Sediment	$D_{24} = U_8 A_w Z_2 + U_9 A_w Z_5$
Sediment-Water	$D_{42} = U_8 A_w Z_2 + U_{10} A_w Z_4$
Soil-Water	$D_{32} = U_{11} A_s Z_2 + U_{12} A_s Z_3$

TABLE 1.5.9
Level III solutions to mass balance equations

Compartment	Mass balance equations
Air	$E_1 + f_2 D_{21} + f_3 D_{31} = f_1 D_{T1}$
Water	$E_2 + f_1 D_{12} + f_3 D_{32} + f_4 D_{42} = f_2 D_{T2}$
Soil	$E_3 + f_1 D_{13} = f_3 D_{T3}$
Sediment	$E_4 + f_2 D_{24} = f_4 D_{T4}$
where	E_i is discharge rate, E_4 usually being zero. $D_{T1} = D_{R1} + D_{A1} + D_{12} + D_{13}$ $D_{T2} = D_{R2} + D_{A2} + D_{21} + D_{23} + D_{24}, (D_{23} = 0)$ $D_{T3} = D_{R3} + D_{A3} + D_{31} + D_{32}, (D_{A3} = 0)$ $D_{T4} = D_{R4} + D_{A4} + D_{42}$
Solutions:	$f_2 = [E_2 + J_1 J_4 / J_3 + E_3 D_{32} / D_{T3} + E_4 D_{42} / D_{T4}] / (D_{T2} - J_2 J_4 / J_3 - D_{24} \cdot D_{42} / D_{T4})$ $f_1 = (J_1 + f_2 J_2) / J_3$ $f_3 = (E_3 + f_1 D_{13}) / D_{T3}$ $f_4 = (E_4 + f_2 D_{24}) / D_{T4}$
where	$J_1 = E_1 / D_{T1} + E_3 D_{31} / (D_{T3} \cdot D_{T1})$ $J_2 = D_{21} / D_{T1}$ $J_3 = 1 - D_{31} \cdot D_{13} / (D_{T1} \cdot D_{T3})$ $J_4 = D_{12} + D_{32} \cdot D_{13} / D_{T3}$

considered here. These calculations show clearly the extent to which intermedia transport occurs. If, for example, the intermedia D values are small compared to the reaction and advection values, the discharged chemical will tend to remain in the discharge or “source” medium with only a small proportion migrating to other media. Conversely, if the intermedia D values are relatively large, the chemical becomes very susceptible to intermedia transport. This behavior is observed for persistent substances such as PCBs, which have very low rates of reaction.

A direct assessment of multimedia behavior is thus possible by examining the proportions of chemical found at steady state in the “source” medium and in other media. For example, when discharged to water, an appreciable fraction of the benzene is found in air, whereas for atrazine, only a negligible fraction of atrazine reaches air.

Linear Additivity or Superposition of Results

Because these equations are entirely linear, the solutions can be scaled linearly. The concentrations resulting from a discharge of 2000 kg/h are simply twice those of 1000 kg/h. Further, if discharge of 1000 kg/h to air causes 500 kg in water and discharge of 1000 kg/h to soil causes 100 kg in water, then if both discharges occur simultaneously, there will be 600 kg in water. If the discharge to soil is increased to 3000 kg/h, the total amount in the water will rise to (500 + 300) or 800 kg. It is thus possible to deduce the amount in any medium arising from any combination of discharge rates by scaling and adding the responses from the unit inputs. This “linear additivity principle” is more fully discussed by Stiver and Mackay (1989).

The persistence or residence time of the chemical is independent of the emission rate, but it does depend on the “mode of entry, i.e., into which compartment the chemical is emitted.”

In the diagrams presented later, these three-unit (1000 kg/h) responses are given. Also, an illustrative “three discharge” mass balance is given in which a total of 1000 kg/h is discharged, but in proportions judged to be typical of chemical use and discharge to the environment. For example, benzene is believed to be mostly discharged to air with minor amounts to soil and water.

Also given in the tables are the rates of reaction, advection and intermedia transport for each case.

The reader can deduce the fate of any desired discharge pattern by appropriate scaling and addition. It is important to emphasize that because the values of transport velocity parameters are only illustrative, actual environmental conditions may be quite different; thus, simulation of conditions in a specific region requires determination of appropriate parameter values as well as the site-specific dimensions, reaction rate constants and the physical-chemical properties which prevail at the desired temperature.

In total, the aim is to convey an impression of the likely environmental behavior of the chemical in a readily assimilable form.

1.6 DATA SOURCES AND PRESENTATION

1.6.1 DATA SOURCES

Most physical properties such as molecular weight (MW, g/mol), melting point (m.p., °C), boiling point (b.p., °C), and density have been obtained from commonly used handbooks such as the *CRC Handbook of Chemistry and Physics* (Weast 1972, 1982; Lide 2003), Lange's *Handbook of Chemistry* (Dean 1979, 1985, 1992), Dreisbach's *Physical Properties of Chemical Compounds*, Vol. I, II and III (1955, 1959, 1961), Organic Solvents, Physical Properties and Methods of Purification (Riddick et al. 1986), *The Merck Index* (Windholz 1983, Budavari 1989) and several handbooks and compilations of chemical property data for pesticides. Notable are the text by Hartley and Graham-Bryce (1980), the *Agrochemicals Handbook* (Hartley and Kidd 1987), the *Pesticide Manual* (Worthing and co-workers 1983, 1987, 1991, Tomlin 1994), the *CRC Handbook of Pesticides* (Milne 1995), the *Agrochemicals Desk Reference* (Montgomery 1993) and the SCS/ARS/CES Pesticide Properties Database by Wauchope and co-workers (Wauchope et al. 1992, Augustijn-Beckers et al. 1994, Hornsby et al. 1996). Other physical-chemical properties such as aqueous solubility, vapor pressure, octanol-water partition coefficient, Henry's law constant, bioconcentration factor and sorption coefficient have been obtained from scientific journals or other environmental handbooks, notably Verschueren's *Handbook of Environmental Data on Organic Chemicals* (1977, 1983) and Howard and co-workers' *Handbook of Environmental Fate and Exposure Data*, Vol. I, II, III and IV (1989, 1990, 1991 and 1993). Other important sources of vapor pressure are the *CRC Handbook of Chemistry and Physics* (Weast 1972, 1982), Lange's *Handbook of Chemistry* (Dean 1992), the *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds* (Zwolinski and Wilhoit 1971), the *Vapor Pressure of Pure Substances* (Boublik et al. 1973, 1984), the *Handbook of the Thermodynamics of Organic Compounds* (Stephenson and Malanowski 1987). For aqueous solubilities, valuable sources include the *IUPAC Solubility Data Series* (Barton 1984, Horvath and Getzen 1985, Shaw 1989a,b) and Horvath's *Halogenated Hydrocarbons, Solubility-Miscibility with Water* (Horvath 1982). Octanol-water partition coefficients are conveniently obtained from the compilation by Leo et al. (1971), Hansch and Leo (1979), Hansch et al. (1995), and Sangster (1989, 1993), or can be calculated from molecular structure by the methods of Hansch and Leo (1979) or Rekker (1977). Lyman et al. (1982) and Boethling and Mackay (2000) also outline methods of estimating solubility, K_{ow} , vapor pressure, and the bioconcentration factor for organic chemicals. The recent *Handbook of Environmental Degradation Rates* by Howard et al. (1991) is a valuable source of rate constants and half-lives.

The most reliable sources of data are the original citations of valuable experimental data in the reviewed scientific literature. Particularly reliable are those papers which contain a critical review of data from a number of sources as well as independent experimental determinations. Calculated or correlated values are viewed as being less reliable. The aim

in this work has been to gather sufficient experimental data with a list of citations to interpret them and select a “best” or “most likely” value.

1.6.2 DATA PRESENTATION

Chemical Properties.

The emphasis in this handbook is on experimentally determined values rather than estimated values. The latter are included when there is a lack of experimental data. Included in the experimental data are indirect measurements using GC or HPLC retention times.

The names, formula, melting and boiling point and density data are self-explanatory.

The molar volumes are in some cases at the stated temperature and in other cases at the normal boiling point. Certain calculated molecular volumes are also used; thus the reader is cautioned to ensure that when using a molar volume in any correlation, it is correctly selected. In the case of polynuclear aromatic hydrocarbons, the Le Bas molar volume is regarded as suspect because of the compact nature of the multi-ring compounds. It should thus be regarded as merely an indication of relative volume, not an absolute volume.

Heats of fusion, ΔH_{fus} , are generally expressed in kcal/mol or kJ/mol and entropies of fusion, ΔS_{fus} in cal/mol·K (e.u. or entropy unit) or J/mol·K. The fugacity ratio F , as discussed in Section 1.2.8, is used to calculate the supercooled liquid vapor pressure or solubility for correlation purposes. In the case of liquids such as benzene, it is 1.0. For solids it is a fraction representing the ratio of solid-to-liquid solubility or vapor pressure.

A wide variety of solubilities (in units of g/m³ or the equivalent mg/L) have been reported. Experimental data have the method of determination indicated. In other compilations of data the reported value has merely been quoted from another secondary source. In some cases the value has been calculated. The abbreviations are generally self-explanatory and usually include two entries, the method of equilibration followed by the method of determination. From these values a single value is selected for inclusion in the summary data table. Vapor pressures and octanol-water partition coefficients are selected similarly.

The reader is advised to consult the original reference when using these values of bioconcentration factors (BCF), bioaccumulation factors (BAF), K_{OC} and K_{OM} , to ensure that conditions are as close as possible to those of specific interest.

The “Environmental Fate Rate Constants” refer to specific degradation processes rather than media. As far as possible the original numerical quantities are given and thus there is a variety of time units with some expressions being rate constants and others half-lives. The conversion is that the rate constant k is $0.693/t_{1/2}$ where $t_{1/2}$ is the half-life.

From these data a set of medium-specific degradation reaction half-lives is selected for use in Levels II and III calculations. Emphasis is placed on the fastest and the most plausible degradation process for each of the environmental compartments considered. Instead of assuming an equal half-life for both the water and soil compartment as suggested by Howard et al. (1991), a slower active class (in the reactivity table described earlier) was assigned for soil and sediment compared to that of the water compartment. This is in part because the major degradation processes are often photolysis (or photooxidation) and biodegradation. There is an element of judgment in this selection, and it is desirable to explore the implications of selecting other values.

The “Half-life in the Environment” data reflect observations of the rate of disappearance of the chemical from a medium, without necessarily identifying the cause of mechanism of loss. For example, loss from water may be a combination of evaporation, biodegradation and photolysis. Clearly these times are highly variable and depend on factors such as temperature, meteorology and the nature of the media. Again, the reader is urged to consult the original references.

1.7 ILLUSTRATIVE QSPR PLOTS AND FATE CALCULATIONS

Illustrative QSPR plots and their interpretation are given in this section, followed by examples of Levels I, II and III fate calculations. A relatively simple evaluation of benzene is given first followed by the more complex evaluation of pentachlorophenol.

1.7.1 QSPR PLOTS FOR MONONUCLEAR AROMATIC HYDROCARBONS

The physical-chemical data for mononuclear aromatics are plotted in the appropriate QSPR plots on [Figures 1.7.1 to 1.7.5](#) (which are also [Figures 3.2.1 to 3.2.5](#) for the mononuclear aromatic hydrocarbons in [Chapter 3](#)). These plots show that the data are relatively “well-behaved,” there being consistency among the reported values for this homologous series. In the case of benzene this QSPR plot is of little value because this is a well-studied chemical, but for other less-studied chemicals the plots are invaluable as a means of checking the reasonableness of data. The plots can also be used,

with appropriate caution, to estimate data for untested chemicals. We do not develop linear regressions of these data since we suggest that the plots be used directly for data estimation purposes. This enables the user to assess into account the values of similarly structured compounds and it gives a direct impression of likely error. We discuss, below, the general nature of the relationships and in particular the slopes of the QSPR plots.

Figures 1.7.1 to 1.7.4 show the dependence of the physical-chemical properties on Le Bas molar volume. Figure 1.7.1 shows that the solubilities of the monoaromatics decrease steadily with increasing molar volume. The vapor pressure data in Figure 1.7.2 are similar, but $\log K_{ow}$ in Figure 1.7.3 increases with increasing molar volume also in a linear fashion.

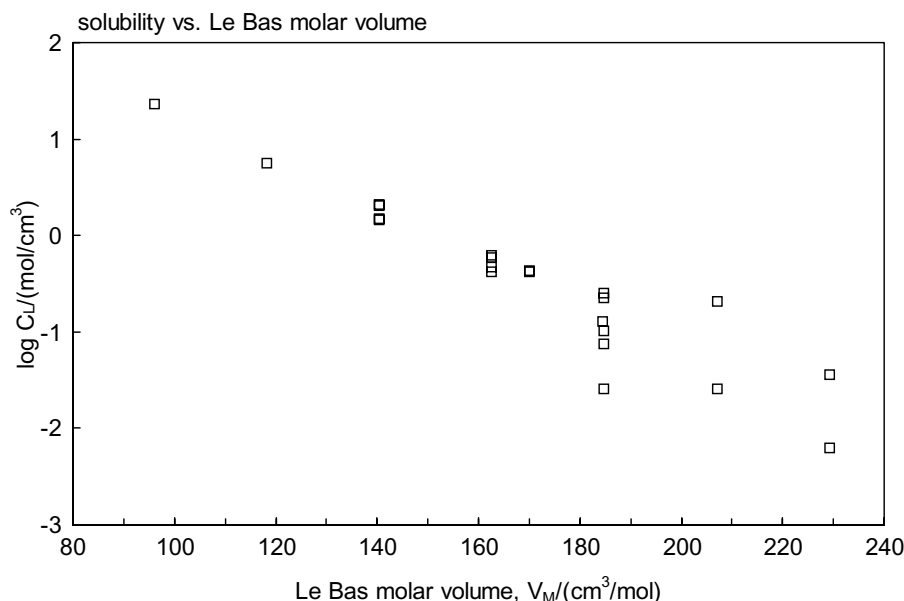


FIGURE 1.7.1 Molar solubility (liquid or supercooled liquid) versus Le Bas molar volume for mononuclear aromatic hydrocarbons.

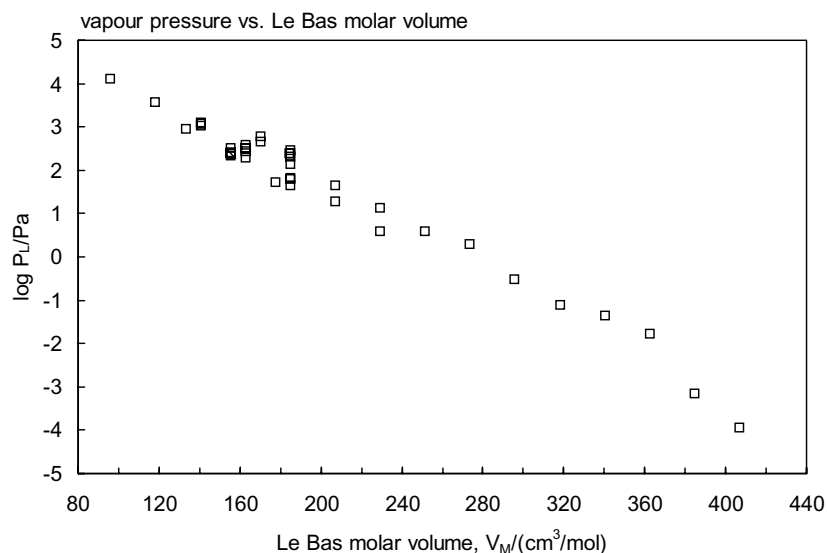


FIGURE 1.7.2 Vapor pressure (liquid or supercooled liquid) versus Le Bas molar volume for mononuclear aromatic hydrocarbons.

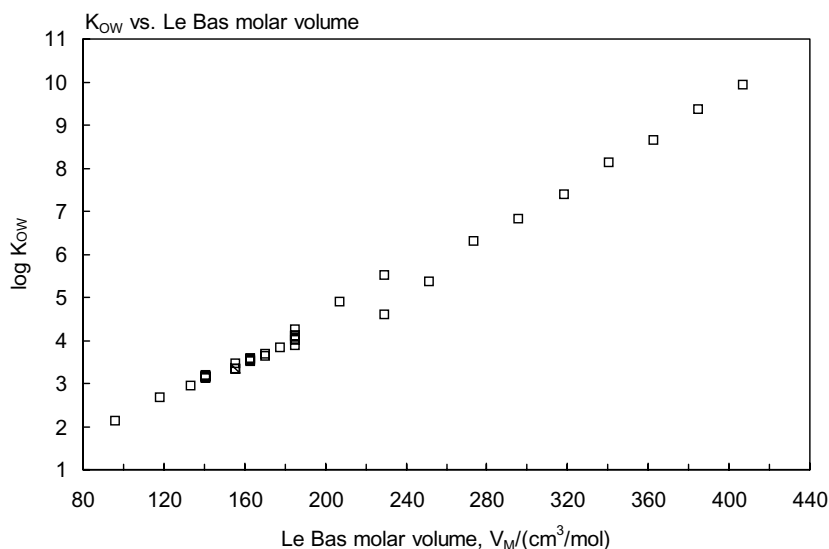


FIGURE 1.7.3 Octanol-water partition coefficient versus Le Bas molar volume for mononuclear aromatic hydrocarbons.

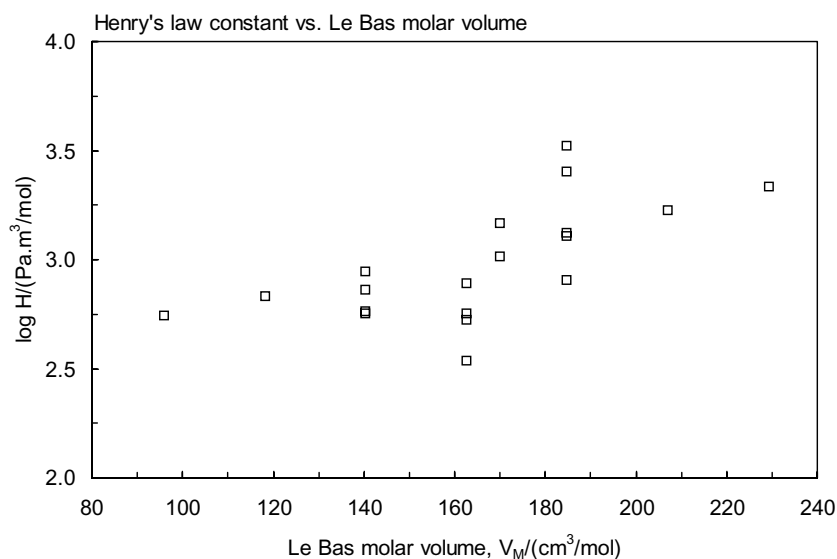


FIGURE 1.7.4 Henry's law constant versus Le Bas molar volume for mononuclear aromatic hydrocarbons.

The plot between Henry's law constant and molar volume (Figure 1.7.4) is more scattered. [Figure 1.7.5](#) shows the often-reported inverse relationship between octanol-water partition coefficient and the supercooled liquid solubility.

The QSPR plots show that an increase in molar volume by 100 cm³/mol generally causes:

- (i) A decrease in log solubility by 2.5 units, i.e., a factor of 10^{2.5} or 316;
- (ii) A decrease in log vapor pressure by 2.2 units, i.e., a factor of 10^{2.2} or 159;
- (iii) An increase in log Henry's law constant of 0.3 (i.e., 2.5 – 2.2) or a factor of 10^{0.3} or 2.0;
- (iv) An increase in log K_{OW} by 2.0 units, i.e., a factor of 100.

The plot of log K_{OW} versus log solubility thus has a slope of approximately 2.0/2.5 or 0.8. This slope of less than 1.0 has been verified experimentally by Chiou et al. (1982) and Bowman and Sans (1983). Its theoretical basis has been discussed in detail by Miller et al. (1985).

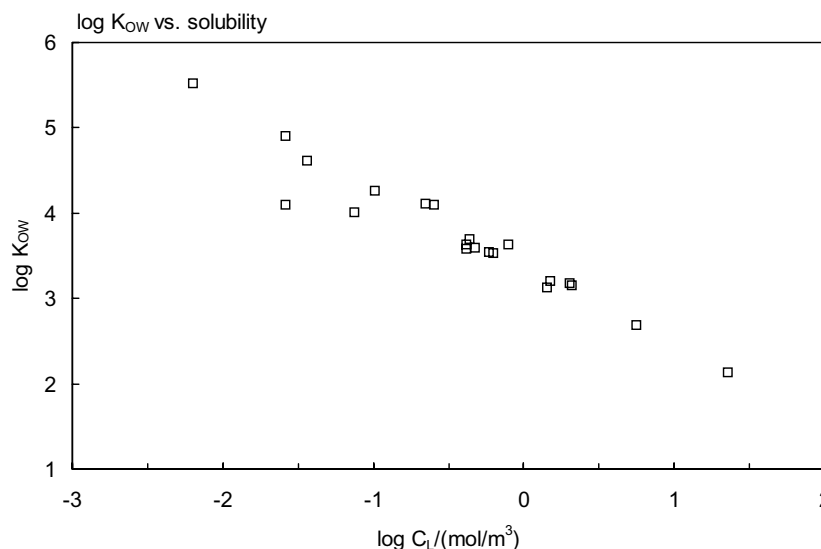


FIGURE 1.7.5 Octanol-water partition coefficient versus molar solubility (liquid or supercooled liquid) for mononuclear aromatic hydrocarbons.

