

CHAPTER 5

EVALUATING ENVIRONMENTAL FATE: Approaches based on chemical structure

by
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5.1 INTRODUCTION

A new chemical is to be manufactured. Will its manufacture or use pose significant environmental or human health risks? If there are risks, what are the exposure pathways? Will the chemical degrade if it is released into the environment or will it persist? If the chemical degrades will the degradation products pose a risk to the environment?

The challenges involved in answering these questions are formidable. Over 8,000 chemicals are produced commercially and every year, a thousand or more new chemicals are developed. For any chemical in use, there are a number of potential risks to human health and the environment. In general, it will not be possible to rigorously and precisely evaluate all possible environmental impacts. Nevertheless, a preliminary screening of the potential environmental impacts of chemicals is necessary and is possible. Preliminary risk screenings allow businesses, government agencies and the public to identify problem chemicals and to identify potential risk reduction opportunities. The challenge is to perform these preliminary risk screenings with a limited amount of information.

The goal of this chapter is to present qualitative and quantitative methods for estimating environmental risks when the only information available is a chemical structure. Many of these methods have been developed by the U.S. Environmental Protection Agency (U.S. EPA) and its contractors. The methods are routinely used in evaluating premanufacture notices submitted under the Toxic Substances Control Act (TSCA). Under the provisions of TSCA, before a new chemical can be manufactured in the United States, a premanufacture notice must be submitted to U.S. EPA. The premanufacture notice specifies the chemical to be manufactured, the quantity to be manufactured and any known environmental impacts as well as potential releases from the manufacturing site. Based on these limited data, the U.S. EPA must assess whether the manufacture or use of the proposed chemical may pose an unreasonable risk to human or ecological health. To accomplish that assessment, a set of tools has been developed that relate chemical structure to potential environmental risks.

Table 5.1-1 identifies the chemical and physical properties that will influence each of the processes that determine environmental exposure and hazard. The Table makes clear that a wide range of properties need to be estimated to perform a screening level assessment of environmental risks.

Table 5.1-1 Chemical properties needed to perform environmental risk screenings

<i>Environmental Process</i>	<i>Relevant Properties</i>
Dispersion and fate	Volatility, density, melting point, water solubility, effectiveness of wastewater treatment
Persistence in the environment	Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation, and adsorption
Uptake by organisms	Volatility, lipophilicity, molecular size, degradation rate in organism
Human uptake	Transport across dermal layers, transport rates across lung membrane, degradation rates within the human body
Toxicity and other health effects	Dose-response relationships

The first group of properties that must be estimated in an assessment of environmental risk are the basic physical and chemical properties that describe a chemical's partitioning between solid, liquid and gas phases. These include melting point, boiling point, vapor pressure and water solubility. Additional molecular properties, related to phase partitioning, that are frequently used in assessing the environmental fate of chemicals include octanol-water partition coefficient, soil sorption coefficients, Henry's law constants and bioconcentration factors. (Each of these properties is defined in Section 5.2). Once the basic physical and chemical properties are defined, a series of properties that influence the fate of chemicals in the environment are estimated. These include estimates of the rates at which chemicals will react in the atmosphere, the rates of reaction in aqueous environments and the rate at which the compounds will be metabolized by organisms. If environmental concentrations can be estimated based on release rates and environmental fate properties, then human exposures to the chemicals can be estimated. Finally, if exposures and hazards are known, then risks to humans and the environment can be estimated.

The remainder of this chapter describes estimation tools for the properties outlined above. Section 5.2 describes estimation tools for physical and chemical properties. Section 5.3 describes how properties that influence environmental fate are estimated. Methods for estimating hazards to ecosystems are discussed in Section 5.4, and Section 5.5 presents simple models that can be used to characterize the environmental partitioning of chemicals. Finally, Section 5.6 describes how chemical property data can be used to classify the risks associated with chemicals.

5.2 CHEMICAL AND PHYSICAL PROPERTY ESTIMATION

Although many chemical and physical properties can influence the way in which a chemical partitions in the environment, most screening level evaluations focus on only a small number of properties. These properties describe the partitioning of chemicals between solid, liquid and gaseous phases and include melting point, boiling point, and vapor pressure. Additional molecular properties, related to phase partitioning, that are frequently used in assessing the environmental fate of chemicals include Henry's law constants, octanol-water partition coefficient, water solubility, soil sorption coefficients and bioconcentration factors. Table 5.2-1 lists the definition of each of these properties and describes the significance of the property in estimating environmental fate.

Our goal in this section is to describe how each of these properties can be estimated based on the structure of the chemical. The review of estimation methods will not be comprehensive. Rather, the focus is on presenting commonly used methods that can produce property estimates based only on the chemical structure of the target compound. More complete presentations are available in texts on environmental property estimation (e.g., Lyman, et al., 1990). More complete compilations of data are available from Howard (1997), Mackay, et al., (1992), Reinhard and Drefahl (1999) and the sources listed at the end of the Chapter.

The methods described in this section generally assume that a molecule is composed of a collection of functional groups or molecular fragments and that each fragment contributes in a well-defined manner to the properties of the molecule. These methods are generally described as group contribution methods, structure activity relationships (SARs) or quantitative structure activity relationships (QSARs).

Table 5.2-1 Properties that influence environmental phase partitioning

<i>Property</i>	<i>Definition</i>	<i>Significance in estimating environmental fate and risks</i>
Melting point (T_m)	Temperature at which solid and liquid coexist at equilibrium	Sometimes used as a correlating parameter in estimating other properties for compounds that are solids at ambient or near-ambient conditions
Boiling point (T_b)	Temperature at which the vapor pressure of a compound equals atmospheric pressure; normal boiling points (temperature at which pressure equals one atmosphere) will be used in this text	Characterizes the partitioning between gas and liquid phases; frequently used as a correlating variable in estimating other properties
Vapor pressure (P_{vp})	Partial pressure exerted by a vapor when the vapor is in equilibrium with its liquid	Characterizes the partitioning between gas and liquid phases
Henry's law constant (H)	Equilibrium ratio of the concentration of a compound in the gas phase to the concentration of the compound in a dilute aqueous solution (sometimes reported as $\text{atm}\cdot\text{m}^3/\text{mol}$; dimensionless form will be used in this text)	Characterizes the partitioning between gas and aqueous phases
Octanol-water partition coefficient (K_{ow})	Equilibrium ratio of the concentration of a compound in octanol to the concentration of the compound in water	Characterizes the partitioning between hydrophilic and hydrophobic phases in the environment and the human body; frequently used as a correlating variable in estimating other properties
Water solubility (S)	Equilibrium solubility in mol/L	Characterizes the partitioning between hydrophilic and hydrophobic phases in the environment
Soil sorption coefficient (K_{oc})	Equilibrium ratio of the mass of a compound adsorbed per unit weight of organic carbon in a soil (in $\mu\text{g}/\text{g}$ organic carbon) to the concentration of the compound in a liquid phase (in $\mu\text{g}/\text{ml}$)	Characterizes the partitioning between solid and liquid phases in soil which in turn determines mobility in soils; frequently estimated based on octanol-water partition coefficient, and water solubility
Bioconcentration factor (BCF)	Ratio of a chemical's concentration in the tissue of an aquatic organism to its concentration in water (reported as	Characterizes the magnification of concentrations through the food chain

	L/kg)
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Boiling point and melting point

As a first example of a structure activity relationship, consider the estimation of boiling point (at one atmosphere pressure). Boiling point is influenced by molecular weight and intermolecular attractions. It can be estimated using a relatively simple group contribution method, developed by Joback and Reid (1987) and modified by Stein and Brown (1994), that relates the boiling point to the number and type of functional groups present in the molecule.

$$T_b \text{ (K)} = 198.2 + \sum n_i g_i \quad \text{(Eqn. 5-1)}$$

where T_b is the normal boiling point (at one atmosphere pressure) in degrees Kelvin, n_i is the number of groups of type i in the molecule, g_i is the contribution of each group to the boiling point, and the summation is taken over all groups. The boiling point predicted by equation 5-1 is corrected using one of the following equations:

$$T_b \text{ (corrected)} = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 \quad [T_b \leq 700\text{K}] \quad \text{(Eqn. 5-2)}$$

$$T_b \text{ (corrected)} = T_b - 282.7 + 0.5209T_b \quad [T_b > 700\text{K}] \quad \text{(Eqn. 5-3)}$$

Structural groups and group contributions (g_i) for boiling point estimation are listed in Table 5.2-2. When tested against a set of more than 4000 organic compounds, this method yielded an average error of 3.2% (Stein and Brown, 1994).

Although equations 5-1 to 5-3 are not the only method or even the most accurate method for estimating boiling point (for a more complete discussion, see Reid, et al., 1987), the approach does illustrate the basic principles of a group contribution method. Each functional group in a molecule is assumed to make a well defined contribution (in this case, g_i) to the property. The group contributions may be simply added together, as in Equation 5-1, or a more complex mathematical form may be used. The application of the method is illustrated in Example 5.2-1.

Table 5.2-2 Structural groups and group contributions for boiling point estimation (Stein and Brown, 1994)

Structural group	Contribution (g _i) to normal boiling point	Structural group	Contribution (g _i) to normal boiling point
<i>Carbon groups</i>		<i>Nitrogen groups</i>	
-CH ₃	21.98	-NH ₂	61.98
>CH ₂	24.22	Aromatic-NH ₂	86.63
>C _{ring} H ₂	26.44	>NH	45.28
>CH-	11.86	>N _{ring} H	65.50
>C _{ring} H-	21.66	>N-	25.78
>C<	4.50	>N _{ring} -	32.77
>C _{ring} <	11.12	>NOH	104.87
=CH ₂	16.44	>NNO	184.68
=CH-	27.95	anN	39.88
=C _{ring} H-	28.03	=NH	73.40
=C<	23.58	=N-	31.32
=C _{ring} <	28.19	=N _{ring} -	43.54
aaCH*	28.53	=N _{ring} N _{ring} H-	179.43
aaC-	30.76	-N _{ring} =C _{ring} N _{ring} H-	284.16
AaaC	45.46	-N=NNH-	257.29
≡CH	21.71	-N=N-	90.87
≡C-	32.99	-NO	30.91
		-NO ₂	113.99
<i>Oxygen groups</i>		-CN	119.16
-OH	106.27	Aromatic-CN	95.43
Primary -OH	88.46		
Secondary -OH	80.63	<i>Halogen groups</i>	
Tertiary -OH	69.32	-F	0.13
Aromatic -OH	70.48	Aromatic-F	-7.81
-O-	25.16	-Cl	34.08
-O _{ring} -	32.98	Primary-Cl	62.63
-OOH	72.92	Secondary-Cl	49.41
		Tertiary-Cl	36.23
<i>Carboxyl groups</i>		Aromatic-Cl	36.79
-CHO	83.38	-Br	76.28
>CO	71.53	Aromatic-Br	61.85
>C _{ring} O	94.76	-I	111.67
-C(O)O-	78.85	Aromatic-I	99.93
-C _{ring} (O)O _{ring} -	172.49		
-C(O)OH	169.83	<i>Sulfur groups</i>	
-C(O)NH ₂	230.39	-SH	81.71
-C(O)NH-	225.09	Aromatic-SH	77.49
-C _{ring} (O)N _{ring} H-	246.13	-S-	69.42
-C(O)N<	142.77	-S _{ring} -	69.00
-C _{ring} (O)N _{ring} <	180.22	>SO	154.50
		>SO ₂	171.58
		>CS	106.20
		>C _{ring} S	179.26

*The symbol a denotes an aromatic bond

Example 5.2-1

Estimate the normal boiling point for ethanol, toluene and acetaldehyde.

Solution

a.) Ethanol has the molecular structure $\text{CH}_3\text{-CH}_2\text{-OH}$. Referring to the groups in Table 5.2-2, this structure can be represented by one $-\text{CH}_3$ group, one $-\text{CH}_2$ group and one $-\text{OH}$ group. The uncorrected normal boiling point, from equation 5-1 is given by:

$$T_b (\text{K}) = 198.2 + 21.98 + 24.22 + 88.46 = 332.9 \text{ K}$$

The corrected value is:

$$T_b (\text{corrected}) = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 = 338.3 \text{ K}$$

The actual boiling point is 351 K, so the predicted value is in error by -3.6 %

b.) Toluene has the molecular structure $\text{CH}_3\text{-C}_6\text{H}_5$. Referring to the groups in Table 5.2-2, this structure can be represented by one $-\text{CH}_3$ group, one $-\text{aaC-}$ group (a substituted carbon bound to two aromatic carbons) and five $-\text{aaCH}$ groups. The uncorrected normal boiling point, from equation 5-1 is given by:

$$T_b (\text{K}) = 198.2 + 21.98 + 30.76 + 5(28.53) = 393.6 \text{ K}$$

The corrected value is:

$$T_b (\text{corrected}) = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 = 398.9 \text{ K}$$

The actual boiling point is 384 K, so the predicted value is in error by +3.9%

c.) Acetaldehyde has the molecular structure $\text{CH}_3\text{-CH=O}$. Referring to the groups in Table 5.2-2, this structure can be represented by one $-\text{CH}_3$ group and one $-\text{CHO}$ group. The uncorrected normal boiling point, from equation 5-1 is given by:

$$T_b (\text{K}) = 198.2 + 21.98 + 83.38 = 303.6 \text{ K}$$

The corrected value is:

$$T_b (\text{corrected}) = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 = 307.0 \text{ K}$$

The actual boiling point is 294 K, so the predicted value is in error by +4.2%

While group contribution methods can produce accurate estimates of chemical and physical properties, it is important to recognize their limitations. Group contribution equations are empirical. They are designed to accurately reflect a particular set of property data. If a group contribution method is used to estimate the properties of molecules that have structures significantly different than those used in the original data set, substantial errors can result. Consider, for example, what might happen if a group contribution method, originally developed with data on alcohols, were used to estimate the properties of glycols. Since glycols have two hydroxyl groups per molecule, they can form chains of molecules (n-mers) held together by hydrogen bonding forces. In contrast, alcohols, with only one hydroxyl group per molecule, can only form dimers in solution. A group contribution method for boiling point, developed with data on alcohols, would likely underpredict the boiling point of glycols (see Example 5.2-2).

Example 5.2-2

Estimate the normal boiling point for ethylene glycol.

Solution

a.) Ethylene glycol has the molecular structure HO-CH₂-CH₂-OH. Referring to the groups in Table 5.2-2, this structure can be represented by two -CH₂ groups and two -OH groups. The uncorrected normal boiling point, from equation 5-1 is given by:

$$T_b \text{ (K)} = 198.2 + 2(24.22) + 2(88.46) = 424 \text{ K}$$

The corrected value is:

$$T_b \text{ (corrected)} = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 = 427 \text{ K}$$

The actual boiling point is 470 K, so the predicted value is in error by -9 %

Melting point

As shown in Example 5.2-1, the estimation of boiling point, using equations 5-1 to 5-3, is relatively straightforward. Boiling points, in turn, can be used to estimate a variety of other properties. One property, which is occasionally used in estimating the phase partitioning of solids, is melting point. Melting point is sometimes expressed as a simple fraction of boiling point (Lyman, 1985):

$$T_m \text{ (K)} = 0.5839 T_b \text{ (K)} \quad \text{(Eqn. 5-4)}$$

Vapor pressure

The vapor pressure of a chemical plays a significant role in its environmental partitioning. High vapor pressure materials will generally have higher atmospheric concentrations than lower vapor pressure materials, and therefore, have the potential to be transported over long distances as gases or inhaled as gases. The temperature dependence of vapor pressure also plays a role in environmental transport and partitioning. If a chemical's vapor pressure varies significantly between daytime and nighttime conditions, strong daily cycling of the chemical between environmental media can be expected assuming no degradation or soil adsorption. Finally, vapor pressures are used in a variety of ways in estimations of exposure and environmental risk. Therefore, reliable estimates of vapor pressure, over a range of temperatures, will be important in screening chemicals for environmental risk.

A number of approaches are available for estimating vapor pressures. Some approaches are based on critical temperatures and pressures; others rely on heats of vaporization (Lyman, et al., 1990). Still other methods use estimates of vapor pressure at a reference temperature (such as the boiling point) to estimate vapor pressure. The methods based on boiling point and heat of vaporization will be the focus of this section—not because they are necessarily more accurate than the other methods, rather, because they are conveniently estimated from chemical structure.

One method for estimating vapor pressure from boiling point and heat of vaporization uses the mathematical form associated with the Antoine equation:

$$\ln P_{vp} = A + B/(T - C) \quad (\text{Eqn. 5-5})$$

Where P_{vp} is the vapor pressure, A and C are empirical constants, B is a parameter that is related to the heat of vaporization and T is absolute temperature. A derivation of this equation based on thermodynamic concepts is available in Lyman, et al. (1990) and in most thermodynamic textbooks.

Note that if we apply Equation 5-5 at the boiling point and define the units of vapor pressure as atmospheres, then:

$$\ln (1 \text{ atm}) = 0 = A + B/(T_b - C) \quad (\text{Eqn. 5-6})$$

Equation 5-6 can be used to express the parameter B in terms of A, C and T_b . Lyman, et al. (1990) provide a derivation of the following equation,

$$\ln P_{vp} (\text{atm}) = \frac{[A(T_b - C)^2]}{[0.97 R T_b]} * [1/(T_b - C) - 1/(T - C)] \quad (\text{Eqn. 5-7})$$

where R is the gas constant ($1.987 \text{ l-atm } ^\circ\text{K}^{-1}\text{mol}^{-1}$). Empirical correlations are available for estimating the parameters A and C from boiling point:

$$C = -18 + 0.19 T_b \quad (\text{Eqn. 5-8})$$

$$A = K_F (8.75 + R \ln T_b) \quad (\text{Eqn. 5-9})$$

Equations 5-7 through 5-9 allow vapor pressure to be estimated, as a function of temperature, based only on the boiling point and the parameter K_F . Values of K_F are given in Tables 5.2-3 and 5.2-4. For any compound not given in the Tables, assume $K_F = 1.06$.

Equations 5-7 through 5-9 work well in estimating vapor pressures that range from 10^{-2} to one atmosphere, yielding average errors of 2.7%. The performance deteriorates at lower pressures, with average errors of 86% for vapor pressures ranging from 10^{-6} to 10^{-2} atmosphere (Lyman, et al., 1990).

For solids, a slightly different form is generally used:

$$\ln P = -(4.4 + \ln T_b)[1.803 (T_b/T - 1) - 0.803 \ln(T_b/T)] - 6.8 (T_m/T - 1) \quad (\text{Eqn. 5-10})$$

where P is the vapor pressure in atmospheres, T_b is the normal boiling point (K), T is the temperature at which the vapor pressure is to be evaluated (K), and T_m is the melting point (K).

Care must be taken in defining the units for Equations 5-7 through 5-10. Example 5.2-3 illustrates the proper use of units.

Example 5.2-3

Estimate the vapor pressure at 298 K for toluene (a liquid) and naphthalene (a solid).

Solution

Toluene has the molecular structure $\text{CH}_3\text{-C}_6\text{H}_5$ and in Example 5.2-1, its boiling point was estimated to be 399 K. The experimental value for the boiling point is 384 K. We will estimate the vapor pressure using both the predicted and the experimental value for boiling point. Using the predicted value of 399 K:

$$C = -18 + 0.19 T_b = 57.8$$

$$A = K_F (8.75 + R \ln T_b) = 1.0(8.75 + 1.987 * \ln (399)) = 20.6$$

$$\ln P_{vp} = \frac{[A(T_b - C)^2]}{[0.97 R T_b]} \left[\frac{1}{T_b - C} - \frac{1}{T - C} \right] = \frac{[20.6 * (399 - 57.8)^2]}{[0.97 * 1.987 * 399]} \left[\frac{1}{341} - \frac{1}{240} \right]$$

$$\ln P_{vp} = -3.83; \quad P_{vp} = 0.021 \text{ atm} = 16 \text{ mm Hg}$$

Repeating the calculation for the experimental boiling point leads to a vapor pressure estimate of 19 mm Hg.

Naphthalene has the formula C_{10}H_8 and is a solid with a melting point of 81°C . The boiling point can be estimated from the methods described earlier in this section. The uncorrected group contribution estimate is:

$$T_b = 198.2 + 2(45.46) + 8(28.53) = 517 \text{ K}$$

The corrected value is: $T_b = 505 \text{ K}$

Applying Equation 5-10:

$$\ln P = -(4.4 + \ln T_b) [1.803 (T_b / T - 1) - 0.803 \ln(T_b / T)] - 6.8 (T_m / T - 1)$$

$$\ln P = -(4.4 + \ln 505) [1.803 (505 / 298 - 1) - 0.803 \ln(505 / 298)] - 6.8 (354 / 298 - 1)$$

$$P = 4.4 * 10^{-5} \text{ atm} = 0.03 \text{ mm Hg}$$

Table 5.2-3 Factors (K_F) used in estimating boiling points (Lyman, et al., 1990)*Number of carbon atoms in compound*

Compound type	1	2	3	4	5	6	7	8	9	10	11	12-20
<i>Hydrocarbons (consider a phenyl group as a single carbon atom)</i>												
n-alkanes	0.97	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkane isomers				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Mono- and diolefins and isomers		1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.00
Cyclic saturated hydrocarbons			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkyl derivatives of cyclic saturated hydrocarbons				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
<i>Halides</i>												
Monochlorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01
Moniodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03	1.03	1.02	1.02	1.01
Mixed halides (completely halogenated)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Perfluorocarbons	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
<i>Compounds containing a keto group</i>												
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Ketones			1.08	1.07	1.06	1.06	1.05	1.04	1.04	1.03	1.02	1.01
aldehydes		1.09	1.08	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
<i>Nitrogen compounds</i>												
Primary amines	1.16	1.13	1.12	1.11	1.10	1.10	1.09	1.09	1.08	1.07	1.06	1.05
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05	1.05	1.04	1.04	1.03
Tertiary amines			1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Nitriles		1.05	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
<i>Sulfur compounds</i>												
Mercaptans	1.05	1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Sulfides		1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
<i>Alcohols and Miscellaneous compounds</i>												
Alcohols (single -OH group)	1.22	1.31	1.31	1.31	1.31	1.30	1.29	1.28	1.27	1.26	1.24	1.24
Diols		1.33	1.33	1.33	1.33	1.33	1.33	1.33				
Triols			1.38	1.38	1.38							
Cyclohexanol, cyclohexyl methyl alcohol, etc.						1.20	1.20	1.21	1.24	1.26		

Aliphatic esters		1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Oxides (cyclic ethers)		1.08	1.07	1.06	1.05	1.05	1.04	1.03	1.02	1.01	1.01	1.01

Table 5.2-4 Factors (K_F) used in estimating boiling points for aromatics (Lyman, et al., 1990)

<i>Compound type</i>	K_F
Phenols (single –OH)	1.15
Phenols (more than one –OH)	1.23
Anilines (single –NH ₂)	1.09
Anilines (more than one –NH ₂)	1.14
N-substituted anilines (C ₆ H ₅ NHR)	1.06
Naphthols (single –OH)	1.09
Naphthylamines (single –NH ₂)	1.06
N-substituted naphthylamines	1.03

Octanol-water partition coefficient

While melting points, boiling points and vapor pressures are familiar properties used in many applications, properties such as the octanol-water partition coefficient are more specialized parameters used in environmental fate modeling. The octanol-water partition coefficient is used to characterize the partitioning of a molecule between largely aqueous phases, such as rivers and lakes, and largely hydrophobic phases, such as the organic fraction of sediments suspended in water bodies. Because the octanol-water partition coefficient (K_{ow}) characterizes partitioning between aqueous and organic, lipid-like phases, it is used to estimate a variety of toxicological, and environmental fate parameters. Therefore, accurate estimates of K_{ow} are critical to successful estimates of other environmental properties.

One specific and simple use of the octanol-water partition coefficient is as a gauge for the potential for bioaccumulation. If a chemical tends to partition into the organic phase (is lipophilic), then the chemical can be stored in fatty tissue of fish and will bioaccumulate in animals that consume the fish. Table 5.2-5 describes the approximate relationship between K_{ow} and bioaccumulation.

Table 5.2-5 Classification criteria for bioaccumulation

<i>Bioaccumulation potential</i>	
High Potential	$8.0 > \text{Log } K_{ow} > 4.3$
Moderate Potential	$4.3 > \text{Log } K_{ow} > 3.5$
Low Potential	$3.5 > \text{Log } K_{ow}$

Group contribution methods (structure activity relationships) have been developed for octanol-water partition coefficients (Meylan and Howard, 1995), and they have a form very similar to the form used for boiling point.

$$\log K_{ow} = 0.229 + \sum n_i f_i \quad (\text{Eqn. 5-11})$$

where $\log K_{ow}$ is the base 10 logarithm of the ratio of the chemical's concentration in octanol to the chemical's concentration in water, n_i is the number of groups of type i in the molecule, f_i is the contribution of each group to the partition coefficient, and the summation is taken over all groups. Structural groups and group contributions (f_i) for estimating octanol-water partition coefficients are listed in Table 5.2-6.

Just as was done for boiling point, corrections are introduced to the preliminary estimate. In this case corrections account for the unusual behavior of selected functional groups. The equation for estimating the corrected value of K_{ow} is:

$$\log K_{ow} = 0.229 + \sum n_i f_i + \sum n_j c_j \quad (\text{Eqn. 5-12})$$

where n_j is the number of groups of type j in the molecule, c_j is the correction factor for each group, and the summation is taken over all groups that have correction factors. Structural groups and correction factors (c_j) are listed in Table 5.2-7. The method yields a mean error of 0.31 log units (Meylan and Howard, 1995).