Similar inferences can be made for other homologous series such as the chlorobenzenes and PCBs. In such cases the property change caused by substitution of one chlorine can be deduced as is illustrated later for chlorophenols.

The “Half-life in the Environment” and “Environmental Fate Rate Constants” are medium-specific degradation reaction half-lives selected for use in Level II and Level III calculations. As discussed earlier, emphasis was based on the fastest and the most plausible degradation process for each of the environmental compartments considered.

In summary, the physical-chemical and environmental fate data listed result in the tabulated selected values of solubility, vapor pressure, K_{ow} , dissociation constant where appropriate and reaction half-lives at the end of each chapter. These values are used in the evaluative environmental calculations.

1.7.2 EVALUATIVE CALCULATIONS FOR BENZENE

The illustrative evaluative environmental calculations described here are presented in the following format. Levels I, II and III diagrams are assigned to separate pages, and the physical-chemical properties are included in the Level I diagram. Two types of Level III diagrams are given; one depicts the transport processes and the other the distribution among compartments.

Level I

The Level I calculation suggests that if 100,000 kg (100 tonnes) of benzene are introduced into the 100,000 km² environment, 99% will partition into air at a concentration of 9.9×10^{-7} g/m³ or about 1 µg/m³. The water will contain nearly 1% at a low concentration of 4 µg/m³ or equivalently 4 ng/L. Soils would contain 5×10^{-6} µg/g and sediments about 9.7×10^{-6} µg/g. These values would normally be undetectable as a result of the very low tendency of benzene to sorb to organic matter in these media. The fugacity is calculated to be 3.14×10^{-5} Pa. The dimensionless soil-water and sediment-water partition coefficients or ratios of Z values are 2.6 and 5.3 as a result of a K_{oc} of about 55 and a few percent organic carbon in these media. There is little evidence of bioconcentration with a very low fish concentration of 3.0×10^{-5} µg/g. The pie chart in Figure 1.7.6 clearly shows that air is the primary medium of accumulation.

Level II

The Level II calculation includes the half-lives of 17 h in air, 170 h in water, 550 h in soil and 1700 h in sediment. No reaction is included for suspended sediment or fish. The input of 1000 kg/h results in an overall fugacity of 6×10^{-6} Pa, which is about 20% of the Level I value. The concentrations and amounts in each medium are thus about 20% of the Level I values. The relative mass distribution is identical to Level I. The primary loss mechanism is reaction in air, which accounts for 802 kg/h or 80.2% of the input. Most of the remainder is lost by advective outflow. The water, soil and sediment loss processes are unimportant largely because so little of the benzene is present in these media, but also

Chemical name: Benzene
 Fugacity Level I calculations: (six-compartment model)

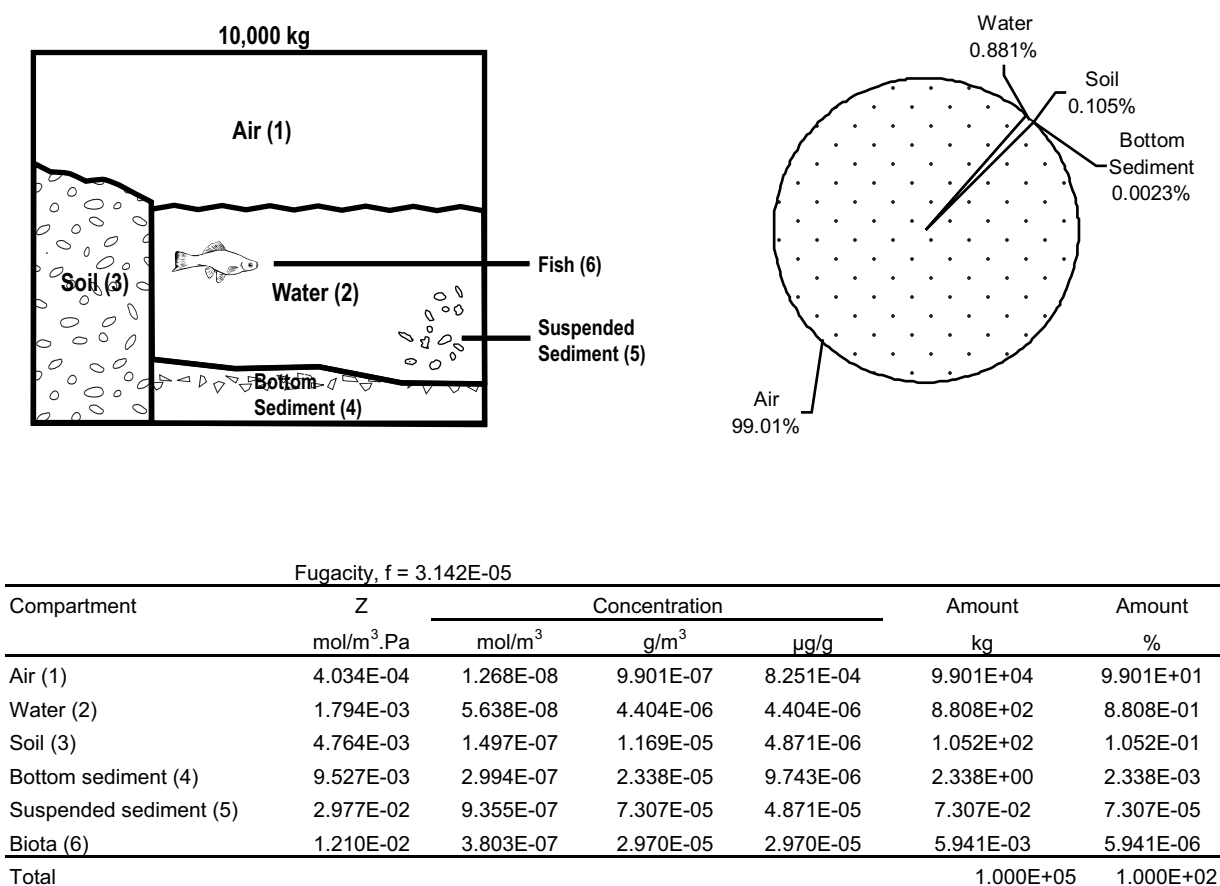


FIGURE 1.7.6 Level I fugacity calculations for benzene in a generic environment.

because of the slower reaction and advection rates. The overall residence time is 19.9 h; thus, there is an inventory of benzene in the system of 19.9×1000 or 19900 kg. The pie chart in Figure 1.7.7 illustrates the dominance of air reaction and advection.

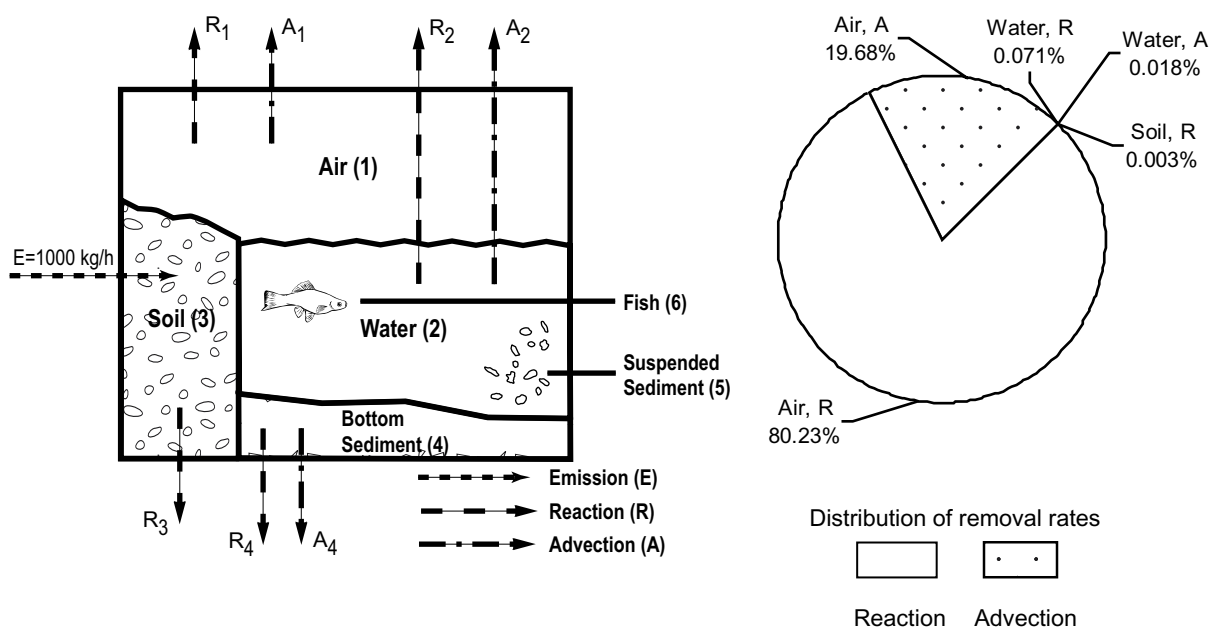
If the primary loss mechanism of atmospheric reaction is accepted as having a 17h half-life, the D value is 1.6×10^9 mol/Pa·h. For any other process to compete with this would require a value of at least 10^8 mol/Pa·h. This is achieved by advection (4×10^8), but the other processes range in D value from 19 (advection in bottom sediment) to 1.5×10^6 (reaction in water) and are thus a factor of over 100 or less. The implication is that the water reaction rate constant would have to be increased 100-fold to become significant. The soil rate constant would require an increase by 10^4 and the sediment by 10^6 . These are inconceivably large numbers corresponding to very short half-lives, thus the actual values of the rate constants in these media are relatively unimportant in this context. They need not be known accurately. The most sensitive quantity is clearly the atmospheric reaction rate.

The amounts in the compartments can be calculated easily from the total amount and the percentages of mass distribution in Level I. For example, the amount in water is 0.881% of 19877 kg or 175 kg.

Level III

The Level III calculation includes an estimation of intermedia transport. Examination of the magnitude of the intermedia D values given in the fate diagram (Figure 1.7.8) suggests that air-water and air-soil transport are most important with water-sediment and soil-water transport being negligible in potential transfer rate. The magnitude of these larger intermedia

Chemical name: Benzene
Fugacity Level II calculations: (six-compartment model)



Compartment	Half-life h	D Value		Concentration mol/m ³	Loss		Total Removal %
		Reaction mol/Pa.h	Advection mol/Pa.h		Reaction kg/h	Advection kg/h	
Air (1)	17	1.645E+09	4.034E+08	2.520E-09	8.023E+02	1.968E+02	9.991E+01
Water (2)	170	1.463E+06	3.589E+05	1.121E-08	7.137E-01	1.751E-01	8.888E-02
Soil (3)	550	5.402E+04	-	2.975E-08	2.635E-02	-	2.635E-03
Bottom sediment (4)	1700	3.884E+02	1.905E+01	5.950E-08	1.895E-04	9.296E-06	1.988E-05
Suspended sediment (5)	170	1.214E+02	2.977E+01	1.859E-07	5.921E-05	1.452E-05	7.373E-06
Biota (6)	170	9.867E+00	2.421E+00	7.559E-08	4.814E-06	1.181E-06	5.995E-07

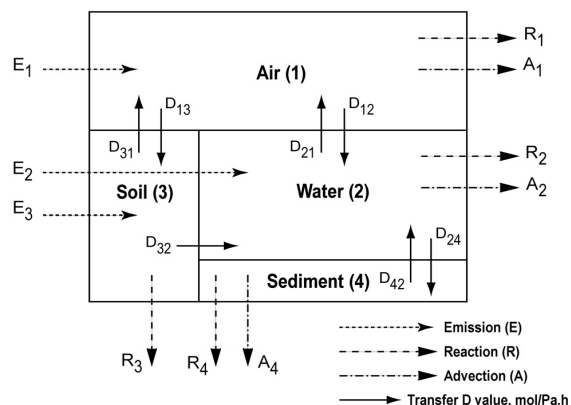
Fugacity, f 6.246E-06 Pa
Total amount, M 2.545E+05 mol
Total amount 1.988E+04 kg
Total reaction D value, D_R 1.646E+09 mol/Pa.h
Total advection D value, D_A 4.038E+08 mol/Pa.h
Total D value, D_T 2.050E+09 mol/Pa.h
Total loss by reaction 8.030E+02 kg/h
Total loss by advection 1.970E+02 kg/h
Total loss 1.000E+03 kg/h
Reaction residence time, t_R 2.475E+01 h
Advection residence time, t_A 1.009E+02 h
Overall residence time, t_O 1.988E+01 h

FIGURE 1.7.7 Level II fugacity calculations for benzene in a generic environment.

transport D values (approximately 10^6 mol/Pa.h) compared to the atmospheric reaction and advection values of 10^8 to 10^9 suggests that reaction and advection will be very fast relative to transport.

The bulk Z values are similar for air and water to the values for the “pure” phases in Levels I and II, but they are lower for soil and sediment because of the “dilution” of the solid phase with air or water.

Chemical name: Benzene
Fugacity Level III calculations: (four-compartment model)



Phase Properties and Rates:

Compartment	Bulk Z mol/m ³ .Pa	Half-life h	D Value	
			Reaction mol/Pa.h	Advection mol/Pa.h
Air (1)	4.034E-04	1.700E+01	1.645E+09	4.034E+08
Water (2)	1.795E-03	1.700E+02	1.463E+06	3.589E+05
Soil (3)	3.001E-03	5.500E+02	6.806E+04	-
Sediment (4)	3.341E-03	1.700E+03	6.810E+02	3.341E+01

Residence time (h)	Emission to			
	(A)ir Only	(W)ater Only	(S)oil Only	A+W+S
Overall residence time	1.977E+01	1.407E+02	8.675E+01	6.274E+01
Reaction residence time	2.462E+01	1.752E+02	1.058E+02	7.796E+01
Advection residence time	1.004E+02	7.142E+02	4.813E+02	3.212E+02

Phase Properties, Compositions, and Transport and Transformation Rates:

Emission Scenario	Emission (kg/h)			Fugacity (Pa)				Concentration (g/m ³)				Amount (kg)				Total Amount (kg)
	E ₁	E ₂	E ₃	f ₁	f ₂	f ₃	f ₄	C ₁	C ₂	C ₃	C ₄	w ₁	w ₂	w ₃	w ₄	
(A)ir Only	1000	0	0	6.249E-06	2.023E-06	5.781E-06	1.556E-06	1.969E-07	2.836E-07	1.355E-06	4.059E-07	1.969E+04	5.673E+01	2.439E+01	2.030E-01	1.977E+04
(W)ater Only	0	1000	0	2.002E-06	4.775E-03	1.852E-06	3.671E-03	6.308E-08	6.693E-04	4.341E-07	9.579E-04	6.308E+03	1.339E+05	7.814E+00	4.790E+02	1.407E+05
(S)oil Only	0	0	1000	5.676E-06	4.999E-05	1.599E-02	3.843E-05	1.788E-07	7.007E-06	3.748E-03	1.003E-05	1.788E+04	1.401E+03	6.746E+04	5.015E+00	8.675E+04
A+W+S	600	300	100	4.918E-06	1.439E-03	1.603E-03	1.106E-03	1.550E-07	2.017E-04	3.757E-04	2.886E-04	1.550E+04	4.033E+04	6.763E+03	1.443E+02	6.274E+04

Emission Scenario	Emission (kg/h)			Loss by Reaction (kg/h)				Loss by Advection (kg/h)			Intermedia Rate of Transport (kg/h)							
	E ₁	E ₂	E ₃	R ₁	R ₂	R ₃	R ₄	A ₁	A ₂	A ₄	T ₁₂	T ₂₁	T ₁₃	T ₃₁	T ₃₂	T ₂₄	T ₄₂	
(A)ir Only	1000	0	0	8.028E+02	2.312E-01	3.073E-02	8.274E-05	1.969E+02	5.673E-02	4.059E-06	4.202E-01	1.358E-01	3.617E-01	3.273E-01	3.648E-03	3.071E-04	2.203E-04	
(W)ater Only	0	1000	0	2.572E+02	5.457E+02	9.845E-03	1.952E-01	6.308E+01	1.339E+02	9.579E-03	1.346E-01	3.204E+02	1.159E-01	1.049E-01	1.169E-03	7.248E-01	5.200E-01	
(S)oil Only	0	0	1000	7.290E+02	5.713E+00	8.499E+01	2.044E-03	1.788E+02	1.401E+00	1.003E-04	3.816E-01	3.354E+00	3.285E-01	9.052E+02	1.009E+01	7.588E-03	5.444E-03	
A+W+S	600	300	100	6.317E+02	1.644E+02	8.521E+00	5.883E-02	1.550E+02	4.033E+01	2.886E-03	3.306E-01	9.653E+01	2.846E-01	9.075E+01	1.011E+00	2.184E-01	1.567E-01	

FIGURE 1.7.8 Level III fugacity calculations for benzene in a generic environment.

The first row describes the condition if 1000 kg/h is emitted into the air. The result is similar to the Level II calculation with 19700 kg in air, 57 kg in water, 24 kg in soil and only 0.2 kg in sediment. It can be concluded that benzene discharged to the atmosphere has very little potential to enter other media. The rates of transfer from air to water and air to soil are both only about 0.4 kg/h. Even if the transfer coefficients were increased by a factor of 10, the rates would remain negligible. The reason for this is the value of the mass transfer coefficients which control this transport process. The overall residence time is 19.8 hours, similar to Level II.

If 1000 kg/h of benzene is discharged to water, as in the second row, there is predictably a much higher concentration in water (by a factor of over 2000). There is reaction of 546 kg/h in water, advective outflow of 134 kg/h and transfer to air of 320 kg/h with negligible loss to sediment. The amount in the water is 134000 kg; thus the residence time in the water is 134 h and the overall environmental residence time is a longer 140 hours. The key processes are thus reaction in water (half-life 170 h), evaporation (half-life 290 h) and advective outflow (residence time 1000 h). The evaporation half-life can be calculated as $(0.693 \times \text{mass in water})/\text{rate of transfer}$, i.e., $(0.693 \times 133863)/320 = 290$ h. Clearly, competition between reaction and evaporation in the water determines the overall fate. Ninety-five percent of the benzene discharged is now found in the water, and the concentration is a fairly high 6.7×10^{-4} g/m³, or 670 ng/L.

The third row shows the fate if discharge is to soil. The amount in soil is 67460 kg, reflecting an overall 87 h residence time. The rate of reaction in soil is only 85 kg/h and there is no advection; thus, the primary loss mechanism is transfer to air (T_{31}) at a rate of 905 kg/h, with a relatively minor 10 kg/h to water by run-off. The net result is that the air concentrations are similar to those for air discharge and the soil acts only as a reservoir. The soil concentration of 3.75×10^{-3} g/m³ or 2.5×10^{-3} µg/g or 2.5 ng/g is controlled almost entirely by the rate at which the benzene can evaporate.

The net result is that benzene behaves entirely differently when discharged to the three media. If discharged to air it reacts rapidly and advects with a residence time of 20 h with little transport to soil or water. If discharged to water it reacts and evaporates to air with a residence time of 140 h. If discharged to soil it mostly evaporates to air with a residence time in soil of 53 h.

The final scenario is a combination of discharges, 600 kg/h to air, 300 kg/h to water, and 100 kg/h to soil. The concentrations, amounts and transport and transformation rates are merely linearly combined versions of the three initial scenarios. For example, the rate of reaction in air is now 632 kg/h. This is 0.6 of the first (air emission) rate of 803 kg/h, i.e., 482 kg/h, plus 0.3 of the second (water emission) rate of 257 kg/h, i.e., 77 kg/h and 0.1 of the third (soil emission) rate of 729 kg/h, i.e., 73 kg yielding a total of $(482 + 77 + 73)$ or 632 kg/h. It is also apparent that the amount in the air of 15500 kg causing a concentration of 0.155 µg/m³ is attributable to emissions to air (0.6×0.197) or 0.118 µg/m³, emissions to water (0.3×0.063) or 0.019 µg/m³ and emissions to soil (0.1×0.179) or 0.018 µg/m³. The concentration in water of 2.0×10^{-4} g/m³ or 202 µg/m³ or ng/L is largely attributable to the discharges to water, which alone cause 0.3×669 or 200 µg/m³. Although more is emitted to air, it contributes less than 1 µg/m³ to the water with soil emissions accounting for about 1 µg/m³. Similarly, the prevailing soil concentration is controlled by the rate of discharge to the soil.