On first inspection, the correction factors listed in Table 5.2-7 may seem a bit baffling and arbitrary, however, more careful analysis reveals rationale behind the corrections. For example, many of the corrections account for electronic interactions between multiple substituents on aromatic rings (e.g., all of the ortho- corrections in Table 5.2-7). Recall from organic chemistry that substituents on aromatic rings can be electron donating or electron withdrawing and that these electronic effects are different at ortho-, meta- and para- positions. Thus, if there are two or more substituents on an aromatic ring, the substituents will interact with one another through their electronic effects on the ring. The corrections in the Table account for this effect. Other corrections in Table 5.2-7 account for other types of interactions between groups and the presence of ring structures. A final type of correction in the Table accounts for the presence of multiple hydrogen bonding groups in a molecule. Molecules with one hydrogen bonding group can form dimers, while molecules with more than one hydrogen bonding group can form n-mers. The potential formation of polymer-like chains held together by hydrogen bonds can dramatically influence chemical and physical properties, necessitating correction factors for molecules containing multiple hydrogen bonding groups.

While a list of correction factors could potentially be endless, in practice, only a few types of corrections are normally accounted for. Ring correction factors, factors accounting for multiple hydrogen bonding groups and corrections for substitution positions are among the most common. Example 5.2-4 illustrates the use of the group contribution method and the application of correction factors.

Table 5.2-6 Structural groups and group contributions for estimating octanol-water partition coefficients (Meylan and Howard, 1995)

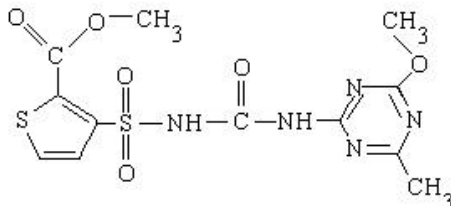
<i>Aromatic atoms</i>	Contribution (f_i) to octanol-water partition coefficient	<i>Aliphatic nitrogen groups</i>	Contribution (f_i) to octanol-water partition coefficient
Carbon	0.2940	-NO ₂ (aliphatic attach.)	-0.8132
Oxygen	-0.0423	-NO ₂ (aromatic attach.)	-0.1823
Sulfur	0.4082	-N=C=S (aliph. attach.)	0.5236
		-N=C=S (arom. attach.)	1.3369
<i>Aromatic nitrogen</i>		-NP	-0.4367
Nitrogen at a fused ring	-0.0001	-N (2 aromatic attach.)	-0.4657
N in a 5 member ring	-0.5262	-N (1 aromatic attach.)	-0.9170
N in a 6 member ring	-0.7324	-N=C (aliph. attach.)	-0.0010
		-NH ₂ (aliphatic attach.)	-1.4148
<i>Aliphatic Carbon</i>		-NH (aliphatic attach.)	-1.4962
-CH ₃	0.5473	-N< (aliphatic attach.)	1.8323
-CH ₂ -	0.4911	-N(O) (nitroso)	-0.1299
-CH<	0.3614	-N=N- (azo)	0.3541
>C<	0.2676		
Other C, no H attached	0.9723	<i>Aliphatic oxygen</i>	
		-OH (nitrogen attach.)	-0.0427
<i>Olefinic/acetylenic C</i>		-OH (P attachment)	0.4750
=C< (2 aromatic bonds)	-0.4186	-OH (olefinic attach.)	-0.8855
=CH ₂	0.5184	-OH (carbonyl attach.)	0.0
=CH- or =C<	0.3836	-OH (aliphatic attach.)	-1.4086
≡CH or ≡C-	0.1334	-OH (aromatic attach.)	-0.4802
		=O	0.0
<i>Carbonyls</i>		-O- (carbonyl attach.)	0.0
-CHO (aliphatic attach.)	-0.9422	-O- (aliphatic attach.)	-1.2566
-CHO (aromatic attach.)	-0.2828	-O- (1 aromatic attach.)	-0.4664
-C(O)OH (aliph. attach)	-0.6895	-O- (2 aromatic attach.)	0.2923
-C(O)OH (arom. attach)	-0.1186		
-NC(O)N- (urea type)	1.0453	<i>Aliphatic sulfur</i>	
NC(O)O (carbamate)	0.1283	-SO ₂ N (aliph. attach)	-0.4351
NC(O)S(thiocarbamate)	0.5240	-SO ₂ N (arom. attach)	-0.2079
-C(O)O- (aliph. attach)	-0.9505	-S- (aliphatic attach.)	-0.4045
-C(O)O- (arom. attach)	-0.7121	-S-S- (disulfide)	0.5497
-C(O)N (aliph. attach)	-0.5236	-SO ₂ OH (sulfonic acid)	-3.1580
-C(O)N (arom. attach)	0.1599		
-C(O)S- (aliph. attach)	-1.100	<i>Halogen groups</i>	
-C(O)- (aliph. attach)	-1.5586	-F (aliph. attach)	-0.0031
-C(O)- (1 arom. attach)	-0.8666	-F (arom. attach)	0.2004
-C(O)- (cyclic, 2 arom. attach)	-0.2063	-Cl (aliph. attach)	0.3102
-C(O)- (olefinic attach)	-1.2700	-Cl (arom. attach)	0.6445
-C(O)- (cyclic, arom., olefinic attach.)	-0.5497	-Cl (olefinic attach)	0.4923
		-Br (aliph. attach)	0.3997
		-Br (arom. attach)	0.8900

Table 5.2-7 Correction factors for estimating octanol-water partition coefficients (Meylan and Howard, 1995)

Structural group	Correction factor
<i>Correction factors involving ortho substituents on aromatic rings</i>	
-COOH/-OH	1.1930
-OH/ester	1.2556
Amino (at 2 position) on pyridine	0.6421
Alkyloxy (or alkylthio) ortho to 1 aromatic nitrogen	0.4549
Alkyloxy ortho to two aromatic nitrogens (or pyrazine)	0.8955
Alkylthio ortho to two aromatic nitrogens (or pyrazine)	0.5415
Carboxamide (-C(O)N) ortho to an aromatic nitrogen	0.6427
Any group other than hydrogen ortho to -NHC(O)C (e.g., 2 methylacetanilide)	-0.5634
Any two groups other than hydrogen ortho to -NHC(O)C (e.g., 2,6 dimethylacetanilide)	-1.1239
Any group other than hydrogen ortho to -C(O)NH (e.g., 2 methylbenzamide)	-0.7352
Any two groups other than hydrogen ortho to -C(O)NH (e.g., 2,6 dimethylbenzamide)	-1.1284
<i>Correction factors involving non-ortho substituents on aromatic rings</i>	
-N</-OH (e.g., 4-aminophenol)	-0.3510
-N</ester (e.g., 4 aminobenzoic acid methyl ester)	0.3953
-OH/ester	0.6487
<i>Correction factors involving ortho or non-ortho substituents on aromatic rings</i>	
-NO ₂ with -OH, -N<, or -N=N-	0.5770
-C≡N with -OH or -N (e.g., cyanophenols)	0.5504
Amino group on triazine, pyrimidine, or pyrazine	0.8566
NC(O)NS on triazine or pyrimidine (2-position)	-0.7500
<i>Additional (non-aromatic) correction factors</i>	
<i>Carbonyl correction factors</i>	
More than one aliphatic -C(O)OH	-0.5865
Cyclic ester (non-olefinic)	-1.0577
Cyclic ester (olefinic)	-0.2969
-C(O)-C-C(O)N	0.9734
<i>Ring correction factors</i>	
triazine ring	0.8856
Pyridine ring (non-fused)	-0.1621
Fused aliphatic ring	-0.3421
<i>Alcohol, ether and nitrogen corrections</i>	
More than one aliphatic -OH	0.4064
-NC(C-OH)C-OH	0.6365
-NCOC	0.5494
HO-CHCOCH-OH	1.0649
HO-CHC(OH)CH-OH	0.5944
-NH-NH-	1.1330
>N-N<	0.7306

Example 5.2-4

Estimate the octanol-water partition coefficient for 1,1 dichloroethylene and the structure shown below (a herbicide).

**Solution**

a.) 1,1-Dichloroethylene has the molecular structure $\text{CH}_2=\text{CCl}_2$. Referring to the groups in Table 5-4, this structure can be represented by one $=\text{CH}_2$ group, one $=\text{CH}-$ or $=\text{C}<$ group and two $-\text{Cl}$ (olefinic attachment) groups. The uncorrected value of K_{ow} from equation 5-4 is given by:

$$\log K_{ow} = 0.229 + 0.5184 + 0.3836 + 2(0.4923) = 2.11$$

$$K_{ow} = 130$$

Dichloroethylene does not contain any groups that have correction terms. The experimental value for $\log K_{ow}$ is 2.13, so the predicted value of K_{ow} is in error by 3.3%

b.) The herbicide can be represented by three $-\text{CH}_3$ groups, one $-\text{NH}-$ (aliphatic attachment), 7 aromatic carbons, 3 aromatic nitrogens, one $-\text{O}-$ (one aromatic attachment) group, one $-\text{N}$ (one aromatic attachment) group, one aromatic sulfur group, one $-\text{C}(=\text{O})\text{O}$ (ester, aromatic attachment) group, one $-\text{SO}_2\text{N}$ (aromatic attachment) group and one $-\text{NC}(=\text{O})\text{N}-$ (urea type carbonyl) group. Note that the $-\text{NC}(=\text{O})\text{N}-$ is listed as a carbonyl group in Table 5-6 and accounts only for the carbonyl ($\text{C}=\text{O}$), not the nitrogens. The uncorrected value of K_{ow} from equation 5-4 is given by:

$$\log K_{ow} = 0.229 + 3(0.5473) - 1.4962 + 7(0.2940) - 3(0.7324) - 0.4664 - 0.9170 + 0.4082 - 0.7121 - 0.2079 + 1.0453 = -0.614$$

The herbicide contains several groups that require correction factors. There is one triazine ring correction, (0.8856), one correction for an amino-type triazine (0.8566), one correction for an alkoxy ortho to two aromatic nitrogens (0.8955) and one correction for a $-\text{NC}(=\text{O})\text{NS}$ on a triazine (-0.7500). The total of these correction factors is 1.887, leading to

$$\log K_{ow} = 1.273$$

The octanol-water partition coefficient for this compound is strongly pH dependent, but this estimation method leads to reasonable estimates for slightly basic solutions.

Bioconcentration factor

One of the primary reasons for estimating the octanol-water partition coefficient is to assess the partitioning of a chemical between aqueous and lipid phases in living organisms. This partitioning is normally expressed as a BioConcentration Factor (BCF). The BCF is defined as the ratio of a chemical's concentration in the tissue of an aquatic organism to its concentration in water (in L/kg). This parameter is called a bioconcentration factor because high values of BCF indicate that a living organism will tend to extract a material from an aqueous phase, such as ingested water or blood, and concentrate it in lipid tissues (e.g., fats). Thus, high values of BCF can be cause for concern. For example, a compound with a high bioconcentration factor may tend to accumulate in fish, resulting in a health hazard if the fish is eaten.

As shown in Table 5.2-8, BCF values can be used to gauge bioaccumulation potential, just as octanol-water partition coefficients were (Table 5.2-5).

Table 5.2-8 Classification criteria for bioaccumulation

<i>Bioaccumulation potential</i>	
High Potential	BCF>1000
Moderate Potential	1000>BCF>250
Low Potential	250>BCF

Veith and Kosian (1983) propose this correlation between octanol-water partition coefficients and BCF:

$$\log \text{BCF} = 0.79 (\log K_{ow}) - 0.40 \quad (\text{Eqn. 5-13})$$

More recently, correction factors have been introduced into this correlation, in a manner analogous to the estimation methods for K_{ow} . For non-ionic compounds, Meylan, et al. (1997), propose:

$$\log \text{BCF} = 0.77 (\log K_{ow}) - 0.70 + \sum j_j \quad (\text{Eqn. 5-14})$$

where j_j is the correction factor for each group, and the summation is taken over all groups that have correction factors. The correction factors are listed in Table 5.2-9. Mean errors of approximately 0.5 log units can be expected with this method.

Note that there are fewer correction factors in Table 5.2-9 than in Table 5.2-7. This is not because BCF is more straightforward to estimate than K_{ow} . If anything, BCF is more difficult to reliably estimate than K_{ow} because of the variability in lipid tissues. The reason why Table 5.2-9 is relatively sparse is because experimental values, on which the correction factors are based, are considerably scarcer for BCF than for K_{ow} . Therefore, estimates of BCF for structurally complex compounds that typically require correction factors may have considerable uncertainty.

Table 5.2-9 Correction factors for BCF of non-ionic compounds (Meylan and Howard, 1997)

Structural group	Correction factor
Ketone (with one or more aromatic connections)	-0.84
Phosphate ester, O=P(O-R)(O-R)(O-R) where at least two of the R groups are carbon	-0.78
Multihalogenated biphenyls and polyaromatics	0.62
Compounds containing an aromatic ring and an aliphatic alcohol in the form of -CH-OH (e.g., benzyl alcohol)	-0.65
Compounds containing an aromatic alcohol (e.g., phenol) with two or more halogens attached to the aromatic ring	-0.40
Compounds containing an aromatic triazine ring	-0.32
Compounds containing an aromatic ring with a tert-butyl group in an ortho position to a hydroxyl group	-0.45
Compounds containing a phenanthrene ring	0.48
Compounds containing a cyclopropyl ester	-1.65
Compounds with an alkyl chain containing 8 or more -CH ₂ - groups (4 < log K _{ow} < 6)	-1.00
Compounds with an alkyl chain containing 8 or more -CH ₂ - groups (6 < log K _{ow} < 10)	-1.50
Azo compounds	Log BCF = 1

Example 5.2-5

Estimate the bioconcentration factor for 2,2,4 trimethyl-1,3 pentanediol, and 2, 4',5 trichlorobiphenyl.