In this multimedia discharge scenario the overall residence time is 59 hours, which can be viewed as 60% of the air residence time of 19.7 h, 30% of the water residence time of 140 h and 10% of the overall soil residence time of 53 h. The overall amount in the environment of 59,000 kg is thus largely controlled by the discharges to water, which account for (0.3×133863) or 40,000 kg.

Figure 1.7.9 shows the distributions of mass and removal process rates for these four scenarios. Clearly, when benzene is discharged into a specific medium, most of the chemical is found in that medium. Only in the case of discharges to soil is an appreciable fraction found in another compartment, namely air. This is because benzene evaporates fairly rapidly from soil without being susceptible to reaction or advection.

Finally, it is interesting to note that the fugacity in this final case (in units of mPa) are for the four media 5.0×10^{-3} , 1.4, 1.6 and 1.1. The soil, sediment and water are fairly close to equilibrium, with the air notably “under-saturated” by a factor of about 200. This is the result of the rapid loss processes from air.

1.7.3 QSPR PLOTS FOR CHLOROPHENOLS AND ALKYLPHENOLS

These QSPR (quantitative structure-property relationship) plots display the usual approximately linear relationships similar to those of the alkyl and chlorinated aromatic hydrocarbons.

Most acid dissociation constants pK_a exceed environmental pH values, the exceptions being the highly chlorinated phenols. As a result, these substances tend to have higher apparent solubilities in water because of dissociation. The structure-property relationships apply to the un-ionized or protonated species; thus, experimental data should preferably be “corrected” to eliminate the effect of ionization, thus eliminating pH effects.

Chemical name: Benzene
Level III Distribution

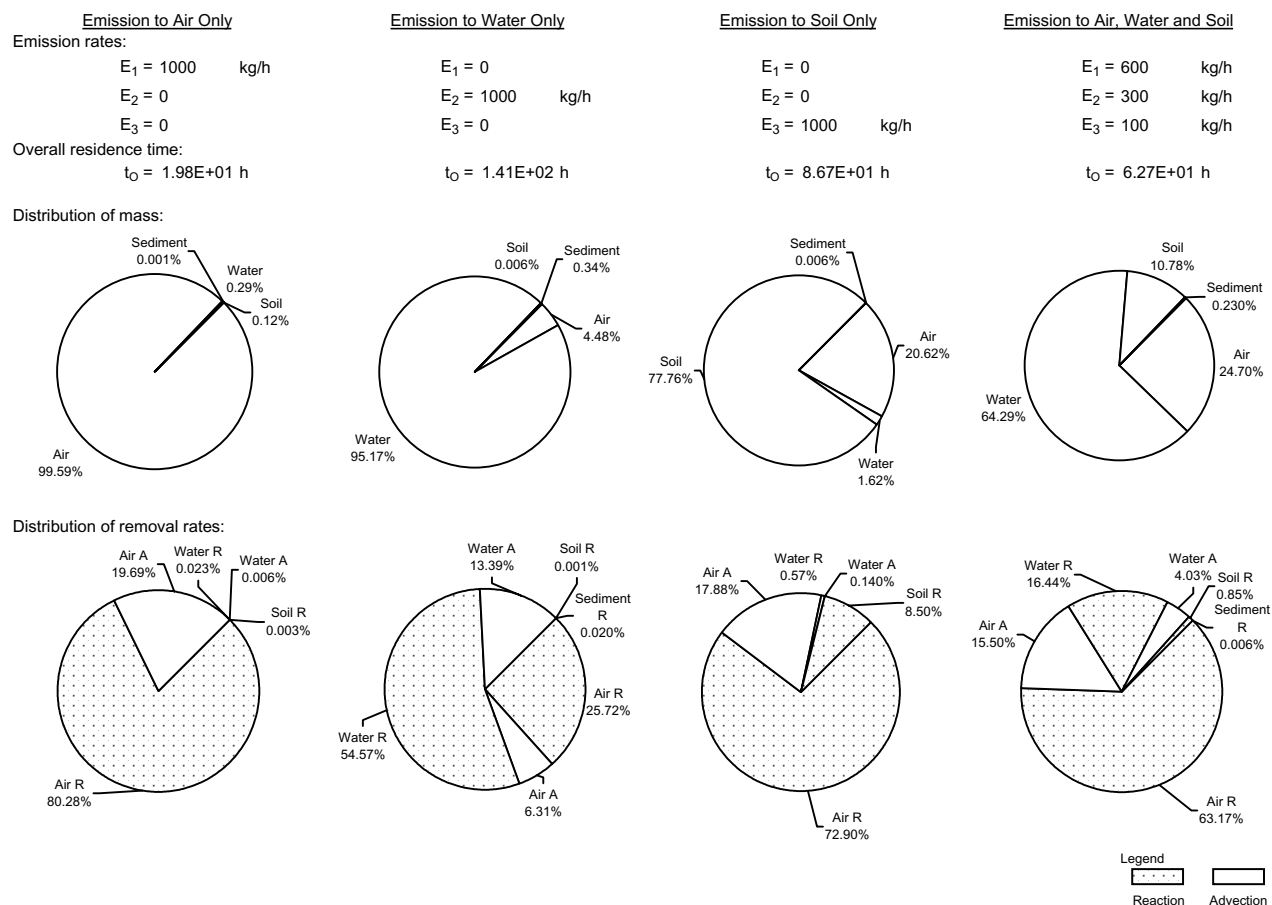


FIGURE 1.7.9 Level III fugacity distributions of benzene for four emission scenarios.

Figure 1.7.10 shows that the chlorophenol solubilities behave similarly to other chemical series with slopes of about 0.62 log units per 20.9 cm³/mol, which is the volume difference resulting from substitution by one chlorine. The result is a factor of 10^{0.62} or 4.2 drop in solubility per chlorine. The alkylphenols have a lower slope of about 0.5 per CH₂ and usually have higher solubilities at the same molar volume. The two sets of data are, however, generally similar.

The vapor pressure data in Figure 1.7.11 show a slope of about 0.60 log units per 20.9 cm³/mol (i.e., a factor of 4.0) per chlorine. There is a lower slope for the alkylphenols, and they usually have higher vapor pressures, especially for the larger molecules.

The K_{OW} data in Figure 1.7.12 show that the chlorophenols and alkylphenols differ in properties, there being more uncertainty about the K_{OW} of the longer-chain phenols. The chlorophenols tend to partition more into octanol at the same molar volume and are thus expected to be more bioaccumulative. The slope of the chlorophenol line is about 0.78 log units per chlorine or a factor of 6.0. The alkylphenol slope is lower and about 0.36 log units per CH₂, i.e., a factor of 2.3.

The Henry's law constant data calculated as the ratio of vapor pressure to solubility in Figure 1.7.13 are quite scattered. There is little systematic variation with molar volume. Most values of log H lie between -0.1 to -0.8, i.e., H lies between 0.8 and 0.08, and the resulting air-water partition coefficient K_{AW} or H/RT thus lies between 3 × 10⁻⁴ and 3 × 10⁻⁵.

Figure 1.7.14, the plot of log K_{OW} versus log solubility, shows a relatively high slope of 1.25 for the chlorophenols and a lower slope of 0.70 for the alkylphenols.

Addition of a chlorine causes a drop in chlorophenol solubility in water by about 0.62 log units, and K_{OW} increases by about 0.78 log units. For the alkylphenols, addition of a methylene causes about a 0.50 log unit drop in solubility in water, and K_{OW} increases by only about 0.36 log units. The slope of the log K_{OW} versus solubility lines are thus about 0.78/0.62 or 1.25 for the chlorophenols and 0.36/0.5 or 0.72 for the alkylphenols. An implication is that since K_{OW} can

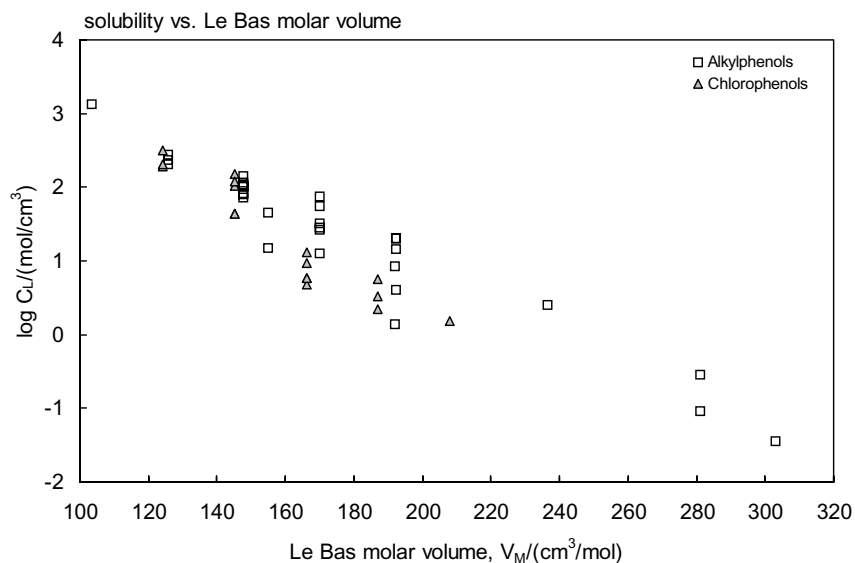


FIGURE 1.7.10 Molar solubility (liquid or supercooled liquid) versus Le Bas molar volume for alkylphenols and chlorophenols.

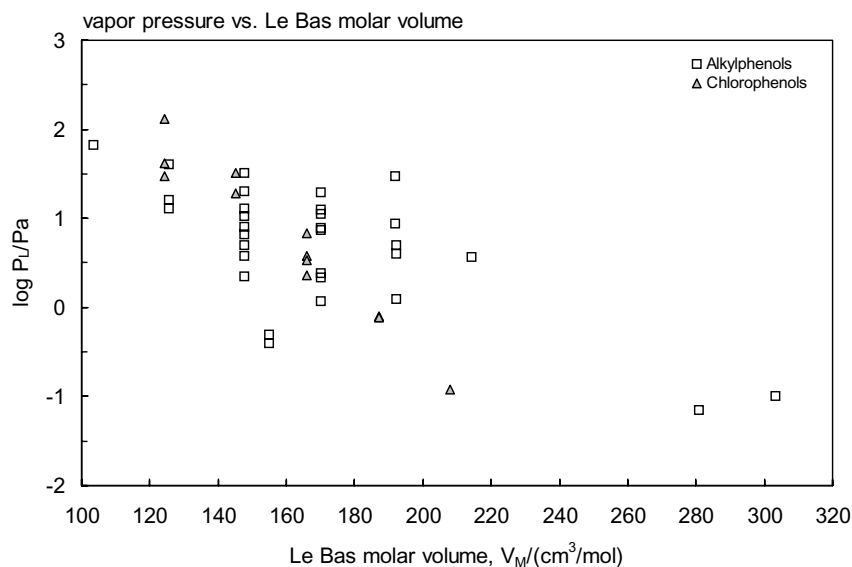


FIGURE 1.7.11 Vapor pressure (liquid or supercooled liquid) versus Le Bas molar volume for alkylphenols and chlorophenols.

be viewed as a ratio of “solubility” in octanol and solubility in water, the solubility of the chlorophenols in octanol increases by $(0.78 - 0.62)$ or 0.16 log unit per chlorine, while for the alkylphenols the corresponding change is $(0.36 - 0.50)$ or -0.14 log unit, or a decrease of a factor of 1.4. The reasons for this difference are not known. The chlorophenols thus appear to have an unusually strong tendency to partition into octanol. Whether or not this tendency applies to lipid phases in biota or to organic carbon is not certain, but such a tendency is obviously of considerable interest when interpreting the toxicity and fate of these chemicals.

These data show clearly that the structure-property relationships which apply to hydrophobic organic chemicals such as the chloro- and alkyl-aromatics also apply to the phenols, but the relationships are more scattered and less well defined. The absolute values of properties differ greatly. This scatter is probably attributable, in part, to insufficient experimental data or errors in experimental measurements, to dissociation and to the greater polar character of these chemicals. It is not recommended that correlations developed for non-polar organic chemicals be applied to the phenols. Separate treatment of each homologous series is required.

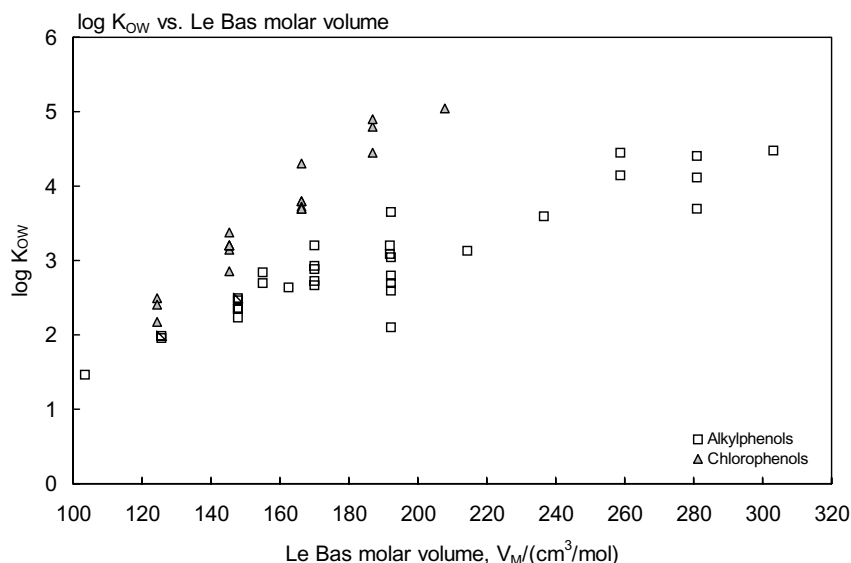


FIGURE 1.7.12 Octanol-water partition coefficient versus Le Bas molar volume for alkylphenols and chlorophenols.

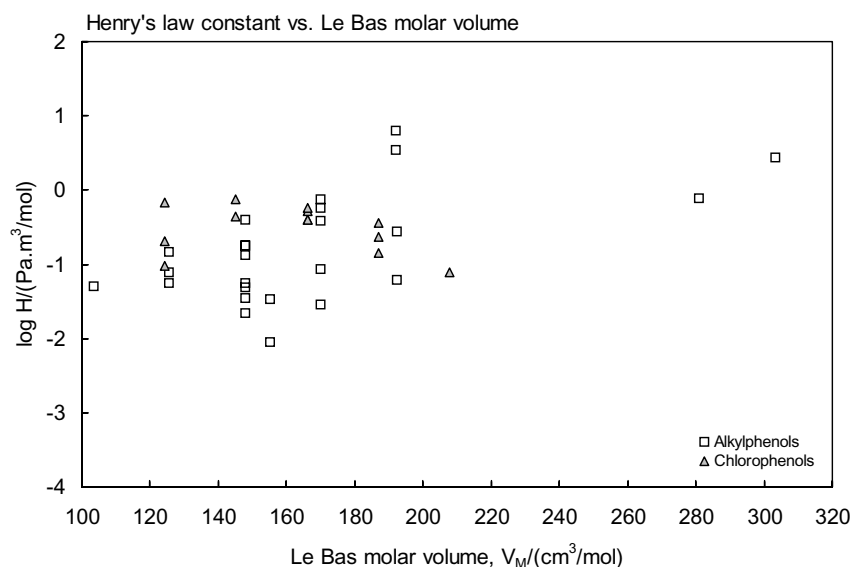


FIGURE 1.7.13 Henry's law constant versus Le Bas molar volume for alkylphenols and chlorophenols.

1.7.4 EVALUATIVE CALCULATIONS FOR PENTACHLOROPHENOL

For dissociating compounds the environmental pH is specified and the calculation of Z values has been modified to include ionic species as discussed in Section 1.2.4. Generally, if discharge is to a compartment such as water, most chemical will be found in that compartment, and will react there, but a quantity does migrate to other compartments and is lost from these media. Three pie charts corresponding to discharges of 1000 kg/h to air, water and soil are included. The percentage emission in each medium in this case has been selected to be 5, 25 and 70% discharged to air, water and soil, respectively. A fourth pie chart with discharges to all three compartments is also given. This latter chart is in principle the linear sum of the first three, but since the overall residence times differ, the diagram with the longer residence time, and greater resident mass, tends to dominate.

Figures 1.7.15 to 1.7.18 show the mass distributions obtained in Level I calculations and the removal distribution from Level II fugacity calculation of pentachlorophenol (PCP) at two different environmental pHs for the generic

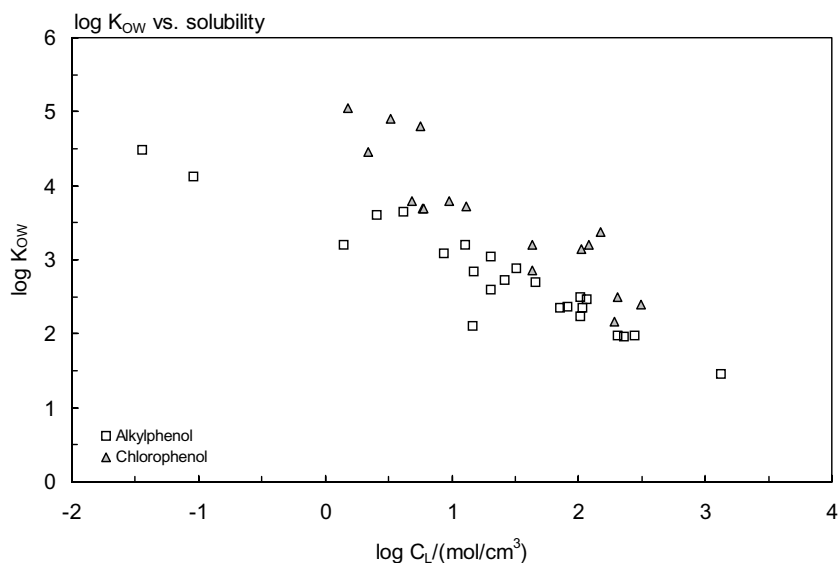


FIGURE 1.7.14 Octanol-water partition coefficient versus molar solubility (liquid or supercooled liquid) for alkylphenols and chlorophenols.

environment. Figures 1.7.19 to 1.7.22 show the corresponding Level III fugacity calculations. Both mass and removal distributions are shown in these figures for the four scenarios of discharges to air, water, soil, and mixed compartments.

Level I

The Level I calculations for environmental pHs of 5.1 and 7 suggest that if 100,000 kg (100 tonnes) of pentachlorophenol (PCP) are introduced into the 100,000 km² environment, most PCP will tend to be associated with soil. This is especially the case at low pH when the protonated form dominates. Very little partitions into air and only about 1% partitions into water. Soil contains most of the PCP. Sediments contain about 2%. There is evidence of bioconcentration with a rather high fish concentration. Note that only four media (air, water, soil and bottom sediment) are depicted in the pie chart; therefore, the sum of the percent distribution figures is slightly less than 100%. The air-water partition coefficient is very low. As pH increases, dissociation increases and there is a tendency for partitioning to water to become more important. Essentially, the capacity of water for the chemical increases. Partitioning to air is always negligible.

Level II

The Level II calculations at pH 5.1 include the reaction half-lives of 550 h in air, 550 h in water, 1700 h in soil and 5500 h in sediment. No reaction is included for suspended sediment or fish. The steady-state input of 1000 kg/h results in an overall fugacity of 3.43×10^{-8} Pa, which is about 24 times the Level I value. The concentrations and amounts in each medium are thus about 24 times the Level I values. The relative mass distribution is identical to Level I. The primary loss mechanism is reaction in soil, which accounts for 936 kg/h, or 94% of the input. Most of the remainder is lost by reaction and advection in water. The air and sediment loss processes are unimportant largely because so little of the PCP is present in these media. The overall residence time is 2373 h; thus, there is an inventory of PCP in the system of 2373×1000 or 2,373,000 kg.