Solution

- a.) 2,2,4 trimethyl-1,3 pentanediol has the structure
 b.) $\text{HO-CH}_2\text{-(C)(CH}_3)_2\text{-CH(OH)-(CH)(CH}_3\text{)-CH}_3$. Before estimating BCF, it is first necessary to estimate K_{ow} . Referring to the groups in Table 5.2-6, the structure can be represented by four $-\text{CH}_3$ groups, one $-\text{CH}_2-$ group, one $>\text{C}<$ group, two $-\text{CH}<$ groups and two $-\text{OH}$ groups (aliphatic attachment). The uncorrected value of K_{ow} from equation 5-4 is given by:

$$\log K_{ow} = 0.229 + 4(0.5473) + 0.4911 + 0.2676 + 2(0.3614) + 2(-1.4086) = 1.08$$

$$K_{ow} = 12.1$$

2,2,4 trimethyl-1,3 pentanediol requires a correction for molecules containing two or more aliphatic $-\text{OH}$ (0.4064). The corrected value for $\log K_{ow}$ is 1.49. The experimental value for $\log K_{ow}$ is 1.24. Using the corrected calculated value of $\log K_{ow}$ and equation 5-13 (Eqn. 5-14 does not apply since none of the correction factors in Table 5.2-9 are appropriate), proceed to calculate BCF for 2,2,4 trimethyl-1,3 pentanediol.

$$\log \text{BCF} = 0.79(1.49) - 0.40 = 0.7771$$

$$\text{BCF} = 5.99$$

Referring to Table 5.2-8, we see that since the BCF of 2,2,4 trimethyl-1,3 pentanediol is less than 250, it has low potential for bioaccumulation.

- b.) 2,4',5 trichlorobiphenyl can be represented by 12 aromatic carbons and 3 $-\text{Cl}$ (aromatic attachment) groups. The uncorrected value of K_{ow} from equation 5-4 is given by:

$$\log K_{ow} = 0.229 + 12(0.2940) + 3(.6445) = 5.69$$

No corrections are required. The experimental value for $\log K_{ow}$ is 5.81. Using this uncorrected calculated value of $\log K_{ow}$ and equation 5-14, proceed to calculate BCF for 2,4',5 trichlorobiphenyl. With the correction factor from Table 5.2-9 for multihalogenated biphenyls and polyaromatics (0.62), equation 5-14 becomes:

$$\log \text{BCF} = 0.77(5.69) - 0.70 + 0.62 = 4.30$$

$$\text{BCF} = 20000$$

Referring to Table 5.2-9, it is evident that 2,4',5 trichlorobiphenyl has a very high potential for bioaccumulation.

Water Solubility

In assessing environmental transport and partitioning, it is often necessary to predict maximum, or saturation, concentrations. In the gas phase this is done by estimating vapor pressure. In aqueous phases, saturation concentrations are estimated using water solubilities.

Water solubility can be estimated in many ways. Activity coefficients, solubility parameters and other chemical and structural properties can be used as a basis for estimating water solubility. For environmental applications, however, water solubility is most often estimated based on octanol-water partition coefficients. This is not because K_{ow} is the most accurate or reliable parameter for estimating water solubility. Rather, it is a matter of convenience. K_{ow} is used to estimate a wide variety of parameters in evaluating environmental fate and risk. Therefore, K_{ow} is generally available in environmental assessments, while properties such as activity coefficients are not frequently calculated in environmental screening studies. Table 5.2-10 classifies the numerical values for solubility (S) into general solubility categories.

Table 5.2-10 Classification criteria for water solubility

<i>Water Solubility</i>	
Very Soluble	$S > 10,000$ ppm
Soluble	$1,000 < S < 10,000$ ppm
Moderately Soluble	$100 < S < 1,000$ ppm
Slightly Soluble	$0.1 < S < 100$ ppm
Insoluble	$S < 0.1$ ppm

Meylan, et al. (1996) have used K_{ow} , along with correction factors, to estimate water solubilities. Their correlations are:

$$\log S = 0.342 - 1.0374 \log K_{ow} - 0.0108(T_m - 25) + \sum h_j \quad (\text{Eqn. 5-15})$$

$$\log S = 0.796 - 0.854 \log K_{ow} - 0.00728(MW) + \sum h_j \quad (\text{Eqn. 5-16})$$

$$\log S = 0.693 - 0.96 \log K_{ow} - 0.0092(T_m - 25) - 0.00314(MW) + \sum h_j \quad (\text{Eqn. 5-17})$$

Where S is the water solubility in mol/L; K_{ow} is the octanol-water partition coefficient, T_m is the melting point in °C, MW is the molecular weight, and h_j is the correction factor for each group, and the summation is taken over all groups that have correction factors. Note that the correction factors are different for each equation. They are listed in Table 5.2-11. Mean errors are in the range of 0.3 to 0.4 log units.

Any of the three equations can be used, but generally, if more information is available for the correlation (Equations 5-16 or 5-17), the estimate is more accurate.

Table 5.2-11 Correction factors for estimating water solubility (Meylan, et al., 1996)

Structural group	Correction factor (Eqn. 5-15)	Correction factor (Eqn. 5-16)
Aliphatic alcohols with one –OH attached to aliphatic carbon, except acetamide, amino, azo or –S=O compounds	0.466	0.510
Aliphatic acids with acid attached to aliphatic group, except amino acids and compounds with C(O)-N-C-COOH	0.689	0.395
Primary, secondary and tertiary aliphatic, liquid amines	0.883	1.008
Aromatic acids except amino-substituted compounds	1.104	-
Phenols, except amino-phenols	1.092	0.580
Alkylpyridines	1.293	1.300
Azo compounds (-C-N=N-C-)	-0.638	-0.432
Nitrile compounds except (N-C-CN)	-0.381	-0.265
Hydrocarbons (aliphatics containing only carbon and hydrogen)	-0.112	-0.537
Aliphatic and aromatic nitro compounds, except aromatic compounds with –OH or amino substitutions	-0.555	-0.390
Aromatic sulfonamide and aliphatic compounds with S-(O)-C-C(O)-C	-1.187	-1.051
Alkanes with two or more fluorines	-0.832	-0.742
Polyaromatic hydrocarbons	-	-1.110
Compounds with two or more aliphatic N, one attached to C(O), S(O) or C(=S); compounds with 4 or more aromatic N, compounds with 2 or more aromatic N and one or more aliphatic N attached to C(O), S(O) or C(=S); except N in nitrile, nitro, azo, barbituate and metal compounds	-	-1.310
Amino acids	-	-2.070

Example 5.2-5

Estimate the water solubility of 2-hexanol and diphenyl ether.

Solution

a.) 2-hexanol has the molecular structure $\text{CH}_3\text{-(CH-OH)-C}_4\text{H}_9$. Before estimating water solubility, we must estimate K_{ow} . Referring to the groups in Table 5.2-6, this structure can be represented by two $-\text{CH}_3$ groups, three $-\text{CH}_2-$ groups, one $-\text{CH}-$ group and one $-\text{OH}$ (aliphatic attachment) group. The uncorrected value of K_{ow} from Equation 5-11 is given by:

$$\log K_{ow} = 0.229 + 2(0.5473) + 3(0.4911) + 0.3614 - 1.4086 = 1.75$$

2-hexanol does not contain any groups that have correction terms. The experimental value for $\log K_{ow}$ is 1.76, so the predicted value of K_{ow} is in error by -0.6%

The water solubility can be estimated from Equation 5-16 with a correction term for one aliphatic $-\text{OH}$ group.

$$\text{Log } S = 0.796 - 0.854 (\log K_{ow}) - 0.00728(\text{MW}) + \sum h_j$$

$$\text{Log } S = 0.796 - 0.854 (1.75) - 0.00728(102.2) + 0.510 = -0.932$$

$$S = 0.12 \text{ mol/L}$$

b.) Diphenyl ether has the molecular structure $\text{C}_6\text{H}_5\text{-O-C}_6\text{H}_5$. Before estimating water solubility, we must estimate K_{ow} . Referring to the groups in Table 5.2-6, this structure can be represented by twelve aromatic carbons and one $-\text{O}-$ group (two aromatic attachments) group. The uncorrected value of K_{ow} from equation 5-11 is given by:

$$\log K_{ow} = 0.229 + 12 (0.2940) + 0.2923 = 4.05$$

Diphenyl ether does not contain any groups that have correction terms. The experimental value for $\log K_{ow}$ is 4.21, so the predicted value of K_{ow} is in error by -3.8%

The water solubility can be estimated from Equation 5-16. There are no correction terms that apply.

$$\text{Log } S = 0.796 - 0.854 (\log K_{ow}) - 0.00728(\text{MW}) + \sum h_j$$

$$\text{Log } S = 0.796 - 0.854 (4.05) - 0.00728(170.2) + 0.0 = -3.90$$

$$S = 1.2 * 10^{-4} \text{ mol/L}$$

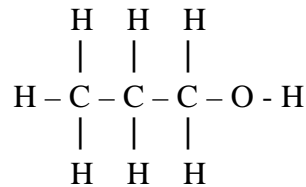
Henry's Law Constant

The Henry's Law constant, as commonly used in describing environmental fate, is the ratio of a compound's concentration in air to its concentration in water, at equilibrium. In other words, it shows a compound's affinity for air over water. Therefore, compounds with high values of Henry's Law constant (H) tend to partition into the air, while compounds with low values of H tend to partition into the water. H is generally expressed either as a dimensionless ratio, or in units of atm-m³/mole. Table 5.2-12 classifies Henry's law coefficients into a set of volatility categories.

Table 5.2-12 Classification criteria for volatility

Volatility (H in atm-m ³ /mole)	
Very Volatile	$H > 10^{-1}$
Volatile	$10^{-1} > H > 10^{-3}$
Moderately Volatile	$10^{-3} > H > 10^{-5}$
Slightly Volatile	$10^{-5} > H > 10^{-7}$
Nonvolatile	$10^{-7} > H$

A group contribution method can also be used to estimate the value of Henry's Law constant. In this case, the group contribution method is structured differently than the previous methods. The structural elements are bonds, rather than functional groups. Consider 1-propanol as an example of how a bond approach differs from a functional group approach to structural characterization.



Using the groups from Table 5.2-2, 1-propanol would consist of one –CH₃ group, two >CH₂ groups, and one primary –OH group. Expressed as a collection of bonds, 1-propanol consists of 7 C-H bonds, 2 C-C bonds, one C-O bond and one O-H bond.

A preliminary estimate of the Henry's Law constant is obtained by summing each of the bond contributions. This preliminary estimate is then adjusted by correction factors for selected functional groups (Meylan and Howard, 1991).

$$-\log H = \log (\text{air-water partition coefficient}) = \sum n_i h_i + \sum n_j c_j \quad (\text{Eqn. 5-18})$$

where H is the dimensionless Henry's Law constant, n_i is the number of bonds of type i in the molecule, h_i is the bond contribution to the air-water partition coefficient, n_j is the number of groups of type j in the molecule, c_j is the correction factor for each group, and the summations are taken over all bonds and all groups that have correction factors. Bond contributions (h_i) and correction factors (c_j) are listed in Tables 5.2-13 and 5.2-14. Mean

errors in log units range from 0.06 for alkanes and alkylbenzenes to 0.4 for haloalkenes (Meylan and Howard, 1991).