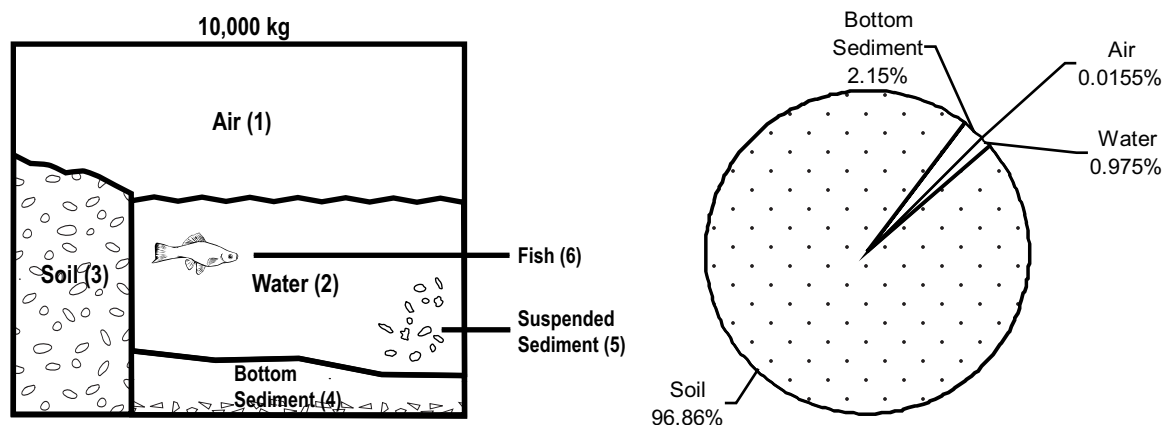
The primary loss mechanism of soil reaction has a D value of 1.03×10^{11} ; thus, for any other process to compete with this would require a D value of at least 10^{10} mol/Pa·h. The next largest D values are 3.19×10^9 and 2.53×10^9 for reaction and advection in water, which are about a factor of 30 smaller. Only if the water advection or reaction rates are increased by about this factor will these processes become significant. As pH increases, reaction in, and advection from, water increase in importance.

Level III

The Level III diagrams (Figures 1.7.19 to 1.7.22 for the two pHs) are regarded as the most realistic depictions of chemical fate.

This calculation includes an estimation of intermedia transport. Examination of the magnitude of the intermedia D values given in the fate diagrams suggest that water-sediment and air-soil transport are most important, with soil-water, and air-water exchange being slower. This chemical tends to be fairly immobile in terms of intermedia transport.

Chemical name: Pentachlorophenol
 Fugacity Level I calculations: (six-compartment model) at data pH of 5.1



Physical-chemical properties:

Molecular weight (g/mol)
 Melting point ($^{\circ}\text{C}$)
 Solubility (g/m^3)
 Vapor pressure (Pa)
 $\log K_{\text{OW}}$
 Fugacity ratio, F
 Dissociation const, pKa

266.34
 174
 14
 4.15E-03
 5.05
 3.36E-02
 4.74

Partition coefficients:

Henry's law constant
 Air/water
 Organic carbon, K_{OC}
 Bioconcentration factor, BCF
 Soil/water
 Sediment/water
 Suspended sediment/water
 Aerosol/water

7.90E-02
 3.19E-05
 4.60E+04
 5.61E+03
 2.21E+03
 4.42E+03
 1.38E+04
 4.86E+07

Z values in water:

at data pH
 neutral
 ionic
 total
 at environ. pH
 neutral
 ionic
 total

Compartment	Z mol/m ³ .Pa	Concentration			Amount	
		mol/m ³	g/m ³	μg/g	kg	%
Air (1)	4.03E-04	5.82E-13	1.55E-10	1.31E-07	1.55E+01	1.55E-02
Water (2)	1.27E+01	1.83E-08	4.87E-06	4.87E-06	9.74E+02	9.74E-01
Soil (3)	2.80E+04	4.04E-05	1.08E-02	4.48E-03	9.68E+04	9.68E+01
Bottom sediment (4)	5.59E+04	8.80E-05	2.15E-02	8.96E-03	2.15E+03	2.15E+00
Suspended sediment (5)	1.75E+05	2.52E-04	6.72E-02	4.48E-02	6.72E+01	6.72E-02
Biota (6)	7.11E+04	1.03E-04	2.73E-02	2.73E-02	5.46E+00	5.46E-03
Total					1.00E+05	1.00E+02

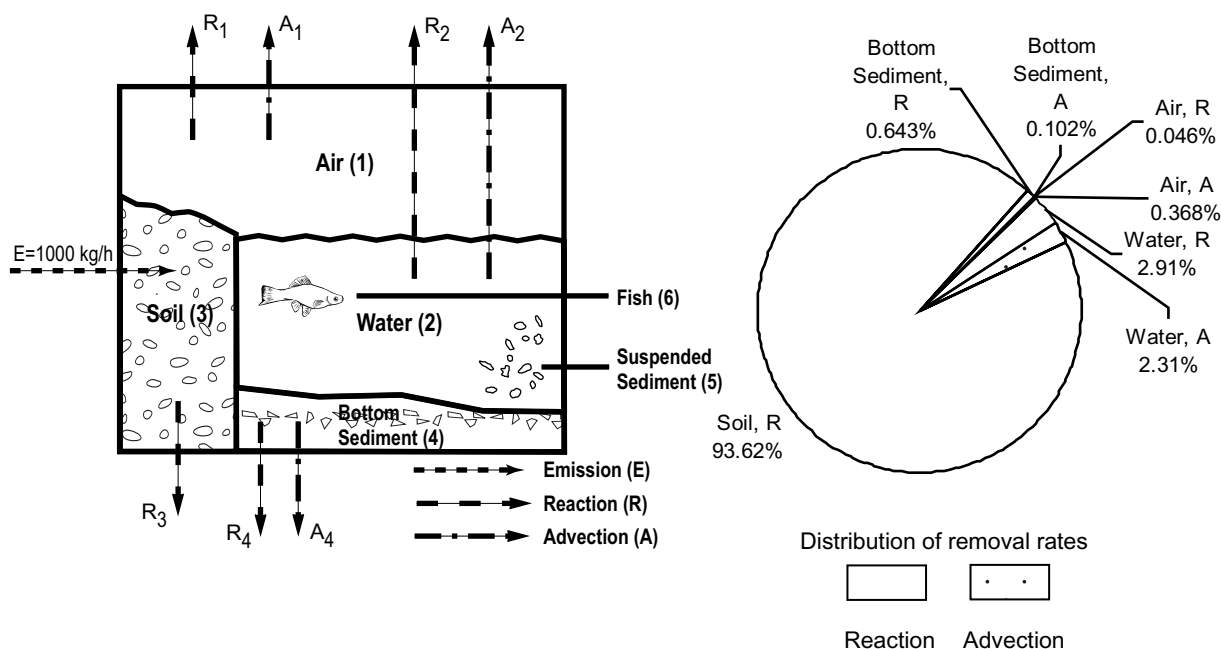
FIGURE 1.7.15 Level I fugacity calculations for PCP at data determination pH of 5.1.

The bulk Z values are similar for air and water to the values for the “pure” phases in Level I and II, but they are lower for soil and sediment because of the “dilution” of the solid soil and sediment phases with air or water.

The complete discussion of PCP fate as deduced in these calculations is beyond our scope, but to assist the reader we describe the behavior at a pH of 5.1 in some detail below.

These tabulated data are given in numerical and pictorial form in Figures 1.7.19 to 1.7.22. The first row of figures at the foot of Figure 1.7.19 describes the condition if 1000 kg/h is emitted to the air. The result is similar to the Level II calculation with 65780 kg in air, 21070 kg in water, 504700 kg in soil and only 40800 kg in sediment. It can be concluded that PCP discharged to the atmosphere has fairly high potential to enter other media. The rate of transfer from air to

Chemical name: Pentachlorophenol
Fugacity Level II calculations: (six-compartment model) at data pH of 5.1



Compartment	Half-life h	D Value		Concentration mol/m ³	Loss		Total Removal %
		Reaction mol/Pa.h	Advection mol/Pa.h		Reaction kg/h	Advection kg/h	
Air (1)	550	5.08E+07	4.03E+08	1.38E-11	4.64E-01	3.68E+00	4.14E-01
Water (2)	550	3.19E+09	2.53E+09	4.34E-07	2.91E+01	2.31E+01	5.22E+00
Soil (3)	1700	1.03E+11	-	9.58E-04	9.36E+02	-	9.36E+01
Bottom sediment (4)	5500	7.05E+08	1.12E+08	1.92E-03	6.43E+00	1.02E+00	7.45E-01
Suspended sediment (5)	-	-	-	5.99E-03	-	-	-
Biota (6)	-	-	-	2.43E-03	-	-	-

Fugacity, f	3.43E-08 Pa
Total amount, M	8.91E+06 mol
Total amount	2.37E+06 kg
Total reaction D value, D _R	1.06E+11 mol/Pa.h
Total advection D value, D _A	2.94E+09 mol/Pa.h
Total D value, D _T	1.09E+11 mol/Pa.h
Total loss by reaction	9.72E+02 kg/h
Total loss by advection	2.78E+01 kg/h
Total loss	1.00E+03 kg/h
Reaction residence time, t _R	2.44E+03 h
Advection residence time, t _A	8.53E+04 h
Overall residence time, t _O	2.37E+03 h

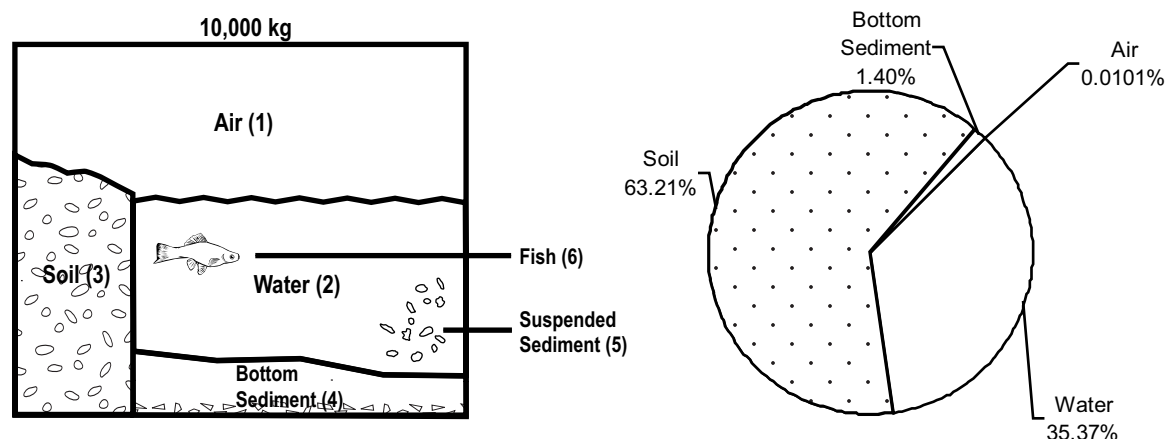
FIGURE 1.7.16 Level II fugacity calculations for PCP at data determination pH of 5.1.

water (T_{12}) is about 54 kg/h and that from air to soil (T_{13}) 206 kg/h. The reason for this is the value of the mass transfer coefficients which control this transport process. The overall residence time is 632 h.

If 1000 kg/h of PCP is discharged to water, as in the second row, there is, as expected, a much higher concentration in water. There is reaction of 494 kg/h in water, advective outflow of 392 kg/h and transfer to air (T_{21}) of 2.90 kg/h with

Chemical name: Pentachlorophenol

Fugacity Level I calculations: (six-compartment model) at environmental pH of 7



Physical-chemical properties:

Molecular weight (g/mol)
Melting point ($^{\circ}\text{C}$)
Solubility (g/m^3)
Vapor pressure (Pa)
 $\log K_{OW}$
Fugacity ratio, F
Dissociation const, pKa

Partition coefficients:

Henry's law constant
Air/water
Organic carbon, K_{OC}
Bioconcentration factor, BCF
Soil/water
Sediment/water
Suspended sediment/water
Aerosol/water

Z values in water:

at data pH
neutral
ionic
total
at environ. pH
neutral
ionic
total

Fugacity, $f =$		9.43E-10				
Compartment	Z	Concentration			Amount	Amount
	$\text{mol}/\text{m}^3 \cdot \text{Pa}$	mol/m^3	g/m^3	$\mu\text{g}/\text{g}$	kg	%
Air (1)	4.03E-04	3.80E-13	1.01E-10	8.54E-08	1.01E+01	1.01E-02
Water (2)	7.04E+02	6.64E-07	1.77E-04	1.77E-04	3.54E+04	3.54E+01
Soil (3)	2.80E+04	2.64E-05	7.02E-03	2.93E-03	6.32E+04	6.32E+01
Bottom sediment (4)	5.59E+04	5.27E-05	1.40E-02	5.85E-03	1.40E+03	1.40E+00
Suspended sediment (5)	1.75E+05	1.65E-04	4.39E-02	2.93E-02	4.39E+01	4.39E-02
Biota (6)	7.11E+04	6.70E-05	1.78E-02	1.78E-02	3.57E+00	3.57E-03
Total					1.00E+05	1.00E+02

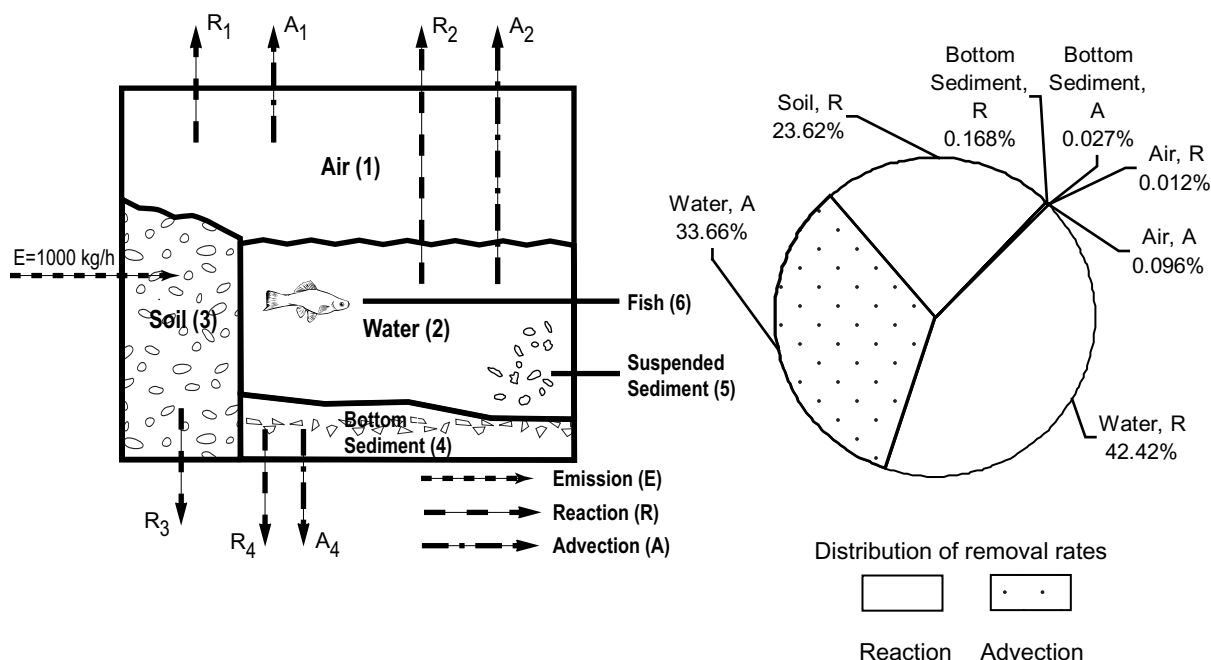
FIGURE 1.7.17 Level I fugacity calculations for PCP at environmental pH of 7.

substantial loss of 128 kg/h to sediment. The amount in the water is 392,200 kg; thus, the residence time in the water is 392 h, and the overall environmental residence time is a longer 1153 h. The key processes are thus reaction in water (half-life 550 h) and advective outflow (residence time 1000 h). The evaporation half-life can be calculated as $(0.693 \times \text{mass in water})/\text{rate of transfer}$, i.e., $(0.693 \times 392,200)/2.90 = 93700$ h. Clearly competition between advection and reaction in the water determines the overall fate. Thirty-four percent of the PCP discharged is now found in the water and the concentration is fairly high, namely $1.96 \times 10^{-3} \text{ g}/\text{m}^3$ or $1.96 \mu\text{g}/\text{L}$.

The third row shows the fate if PCP is discharged to soil. The amount in soil is 245100 kg, with only 7.43 kg in air. The overall residence time is 2452 hours, which is largely controlled by the reaction rate in soil. The rate of reaction in soil is 999 kg/h and there is no advection; thus, the other loss mechanism is transfer to air (T_{31}) at a rate of 0.11 kg/h, with a relatively minor 0.8 kg/h to water by run-off. The soil concentration of $0.136 \text{ g}/\text{m}^3$ is controlled almost entirely by the rate at which the PCP reacts.

Chemical name: Pentachlorophenol

Fugacity Level II calculations: (six-compartment model) at environmental pH of 7



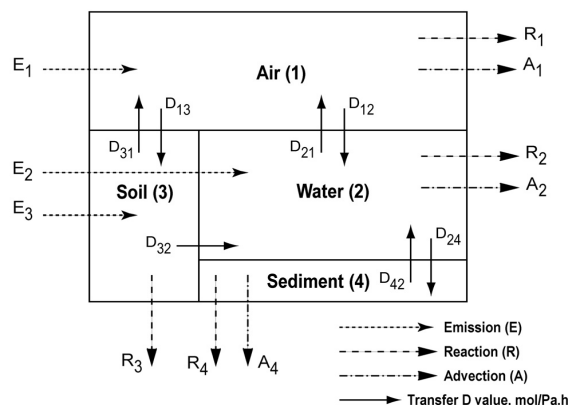
Compartment	Half-life h	D Value		Concentration mol/m ³	Loss		Total Removal %
		Reaction mol/Pa.h	Advection mol/Pa.h		Reaction kg/h	Advection kg/h	
Air (1)	550	5.08E+07	4.03E+08	3.59E-12	1.20E-01	9.56E-01	1.08E-01
Water (2)	550	1.77E+11	1.41E+11	6.26E-06	4.20E+02	3.34E+02	7.54E+01
Soil (3)	1700	1.03E+11	-	2.49E-04	2.34E+02	-	2.43E+01
Bottom sediment (4)	5500	7.05E+08	1.12E+08	4.97E-04	1.67E+00	2.65E-01	1.93E-01
Suspended sediment (5)	-	-	-	1.55E-03	-	-	-
Biota (6)	-	-	-	6.32E-04	-	-	-

Fugacity, f	8.89E-09 Pa
Total amount, M	3.54E+06 mol
Total amount	9.44E+05 kg
Total reaction D value, D_R	2.80E+11 mol/Pa.h
Total advection D value, D_A	1.41E+11 mol/Pa.h
Total D value, D_T	4.21E+11 mol/Pa.h
Total loss by reaction	6.65E+02 kg/h
Total loss by advection	3.35E+02 kg/h
Total loss	1.00E+03 kg/h
Reaction residence time, t_R	1.42E+03 h
Advection residence time, t_A	2.82E+03 h
Overall residence time, t_O	9.44E+02 h

FIGURE 1.7.18 Level II fugacity calculations for PCP at environmental pH of 7.

The net result is that PCP behaves entirely differently when discharged to the three media. If discharged to air, it advects rapidly and reacts with a residence time of 632 h or about 26.3 days, with substantial transport to soil or water. If discharged to water, it reacts and evaporates to air with a residence time of 1153 h or 48 days. If discharged to soil, it mostly reacts with an overall residence time of about 2452 h or 102 days.

Chemical name: Pentachlorophenol
 Fugacity Level III calculations: (four-compartment model) at data pH of 5.1



Phase Properties and Rates:

Compartment	Bulk Z mol/m ³ .Pa	Half-life h	D Value	
			Reaction mol/Pa.h	Advection mol/Pa.h
Air (1)	4.038E-04	5.500E+02	5.09E+07	4.04E+08
Water (2)	1.361E+01	5.500E+02	3.43E+09	2.72E+09
Soil (3)	1.399E+04	1.700E+03	1.03E+11	-
Sediment (4)	1.120E+04	5.500E+03	7.05E+08	1.12E+08

Residence time (h)	Emission to			
	(A)ir Only	(W)ater Only	(S)oil Only	A+W+S
Overall residence time	6.324E+02	1.153E+03	2.452E+03	2.036E+03
Reaction residence time	1.974E+03	1.952E+03	2.453E+03	2.358E+03
Advection residence time	9.304E+02	2.817E+03	6.090E+06	1.491E+04

Phase Properties, Compositions, and Transport and Transformation Rates:

Emission Scenario	Emission (kg/h)			Fugacity (Pa)				Concentration (g/m ³)				Amount (kg)				Total Amount (kg)
	E ₁	E ₂	E ₃	f ₁	f ₂	f ₃	f ₄	C ₁	C ₂	C ₃	C ₄	w ₁	w ₂	w ₃	w ₄	
(A)ir Only	1000	0	0	6.116E-06	2.907E-08	7.526E-09	2.736E-08	6.578E-07	1.054E-04	2.804E-02	8.160E-02	6.578E+04	2.107E+04	5.047E+05	4.080E+04	6.324E+05
(W)ater Only	0	1000	0	1.772E-08	5.410E-07	2.180E-11	5.092E-07	1.905E-09	1.961E-03	8.122E-05	1.519E+00	1.905E+02	3.922E+05	1.462E+03	7.593E+05	1.153E+06
(S)oil Only	0	0	1000	6.909E-10	4.359E-10	3.655E-08	4.103E-10	7.430E-11	1.580E-06	1.362E-01	1.224E-03	7.430E+00	3.160E+02	2.451E+06	6.118E+02	2.452E+06
A+W+S	50	250	700	3.107E-07	1.370E-07	2.597E-08	1.290E-07	3.342E-08	4.966E-04	9.674E-02	3.846E-01	3.342E+03	9.933E+04	1.741E+06	1.923E+05	2.036E+06

Emission Scenario	Emission (kg/h)			Loss by Reaction (kg/h)				Loss by Advection (kg/h)			Intermedia Rate of Transport (kg/h)							
	E ₁	E ₂	E ₃	R ₁	R ₂	R ₃	R ₄	A ₁	A ₂	A ₄	T ₁₂	T ₂₁	T ₁₃	T ₃₁	T ₃₂	T ₂₄	T ₄₂	
(A)ir Only	1000	0	0	8.288E+01	2.655E+01	2.06E+02	5.141E+00	6.578E+02	2.107E+01	8.160E-01	5.358E+01	1.557E-01	2.059E+02	2.278E-02	1.647E-01	6.864E+00	9.076E-01	
(W)ater Only	0	1000	0	2.401E-01	4.942E+02	5.96E-01	9.567E+01	1.905E+00	3.922E+02	1.519E+01	1.552E-01	2.897E+00	5.965E-01	6.599E-05	4.770E-04	1.278E+02	1.689E+01	
(S)oil Only	0	0	1000	9.362E-03	3.982E-01	9.99E+02	7.709E-02	7.430E-02	3.160E-01	1.224E-02	6.052E-03	2.334E-03	2.326E-02	1.106E-01	7.999E-01	1.029E-01	1.361E-02	
A+W+S	50	250	700	4.211E+00	1.252E+02	7.10E+02	2.423E+01	3.342E+01	9.933E+01	3.846E+00	2.722E+00	7.337E-01	1.046E+01	7.861E-02	5.863E-01	3.235E+01	4.277E+00	

FIGURE 1.7.19 Level III fugacity calculations for PCP at pH of 5.1.

Chemical name: Pentachlorophenol
 Level III Distribution at data pH of 5.1

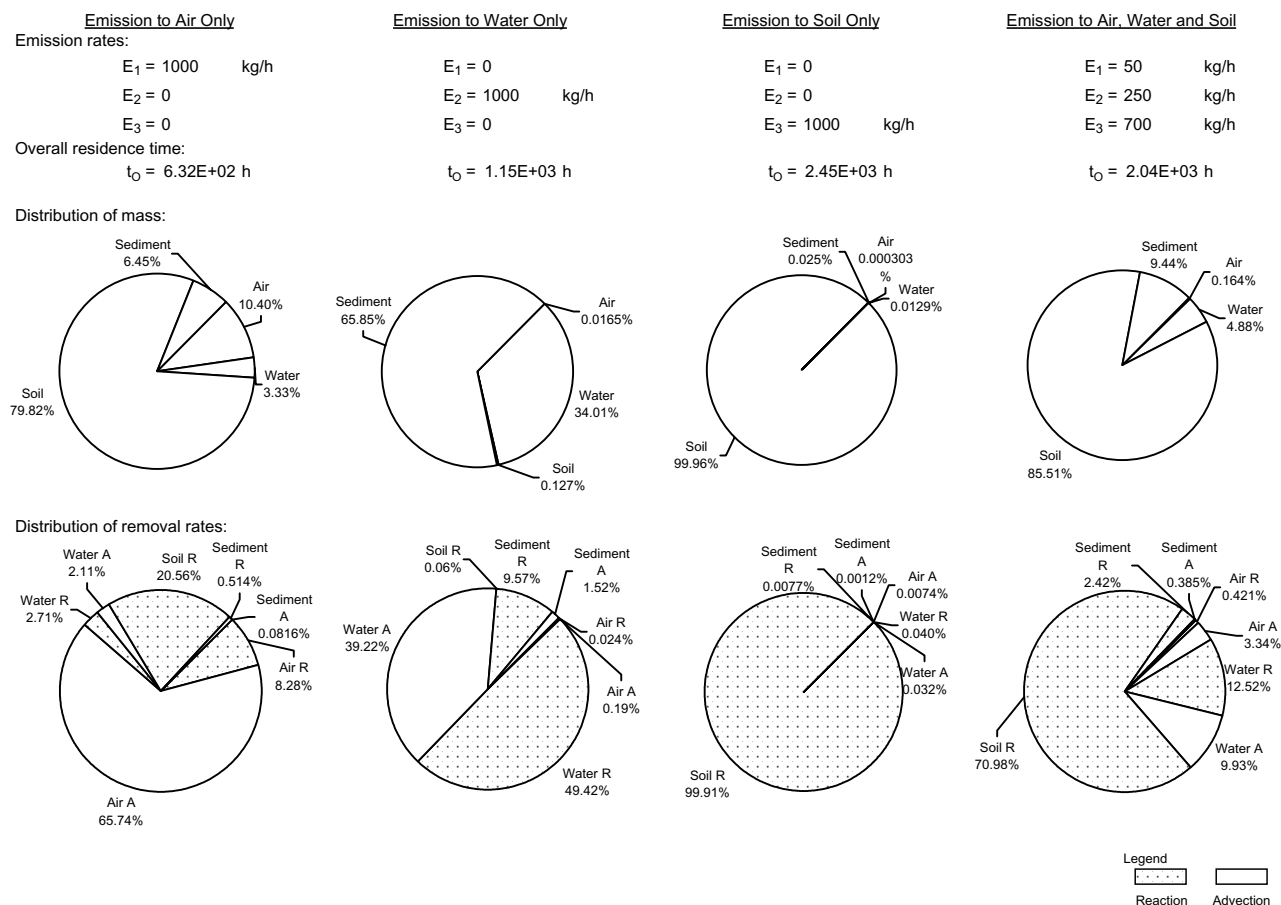


FIGURE 1.7.20 Level III fugacity distributions of PCP for four emission scenarios at pH of 5.1.

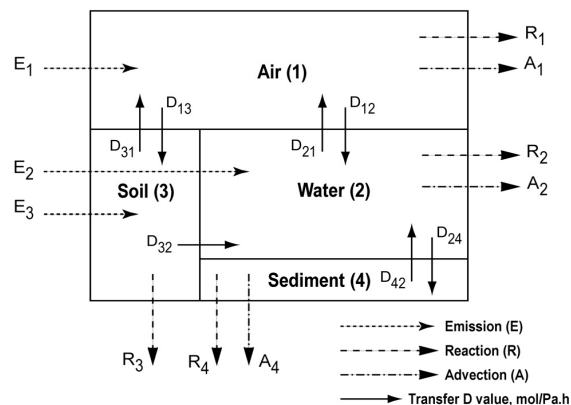
The final scenario is a combination of discharges, 50 kg/h to air, 250 kg/h to water, and 700 kg/h to soil (which are different from the often assumed equal emissions). The concentrations, amounts and transport and transformation rates are merely linearly combined versions of the three initial scenarios. For example, the rate of reaction in air is now 4.21 kg/h. This is 0.05 of the first (air emission) rate of 82.9 kg/h, i.e., 4.14 kg/h, plus 0.25 of the second (water emission) rate of 0.24 kg/h, i.e., 0.06 kg/h and 0.7 of the third (soil emission) rate of 0.0094 kg/h, i.e., 0.0066 kg/h yielding a total of $(4.14 + 0.06 + 0.0066)$ or 4.21 kg/h. It is also apparent that the amount in the air of 3342 kg causing a concentration of 3.342×10^{-8} g/m³ or 33 ng/m³ is attributable to emissions to air (0.05×658 or 33 ng/m³), emissions to water (0.25×1.9 or 0.5 ng/m³) and emissions to soil (0.7×0.0743 or 0.052 μ g/m³). The concentration in water of 4.97×10^{-4} g/m³, or 497 ng/L, is largely attributable to the discharges to water, which alone cause $0.25 \times 1.96 \times 10^{-3}$ g/m³ or 4.9×10^{-4} g/m³ or 490 μ g/m³, or 490 ng/L. Although more is emitted to soil, it contributes only about 1.1 μ g/m³ to the water with air emissions accounting for about 5.27 μ g/m³. Similarly, the prevailing soil concentration is controlled by the rate of discharge to the soil.

In this multimedia discharge scenario the overall residence time is 2036 h, which can be viewed as the sum of 5% of the air emission residence time of 632 h, 25% of the water emission residence time of 1153 h and 70% of the soil emission residence time of 2452 h. The overall amount in the environment of 2.04×10^6 kg is thus largely controlled by the discharges to soil and water.

Finally, it is interesting to note that the fugacities in this final case (in units of μ Pa) are for the four media: 0.31 (air), 0.137 (water), 0.026 (soil) and 0.129 (sediment). The media are fairly close to equilibrium, i.e., within a factor of about 5 of the average value.

At pH 7, Figure 1.7.21, the capacity of water for PCP increases; thus, the water compartment becomes more important as do intermedia transport processes involving water such as wet deposition in dissolved form and run-off

Chemical name: Pentachlorophenol
 Fugacity Level III calculations: (four-compartment model) at environmental pH of 7



Phase Properties and Rates:

Compartment	Bulk Z mol/m ³ .Pa	Half-life h	D Value	
			Reaction mol/Pa.h	Advection mol/Pa.h
Air (1)	4.038E-04	5.500E+02	5.09E+07	4.04E+08
Water (2)	7.052E+02	5.500E+02	1.78E+11	1.41E+11
Soil (3)	1.420E+04	1.700E+03	1.04E+11	-
Sediment (4)	1.175E+04	5.500E+03	7.40E+08	1.18E+08

Residence time (h)	Emission to			
	(A)ir Only	(W)ater Only	(S)oil Only	A+W+S
Overall residence time	2.074E+03	4.588E+02	2.393E+03	1.894E+03
Reaction residence time	2.319E+03	8.218E+02	2.426E+03	2.164E+03
Advection residence time	1.961E+04	1.039E+03	1.805E+05	1.515E+04

Phase Properties, Compositions, and Transport and Transformation Rates:

Emission Scenario	Emission (kg/h)			Fugacity (Pa)				Concentration (g/m ³)				Amount (kg)				Total Amount (kg)
	E ₁	E ₂	E ₃	f ₁	f ₂	f ₃	f ₄	C ₁	C ₂	C ₃	C ₄	w ₁	w ₂	w ₃	w ₄	
(A)ir Only	1000	0	0	4.907E-07	1.408E-09	2.958E-08	1.328E-09	5.278E-08	2.645E-04	1.118E-01	4.158E-03	5.278E+03	5.290E+04	2.013E+06	2.078E+03	2.074E+06
(W)ater Only	0	1000	0	3.097E-11	1.175E-08	1.867E-12	1.108E-08	3.331E-12	2.207E-03	7.060E-06	3.467E-02	3.331E-01	4.413E+05	1.271E+02	1.733E+04	4.588E+05
(S)oil Only	0	0	1000	6.453E-10	3.510E-10	3.497E-08	3.309E-10	6.940E-11	6.592E-05	1.322E-01	1.036E-03	6.940E+00	1.318E+04	2.380E+06	5.178E+02	2.393E+06
A+W+S	50	250	700	2.500E-08	3.253E-09	2.596E-08	3.067E-09	2.688E-09	6.110E-04	9.814E-02	9.600E-03	2.688E+02	1.222E+05	1.766E+06	4.800E+03	1.894E+06

Emission Scenario	Emission (kg/h)			Loss by Reaction (kg/h)				Loss by Advection (kg/h)			Intermedia Rate of Transport (kg/h)						
	E ₁	E ₂	E ₃	R ₁	R ₂	R ₃	R ₄	A ₁	A ₂	A ₄	T ₁₂	T ₂₁	T ₁₃	T ₃₁	T ₃₂	T ₂₄	T ₄₂
(A)ir Only	1000	0	0	6.650E+00	6.665E-02	8.21E+02	2.618E-01	5.278E+01	5.290E+01	4.156E-02	9.470E+01	7.565E-03	8.470E+02	1.112E+00	2.517E+01	5.920E-01	2.886E-01
(W)ater Only	0	1000	0	4.197E-04	5.561E+02	5.18E-02	2.184E+00	3.331E-03	4.413E+02	3.467E-01	5.977E-03	6.312E-02	5.346E-02	7.020E-05	1.589E-03	4.939E+00	2.408E+00
(S)oil Only	0	0	1000	8.745E-03	1.661E+01	9.70E+02	6.525E-02	6.940E-02	1.318E+01	1.036E-02	1.245E-01	1.885E-03	1.114E+00	1.315E+00	2.975E+01	1.475E-01	7.193E-02
A+W+S	50	250	700	3.387E-01	1.540E+02	7.20E+02	6.048E-01	2.688E+00	1.222E+02	9.600E-02	4.823E+00	1.748E-02	4.314E+01	9.758E-01	2.208E+01	1.368E+00	6.667E-01

FIGURE 1.7.21 Level III fugacity calculations for PCP at pH of 7.

Chemical name: Pentachlorophenol
 Level III Distribution at environmental pH of 7

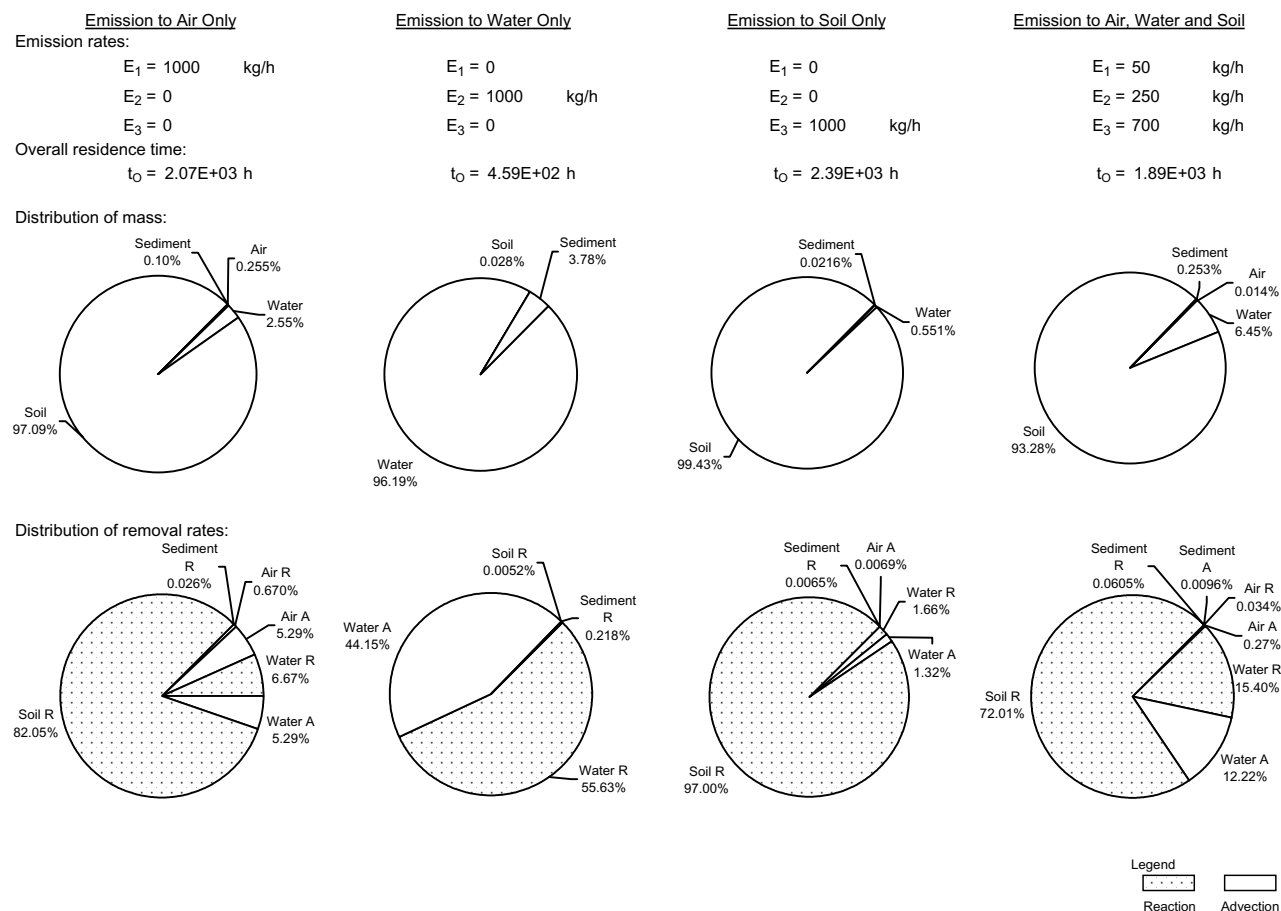


FIGURE 1.7.22 Level III fugacity distributions of PCP for four emission scenarios at pH of 7.

from soil to water. The net effect is that if discharged to air, the amounts transferred to soil and water increase as does the overall residence time. If discharged to water, there is less water to sediment transfer because of the reduced apparent hydrophobicity, and the residence time decreases. If discharged to soil, there is little effect of the pH increase because the PCP tends to remain there.

Similar diagrams could be prepared for other phenolic compounds at a range of pH values. The results suggest that the same broad patterns of behavior apply as for PCP but the residence times are generally shorter because of reduced hydrophobicity and more rapid reactions. The lower chlorinated phenols are relatively short-lived and are not subject to appreciable intermedia transport, i.e., when discharged to a medium they tend to remain there until degraded or advected. The longest persistence occurs when the chemical is present in soils.

Such simulations suggest that because of their relatively high water solubility which in combination with low vapor pressure causes low air-water partition coefficients, the phenols tend to remain in water or in soil and show little tendency to evaporate. Their environmental fate tends to be dominated by reaction in soil and water, and for the more sorptive species, in sediments. Their half-lives are relatively short, because of their susceptibility to degradation.

It is believed that examining these three behavior profiles, and their combination in the fourth, illustrate and explain the environmental fate characteristics of this and other chemicals. Important intermedia transport processes and levels in various media that arise from discharges into other media become clear. It is believed that the broad characteristics of environmental fate as described in the generic environment are generally applicable to other environments, albeit with differences attributable to changes in volumes, temperature, flow rates and compartment compositions.