Table 5.2-13 Structural groups and group contributions for estimating Henry's Law constants (Meylan and Howard, 1991)

Bond type	Contribution (h_i) to Henry's Law constant	Bond type	Contribution (h_i) to Henry's Law constant
C-H	-0.1197	C _{aromatic} -OH	0.5967
C-C	0.1163	C _{aromatic} -O	0.3473
C-C _{aromatic}	0.1619	C _{aromatic} - N _{aromatic}	1.6282
C-C _{olefinic}	0.0635	C _{aromatic} - S _{aromatic}	0.3739
C-C _{acetylenic}	0.5375	C _{aromatic} - O _{aromatic}	0.2419
C-CO	1.7057	C _{aromatic} - S	0.6345
C-N	1.3001	C _{aromatic} - N	0.7304
C-O	1.0855	C _{aromatic} - I	0.4806
C-S	1.1056	C _{aromatic} - F	-0.2214
C-Cl	0.3335	C _{aromatic} - C _{olefinic}	0.4391
C-Br	0.8187	C _{aromatic} - CN	1.8606
C-F	-0.4184	C _{aromatic} - CO	1.2387
C-I	1.0074	C _{aromatic} - Br	0.2454
C-NO ₂	3.1231	C _{aromatic} - NO ₂	2.2496
C-CN	3.2624	CO-H	1.2102
C-P	0.7786	CO-O	0.0714
C=S	-0.0460	CO-N	2.4261
C _{olefinic} -H	-0.1005	CO-CO	2.4000
C _{olefinic} = C _{olefinic}	0.0000	O-H	3.2318
C _{olefinic} - C _{olefinic}	0.0997	O-P	0.3930
C _{olefinic} -CO	1.9260	O-O	-0.4036
C _{olefinic} -Cl	0.0426	O=P	1.6334
C _{olefinic} -CN	2.5514	N-H	1.2835
C _{olefinic} -O	0.2051	N-N	1.0956
C _{olefinic} -F	-0.3824	N=O	1.0956
C _{acetylenic} -H	0.0040	N=N	0.1374
C _{acetylenic} ≡ C _{acetylenic}	0.0000	S-H	0.2247
C _{aromatic} -H	-0.1543	S-S	-0.1891
C _{aromatic} - C _{aromatic} (fused)	0.2638	S-P	0.6334
C _{aromatic} - C _{aromatic} (ext.)	0.1490	S=P	-1.0317
C _{aromatic} - Cl	-0.0241		

Table 5.2-14 Correction factors for Henry's law constants (Meylan and Howard, 1991)

Structural group	Correction factor
Linear or branched alkane	-0.75
Cyclic alkane	-0.28
Monoolefin	-0.20
Cyclic monoolefin	0.25
Linear or branched aliphatic alcohol	-0.20
Adjacent aliphatic ethers (-C-O-C-O-C-)	-0.70
Cyclic monoether	0.90
Epoxide	0.50
Each additional aliphatic -OH above one	-3.00
Each additional aromatic nitrogen within a single ring above one	-2.50
A fluoroalkane with only one fluorine	0.95
A chloroalkane with only one chlorine	0.50
A fully chlorinated chloroalkane	-1.35
A fully fluorinated fluoroalkane	-0.60
A fully halogenated haloalkane	-0.90

Example 5.2-6

Estimate the Henry's law constant for 1-propanol.

Solution

1-propanol consists of 7 C-H bonds, 2 C-C bonds, one C-O bond and one O-H bond.

The uncorrected value of log (air to water partition constant) is given by:

$$-\log H = \log (\text{air-water partition coefficient}) = 7(-0.1197) + 2(0.1163) + 1.0855 + 3.2318 = 3.7112$$

The correction is for linear or branched alcohols (-0.20) giving a net value of 3.5112 for $\log H^{-1}$. The experimental value is 3.55, an error of -1.1% in the logarithm of the air to water partition constant. Note that this is a dimensionless value (mol/m^3 divided by mol/m^3). To convert to units of atmospheres- m^3/mol , the dimensionless value should be adjusted using the ideal gas law, the gas constant and the temperature.

Soil sorption Coefficients

Soil-water partitioning is generally described using soil sorption coefficients. The coefficient (K_{oc}) is defined as the ratio of the mass of a compound adsorbed per unit weight of organic carbon in a soil (in $\mu\text{g/g}$ organic carbon) to the concentration of the compound in a liquid phase (in $\mu\text{g/ml}$). Values of K_{oc} are categorized in Table 5.2-15.

Table 5.2-15 Classification criteria for soil sorption

<i>Soil Sorption</i>	
Very Strong Sorption	$\text{Log } K_{oc} > 4.5$
Strong Sorption	$4.5 > \text{Log } K_{oc} > 3.5$
Moderate Sorption	$3.5 > \text{Log } K_{oc} > 2.5$
Low Sorption	$2.5 > \text{Log } K_{oc} > 1.5$
Negligible Sorption	$1.5 > \text{Log } K_{oc}$

The property estimation methods just described for water solubility, bioconcentration factor, and Henry's Law constant used the octanol-water partition coefficient as the primary correlating variable. This was possible because both the properties of interest and the correlating variable were bulk properties. Correlations for soil sorption coefficients, based on octanol-water partition coefficients and water solubility, are also available.

Lyman, et al. (1990) have given the following equations for octanol-water partition coefficient estimation.

$$\log K_{oc} = 0.544 \log K_{ow} + 1.377 \quad (\text{Eqn. 5-19})$$

$$\log K_{oc} = -0.55 \log S + 3.64 \quad (\text{Eqn. 5-20})$$

These equations, however, are restricted to quite specific classes of compounds. They are limited in their applicability because of the nature of soil sorption. The soil sorption coefficient describes the physical adsorption and chemical absorption of a compound onto a surface. The coefficient therefore depends not only bulk properties, but also on steric properties that influence the interaction of a molecule with a surface. Meylan, et al., (1992) have proposed a relatively simple correlation for estimating soil sorption coefficients that incorporates both bulk and steric effects through a structural parameter called the molecular connectivity.

$$\log K_{oc} = 0.53^1\chi + 0.62 + \sum n_j P_j \quad (\text{Eqn. 5-21})$$

where K_{oc} is the soil sorption coefficient expressed as the ratio of the mass of a compound adsorbed per unit weight of organic carbon in a soil (in $\mu\text{g/g}$ organic carbon) to the concentration of the compound in a liquid phase (in $\mu\text{g/ml}$); $^1\chi$ is the first order molecular connectivity index, as described in the Appendix to this chapter; n_j is the number of groups of type j in the molecule; P_j is the correction factor for each group, and the summation is taken over all groups that have correction factors. The correction factors are listed in Table 5.2-16. Mean errors of approximately 0.6 log units can be expected.

Table 5.2-16 Correction factors for soil sorption coefficients (Meylan and Howard, 1992)

Structural group	Correction factor
<i>N containing groups</i>	
azo	-1.028
<i>N, C containing groups</i>	
Nitrile/cyanide	-0.722
Nitrogen bound to noncyclic aliphatic C	-0.124
Nitrogen bound to cycloalkane	-0.822
Nitrogen bound to non-fused aromatic ring	-0.777
Pyridine ring with no other fragments	-0.700
Aromatic ring with 2 nitrogens	-0.965
Triazine ring	-0.752
<i>N, O containing groups</i>	
nitro	-0.632
<i>N, C, O containing groups</i>	
Urea group (N-CO-N)	-0.922
Acetamide (N-CO-C)	-0.811
Uracil (-N-CO-N-CO-C=C- ring)	-1.806
N-CO-O-N-	-1.920
Carbamate (N-CO-O-phenyl)	-2.002
N-phenyl carbamate	-1.025
<i>C, O containing groups</i>	
Aromatic ether	-0.643
Aliphatic ether	-1.264
Ketone	-1.248
Ester	-1.309
Aliphatic alcohol	-1.519
Carboxylic acid	-1.751
Carbonyl	-1.200
<i>P, O containing groups</i>	
Aliphatic organophosphorus, P=O	-1.698
Aromatic organophosphorus, P=O	-2.878
<i>P, S containing groups</i>	
P=S	-1.263
<i>C, S containing groups</i>	
Thiocarbonyl	-1.100
<i>S, O containing groups</i>	
sulfone	-0.995

Example 5.2-7

Estimate the soil sorption coefficient of 2-hexanol.

Solution

a.) As noted in Example problem 5.2-5, 2-hexanol has the molecular structure $\text{CH}_3\text{-(CH-OH)-C}_4\text{H}_9$. $\log K_{ow}$ was estimated to be 1.75 and $\log S$ was estimated to be -0.932.

Estimating soil sorption coefficients using Equation 5-19 and Equation 5-20:

$$\text{Log } K_{oc} = 0.544 \log K_{ow} + 1.377 = 2.329$$

$$\text{Log } K_{oc} = -0.55 \log S + 3.64 = 4.15$$

Both of these estimates are substantially different from the experimental value of 1.01. Using instead a correlation based on molecular connectivity (Equation 5-21):

$$\text{Log } K_{oc} = 0.53^1\chi + 0.62 + \sum n_j P_j$$

Where the value of $^1\chi$ is 3.27 gives an uncorrected value of 2.35. Adding in the correction term for an aliphatic alcohol (-1.519) yields an estimate of 0.83.

Summary

This section has examined methods for estimating chemical and physical properties that influence phase partitioning in the environment. These methods will serve as the basis for estimation of a broad range of parameters that describe environmental persistence and environmental impacts. Therefore, any errors or uncertainties associated with the estimates described in this section are likely to propagate through the entire environmental assessment.

Section 5.2 Questions for Discussion

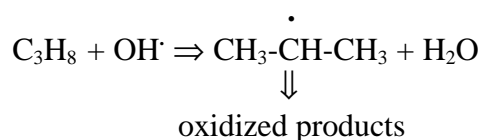
1. How would you estimate properties for molecules that contain groups that are not explicitly represented in the group contribution methods (for example, could you estimate the Henry's Law constant for the herbicide listed in Example 5.2-3)?
2. The methodologies presented in this chapter are only a small selection of the group contribution methods available for these properties. How would you select the most accurate estimation methods?
3. Do the functional forms of the group contribution methods seem appropriate? For example, is it reasonable to assume that a boiling point estimation method should be a simple linear function? Would this approach work equally well for carboxylic acids and dicarboxylic acids? Would it work equally well for alcohols and glycols?
4. Can you rationalize the values of the group contributions? For example, does it make sense that the -OH group has a large positive group contribution for boiling point?

5.3 ESTIMATING ENVIRONMENTAL PERSISTENCE

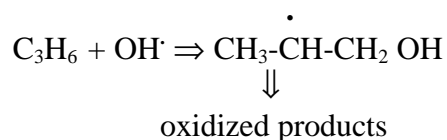
Section 5.2 described estimation tools for properties that influence the phase partitioning of chemicals in the environment. This section will examine methods for estimating the persistence of chemicals in the atmosphere and in aqueous and sediment environments. These methods are, by necessity, extremely simplified attempts to characterize the complex chemistries that occur in ambient environments. Thus, they should not be viewed as precise tools for estimating environmental lifetimes of chemicals. Rather, they should be viewed as semi-quantitative screening tools for ranking relative persistence.

Estimating atmospheric lifetimes

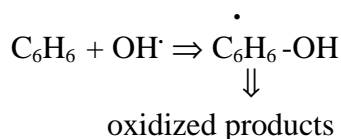
Chemicals emitted to the atmosphere undergo oxidation through a wide range of processes. One of the critical steps in these oxidations, particularly for organic compounds, is the rate of reaction with the hydroxyl radical. Hydroxyl radicals are extremely reactive species and can abstract hydrogen from saturated organics, add to double bonds or add to aromatic rings. Some of these reactions are shown below.



Hydrogen abstraction from propane



Hydroxyl radical addition to propene



Hydroxyl radical addition to an aromatic ring

These reactions with hydroxyl radicals are often the first step in a series of reactions that lead to the oxidation of organics in the atmosphere. We will not examine the details of these pathways (the interested reader is referred to Seinfeld and Pandis, 1998), however, the relative rate at which a hydroxyl radical reacts with a compound is a semi-quantitative indicator of how long the compound will persist in the atmosphere. For example, for the three reactions listed above (hydrogen abstraction from propane, addition to propene and addition to benzene), the rates of reaction are 1.2×10^{12} , 26.0×10^{12} , and 2.0×10^{12} $\text{cm}^3/\text{molecule}\cdot\text{sec.}$, respectively. This indicates that if reaction with a hydroxyl radical is the dominant reaction pathway leading to oxidation in the atmosphere, then the rates of disappearance should be in the ratio 1.2 : 26 : 2. As shown in Example 5.3-1, this implies a ratio of atmospheric lifetimes of 106 hours : 5 hours : 64 hours:

So, one method of assessing atmospheric lifetimes is to estimate rate of reaction with hydroxyl radical. Once again, group contribution methods are a viable approach. The mechanics of the method are similar to those discussed in Section 5.2. A molecule is divided into a collection of functional groups and each group makes a defined contribution to the overall rate of reaction. The method is slightly different than the methods discussed in Section 5.2, however, in that a single compound might have multiple rate parameters. Consider, for example, the reactions of propene. Hydroxyl radical can add to the double bond of propene. To estimate that rate constant we would note that the olefinic group in propene has the structure ($\text{CH}_2=\text{CH}-$), and based on the data in Table 5.3-1, the rate constant for hydroxyl radical addition would be 26.3×10^{12} $\text{cm}^3/\text{molecule}\cdot\text{sec.}$ But hydroxyl radical can also abstract hydrogen from the terminal methyl group. This reaction, however, occurs much more slowly than the addition reaction. The group contribution for abstraction from a terminal methyl group is only 0.136×10^{12} $\text{cm}^3/\text{molecule}\cdot\text{sec.}$ Thus, although propene can react via two pathways, only one is significant.

Identifying and estimating the rates of hydroxyl radical reactions with all of the functional groups in a molecule requires extensive experience. In this chapter, we will limit our estimations to addition reactions for olefins, and abstraction reactions. The group contributions for estimating these rates are listed in Tables 5.3-1 to 5.3-3. As with the property estimations described in Section 5.2, there are correction factors that can be applied to the estimations. These correction factors account for the electron donating and withdrawing characteristics of substituent groups, ring strain energy and other parameters. A detailed discussion of these correction factors is beyond the scope of this chapter. Examples 5.3-1 and 5.3-2 illustrate how the basic estimations of hydroxyl radical reaction rates and atmospheric half-life are performed and provides simple illustrations of how the correction factors are applied.

Example 5.3-1

Using the rate of reaction of propene with the hydroxyl radical, estimate the atmospheric half-life of propylene.