1.8 REFERENCES

- Abernethy, S., Mackay, D., McCarty, L. S. (1988) Volume fraction correlation for narcosis in aquatic organisms: The key role of partitioning. *Environ. Toxicol. Chem.* 7, 469–481.
- Abramowitz, R., Yalkowsky, S. H. (1990) Estimation of aqueous solubility and melting point of PCB congeners. *Chemosphere* 21, 1221–1229.
- Alaee, M., Whittall, R.M., Strachan, W.M.J. (1996) The effect of water temperature and composition on Henry's law constant for various PAH's. *Chemosphere* 32, 1153–1164.
- Almgren, M., Grieser, F., Powell, J. R., Thomas, J. K. (1979) A correlation between the solubility of aromatic hydrocarbons in water and micellar solutions, with their normal boiling points. *J. Chem. Eng. Data* 24, 285–287.
- Al-Sahhaf, T. A. (1989) Prediction of the solubility of hydrocarbons in water using UNIFAC. *J. Environ. Sci. Health A24*, 49–56.
- Altshuller, A. P. (1980) Lifetimes of organic molecules in the troposphere and lower stratosphere. *Adv. Environ. Sci. Technol.* 10, 181–219.
- Altshuller, A. P. (1991) Chemical reactions and transport of alkanes and their products in the troposphere. *J. Atmos. Chem.* 12, 19–61.
- Ambrose, D. (1981) Reference value of vapor pressure. The vapor pressures of benzene and hexafluorobenzene. *J. Chem. Thermodyn.* 13, 1161–1167.
- Ambrose, D., Lawrenson, L. J., Sprake, C. H. S. (1975) The vapour pressure of naphthalene. *J. Chem. Thermodyn.* 7, 1173–1176.
- Amidon, G. L., Yalkowsky, S. H., Anik, S. T., Leung, S. (1975) Solubility of nonelectrolytes in polar solvents. V. Estimation of the solubility of aliphatic monofunctional compounds in water using a molecular surface area approach. *J. Phys. Chem.* 9, 2239–2245.
- Amidon, G. L., Anik, S. T. (1981) Application of the surface area approach to the correlation and estimation of aqueous solubility and vapor pressure. Alkyl aromatic hydrocarbons. *J. Chem. Eng. Data* 26, 28–33.
- Amidon, G. L., Williams, N. A. (1982) A solubility equation for non-electrolytes in water. *Intl. J. Pharm.* 11, 156–249.
- Anderson, E., Veith, G. D., Weininger, D. (1987) *SMILES: A Line Notation and Computerized Interpreter for Chemical Structures*. EPA Environmental Research Brief, U.S. EPA, EPA/600/M-87/021.
- Andren, A. W., Doucette, W. J., Dickhut, R. M. (1987) Methods for estimating solubilities of hydrophobic organic compounds: Environmental modeling efforts. In: *Sources and Fates of Aquatic Pollutants*. Hites, R. A., Eisenreich, S. J., Eds., pp. 3–26, Advances in Chemistry Series 216, American Chemical Society, Washington, D.C.
- Arbuckle, W. B. (1983) Estimating activity coefficients for use in calculating environmental parameters. *Environ. Sci. Technol.* 17, 537–542.
- Arbuckle, W. B. (1986) Using UNIFAC to calculate aqueous solubilities. *Environ. Sci. Technol.* 20, 1060–1064.
- Arcand, Y., Hawari, J., Guiot, S. R. (1995) Solubility of pentachlorophenol in aqueous solutions: the pH effect. *Water Res.* 29, 131–136.
- Arnold, D.S., Plank, C.A., Erickson, E.E., Pike, F.P. (1958) Solubility of benzene in water. *Chem. Eng. Data Ser.* 3, 253–256.
- Ashworth, R. A., Howe, G. B., Mullins, M. E., Roger, T. N. (1988) Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Hazard. Materials* 18, 25–36.
- Atkinson, R. (1985) Kinetics and mechanisms of the gas phase reaction of hydroxyl radicals with organic compounds under atmospheric conditions. *Chem. Rev.* 85, 69–201.
- Atkinson, R. (1987) A structure-activity relationship for the estimation of the rate constants for the gas phase reactions of OH radicals with organic compounds. *Int. J. Chem. Kinetics* 19, 790–828.
- Atkinson, R. (1989) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. *J. Phys. Chem. Ref. Data Monograph No. 1*, 1–246.
- Atkinson, R. (1990) Gas-phase tropospheric chemistry of organic compounds, a review. *Atmos. Environ.* 24A, 1–41.
- Atkinson, R. (1991) Kinetics and mechanisms of the gas-phase reactions of the NO₃ radicals with organic compounds. *J. Phys. Chem. Data* 20, 450–507.
- Atkinson, R., Carter, W. L. (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.* 84, 437–470.
- Augustijn-Beckers, P. W. M., Hornsby, A. G., Wauchope, R. D. (1994) The SCS/ARS/CES pesticide properties database for environmental decision making. II. Additional compounds. *Rev. Environ. Contam. Toxicol.* 137, 1–82.
- Bahnick, D. A., Doucette, W. J. (1988) Use of molecular connectivity indices to estimate soil sorption coefficients for organic chemicals. *Chemosphere* 17, 1703–1715.
- Balson, E. W. (1947) Studies in vapour pressure measurement. Part III. An effusion manometer sensitive to 5×10^{-6} millimetres of mercury: vapour pressure of D.D.T. and other slightly volatile substances. *Trans. Farad. Soc.* 43, 54–60.
- Banerjee, S. (1985) Calculation of water solubility of organic compounds with UNIFAC-derived parameters. *Environ. Sci. Technol.* 19, 369–370.
- Banerjee, S., Howard, P. H. (1988) Improved estimation of solubility and partitioning through correction of UNIFAC-derived activity coefficients. *Environ. Sci. Technol.* 22, 839–841.
- Banerjee, S., Howard, P. H., Lande, S. S. (1990) General structure-vapor pressure relationships for organics. *Chemosphere* 21, 1173–1180.
- Banerjee, S., Yalkowsky, S. H., Valvani, S. C. (1980) Water solubility and octanol/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlation. *Environ. Sci. Technol.* 14, 1227–1229.
- Barton, A.F.M. (1984) IUPAC Solubility Data Series Vol. 15. *Alcohols With Water*. Pergamon Press Inc., Oxford, England, U.K.

- Betterton, E. A., Hoffmann, M. R. (1988) Henry's law constants of some environmentally important aldehydes. *Environ. Sci. Technol.* 22, 1415–1418.
- Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E. (2000) Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.* 34, 699–703.
- Bidleman, T. F. (1984) Estimation of vapor pressures for nonpolar organic compounds by capillary gas chromatography. *Anal. Chem.* 56, 2490–2496.
- Boethling, R.S., Mackay, D. Eds. (2000) Handbook of Property Estimation Methods: Environmental and Health Sciences. CRC Press, Boca Raton, FL.
- Bohon, R. L., Claussen, W. F. (1951) The solubility of aromatic hydrocarbons in water. *J. Am. Chem. Soc.* 73, 1571–1576.
- Bondi, A. (1964) van der Waals volumes and radii. *J. Phys. Chem.* 68, 441–451.
- Booth, H. S., Everson, H. E. (1948) Hydrotropic solubilities: solubilities in 40 percent sodium xylenesulfonate. *Ind. Eng. Chem.* 40, 1491–1493.
- Boublik, T., Fried, V., Hala, E. (1973) *The Vapor Pressure of Pure Substances*, Elsevier, Amsterdam, The Netherlands.
- Boublik, T., Fried, V., Hala, E. (1984) *The Vapor Pressure of Pure Substances*, 2nd revised Edition, Elsevier, Amsterdam, The Netherlands.
- Bowman, B. T., Sans, W. W. (1983) Determination of octanol-water partitioning coefficient (K_{OW}) of 61 organophosphorus and carbamate insecticides and their relationship to respective water solubility (S) values. *J. Environ. Sci. Health B18*, 667–683.
- Bradley, R. S., Cleasby, T. G. (1953) The vapour pressure and lattice energy of some aromatic ring compounds. *J. Chem. Soc.* 1953, 1690–1692.
- Breton, R., Schuurmann, G., Purdy, R. (2003) Proceedings 10th International Quantitative Structure Activity Relationships workshop. *QSAR and Combinatorial Science* 22, 1–409.
- Briggs, G. G. (1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *J. Agric. Food Chem.* 29, 1050–1059.
- Brodsky, J., Ballschmiter, K. (1988) Reversed phase liquid chromatography of PCBs as a basis for the calculation of water solubility and log K_{OW} for polychlorobiphenyls. *Fresenius Z. Anal. Chem.* 331, 295–301.
- Bruggeman, W. A., van der Steen, J., Hutzinger, O. (1982) Reversed-phase thin-layer chromatography of polynuclear aromatic hydrocarbons and chlorinated biphenyls. Relationship with hydrophobicity as measured by aqueous solubility and octanol-water partition coefficient. *J. Chromatogr.* 238, 335–346.
- Budavari, S., Editor (1989) *The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals*. 11th Edition, Merck & Co., Rahway, New Jersey.
- Burkhard, L.P. (1984) Physical-Chemical Properties of the Polychlorinated Biphenyls: Measurement, Estimation, and Application to Environmental Systems. Ph.D. Thesis, University of Wisconsin-Madison, Wisconsin.
- Burkhard, L. P., Andren, A. W., Armstrong, D. E. (1985a) Estimation of vapor pressures for polychlorinated biphenyls: A comparison of eleven predictive methods. *Environ. Sci. Technol.* 19, 500–507.
- Burkhard, L. P., Armstrong, D. E., Andren, A. W. (1985b) Henry's law constants for polychlorinated biphenyls. *Environ. Sci. Technol.* 19, 590–595.
- Burkhard, L. P., Kuehl, D. W., Veith G. D. (1985c) Evaluation of reversed phase liquid chromatograph/mass spectrometry for estimation of n-octanol/water partition coefficients of organic chemicals. *Chemosphere* 14, 1551–1560.
- Burnett, M. G. (1963) Determination of partition coefficients in infinite dilution by the gas chromatographic analysis of the vapor above dilute solutions. *Anal. Chem.* 35, 1567–1570.
- Butler, J. A. V., Ramchandani, C. N., Thomson, D. W. (1935) The solubility of non-electrolytes. Part I. The free energy of hydration of some aliphatic alcohols. *J. Chem. Soc.* 280–285.
- Buttery, R. B., Ling, L. C., Guadagni, D. G. (1969) Volatilities of aldehydes, ketones, and esters in dilute water solution. *J. Agric. Food Chem.* 17, 385–389.
- Buxton, G. V., Greenstock, G. L., Helman, W. P., Ross, A. B. (1988) Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solutions. *J. Phys. Chem. Ref. Data* 17, 513–886.
- Chao, J., Lin, C.T., Chung, T.H. (1983) Vapor pressure of coal chemicals. *J. Phys. Chem. Ref. Data* 12, 1033–1063.
- Chickos, J.S., Acree, W.E., Jr., Liebman, J.F. (1999) Estimating solid-liquid phase change enthalpies and entropies. *J. Phys. Chem. Ref. Data* 28, 1535–1673.
- Chiou, C. T. (1985) Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol.* 19, 57–62.
- Chiou, C. T., Freed, V. H., Schmedding, D. W. (1977) Partition coefficient and bioaccumulation of selected organic chemicals. *Environ. Sci. Technol.* 11, 475–478.
- Chiou, C. T., Schmedding, D. W., Manes, M. (1982) Partitioning of organic compounds in octanol-water system. *Environ. Sci. Technol.* 16, 4–10.
- Choi, J., Amoine, S. (1974) Adsorption of pentachlorophenol by soils. *Soil Sci. Plant Nutr.* 20, 135–144.
- Clark, E.C.W., Glew, D.N. (1966) Evaluation of thermodynamic functions from equilibrium constants. *Trans. Farad. Soc.* 62, 539–547.
- Cole, J.G., Mackay, D. (2000) Correlating environmental partitioning properties of organic compounds: The “three solubility approach”. *Environ. Toxicol. Chem.* 19, 265–270.
- Davies, R. P., Dobbs, A. J. (1984) The prediction of bioconcentration in fish. *Water Res.* 18, 1253–1262.

- Davis, W. W., Krahle, M. E., Clowes, G. H. (1942) Solubility of carcinogenic and related hydrocarbons in water *J. Am. Chem. Soc.* 64, 108–110.
- Davis, W. W., Parke, Jr., T. V. (1942) A nephelometric method for determination of solubilities of extremely low order. *J. Am. Chem. Soc.* 64, 101–107.
- Dean, J. D., Ed. (1979) *Lange's Handbook of Chemistry*. 12th Edition, McGraw-Hill, New York.
- Dean, J. D., Ed. (1985) *Lange's Handbook of Chemistry*. 13th Edition, McGraw-Hill, New York.
- Dean, J. D., Ed. (1992) *Lange's Handbook of Chemistry*. 14th Edition, McGraw-Hill, New York.
- Dearden, J. C. (1990) Physico-chemical descriptors. In: *Practical Applications of Quantitative Structure-Activity Relationships (QSAR) in Environmental Chemistry and Toxicology*. Karcher, W. and Devillers, J., Eds., pp. 25–60. Kluwer Academic Publisher, Dordrecht, The Netherlands.
- De Bruijn, J., Busser, G., Seinen, W., Hermens, J. (1989) Determination of octanol/water partition coefficient for hydrophobic organic chemicals with the “slow-stirring” method. *Environ. Toxicol. Chem.* 8, 499–512.
- De Bruijn, J., Hermens, J. (1990) Relationships between octanol/water partition coefficients and total molecular surface area and total molecular volume of hydrophobic organic chemicals. *Quant. Struct.-Act. Relat.* 9, 11–21.
- De Kruif, C. G. (1980) Enthalpies of sublimation and vapour pressures of 11 polycyclic hydrocarbons. *J. Chem. Thermodyn.* 12, 243–248.
- Dobbs, A. J., Grant, C. (1980) Pesticide volatilization rate: a new measurement of the vapor pressure of pentachlorophenol at room temperature. *Pestic. Sci.* 11, 29–32.
- Dobbs, A. J., Cull, M. R. (1982) Volatilization of chemical relative loss rates and the estimation of vapor pressures. *Environ. Pollut. Ser.B.*, 3, 289–298.
- Doucette, W. J., Andren, A. W. (1987) Correlation of octanol/water partition coefficients and total molecular surface area for highly hydrophobic aromatic compounds. *Environ. Sci. Technol.* 21, 521–524.
- Doucette, W. J., Andren, A. W. (1988a) Aqueous solubility of selected biphenyl, furan, and dioxin congeners. *Chemosphere* 17, 243–252.
- Doucette, W. J., Andren, A. W. (1988b) Estimation of octanol/water partition coefficients: Evaluation of six methods for highly hydrophobic aromatic hydrocarbons. *Chemosphere* 17, 345–359.
- Dreisbach, R. R. (1955) *Physical Properties of Chemical Compounds*. No. 15 of the Adv. in Chemistry Series, American Chemical Society, Washington, D.C.
- Dreisbach, R. R. (1959) *Physical Properties of Chemical Compounds-II*. No. 22, Adv. in Chemistry Series, American Chemical Society, Washington, D.C.
- Dreisbach, R. R. (1961) *Physical Properties of Chemical Compounds-III*. No. 29, Adv. in Chemistry Series, American Chemical Society, Washington, D.C.
- Dunnivant, F. M., Coate, J. T., Elzerman, A. W. (1988) Experimentally determined Henry's law constants for 17 polychlorobiphenyl congeners. *Environ. Sci. Technol.* 22, 448–453.
- Dunnivant, F. M., Elzerman, A. W., Jurs, P. C., Hansen, M. N. (1992) Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 26, 1567–1573.
- Ellgehausen, H., D'Hondt, C., Fuerer, R. (1981) Reversed-phase chromatography as a general method for determining octan-1-ol/water partition coefficients. *Pestic. Sci.* 12, 219–227.
- Ellington, J. J. (1989) *Hydrolysis Rate Constants for Enhancing Property-Reactivity Relationships*. U.S. EPA, EPA/600/3-89/063, Athens, GA.
- Ellington, J. J., Stancil, Jr., F. E., Payne, W. D. (1987a) *Measurements of Hydrolysis Rate Constant for Evaluation of Hazardous Land Disposal: Volume I. Data on 32 Chemicals* U.S. EPA, EPA/600/3-86/043, Athens, GA.
- Ellington, J. J., Stancil, Jr., F. E., Payne, W. D., Trusty, C. D. (1987b) *Measurements of Hydrolysis Rate Constant for Evaluation of Hazardous Land Disposal: Volume II. Data on 54 Chemicals*. U.S. EPA, EPA/600/3-88/028, Athens, GA.
- Ellington, J. J., Stancil, Jr., F. E., Payne, W. D., Trusty, C. D. (1988) *Interim Protocol for Measurement Hydrolysis Rate Constants in Aqueous Solutions*. USEPA, EPA/600/3-88/014, Athens, GA.
- Fendinger, N. J., Glotfelty, D. E. (1988) A laboratory method for the experimental determination of air-water Henry's law constants for several pesticides. *Environ. Sci. Technol.* 22, 1289–1293.
- Fendinger, N. J., Glotfelty, D. E. (1989) A comparison of two experimental techniques for determining air-water Henry's laws constants. *Environ. Sci. Technol.* 23, 1528–1531.
- Fendinger, N. J., Glotfelty, D. E. (1990) Henry's law constants for selected pesticides, PAHs and PCBs. *Environ. Toxicol. Chem.* 9, 731–735.
- Finizio, A., Di Guardo, A., Vighi, M. (1994) Improved RP-HPLC determination of K_{ow} for some chloroaromatic chemicals using molecular connectivity indices. *SAR & QSAR in Environ. Res.* 2, 249–260.
- Finizio, A., Mackay, D., Bidleman, T.F., Harner, T. (1997) Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols. *Atmos. Environ.* 31, 2289–2296.
- Foreman, W. T., Bidleman, T. F. (1985) Vapor pressure estimates of individual polychlorinated biphenyls and commercial fluids using gas chromatographic retention data. *J. Chromatogr.* 330, 203–216.
- Fredenslund, A., Jones, R. L., Prausnitz, J. M. (1975) Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* 21, 1086–1099.

- Fujita, T., Iwasa, J., Hansch, C. (1964) A new substituent constant, " π " derived from partition coefficients. *J. Am. Chem. Soc.* 86, 5175–5180.
- Garst, J.E. (1984) Accurate, wide-range, automated, high-performance chromatographic method for the estimation of octanol/water partition coefficients. II: Equilibrium in partition coefficient measurements, additivity of substituent constants, and correlation of biological data. *J. Pharm. Sci.* 73, 1623–1629.
- Garten, C. T., Trabalka, J. R. (1983) Evaluation of models for predicting terrestrial food chain behavior of xenobiotics. *Environ. Sci. Technol.* 17, 590–595.
- Gerstl, Z., Helling, C. S. (1984) Evaluation of molecular connectivity as a predictive method for the adsorption of pesticides by soils. *J. Environ. Sci. Health B22*, 55–69.
- Glew, D.N., Roberson, R.E. (1956) The spectrophotometric determination of the solubility of cumene in water by a kinetic method. *J. Phys. Chem.* 60, 332–337.
- Gmehling, J., Rasmussen, P., Fredenslund, A. (1982) Vapor-liquid equilibria by UNIFAC group contribution. Revision and extension. 2 *Ind. Eng. Chem. Process Des. Dev.* 21, 118–127.
- Gossett, R. (1987) Measurement of Henry's law constants for C_1 and C_2 chlorinated hydrocarbons. *Environ. Sci. Technol.* 21, 202–208.
- Gross, P. M., Saylor, J. H. (1931) The solubilities of certain slightly soluble organic compounds in water. *J. Am. Chem. Soc.* 1931, 1744–1751.
- Gückel, W., Rittig, R., Synnatschke, G. (1974) A method for determining the volatility of active ingredients used in plant protection. II. Application to formulated products. *Pestic. Sci.* 5, 393–400.
- Gückel, W., Kästel, R., Lawerenz, J., Synnatschke, G. (1982) A method for determining the volatility of active ingredients used in plant protection. Part III: The temperature relationship between vapour pressure and evaporation rate. *Pestic. Sci.* 13, 161–168.
- Hafkenschied, T. L., Tomlinson, E. (1981) Estimation of aqueous solubilities of organic non-electrolytes using liquid chromatographic retention data. *J. Chromatogr.* 218, 409–425.
- Hamaker, J. W., Kerlinger, H. O. (1969) Vapor pressures of pesticides. *Adv. Chem. Ser.* 86, 39–54.
- Hamilton, D. J. (1980) Gas chromatographic measurement of volatility of herbicide esters. *J. Chromatogr.* 195, 75–83.
- Hansch, C., Leo, A. (1979) *Substituent Constants for Correlation Analysis in Chemistry and Biology*. Wiley-Interscience, New York.
- Hansch, C., Leo, A. J., Hoekman, D. (1995) *Exploring QSAR, Hydrophobic, Electronic, and Steric Constants*. ACS Professional Reference Book, American Chemical Society, Washington, D.C.
- Hansch, C., Quinlan, J. E., Lawrence, G. L. (1968) The linear-free energy relationship between partition coefficient and aqueous solubility of organic liquids. *J. Org. Chem.* 33, 347–350.
- Hansen, H. K., Schiller, M., Gmehling, J. (1991) Vapor-liquid equilibria by UNIFAC group contribution. 5. Revision and extension. *Ind. Eng. Chem. Res.* 30, 2362–2356.
- Harner, T. and Bidleman, T.F. (1996) Measurements of octanol-air partition coefficients for polychlorinated biphenyls. *J. Chem. Eng. Data* 41, 895–899.
- Harner, T. and Mackay, D. (1995) Measurement of octanol-air partition coefficients for chlorobenzenes, PCBs, and DDT. *Environ. Sci. Technol.* 29, 1599–1606.
- Hartley, G. S., Gram-Bryce, I. J. (1980) *Physical Principles of Pesticide Behavior, the Dynamics of Applied Pesticides in the Local Environments in Relation to Biological Response*. Vol. 2, Academic Press, London.
- Hartley, D., Kidd, H., Eds., (1987) *The Agrochemical Handbook*, 2nd ed., The Royal Society of Chemistry, The University of Nottingham, England.
- Hawker, D. W. (1989) The relationship between octan-1-ol/water partition coefficient and aqueous solubility in terms of solvatochromic parameters. *Chemosphere* 19, 1586–1593.
- Hawker, D. W. (1990a) Vapor pressures and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 23, 1250–1253.
- Hawker, D. W. (1990b) Description of fish bioconcentration factors in terms of solvatochromic parameters. *Chemosphere* 20, 267–477.
- Hawker, D. W., Connell, D. W. (1988) Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 22, 382–387.
- Heidman, J. L., Tsonopoulos, C., Brady, C. J., Wilson, G. M. (1985) High-temperature mutual solubilities of hydrocarbons and water. *AIChE J.* 31, 376–384.
- Hermann, R. B. (1971) Theory of hydrophobic bonding. II. The correlation of hydrocarbon solubility in water with solvent cavity surface area. *J. Phys. Chem.* 76, 2754–2758.
- Hermens, J. L. M., Opperhuizen, A., Eds. (1991) *QSAR in Environmental Toxicology IV*. Elsevier, Amsterdam, The Netherlands. Also published in *Sci. Total Environ.* vol. 109/110.
- Hildebrand, J. H., Prausnitz, J. M., Scott, R. L. (1970) *Regular and Related Solutions. The Solubility of Gases, Liquids, and Solids*. Van Nostrand Reinhold. Co., New York.
- Hinckley, D. A., Bidleman, T.F., Foreman, W.T. (1990) Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data. *J. Chem. Eng. Data* 35, 232–237.
- Hine, J., Mookerjee, P. K. (1975) The intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions. *J. Org. Chem.* 40, 292–298.
- Hippelein, M. and McLachlan, M.S. (1998) Soil air partitioning of semivolatile organic chemicals. 1. Method development and influence of physical chemical properties. *Environ. Sci. Technol.* 32, 310–316.