Solution:

The rate of reaction implies a rate of disappearance of propene:

$$(d[C_{\text{propene}}]/dt) = k [\text{OH}\cdot] [C_{\text{propene}}]$$

where $[\text{OH}\cdot]$ is the concentration of the hydroxyl radical and $[C_{\text{propene}}]$ is the concentration of propene.

Assuming that the concentration of hydroxyl radical is steady state - the pseudosteady-state assumption (see, for example, Fogler, 1995) – leads to the following expression for the concentration of propene:

$$\ln ([C_{\text{propene}}]/[C_{0\text{-propene}}]) = -(k [\text{OH}\cdot])t$$

Where $[C_{0\text{-propene}}]$ is the initial concentration of propene, $(k [\text{OH}\cdot])$ is the rate constant multiplied by the steady state concentration of hydroxyl radicals and t is the time of reaction.

Since $([C_{\text{propene}}]/[C_{0\text{-propene}}]) = 1/2$ when the concentration has reached one half of its original value, the half life is given by:

$$t_{1/2} = \ln(2) / (k [\text{OH}\cdot])$$

Assuming a value of 1.5×10^6 molecules/cm³ for the concentration of the hydroxyl radical (while 1.5×10^6 molecules/cm³ is a typical value – summertime concentrations in urban areas can reach 10^7 molecules/cm³) and a value of 26×10^{-12} cm³/molecule-sec for k :

$$t_{1/2} = \ln(2) / (39 \times 10^{-6} \text{ sec}^{-1})$$

So, the half life for propene in the atmosphere is:

$$t_{1/2} = 5.0 \text{ hr}$$

Repeating this calculation for propane and benzene, with reaction rates of 1.2×10^{-12} and 2.0×10^{-12} cm³/molecule-sec, leads to atmospheric half lives of 106 and 64 hours, respectively.

Example 5.3-2a

Estimate the rate of reaction of octane with the hydroxyl radical.

Solution

Octane has the molecular structure $\text{CH}_3\text{-(CH}_2\text{)}_6\text{-CH}_3$. Since there are no aromatic, olefinic or acetyl groups, the primary reaction pathway will be hydrogen atom abstraction. Referring to the groups in Table 5.3-1, this structure can be represented by two -CH₃ groups and six -CH₂ groups.

Both of the -CH₃ groups are bound to -CH₂ groups, so the abstraction rate from the -CH₃ groups is the group contribution for -CH₃ multiplied by the substituent factor for the -CH₂ group:

$$K(-\text{CH}_3) F(-\text{CH}_2) = 0.136 (1.23)$$

Two of the -CH₂ groups are bound to one -CH₂ group and one -CH₃ group, so the abstraction rate from these -CH₂ groups is the group contribution for -CH₂ multiplied by the substituent factors for the -CH₂ group and the -CH₃ group:

$$K(-\text{CH}_2) F(-\text{CH}_3) F(-\text{CH}_2) = 0.934 (1.00) (1.23)$$

Four of the -CH₂ groups are bound to one -CH₂ group and one -CH₂ group, so the abstraction rate from these -CH₂ groups is the group contribution for -CH₂ multiplied twice by the substituent factor for the -CH₂ group:

$$K(-\text{CH}_2) F(-\text{CH}_2) F(-\text{CH}_2) = 0.934 (1.23) (1.23)$$

The sum of the contributions from each of these groups:

$$k = [2(0.136)(1.23) + 2(.934)(1.00)(1.23) + 4(0.934)(1.23)(1.23)] * 10^{-12} \text{ cm}^3/\text{molecule-sec}$$

$$k = 8.28 * 10^{-12} \text{ cm}^3/\text{molecule-sec}$$

The experimental value is $8.68 * 10^{-12} \text{ cm}^3/\text{molecule-sec}$

Table 5.3-1 Group contributions and substituent factors for hydrogen abstraction rate constants (Kwok and Atkinson, 1995)

Structural group	Group rate constant 10^{-12} cm ³ /molecule-sec
<i>Group contributions</i>	
K(-CH ₃)	0.136
K(-CH ₂ -)	0.934
K(>CH-)	1.94
K(>C<)	0
K(-OH)	0.14
K(-NH ₂) (aliphatic)	21
K(-NH-) (aliphatic)	63
K(>N-) (aliphatic)	66
K(-SH) (aliphatic)	32.5
K(-S-)	1.7
K(-S-S-)	225
K(>N-NO)	0
K(>N-NO ₂)	1.3
K(P(=O))	0
K(P(=S))	53
<i>Substituent factors</i>	F(X) at 298 K
F(-CH ₃)	1.00
F(-CH ₂ -)	1.23
F(>CH-)	1.23
F(>C<)	1.23
F(-OH)	3.5
F(-F)	0.094
F(-Cl)	0.38
F(-Br)	0.28
F(-C(O)OH)	0.74

Table 5.3-2 Group contributions to rate constants for hydroxyl radical additions to olefins and acetylenes (Kwok and Atkinson, 1995)

Structural group	Group rate constant $10^{-12} \text{ cm}^3/\text{molecule-sec}$
CH ₂ =CH-	26.3
CH ₂ =C<	51.4
-CH=CH- (cis-)	56.4
-CH=CH- (trans-)	64.0
-CH=C<	86.9
>C=C<	110.0
-CH=CH- (cyclic)	56.4
CH≡C-	7.0
-C≡C-	27.0
<i>Substituent factors</i>	F(X) at 298 K
F(-CH ₃)	1.00
F(-CH ₂ -)	1.00
F(>CH-)	1.00
F(>C<)	1.00
F(-F)	0.21
F(-Cl)	0.21
F(-Br)	0.26
F(-Phenyl)	1.00

Table 5.3-3 Group contributions for rate constants for hydroxyl radical additions to (-C=C=C-) (Kwok and Atkinson, 1995)

Structural group	Group rate constant $10^{-12} \text{ cm}^3/\text{molecule-sec}$
(CH ₂ =C=CH-)	31.0
(-CH=C=CH-)	57.0
(CH ₂ =C=C<)	57.0
(-CH=C=C<)	85.0
(>C=C=C<)	110.

Example 5.3-2b

Estimate the rate of reaction of cis-2-butene with the hydroxyl radical.

Solution

Cis-2-butene has the molecular structure $\text{CH}_3\text{-}(\text{CH}=\text{CH})\text{-CH}_3$. Since there are no aromatic groups, the primary reaction pathways will be hydrogen atom abstraction and hydrogen addition to the double bond. The rate of addition is given simply by the rate constant for addition to the cis ($-\text{CH}=\text{CH}-$) structure: $56.4 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$. The substituent factors are both 1.00.

The rate of abstraction is the rate due to abstraction from the two $-\text{CH}_3$ groups. Both of the $-\text{CH}_3$ groups are bound to $=\text{CH}$ groups, so the abstraction rate from the $-\text{CH}_3$ groups would be the group contribution for $-\text{CH}_3$ multiplied by the substituent factor for the $=\text{CH}-$ group, if it were available. Since it is not available, a value of 1.0 will be assumed:

$$K(-\text{CH}_3) F(-\text{CH}_2) = 0.136 (1.0)$$

The sum of the contributions from each of these routes:

$$k = [56.4 + 2(0.136)(1.0)] \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$$

$$k = 56.7 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$$

Estimating lifetimes in aqueous environments

Chemicals emitted to aqueous environments undergo a wide range of reactions. One of the most significant reaction pathways is hydrolysis, which can be catalyzed by acids and bases; hydrolysis can also occur in neutral waters. Calculating the rate at which a compound reacts (or breaks down) in water helps in estimating the concentration of that compound in the surface waters of the environment.

Hydrolysis rates can be estimated for a limited number of compound types using correlations based on structure-activity relationships (Mill, et al., 1987). The structure-activity relationships are generally based on linear free energy relationships. A linear free energy relationship assumes that the ratio of a rate constant to some reference rate is linearly proportional to a structural parameter that in some way characterizes the free energy of the transition state for the reaction. So, for hydrolysis reactions, the rate of hydrolysis can be correlated using an equation like 5-22.

$$\log (\text{hydrolysis rate}) = \log (\text{hydrolysis rate of a reference compound}) + \text{Constant} * \sigma$$

$$\log (\text{hydrolysis rate}) = A + B\sigma \quad (\text{Eqn. 5-22})$$

where σ is a structural parameter commonly used in linear free energy relationships, the Hammett constant. The Hammett constant characterizes the electron donating or electron withdrawing properties of a functional group. The details of estimating the Hammett constant and other parameters used in hydrolysis rate estimations are beyond the scope of this chapter, and it should be noted that empirical values for the constants A and B in Equation 5-22 must be determined for individual classes of reactants (e.g., the values for esters would be different than the values for epoxides). The parameter A is reaction and compound class specific because it depends on the reference reaction chosen. The parameter B is reaction and compound class specific because the dependence of rate on structural features depends on the type of reaction being considered.

An added complexity is that rates of reactions, such as hydrolysis, depend not just on the structure of the reactant, but also on the characteristics (e.g., pH) of the receiving waters. Thus, an estimate of hydrolysis rates requires both good rate estimation methods – which are scarce – and a detailed understanding of local environmental conditions.

Estimating overall biodegradability

In addition to all of the reactions that may occur with other chemicals in the atmosphere and in aqueous environments, we must also be concerned with the rate at which compounds are metabolized by living organisms. Developing an overall assessment of biodegradation will be difficult. Nevertheless, semi-quantitative assessments are possible. An ideal framework for estimating biodegradation would distinguish between the initial structural change of the compound (primary biodegradation) and the complete conversion to stable reaction products such as CO₂ and H₂O (ultimate biodegradation). It would also distinguish between aerobic (oxygen present) and anaerobic degradation.

Unfortunately, primary and ultimate, aerobic and anaerobic biodegradation rates are available for only a small number of compounds. Therefore, the approach described in previous sections – statistical regression of measured environmental data to yield group contribution parameters – will not work because there are not enough biodegradation data. Nevertheless, it is extremely important to have a qualitative sense of the persistence of compounds in the environment, and biodegradation is one of the most significant removal pathways for compounds in ambient environments. One pragmatic response to this problem has been to rely on estimations of biodegradation by expert panels. As described by Howard, et al. (1992) and Boethling, et al., (1994), expert panels can provide estimates of whether biodegradation occurs over hours, days, weeks, months or longer. These expert assessments can then be used as the basis for a group contribution method for biodegradation.

One such method (Boethling, et al., 1994) involves calculating an index that characterizes aerobic biodegradation rate in ambient environments.

$$I = 3.199 + a_1f_1 + a_2f_2 + \dots + a_n f_n + a_m MW \quad (\text{Eqn. 5-23})$$

where I is an indicator of the aerobic biodegradation rate. A value of 5 indicates that the compound is expected to degrade over hours; a value of 4 corresponds to a lifetime of days; 3, 2 and 1 correspond to weeks, months, and longer, respectively. These values of I should not be viewed as an accurate quantitative predictor of biodegradation rate. Rather, they should be viewed as a relative ranking of the probability that a material will biodegrade. The parameter f_n is the number of groups of type n in the molecule, and a_n is the contribution of group n to degradation rate. Group contribution parameters are listed in Table 5.3-4 and sample calculations are given in Example 5.3-3.

Table 5.3-4 Group contributions to ultimate aerobic biodegradation index (Boethling, et al., 1994)

Structural group	Group contribution (a_n)
<i>Molecular weight</i>	-0.00221
<i>Functional groups</i>	
Unsubstituted mono-, di-, or tri-aromatic ring	-0.586
Unsubstituted phenyl group	0.022
Aromatic acid (-COOH)	0.088
Linear 4 carbon terminal chain (-CH ₂ -CH ₂ -CH ₂ -CH ₃)	0.298
Aliphatic acid (-COOH)	0.365
Alkyl substituent on a ring	-0.075
Aromatic F	-0.407
Aromatic I	-0.045
Tetra aromatic or larger ring	-0.799
Aromatic amine	-0.135
Aliphatic amine	0.024
Aliphatic Cl	-0.173
Aromatic Cl	-0.207
Aromatic -OH	0.056
Aliphatic -OH	0.160
Aliphatic ether	-0.0087
Aromatic ether	-0.058

Example 5.3-3

Estimate the biodegradation index for 1-propanol and diphenyl ether.

Solution

a.) 1-propanol has a molecular weight of 60 and contains an aliphatic -OH. Its biodegradation index is:

$$I = 3.199 + 0.160 - 0.00221 (60) = 3.22$$

This implies a lifetime of weeks.

b.) diphenyl ether has a molecular weight of 170 and contains an aromatic ether and two mono-aromatic rings. Its biodegradation index is:

$$I = 3.199 + 2(0.022) - 0.058 - 0.00221 (170) = 2.81$$

This implies a lifetime of weeks; literature data indicate a lifetime of months.

Summary

This section has provided a limited introduction to methods for estimating environmental persistence. The methods are generally specific to a particular environmental medium (air, water, or sediment/soil) and to particular reaction pathways (e.g., reaction with hydroxyl radical in the atmosphere or hydrolysis in aqueous environments). Often the methods will depend on local characteristics, such as the acidity or alkalinity of water body and the concentration of oxidizing species in the atmosphere. With all of these restrictions, the appropriate use of these methods in performing screening assessments is simply for relative rankings of environmental persistence.

Section 5.3 Questions for Discussion

1. When we examine atmospheric oxidation, we monitor only the disappearance of the chemical of interest. Should we be concerned about the reaction products that are formed?
2. The methodologies presented in this chapter represent only a small fraction of possible environmental degradation pathways. How would you use these limited data to perform an overall assessment of environmental persistence?

5.4 ESTIMATING ECOSYSTEM RISKS

Structure activity relationships may also be used to assess ecosystem and human health impacts. The range and variety of such relationships are enormous. Therefore, this section will present only a few, simple relationships that are used to assess ecosystem risk. For a more comprehensive review, the interested reader is referred to extensive literature on structure activity relationships (e.g., Hansch, et al., 1995a,b), as well as extensive literature of experimental data (see, for example, on line databases of the U.S. EPA available at the EPA website: www.epa.gov, or the databases cited at the end of this Chapter).

In assessing ecosystem hazard, the standard practice is to estimate toxicity for a variety of species. For example, mortality for daphnids, fish and guppies are frequently used in assessing the ecosystem hazard of chemicals described in premanufacture notices submitted to the U.S. EPA under the Toxic Substances Control Act. The mortality for guppies can be correlated with the octanol-water partition coefficient using equation 5-24

$$\log (1/LC_{50}) = 0.871 \log K_{ow} - 4.87 \quad (\text{Eqn. 5-24})$$

where LC_{50} is the concentration that is lethal to 50% of the population over a 14 day exposure (expressed in $\mu\text{mol/L}$). This equation was developed using data from a variety of different compounds, including chlorobenzenes, chlorotoluenes, chloroalkanes, diethyl ether and acetone (Konemann, 1981).

Other equations used to estimate ecosystem hazard are specific to certain compound classes. For example, toxicities for daphnids and fish can be estimated for more than 50 different compound classes. The correlations for acrylates are given below:

$$\log LC_{50} = 0.00886 - 0.51136 \log K_{ow} \quad (\text{Eqn. 5-25})$$

(Daphnids, mortality after 48 hr exposure)

$$\log LC_{50} = -1.46 - 0.18 \log K_{ow} \quad (\text{Eqn. 5-26})$$

(Fish, mortality after 96 hr exposure)

where LC_{50} is expressed in units of millimoles/L.

Example 5.4-1

Compare the fish, guppy and daphnid mortalities for an acrylate with $\log K_{ow} = 1.28$ (e.g. methyl methacrylate)

Solution

The concentrations yielding 50% mortality are:

Guppies (14 day): 5690 $\mu\text{mol/L}$

Daphnids (48 hour): 0.226 millimoles/L = 226 $\mu\text{mol/L}$

Fish (96 hour): 0.020 millimoles/L = 20 $\mu\text{mol/L}$

Section 5.4 Questions for Discussion

1. Why are ecotoxicities evaluated for immature amphibians and similar biota?
2. Why are the lethal concentrations negatively correlated with the octanol-water partition coefficient for these species?

5.5 USING PROPERTY ESTIMATES TO ESTIMATE ENVIRONMENTAL FATE AND EXPOSURE

The previous sections have described methods that can be used to estimate the properties that will govern a chemical's environmental partitioning and fate. This section will illustrate, through a few simple examples, how those properties can be employed to estimate partitioning and fate. These properties will also be used to estimate exposures, in Chapter 6.

Consider, for example, the problem of estimating exposure to a chemical via inhalation. To calculate inhalation exposure, it is necessary to know the atmospheric concentrations. Breathing rates are multiplied by atmospheric chemical concentrations to determine inhalation exposures. The atmospheric chemical concentration depends on emission rate, mixing rate and atmospheric lifetime. A simple case study is given in Example 5.5-1.

Example 5.5-1

Propylene is emitted at a rate of 10 metric tons per year into an airshed that has a volume of 10^4 cubic kilometers. Assume that the airshed has a residence time of one day and is well mixed. Calculate the steady state concentration of propylene, accounting for chemical reaction. Calculate an inhalation exposure for an adult, assuming an inhalation rate of 20 l/min.

Solution

a.) Perform a mass balance to calculate the steady state concentration of propylene:

$$\text{In} - \text{out} - \text{disappearance due to reaction} = 0$$

$$\text{In} = 10^4 \text{ kilogram/yr} = 7.5 * 10^{-3} \text{ gram moles/sec}$$

(based on a molecular weight of 42)

$$\begin{aligned} \text{Out} &= \text{flow rate} * \text{steady state concentration of propylene} \\ &= 10^4 \text{ cubic kilometers/day} * C_{\text{propylene, ss}} = 1.16 * 10^{14} \text{ cm}^3/\text{sec} * C_{\text{propylene, ss}} \end{aligned}$$

$$\begin{aligned} \text{Disappearance due to reaction} &= \text{Volume} * \text{rate} \\ &\text{(note that the rate of reaction for propylene was discussed in Section 5.3)} \\ &= 10^4 \text{ cubic kilometers} * 26 * 10^{-12} \text{ cm}^3/\text{molecule-sec} * 1.5 * 10^6 \text{ molecule/cm}^3 * C_{\text{propylene, ss}} \\ &= 10^{19} \text{ cm}^3 * 39 * 10^{-6} / \text{sec} * C_{\text{propylene, ss}} \end{aligned}$$

$$C_{\text{propylene, ss}} = 1.5 * 10^{-17} \text{ moles/cm}^3$$

Assuming one mole of air occupies $22,400 \text{ cm}^3$ at ambient conditions,

$$C_{\text{propylene, ss}} = 3.3 * 10^{-13} \text{ moles propylene/mole air} = 0.3 \text{ ppt}$$

The exposure, assuming an inhalation rate of 20 L/min is :

$$20000 * 1.5 * 10^{-17} \text{ moles/cm}^3 = 7.5 * 10^{-14} \text{ moles/min} = 6.4 * 10^{-6} \text{ g/yr}$$

Far more sophisticated models than the well-mixed box model, used in Example 5.5-1, can be used to estimate atmospheric concentrations and inhalation rates. Many such models are available and calculating atmospheric concentrations, in order to estimate inhalation rates, is done relatively routinely. The problems associated with estimating environmental exposures via other routes become far more complex. Consider the relatively simple example of calculating exposure through drinking contaminated surface water. Assume that a chemical is released to a river upstream of the intake to a public drinking water treatment plant. To evaluate the exposure we would need to determine:

- What fraction of the chemical was adsorbed by river sediments?
- What fraction of the chemical was volatilized to the atmosphere?
- What fraction of the chemical was taken up by living organisms?
- What fraction of the chemical was biodegraded or was lost through other reactions?
- What fraction of the chemical was removed by the treatment processes in the public water system?

Thus, exposure estimates will require information on the soil sorption coefficient, vapor pressure, water solubility, bioconcentration factor, and biodegradability of the compound, as well as river flow rates, surface area, sediment concentration and other parameters. A simple, yet typical, set of calculations is shown in Examples 5.5-2 through 5.5-4.

Example 5.5-2

Assume that a chemical, with a molecular weight of 150, is released at a rate of 300 kg/day to a river, 100 km upstream of the intake to a public water system. Estimate the initial partitioning of the chemical in the water, sediment and biota.

Data

Water solubility: 100 ppm

Soil sorption coefficient: 10,000

Organic solids concentration in suspended solids: 15 ppm

River flow rate: 500 million liters per day

Bioconcentration factor: 100,000

Biota loading: 100 g per 100 cubic meter

Solution

The ratio of concentrations in water, sediment and biota will be approximately:

$$1 : 10,000 : 100,000$$

Based on the river flow rate the total flow rates of water, sediment and biota are:

Water: (500 million liter/day * 1 kg/liter) = 500 million kg/day

Sediment: 500 million kg/day * 15 kg sediment/ million kg water = 7500 kg sediment/day

Biota: 500 million kg/day * 0.1 kg biota/ million kg water = 50 kg biota/day

Performing a mass balance:

$$300 \text{ kg/day} = 500 \text{ million kg water/day } (C_{\text{water}}) + 7500 \text{ kg sediment/day } (10,000 C_{\text{water}}) + 50 \text{ kg biota/day } (100,000 C_{\text{water}})$$

where (C_{water}) is the chemical concentration in the water phase;

$$(C_{\text{water}}) = 0.5 * 10^{-6} \text{ kg chemical/kg water} = 0.5 \text{ ppm}$$

This is well below the solubility of 100 ppm. The ratio of the mass in water, sediment and biota is:

$$500,000,000 : 75,000,000 : 5,000,000 \\ 84 : 13 : 1$$

Thus, although the concentrations are much higher in the biota and the sediment, more than 80% of the mass remains in the water phase.

Example 5.5-3

For the discharge described in Example 5.5-2, calculate the equilibrium vapor pressure above the river at the discharge point. Is volatilization from the river likely to be significant?

Data

Vapor pressure: 10^{-1} mm Hg
 River flow rate: 500 million liters per day
 River velocity: 0.5 m/sec
 River width: 30 m

Solution

Assuming ideal behavior and the concentration determined in Example 5.5-2, the equilibrium vapor pressure should be:

$$0.5 * 10^{-6} \text{ g chemical/g water} * 1 \text{ mole chemical} / 150 \text{ g} * 18 \text{ g / mole water} * 10^{-1} \text{ mm Hg} \\ = 0.6 * 10^{-9} \text{ mmHg} = 8. * 10^{-12} \text{ atm}$$

To determine if the loss rate is significant, assume that a volume 10 m above the river reached this concentration for the length of the river to the public water system inlet (a total volume of $100,000 * 10 * 30 \text{ m}^3$). Noting that 1 gram-mole of air at standard conditions occupies 22.4 liters:

$$30 * 10^6 \text{ m}^3 * (1 \text{ mole air} / 0.0224 \text{ m}^3) * 8. * 10^{-12} \text{ moles chemical/mole air} * 150 \text{ g/mole} \\ = 1.6 \text{ g}$$

This is the mass required to saturate the atmosphere to a height of 10 m above the river for the 100 km length of the river. Compare this to the total discharge rate of 300 kg/day, and it is clear that volatilization will be negligible.

Example 5.5-4

For the discharge described in Examples 5.5-2 and 5.5-3, estimate what fraction of the initial discharge might still be in the water at the public water intake. If the treatment efficiency of this chemical in the water treatment plant is 95%, what would be the concentration in drinking water?

Data

Biodegradation half life: 300 hours

Solution

Based on a river velocity of 0.5 m/sec and a travel distance of 100 km, the transit time is 2.3 days. If the half life is 300 hours, the disappearance rate constant is (see Example 5.3-1);

$$t_{1/2} = 300 \text{ hours} = \ln(2) / (k)$$

This can be used to calculate the ratio of final to initial concentration:

$$\ln([C]/[C_0]) = -(\ln(2)/300 \text{ hours})t = -(\ln(2)/300 \text{ hours}) 55 \text{ hours}$$

$$([C]/[C_0]) = 0.88$$

The concentration entering the treatment plant is $0.88 * 0.5 \text{ ppm}$.

The concentration in the drinking water is $0.05 * 0.88 * 0.5 \text{ ppm} = 20 \text{ ppb}$

Summary

The purpose of this section has been to illustrate how the properties evaluated in Sections 5.2 and 5.3 can be used to estimate environmental partitioning. Again, the models presented have been simple, demonstrating basic concepts of environmental partitioning, fate and exposure. More complex and accurate models are available, but are beyond the scope of these simple screening methods.

Section 5.5 Questions for Discussion

1. Why is most of the mass of the chemical considered in Example 5.5-2 in the water phase, while the concentrations in the sediment and biota phases are so high?
2. For Example 5.5-3, what vapor pressure would result in significant volatilization rates?
3. How would you develop an accurate estimate for volatilization rate in Example 5.5-3, if the losses were significant?

5.6 CLASSIFYING ENVIRONMENTAL RISKS BASED ON CHEMICAL STRUCTURE

The previous sections have described procedures for estimating the chemical and physical properties that are needed to assess potential environmental risks for chemicals. Our goals in this section are to put these property values in perspective and to introduce the tools that will be needed to perform an overall assessment of environmental hazards.

Three types of criteria are typically considered in risk-based evaluations – persistence, bioaccumulation and toxicity. For any one of these criteria, it may be necessary to consider a number of properties in performing an evaluation. For example, in evaluating persistence, it may be necessary to consider atmospheric half-lives and biodegradation half-lives. In evaluating toxicity, it may be necessary to consider a variety of eco-toxicity measures and human toxicity measures. Because there is such a wide variety of criteria that can be used in evaluating environmental risks – ranging from human carcinogenicity to biodiversity - and because opinions vary widely on the relative importance of the evaluation criteria, *there is no single evaluation methodology that is universally accepted for evaluating the environmental hazards of chemicals.*

Therefore, our approach in this text will be to present approximate classifications that can be used to categorize chemicals according to their persistence, bioaccumulation potential and toxicity. The classifications will group chemicals into categories of high, moderate and low concern, using values established by the U.S. EPA in evaluating chemicals under the Toxic Substances Control Act. For example, Table 5.6-1 is a summary of the categories used to classify the persistence and bioaccumulation of chemicals and Figure 5.6-1 shows distributions of one measure of ecotoxicity.