- Hollifield, H. C. (1979) Rapid nephelometric estimate of water solubility of highly insoluble organic chemicals of environmental interest. *Bull. Environ. Contam. Toxicol.* 23, 579–586.
- Hornsby, A. G., Wauchope, R. D., Herner, A. E. (1996) *Pesticide Properties in the Environment*. Springer-Verlag, New York.
- Horvath, A. L. (1982) *Halogenated Hydrocarbons, Solubility - Miscibility with Water*. Marcel Dekker, New York.
- Horvath, A. L., Getzen, F. W. Eds. (1985) IUPAC Solubility Data Series: Vol. 20. *Halogenated Benzenes, Toluenes and Phenols with Water*. Pergamon Press, Oxford.
- Howard, P. H., Ed. (1989) *Handbook of Fate and Exposure Data for Organic Chemicals. Vol. I. Large Production and Priority Pollutants*. Lewis Publishers, Chelsea, MI.
- Howard, P. H., Ed. (1990) *Handbook of Fate and Exposure Data for Organic Chemicals. Vol. II. Solvents*. Lewis Publishers, Chelsea, MI.
- Howard, P. H., Ed. (1991) *Handbook of Fate and Exposure Data for Organic Chemicals. Vol. III. Pesticides*. Lewis Publishers, Chelsea, MI.
- Howard, P. H., Ed. (1993) *Handbook of Fate and Exposure Data for Organic Chemicals. Vol. IV. Solvents 2*. Lewis Publishers, Chelsea, MI.
- Howard, P. H., Boethling, R. S., Jarvis, W. F., Meylan, W. M., Michalenko, E. M. (1991) *Handbook of Environmental Degradation Rates*. Lewis Publishers, Chelsea, MI.
- Huang, G. -L., Xiao, H., Chi, J., Shiu, W. -Y., Mackay, D. (2000) Effects of pH on the aqueous solubility of selected chlorinated phenols. *J. Chem. Eng. Data* 45, 411–414.
- Hussam, A., Carr, P. W. (1985) A study of a rapid and precise methodology for the measurement of vapor-liquid equilibria by headspace gas chromatography. *Anal. Chem.* 57, 793–801.
- Irmann, F. (1965) Eine einfache korrelation zwischen wasserlöslichkeit und struktur von kohlenwasserstoffen und halogenkohlenwasserstoffen. *Chem.-Ing.-Techn.* 37, 789–798.
- Isnard, P., Lambert, S. (1988) Estimating bioconcentration factors for octanol-water partition coefficient and aqueous solubility. *Chemosphere* 17, 21–34.
- Isnard, P., Lambert, S. (1989) Aqueous solubility/*n*-octanol-water partition coefficient correlations. *Chemosphere* 18, 1837–1853.
- IUPAC Solubility Data Series (1984) Vol. 15: *Alcohols with Water*. Barton, A. F. M., Ed., Pergamon Press, Oxford, England.
- IUPAC Solubility Data Series (1985) Vol. 20: *Halogenated Benzenes, Toluenes and Phenols with Water*. Horvath, A. L., Getzen, F. W., Eds., Pergamon Press, Oxford, England.
- IUPAC Solubility Data Series (1989a) Vol. 37: *Hydrocarbons ($C_5 - C_7$) with Water and Seawater*. Shaw, D. G., Ed., Pergamon Press, Oxford, England.
- IUPAC Solubility Data Series (1989b) Vol. 38: *Hydrocarbons ($C_8 - C_{36}$) with Water and Seawater*. Shaw, D. G., Ed., Pergamon Press, Oxford, England.
- Iwase, K., Komatsu, K., Hirono, S., Nakagawa, S., Moriguchi, I. (1985) Estimation of hydro-phobicity based on the solvent-accessible surface area of molecules. *Chem. Pharm. Bull.* 33, 2114–2121.
- Jafvert, C. T., Westall, J. C., Grieder, E., Schwarzenbach, P. (1990) Distribution of hydrophobic ionogenic organic compounds between octanol and water: organic acids. *Environ. Sci. Technol.* 24, 1795–1803.
- Jaoui, M., Luszczek, M., Rogalski, M. (1999) Liquid-liquid and liquid-solid equilibria of systems containing water and selected chlorophenols. *J. Chem. Eng. Data* 44, 1269–1272.
- Jensen, T., Fredenslund, A., Rasmussen, P. (1981) Pure-compound vapor pressures using UNIFAC group contribution. *Ind. Eng. Chem. Fundam.* 20, 239–246.
- Johnson, C. A., Westall, J. C. (1990) Effect of pH and KCl concentration on the octanol-water distribution of methylanilines. *Environ. Sci. Technol.* 24, 1869–1875.
- Jönsson, J. A., Vejrosta, J., Novak, J. (1982) Air/water partition coefficients for normal alkanes (*n*-pentane to *n*-nonane). *Fluid Phase Equil.* 9, 279–286.
- Jury, W. A., Spencer, W. F., Farmer, W. J. (1983) Behavior assessment model for trace organics in soil: I. Model description. *J. Environ. Qual.* 12, 558–566.
- Jury, W. A., Farmer, W. J., Spencer, W. F. (1984a) Behavior assessment model for trace organics in soil: II. Chemical classification and parameter sensitivity. *J. Environ. Qual.* 13, 567–572.
- Jury, W. A., Farmer, W. J., Spencer, W. F. (1984b) Behavior assessment model for trace organics in soil: III. Application of screening model. *J. Environ. Qual.* 13, 573–579.
- Jury, W. A., Spencer, W. F., Farmer, W. J. (1984c) Behavior assessment model for trace organics in soil: IV. Review of experimental evidence. *J. Environ. Qual.* 13, 580–587.
- Kabadi, V. N., Danner, R. P. (1979) Nomograph solves for solubilities of hydrocarbons in water. *Hydrocarbon Processing*, 68, 245–246.
- Kaiser, K. L. E., Valdmánis, I. (1982) Apparent octanol/water partition coefficients of pentachlorophenol as a function of pH. *Can. J. Chem.* 61, 2104–2106.
- Kamlet, M. J., Doherty, R. M., Veith, G. D., Taft, R. W., Abraham, M. H. (1986) Solubility properties in polymers and biological media. 7. An analysis toxicant properties that influence inhibition of bioluminescence in *Photobacterium phosphoreum* (the Microtox test). *Environ. Sci. Technol.* 20, 690–695.
- Kamlet, M. J., Doherty, R. M., Abraham, M. H., Carr, P. W., Doherty, R. F., Raft, R. W. (1987) Linear solvation energy relationships. Important differences between aqueous solubility relationships for aliphatic and aromatic solutes. *J. Phys. Chem.* 91, 1996–2004.

- Kamlet, M. J., Doherty, R. M., Carr, P. W., Mackay, D., Abraham, M. H., Taft, R. W. (1988) Linear solvation energy relationships. 44. Parameter estimation rules that allow accurate prediction of octanol/water partition coefficients and other solubility and toxicity properties of polychlorinated biphenyls and polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 22, 503–509.
- Karcher, W., Devillers, J., Eds., (1990) *Practical Applications of Quantitative-Structure-Activity Relationships (QSAR) in Environmental Chemistry and Toxicology*. Kluwer Academic Publisher, Dordrecht, The Netherlands.
- Karger, B. L., Castells, R. C., Sewell, P. A., Hartkopf, A. (1971a) Study of the adsorption of insoluble and sparingly soluble vapors at the gas-liquid interface of water by gas chromatography. *J. Phys. Chem.* 75, 3870–3879.
- Karger, B. L., Sewell, P. A., Castells, R. C., Hartkopf, A. (1971b) Gas chromatographic study of the adsorption of insoluble vapors on water. *J. Colloid Interface Sci.* 35(2), 328–339.
- Karickhoff, S. W. (1981) Semiempirical estimation of sorption of hydrophobic pollutants on natural sediments and soil. *Chemosphere* 10, 833–846.
- Karickhoff, S. W., Brown, D. S., Scott, T. A. (1979) Sorption of hydrophobic pollutants on natural water sediments. *Water Res.* 13, 241–248.
- Kenaga, E. E. (1980) Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. *Ecotox. Environ. Saf.* 4, 26–38.
- Kenaga, E. E., Goring, C. A. I. (1980) Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota. In: *Aquatic Toxicology*. ASTM STP 707, Eaton, J. G., Parrish, P. R., Hendrick, A. C., Eds., pp. 78–115, Am. Soc. for Testing and Materials, Philadelphia, PA.
- Kier, L. B., Hall, L. H. (1976) Molar properties and molecular connectivity. In: *Molecular Connectivity in Chemistry and Drug Design*. Medicinal Chem. Vol. 14, pp. 123–167, Academic Press, New York.
- Kier, L. B., Hall, L. H. (1986) *Molecular Connectivity in Structure-Activity Analysis*. Wiley, New York.
- Kikic, I., Alesse, P., Rasmussen, P., Fredenslund, A. (1980) On the combinatorial part of the UNIFAC and UNIQUAC models. *Can. J. Chem. Eng.* 58, 253–258.
- Kim, Y.-H., Woodrow, J. E., Seiber, J. N. (1984) Evaluation of a gas chromatographic method for calculating vapor pressures with organophosphorus pesticides. *J. Chromatogr.* 314, 37–53.
- Klöpffer, W. (1991) Photochemistry in environmental research: Its role in abiotic degradation and exposure analysis. *EPA Newsletter* 41, 24–39.
- Klopman, G., Wang, S., Balthasar, D. M. (1992) Estimation of aqueous solubility of organic molecules by the group contribution approach. Application to the study of biodegradation. *J. Chem. Inf. Comput. Sci.* 32, 474–482.
- Könemann, H., van Leeuwen, K. (1980) Toxicokinetics in fish: accumulation of six chloro-benzenes by guppies. *Chemosphere* 9, 3–19.
- Könemann, H., Zelle, R., Busser, F. (1979) Determination of log P_{oct} values of chloro-substituted benzenes, toluenes and anilines by high-performance liquid chromatography on ODS-silica. *J. Chromatogr.* 178, 559–565.
- Korenman, I.M., Gur'ev, I.A., Gur'eva, Z.M. (1971) Solubility of liquid aliphatic compounds in water. *Russ. J. Phys. Chem.* 45, 1065–1066.
- Lande, S. S., Banerjee, S. (1981) Predicting aqueous solubility of organic nonelectrolytes from molar volume. *Chemosphere* 10, 751–759.
- Leahy, D. E. (1986) Intrinsic molecular volume as a measure of the cavity term in linear solvation energy relationships: octanol-water partition coefficients and aqueous solubilities. *J. Pharm. Sci.* 75, 629–636.
- Lee, L. S., Rao, P. S. C., Nkedi-Kizza, P., Delfino, J. (1990) Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol-water and soil-water systems. *Environ. Sci. Technol.* 24, 654–661.
- Leighton, Jr., D. T., Calo, J. M. (1981) Distribution coefficients of chlorinated hydrocarbons in dilute air-water systems for groundwater contamination applications. *J. Chem. Eng. Data* 26, 382–385.
- Leo, A., Hansch, C., Elkins, D. (1971) Partition coefficients and their uses. *Chem. Rev.* 71, 525–616.
- Lide, D.R., Ed. (2003) *CRC Handbook of Chemistry and Physics*, 84th edition. CRC Press, Boca Raton, FL.
- Lincoff, A. H., Gossett, J. M. (1984) The determination of Henry's law constants for volatile organics by equilibrium partitioning in closed systems. In: *Gas Transfer at Water Surfaces*. Brutsaert, W., Jirka, G. H., Eds., pp. 17–26, D. Reidel Publishing Co., Dordrecht, The Netherlands.
- Lo, J. M., Tseng, C. L., Yang, J. Y. (1986) Radiometric method for determining solubility of organic solvents in water. *Anal. Chem.* 58, 1596–1597.
- Locke, D. (1974) Selectivity in reversed-phase liquid chromatography using chemically bonded stationary phases. *J. Chromatogr. Sci.* 12, 433–437.
- Lohninger, H. (1994) Estimation of soil partition coefficients of pesticides from their chemical structure. *Chemosphere* 29, 1611–1626.
- Lyman, W. J., Reehl, W. F., Rosenblatt, D. H. (1982) *Handbook of Chemical Property Estimation Methods*. McGraw-Hill, New York.
- Mabey, W. J., Mill, T., Podoll, R. T. (1984) *Estimation Methods for Process Constants and Properties used in Fate Assessment*. USEPA, EPA-600/3-84-035, Athens, GA.
- Mackay, D. (1979) Finding fugacity feasible. *Environ. Sci. Technol.* 13, 1218–1223.
- Mackay, D. (1982) Correlation of bioconcentration factors. *Environ. Sci. Technol.* 16, 274–278.
- Mackay, D. (1991) *Multimedia Environmental Models. The Fugacity Approach*. Lewis Publishers, Chelsea, MI.
- Mackay, D. (2001) *Multimedia Environmental Models: The Fugacity Approach*. 2nd edition, Lewis Publishers, CRC Press, Boca Raton, FL.

- Mackay, D., Bobra, A. M., Shiu, W.-Y., Yalkowsky, S. H. (1980) Relationships between aqueous solubility and octanol-water partition coefficient. *Chemosphere* 9, 701–711.
- Mackay, D., Bobra, A. M., Chan, D. W., Shiu, W.-Y. (1982) Vapor pressure correlation for low-volatility environmental chemicals. *Environ. Sci. Technol.* 16, 645–649.
- Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E. (1996) Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ. Toxicol. Chem.* 15, 1627–1637.
- Mackay, D., Paterson, S. (1990) Fugacity models. In: *Practical Applications of Quantitative Structure-Activity Relationships (QSAR) in Environmental Chemistry and Toxicology*. Karcher, W., Devillers, J., Eds., pp. 433–460, Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Mackay, D., Paterson, S. (1991) Evaluating the multimedia fate of organic chemicals: A Level III fugacity model. *Environ. Sci. Technol.* 25, 427–436.
- Mackay, D., Shiu, W. Y. (1977) Aqueous solubility of polynuclear aromatic hydrocarbons. *J. Chem. Eng. Data* 22, 339–402.
- Mackay, D., Shiu, W. Y. (1981) A critical review of Henry's law constants for chemicals of environmental interest. *J. Phys. Chem. Ref. Data* 11, 1175–1199.
- Mackay, D., Shiu, W. Y., Sutherland, R.P. (1979) Determination of air-water Henry's law constants for hydrophobic pollutants. *Environ. Sci. Technol.* 13, 333–337.
- Mackay, D., Shiu, W. Y., Wolkoff, A. W. (1975) Gas chromatographic determination of low concentration of hydrocarbons in water by vapor phase extraction. In: *Water Quality Parameters. ASTM STP 573*, pp. 251–258, American Society for Testing and Materials, Philadelphia, PA.
- Mackay, D., Stiver, W. H. (1991) Predictability and environmental chemistry. In: *Environmental Chemistry of Herbicides*. Vol. II, Grover, R., Cessna, A. J., Eds., pp. 281–297, CRC Press, Boca Raton, FL.
- Macknick, A. B., Prausnitz, J. M. (1979) Vapor pressure of high-molecular weight hydrocarbons. *J. Chem. Eng. Data* 24, 175–178.
- Magnussen, T., Rasmussen, P., Fredenslund, A. (1981) UNIFAC parameter table for prediction of liquid-liquid equilibria. *Ind. Eng. Chem. Process Des. Dev.* 20, 331–339.
- Mailhot, H., Peters, R. H. (1988) Empirical relationships between the 1-octanol/water partition coefficient and nine physicochemical properties. *Environ. Sci. Technol.* 22, 1479–1488.
- May, W. E., Wasik, S. P., Freeman, D. H. (1978a) Determination of the aqueous solubility of polynuclear aromatic hydrocarbons by a coupled-column liquid chromatographic technique. *Anal. Chem.* 50, 175–179.
- May, W. E., Wasik, S. P., Freeman, D. H. (1978b) Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. *Anal. Chem.* 50, 997–1000.
- May, W. E., Wasik, S. P., Miller, M. M., Tewari Y. B., Brown-Thomas, J. M., Goldberg, R. N. (1983) Solution thermodynamics of some slightly soluble hydrocarbons in water. *J. Chem. Eng. Data* 28, 197–200.
- McAuliffe, C. (1966) Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin and aromatic hydrocarbons. *J. Phys. Chem.* 76, 1267–1275.
- McAuliffe, C. (1971) GC determination of solutes by multiple phase equilibration. *Chem. Tech.* 1, 46–51.
- McDuffie, B. (1981) Estimation of octanol/water partition coefficient for organic pollutants using reversed phase HPLC. *Chemosphere* 10, 73–83.
- McLachlan, M.S., Welsch-Pausch, K. and Tolls, J. (1995) Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (Rye Grass). *Environ. Sci. Technol.* 29, 1998–2004.
- McGowan, J.C., Mellors, A. (1986) *Molecular Volumes in Chemistry and Biology-Applications including Partitioning and Toxicity*. Ellis Horwood Limited, Chichester, England.
- Meylan, W. M., Howard, P. H. (1991) Bond contribution method for estimating Henry's law constants. *Environ. Toxicol. Chem.* 10, 1283–1293.
- Meylan, W. M., Howard, P. H., Boethling, R. S. (1992) Molecular topology/fragment contribution for predicting soil sorption coefficient. *Environ. Sci. Technol.* 26, 1560–1567.
- Mill, T. (1982) Hydrolysis and oxidation processes in the environment. *Environ. Toxicol. Chem.* 1, 135–141.
- Mill, T. (1989) Structure-activity relationships for photooxidation processes in the environment. *Environ. Toxicol. Chem.* 8, 31–45.
- Mill, T. (1993) Environmental chemistry. In: *Ecological Risk Assessment*. Suter, II, G.W., Ed., pp. 91–127, Lewis Publishers, Chelsea, MI.
- Mill, T., Mabey, W. (1985) Photodegradation in water. In: *Environmental Exposure from Chemicals*. Vol. 1. Neely, W. B., Blau, G. E., Eds., pp. 175–216, CRC Press, Boca Raton, FL.
- Miller, M. M., Ghodbane, S., Wasik, S. P., Tewari, Y. B., Martire, D. E. (1984) Aqueous solubilities, octanol/water partition coefficients and entropies of melting of chlorinated benzenes and biphenyls. *J. Chem. Eng. Data* 29, 184–190.
- Miller, M. M., Wasik, S. P., Huang, G.-L., Shiu, W.-Y., Mackay, D. (1985) Relationships between octanol-water partition coefficient and aqueous solubility. *Environ. Sci. Technol.* 19, 522–529.
- Milne, G. W. A., Editor (1995) *CRC Handbook of Pesticides*. CRC Press, Boca Raton, FL.
- Montgomery, J. H. (1993) *Agrochemicals Desk Reference. Environmental Data*. Lewis Publishers, Chelsea, MI.
- Munz, C., Roberts, P. V. (1987) Air-water phase equilibria of volatile organic solutes. *J. Am. Water Works Assoc.* 79, 62–69.
- Neely, W. B., Branson, D. R., Blau, G. E. (1974) Partition coefficient to measure bioconcentration potential of organic chemicals in fish. *Environ. Sci. Technol.* 8, 1113–1115.

- Nirmalakhandan, N. N., Speece, R. E. (1988a) Prediction of aqueous solubility of organic chemicals based on molecular structure. *Environ. Sci. Technol.* 22, 328–338.
- Nirmalakhandan, N. N., Speece, R. E. (1988b) QSAR model for predicting Henry's law constant. *Environ. Sci. Technol.* 22, 1349–1357.
- Nirmalakhandan, N. N., Speece, R. E. (1989) Prediction of aqueous solubility of organic chemicals based on molecular structure. 2. Application to PNAs, PCBs, PCDDs, etc. *Environ. Sci. Technol.* 23, 708–713.
- NRCC (1982) *Chlorinated Phenols: Criteria for Environmental Quality*. National Research Council Canada, Publication No. 18578, Ottawa, Canada.
- Ochi, K., Saito, T., Kojima, K. (1996) Measurement and correlation of mutual solubilities of 2-butanol + water. *J. Chem. Eng. Data* 41, 361–364.
- Okouchi, H., Saegusa, H., Nojima, O. (1992) Prediction of environmental parameters by adsorbability index: water solubilities of hydrophobic organic pollutants. *Environ. Intl.* 18, 249–261.
- Oliver, B. G. (1984) The relationship between bioconcentration factor in rainbow trout and physical-chemical properties for some halogenated compounds. In: *QSAR in Environmental Toxicology*. Kaiser, K. L. E., Ed., pp. 300–317, D. Reidel Publishing, Dordrecht, The Netherlands.
- Oliver, B. G., Niimi, A. J. (1988) Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. *Environ. Sci. Technol.* 22, 388–397.
- Osborn, A.G., Douslin, D.R. (1974) Vapor-pressure relations of 15 hydrocarbons. *J. Chem. Eng. Data* 19, 114–117.
- Osborn, A. G., Douslin, D. R. (1975) Vapor pressures and derived enthalpies of vaporization of some condensed-ring hydrocarbons. *J. Chem. Eng. Data* 20, 229–231.
- Owens, J.W., Wasik, S.P., DeVoe, H. (1986) Aqueous solubilities and enthalpies of solution of n-alkylbenzenes. *J. Chem. Eng. Data* 31, 47–51.
- Paterson, S., Mackay, D. (1985) The fugacity concept in environmental modelling. In: *The Handbook of Environmental Chemistry*. Vol. 2/Part C, Hutzinger, O., Ed., pp. 121–140, Springer-Verlag, Heidelberg, Germany.
- Paterson, S., Mackay, D., Bacci, E. and Calamari, D. (1991) Correlation of the equilibrium and kinetics of leaf-air exchange of hydrophobic organic chemicals. *Environ. Sci. Technol.* 25, 866–871.
- Pearlman, R. S. (1980) Molecular surface areas and volumes and their use in structure/activity relationships. In: *Physical Chemical Properties of Drugs*. Yalkowsky, S.H., Sinkula, A.A., Valvani, S.C., Eds., *Medicinal Research Series*, Vol. 10, pp. 321–317, Marcel Dekker, New York.
- Pearlman, R. S. (1986) Molecular surface area and volume: Their calculation and use in predicting solubilities and free energies of desolvation. In: *Partition coefficient, Determination and Estimation*. Dunn, III, W. J., Block, J. H., Pearlman R. S., Eds., pp. 3–20, Pergamon Press, New York.
- Pearlman, R. S., Yalkowsky, S. H., Banerjee, S. (1984) Water solubilities of polynuclear aromatic and heteroaromatic compounds. *J. Phys. Chem. Ref. Data* 13, 555–562.
- Pierotti, C., Deal, C., Derr, E. (1959) Activity coefficient and molecular structure. *Ind. Eng. Chem. Fundam.* 51, 95–101.
- Polak, J., Lu, B. C. Y. (1973) Mutual solubilities of hydrocarbons and water at 0° and 25°C. *Can. J. Chem.* 51, 4018–4023.
- Rapaport, R. A., Eisenreich, S. J. (1984) Chromatographic determination of octanol-water partition coefficients (K_{OW} 's) for 58 polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 18, 163–170.
- Reddy, K. N., Locke, M. A. (1994) Relationships between molecular properties and log p and soil sorption (K_{OC}) of substituted phenylureas: QSAR models. *Chemosphere* 28, 1929–1941.
- Reid, R. C., Prausnitz, J. M., Polling, B. E. (1987) *The Properties of Gases and Liquids*. 4th Edition, McGraw-Hill, New York.
- Rekker, R. F. (1977) *The Hydrophobic Fragmental Constant*. Elsevier, Amsterdam/New York.
- Riddick, J. A., Bunger, W. B., Sakano, T. K. (1986) *Organic Solvents, Physical Properties and Methods of Purification*. 4th Edition, Wiley-Science Publication, John Wiley & Sons, New York.
- Rordorf, B. F. (1985a) Thermodynamic and thermal properties of polychlorinated compounds: the vapor pressures and flow tube kinetic of ten dibenzo-*p*-dioxins. *Chemosphere* 14, 885–892.
- Rordorf, B. F. (1985b) Thermodynamic properties of polychlorinated compounds: the vapor pressures and enthalpies of sublimation of ten dibenzo-*p*-dioxins. *Thermochimica Acta* 85, 435–438.
- Rordorf, B. F. (1986) Thermal properties of dioxins, furans and related compounds. *Chemosphere* 15, 1325–1332.
- Sabljić, A. (1984) Predictions of the nature and strength of soil sorption of organic pollutants by molecular topology. *J. Agric. Food Chem.* 32, 243–246.
- Sabljić, A. (1987) On the prediction of soil sorption coefficients of organic pollutants from molecular structure: Application of molecular topology model. *Environ. Sci. Technol.* 21, 358–366.
- Sabljić, A., Lara, R., Ernst, W. (1989) Modelling association of highly chlorinated biphenyls with marine humic substances. *Chemosphere* 19, 1665–1676.
- Sabljić, A., Güsten, H. (1989) Predicting Henry's law constants for polychlorinated biphenyls. *Chemosphere* 19, 1503–1511.
- Sabljić, A., Güsten, H. (1990) Predicting the night-time NO_3 radical reactivity in the troposphere. *Atmos. Environ.* 24A, 73–78.
- Sangster, J. (1989) Octanol-water partition coefficients of simple organic compounds. *J. Phys. Chem. Ref. Data* 18, 1111–1230.
- Sangster, J. (1993) LOGKOW databank. Sangster Research Laboratory, Montreal, Quebec, Canada.
- Schellenberg, K., Leuenberger, C., Schwarzenbach, R. P. (1984) Sorption of chlorinated phenols by natural sediments and aquifer materials. *Environ. Sci. Technol.* 18, 652–657.

- Schwarz, F. P. (1980) Measurement of the solubilities of slightly soluble organic liquids in water by elution chromatography. *Anal. Chem.* 52, 10–15.
- Schwarz, F. P., Miller, J. (1980) Determination of the aqueous solubilities of organic liquids at 10.0, 20.0, 30.0 °C by elution chromatography. *Anal. Chem.* 52, 2162–2164.
- Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M. (1993) *Environmental Organic Chemistry*. John Wiley & Sons, New York.
- Schwarzenbach, R. P., Stierli, R., Folsom, B. R., Zeyer, J. (1988) Compound properties relevant for assessing the environmental partitioning of nitrophenols. *Environ. Sci. Technol.* 22, 83–92.
- Schwarzenbach, R. P., Westall, J. (1981) Transport of nonpolar compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* 11, 1360–1367.
- Sears, G. W., Hopke, E. R. (1947) Vapor pressures of naphthalene, anthracene and hexachlorobenzene in a low pressure region. *J. Am. Chem. Soc.* 71, 1632–1634.
- Seth, R., Mackay, D., Munthe, J. (1999) Estimation of organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ. Sci. Technol.* 33, 2390–2394.
- Shaw, D.G., Ed. (1989a) IUPAC Solubility Data Series: Vol. 37. *Hydrocarbons (C₅-C₇) with Water and Seawater*, Pergamon Press, Oxford, England.
- Shaw, D.G., Ed. (1989b) IUPAC Solubility Data Series: Vol. 38. *Hydrocarbons (C₈-C₃₆) with Water and Seawater*. Pergamon Press, Oxford, England.
- Shigeoka, T., Sato, Y., Takeda, Y. (1988) Acute toxicity of chlorophenols to green algae, *Selenastrum capricornutum* and *Chlorella vulgaris*, and quantitative structure-activity relationships. *Environ. Toxicol. Chem.* 7, 847–854.
- Shiu, W.-Y., Ma, K.-C., Varhanickova, D., Mackay, D. (1994) Chlorophenols and alkylphenols: A review and correlation of environmentally relevant properties and fate in an evaluative environment. *Chemosphere* 29(6), 1155–1224.
- Shiu, W.-Y., Mackay, D. (1986) A critical review of aqueous solubilities, vapor pressures, Henry's law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. *J. Phys. Chem. Ref. Data* 15, 911–929.
- Shiu, W.-Y., Gobas, F. A. P. C., Mackay, D. (1987) Physical-chemical properties of three congeneric series of chlorinated aromatic hydrocarbons. In: *QSAR in Environmental Toxicology II*. Kaiser, K. L. E., Ed., pp. 347–362, D. Reidel Publishing, Dordrecht, The Netherlands.
- Shiu, W.-Y., Doucette, W., Gobas, F. A. P. C., Mackay, D., Andren, A. W. (1988) Physical-chemical properties of chlorinated dibenzo-*p*-dioxins. *Environ. Sci. Technol.* 22, 651–658.
- Shoeib, M., Harner, T. (2002) Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. *Environ. Toxicol. Chem.* 21, 984–990.
- Sinke, G. C. (1974) A method for measurement of vapor pressures of organic compounds below 0.1 torr. Naphthalene as reference substance. *J. Chem. Thermodyn.* 6, 311–316.
- Smejtek, P., Wang, S. (1993) Distribution of hydrophobic ionizable xenobiotics between water and lipid membranes: pentachlorophenol and pentachlorophenate. A comparison with octanol-water partition. *Arch. Environ. Contam. Toxicol.* 25, 394–404.
- Smith, P.D., Brockway, D.L., Stancil, Jr., F.E. (1987) Effect of hardness, alkalinity and pH on toxicity of pentachlorophenol to *senastrum capricornutum* (printz). *Environ. Toxicol. Chem.* 6, 891–990.
- Sonnefeld, W. J., Zoller, W. H., May, W. E. (1983) Dynamic coupled-column liquid chromatographic determination of ambient temperature vapor pressures of polynuclear aromatic hydrocarbons. *Anal. Chem.* 55, 275–280.
- Spencer, W. F., Cliath, M. M. (1970) Vapor density and apparent vapor pressure of lindane (γ -BHC). *J. Agric. Food Chem.* 18, 529–530.
- Spencer, W. F., Cliath, M. M. (1972) Volatility of DDT and related compounds. *J. Agric. Food Chem.* 20, 645–649.
- Stehly, G. R., Hayton, W. L. (1990) Effect of pH on the accumulation kinetics of pentachlorophenol in goldfish. *Arch. Environ. Contam. Toxicol.* 19, 464–470.
- Stephenson, R. M., Malanowski, A. (1987) *Handbook of the Thermodynamics of Organic Compounds*. Elsevier, New York.
- Stiver, W., Mackay, D. (1989) The linear additivity principle in environmental modelling: Application to chemical behaviour in soil. *Chemosphere* 19, 1187–1198.
- Su, Y., Lei, D.L., Daly, G., Wania, F. (2002) Determination of octanol-air partition coefficient (K_{OA}) values for chlorobenzenes and polychlorinated naphthalenes from gas chromatographic retention times. *J. Chem. Eng. Data*, 47, 449–455.
- Sugiyama, T., Takeuchi, T., Suzuki, Y. (1975) Thermodynamic properties of solute molecules at infinite dilution determined by gas-liquid chromatography. I. Intermolecular energies of *n*-alkane solutes in C₂₈-C₃₆ *n*-alkane solvents. *J. Chromatogr.* 105, 265–272.
- Suntio, L. R., Shiu, W.-Y., Mackay, D. (1988) Critical review of Henry's law constants for pesticides. *Rev. Environ. Contam. Toxicol.* 103, 1–59.
- Swann, R. L., Laskowski, D. A., McCall, P. J., Vander Kuy, K., Dishburger, H. J. (1983) A rapid method for the estimation of the environmental parameters octanol/water partition coefficient, soil sorption constant, water to air ratio, and water solubility. *Res. Rev.* 85, 17–28.
- Szabo, G., Prosser, S., Bulman, R. A. (1990) Determination of the adsorption coefficient (K_{OC}) of some aromatics for soil by RP-HPLC on two immobilized humic acid phases. *Chemosphere* 21, 777–788.
- ten Hulscher, Th.E.M., van der Velde, Bruggeman, W. A. (1992) Temperature dependence of Henry's law constants for selected chlorobenzenes, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* 11, 1595–1603.
- Tesconi, M., Yalkowsky, S.H. (2000) Melting Point, Chapter 1 in Boethling, R.S. and Mackay, D. (Eds). *Handbook of Property Estimation Methods: Environmental and Health Sciences*, CRC Press, Boca Raton, FL.

- Tolls, J. and McLachlan, M.S. (1994) Partitioning of semivolatile organic compounds between air and *Lolium multiflorum* (Welsh Rye Grass). *Environ. Sci. Technol.* 28, 159–166.
- Tomlin, C., Ed. (1994) *The Pesticide Manual (A World Compendium)*, 10th Ed., Incorporating the Agrochemicals Handbook, The British Crop Protection Council and The Royal Society of Chemistry, England.
- Tomlinson, E., Hafkenscheid, T. L. (1986) Aqueous solution and partition coefficient estimation from HPLC data. In: *Partition Coefficient, Determination and Estimation*. Dunn, III, W. J., Block, J. H., Pearlman, R. S., Eds., pp. 101–141, Pergamon Press, New York.
- Tse, G., Orbey, H., Sandler, S. I. (1992) Infinite dilution activity coefficients and Henry's law coefficients for some priority water pollutants determined by a relative gas chromatographic method. *Environ. Sci. Technol.* 26, 2017–2022.
- Tsonopoulos, C., Prausnitz, J. M. (1971) Activity coefficients of aromatic solutes in dilute aqueous solutions. *Ind. Eng. Chem. Fundam.* 10, 593–600.
- Tsonopoulos, C., Wilson, G.M.W. (1983) High-temperature mutual solubilities of hydrocarbons and water. *AIChE. J.* 29, 990–999.
- Tucker, E.E., Christian, S.D. (1979) A prototype hydrophobic interaction. The dimerization of benzene in water. *J. Phys. Chem.* 83, 426–427.
- Tulp, M. T. M., Hutzinger, O. (1978) Some thoughts on the aqueous solubilities and partition coefficients of PCB, and the mathematical correlation between bioaccumulation and physico-chemical properties. *Chemosphere* 7, 849–860.
- Veith, G. D., Austin, N. M., Morris, R. T. (1979) A rapid method for estimating log P for organic chemicals. *Water Res.* 13, 43–47.
- Veith, G. D., Macek, K. J., Petrocelli, S. R., Carroll, J. (1980) An evaluation of using partition coefficients and water solubilities to estimate bioconcentration factors for organic chemicals in fish. In: *Aquatic Toxicology*. ASTM ATP 707, Eaton, J. G., Parrish, P. R., Hendrick, A.C., Eds, pp. 116–129, Am. Soc. for Testing and Materials, Philadelphia, PA.
- Vejrosta, J., Novak, J., Jönsson, J. (1982) A method for measuring infinite-dilution partition coefficients of volatile compounds between the gas and liquid phases of aqueous systems. *Fluid Phase Equil.* 8, 25–35.
- Verschuere, K. (1977) *Handbook of Environmental Data on Organic Chemicals*. Van Nostrand Reinhold, New York.
- Verschuere, K. (1983) *Handbook of Environmental Data on Organic Chemicals*. 2nd Edition, Van Nostrand Reinhold, New York.
- Wakita, K., Yoshimoto, M., Miyamoto, S., Watanabe, H. (1986) A method for calculations of the aqueous solubility of organic compounds by using new fragment solubility constants. *Chem. Pharm. Bull.* 34, 4663–4681.
- Walker, J.D. (Ed.) 2003 Annual review quantitative structure-activity relationships. *Environ. Toxicol. Chem.* 22, 1651–1935.
- Wang, L., Zhao, Y., Hong, G. (1992) Predicting aqueous solubility and octanol/water partition coefficients of organic chemicals from molar volume. *Environ. Chem.* 11, 55–70.
- Warne, M., St. J., Connell, D. W., Hawker, D. W. (1990) Prediction of aqueous solubility and the octanol-water partition coefficient for lipophilic organic compounds using molecular descriptors and physicochemical properties. *Chemosphere* 16, 109–116.
- Wasik, S. P., Miller, M. M., Tewari, Y. B., May, W. E., Sonnefeld, W. J., DeVoe, H., Zoller, W. H. (1983) Determination of the vapor pressure, aqueous solubility, and octanol/water partition coefficient of hydrophobic substances by coupled generator column/liquid chromatographic methods. *Res. Rev.* 85, 29–42.
- Wauchope, R. D., Buttler, T. M., Hornsby, A. G., Augustijn-Beckers, P. W. M., Burt, J. P. (1992) The SCS/ARS/CES pesticide properties database for environmental decision making. *Rev. Environ. Contam. Toxicol.* 123, 1–156.
- Weast, R., Ed. (1972–73) *Handbook of Chemistry and Physics*. 53th Edition, CRC Press, Cleveland, OH.
- Weast, R., Ed. (1982–83) *Handbook of Chemistry and Physics*. 64th Edition, CRC Press, Boca Raton, FL.
- Weil, L., Dure, G., Quentin, K. L. (1974) Solubility in water of insecticide, chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. *Z. Wasser Abwasser Forsch.* 7, 169–175.
- Westall, J. C., Leuenberger, C., Schwarzenbach, R. P. (1985) Influence of pH and ionic strength on the aqueous-nonaqueous distribution of chlorinated phenols. *Environ. Sci. Technol.* 19, 193–198.
- Westcott, J. W., Bidleman, T. F. (1982) Determination of polychlorinated biphenyl vapor pressures by capillary gas chromatography. *J. Chromatogr.* 210, 331–336.
- Westcott, J. W., Simon, J. J., Bidleman, T. F. (1981) Determination of polychlorinated biphenyl vapor pressures by a semimicro gas saturation method. *Environ. Sci. Technol.* 15, 1375–1378.
- Whitehouse, B. G., Cooke, R. C. (1982) Estimating the aqueous solubility of aromatic hydrocarbons by high performance liquid chromatography. *Chemosphere* 11, 689–699.
- Windholz, M., Ed. (1983) *The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals*. 10th Edition, Merck & Co. Rahway, NJ.
- Woodburn, K. B., Doucette, W. J., Andren, A. W. (1984) Generator column determination of octanol/water partition coefficients for selected polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 18, 457–459.
- Worthing, C. R., Walker, S. B., Eds. (1983) *The Pesticide Manual (A World Compendium)*, 7th Edition, The British Crop Protection Council, Croydon, England.
- Worthing, C. R., Walker, S. B., Eds. (1987) *The Pesticide Manual (A World Compendium)*, 8th Edition, The British Crop Protection Council, Croydon, England.
- Worthing, C. R., Hance, R. J., Eds. (1991) *The Pesticide Manual (A World Compendium)*, 9th Edition, The British Crop Protection Council, Croydon, England.
- Yair, O. B., Fredenslund, A. (1983) Extension of the UNIFAC group-contribution method for the prediction of pure-component vapor pressure. *Ind. Eng. Chem. Fundam. Des. Dev.* 22, 433–436.

- Yalkowsky, S. H. (1979) Estimation of entropies of fusion of organic compounds. *Ind. Eng. Chem. Fundam.* 18, 108–111.
- Yalkowsky, S. H., Banerjee, S. (1992) *Aqueous Solubility, Methods of Estimation for Organic Compounds*. Marcel Dekker, New York.
- Yalkowsky, S. H., Valvani, S. C. (1976) Partition coefficients and surface areas of some alkylbenzenes. *J. Med. Chem.* 19, 727–728.
- Yalkowsky, S. H., Valvani, S. C. (1979) Solubility and partitioning. I: Solubility of nonelectrolytes in water. *J. Pharm. Sci.* 69, 912–922.
- Yalkowsky, S. H., Orr, R. J., Valvani, S. C. (1979) Solubility and partitioning. 3. The solubility of halobenzenes in water. *Ind. Eng. Chem. Fundam.* 18, 351–353.
- Yalkowsky, S. H., Valvani, S. S., Mackay, D. (1983) Estimation of the aqueous solubility of some aromatic compounds. *Res. Rev.* 85, 43–55.
- Yoshida, K., Shigeoka, T., Yamauchi, F. (1983) Relationship between molar refraction and n-octanol/water partition coefficient. *Ecotox. Environ. Saf.* 7, 558–565.
- Yoshida, K., Shigeoka, T., Yamauchi, F. (1987) Evaluation of aquatic environmental fate of 2,4,6-trichlorophenol with a mathematical model. *Chemosphere* 16, 2531–2544.
- Zhou, X., Mopper, K. (1990) Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater: Implications for air-sea exchange. *Environ. Sci. Technol.* 24, 1864–1869.
- Zaroogian, G.E., Heltshe, J. F., Johnson, M. (1985) Estimation bioconcentration in marine species using structure-activity models. *Environ. Toxicol. Chem.* 4, 3–12.
- Zwolinski, B. J., Wilhoit, R. C. (1971) *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds*. API-44, TRC Publication No. 101, Texas A&M University, College Station, TX.