These qualitative screenings can be useful in assigning areas of concern. Ranking risks, however, is more problematic, and approximate methods for ranking chemical risks will be described in Chapter 8. For now, Table 5.6-1 and Figure 5.6-1 can be used to provide perspective on the values for properties generated using the methods of Sections 5-2 and 5-3.

Table 5.6-1 Classification criteria for persistence and bioaccumulation

<i>Water Solubility</i>	
Very Soluble	$S > 10,000$ ppm
Soluble	$1,000 < S < 10,000$ ppm
Moderately Soluble	$100 < S < 1,000$ ppm
Slightly Soluble	$0.1 < S < 100$ ppm
Insoluble	$S < 0.1$ ppm
Soil sorption	
Very Strong Sorption	$\text{Log } K_{oc} > 4.5$
Strong Sorption	$4.5 > \text{Log } K_{oc} > 3.5$
Moderate Sorption	$3.5 > \text{Log } K_{oc} > 2.5$
Low Sorption	$2.5 > \text{Log } K_{oc} > 1.5$
Negligible Sorption	$1.5 > \text{Log } K_{oc}$
Biodegradation	
Rapid	$> 60\%$ degradation over 1 week
Moderate	$> 30\%$ degradation over 28 days
Slow	$< 30\%$ degradation over 28 days
Very Slow	$< 30\%$ degradation over more than 28 days
Volatility (H in atm-m ³ /mole)	
Very Volatile	$H > 10^{-1}$
Volatile	$10^{-1} > H > 10^{-3}$
Moderately Volatile	$10^{-3} > H > 10^{-5}$
Slightly Volatile	$10^{-5} > H > 10^{-7}$
Nonvolatile	$10^{-7} > H$
Bioaccumulation potential	
High Potential	$8.0 > \text{Log } K_{oc} > 4.3$ or $\text{BCF} > 1000$
Moderate Potential	$4.3 > \text{Log } K_{ow} > 3.5$ or $1000 > \text{BCF} > 250$
Low Potential	$3.5 > \text{Log } K_{oc}$ or $250 > \text{BCF}$

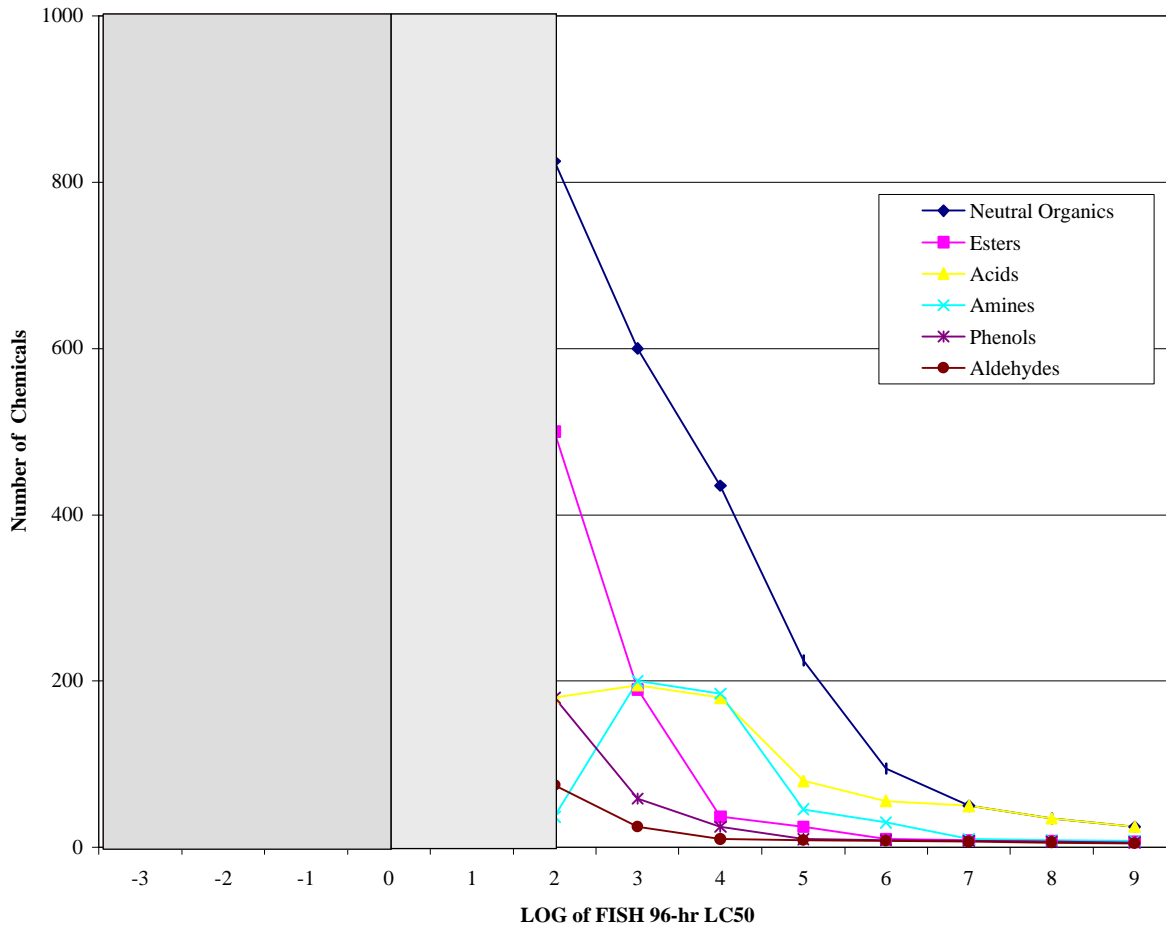


Figure 5.6-1 Distributions of measures of eco-toxicity for several thousand compounds. These distributions can be used to classify compounds into categories of concern. (Note that a high effect concentration implies that a large amount of the material can be released before an effect is observed) (Zeeman, et al., 1993)

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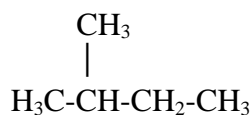
APPENDIX

Appendix A: Molecular Connectivity

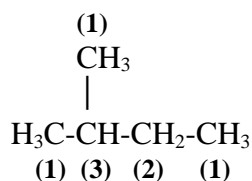
The correlating variables, used in the equations described in this chapter, were primarily bulk properties such as boiling point and octanol-water partition coefficient. While these variables are adequate correlating parameters for many properties, they will not be adequate for properties that depend on molecular topology, such as soil sorption. In situations where a description of molecular topology is required, a simple alternative is to utilize the molecular connectivity (χ).

The concept of molecular connectivity initially appeared in the pharmaceutical literature and a variety of molecular connectivity indices have been used in predicting drug behavior (Kier and Hall, 1986). This text uses only the most basic of molecular connectivity indices – the simple first order molecular connectivity (${}^1\chi$). The goal of this index is to characterize, in a single scalar parameter, the degree of connectedness or the topology of the molecule. A complete description of the rationale behind the molecular connectivity is beyond the scope of this text. The interested reader is referred to Kier and Hall (1986). Instead, the focus here will be on the steps required to calculate ${}^1\chi$.

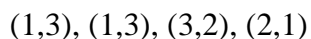
The first step in calculating ${}^1\chi$ is to draw the bond structure of the molecule. For example, isopentane would be drawn as:



The next step is to count the number of bonds to which each carbon is attached (count any heteroatom as a carbon, but ignore bonds to hydrogen). The assignments of this parameter (δ_i , the connectedness of carbon atom i) for each carbon in isopentane are given below.



For each bond, identify the connectedness of the carbons connected by the bond (δ_i , δ_j). For isopentane, these pairs are:



The value of ${}^1\chi$ is calculated using the equation:

$${}^1\chi = \sum(\delta_i^* \delta_j)^{-0.5}$$

$$\text{For isopentane, } {}^1\chi = (1/\sqrt{3}) + (1/\sqrt{3}) + (1/\sqrt{6}) + (1/\sqrt{2}) = 2.68$$

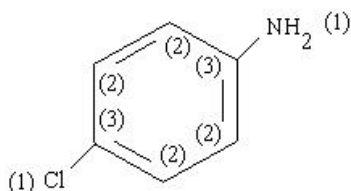
Clearly, this calculation yields a simplistic characterization of complex structural features. Note that isopentene would yield exactly the same value as isopentane, as would 1-chloro, 2 methyl propane. Nevertheless, this simple characterization of molecular topology is often used, as described in Section 5.2, in developing property correlations.

Example 5A-1

Estimate ${}^1\chi$ for 4-chloro-aniline.

Solution

The molecular structure and the connectedness of each carbon or heteroatom are shown below:



The bond pairs, beginning with the amine and continuing clockwise around the molecule, are (1,3), (3,2), (2,2), (2,3), (3,1), (3,2), (2,2), (2,3)

$${}^1\chi = (1/\sqrt{3}) + (1/\sqrt{6}) + (1/\sqrt{4}) + (1/\sqrt{6}) + (1/\sqrt{3}) + (1/\sqrt{6}) + (1/\sqrt{4}) + (1/\sqrt{6}) = 3.787$$

APPENDIX B: Sources of Experimental Property Data (Compiled by David Shonnard)

1. US EPA Integrated Risk Information System (IRIS)
IRIS is a database on the human health effects of chemicals; data, analysis and uncertainty characterizations are provided for hundreds of common chemicals
<http://www.epa.gov/ngispgm3/iris/index.htm>
2. Health Effects Notebook for Hazardous Air Pollutants
Data such as LC50s, Threshold Limit Values and Permissible Exposure Levels (see Chapter 8) are available for approximately 200 chemicals
<http://www.epa.gov/ttn/uatw/hapindex.html>
3. Chemical Health and Safety Data
Health and safety information on thousands of chemicals are available
http://ntp-server.niehs.nih.gov/Main_Pages/Chem-HS.html
4. TRIAGE Chemical Studies Database
Searchable database of scientific studies on the health and environmental effects of chemicals
http://www.epa.gov/docs/8e_triag/
5. The Cumulative Exposure Project – Toxicity Data
Toxicity data on hundreds of compounds
<http://www.epa.gov/CumulativeExposure/resource/toxdata.htm>
6. US EPA ECOTOX Data System
Lethal dose and ecotoxicity data
<http://www.epa.gov/ecotox/>
7. Design Institute for Physical Property Data (American Institute of Chemical Engineers)
(www.aiche.org/dippr/).
8. Syracuse Research Corporation (SRC) environmental databases
Data on many chemical properties relevant to environmental fate
<http://esc-plaza.syrres.com/efdb/>
9. Solvents database
Data on physical and chemical properties, environmental fate and regulation of solvents
<http://solvdb.ncms.org/CAS01.htm>

PROBLEMS

1. Estimate the properties listed in the table given below.

<i>Property</i>	<i>Nitrobenzene</i>
Boiling point (T_b)	
Vapor pressure (P_{vp})	
Henry's Law constant (H)	
Octanol-water partition coefficient (K_{ow})	
Water solubility (S)	
Soil sorption coefficient (K_{oc})	
Atmospheric half life	
Biodegradability	

2. Estimate the properties listed in the table given below. *If group contributions are not available for the necessary groups, use reasonable judgement in estimating parameters.*

<i>Property</i>	<i>2-Chloroaniline</i>
Boiling point (T_b)	
Vapor pressure (P_{vp}) at 300 K	
Henry's Law constant (H)	
Octanol-water partition coefficient (K_{ow})	
Bioconcentration Factor (BCF)	
Water solubility (S)	
Soil sorption coefficient (K_{oc})	
Atmospheric half life	
Biodegradability	

3. Estimate the properties listed in the table given below.

<i>Property</i>	<i>Ethanol</i>	<i>1-propanol</i>	<i>1-hexanol</i>	<i>n-propane</i>	<i>n-hexane</i>
Boiling point (T_b)					
Vapor pressure (P_{vp})					
Henry's Law constant (H)					
Octanol-water partition coefficient (K_{ow})					
Water solubility (S)					
Soil sorption coefficient (K_{oc})					
Atmospheric half life					
Biodegradability					

For each of the properties, comment on whether molecular weight or the presence of a hydrogen bonding group has a more pronounced effect on chemical properties.

4. Benzene in the wastewaters from a manufacturing facility is sent, at a rate of 2000 kg/day, to a publicly owned wastewater treatment works (POTW). The POTW treats the benzene in the wastewater and removes 85% of the organic before discharging to a local river. One hundred kilometers downriver of the discharge point is the intake to a public water system.

- a.) Estimate the fraction of benzene in water, sediment and biotic phases at the discharge point.
- b.) Determine whether volatilization of benzene from the river is likely to be significant.
- c.) Estimate the fraction of the benzene that biodegrades before the effluent reaches the water intake.
- d.) Estimate the potential toxicity of the releases to aquatic life.

Data

River flow rate: 1250 million liter per day

River velocity: 0.5 m/sec

River width: 50 m

Organic solids concentration in suspended sediment: 15 ppm

Biota concentration: 100 g per 100 cubic meter

5. During pesticide application, 1 kg of hexachlorobenzene is accidentally applied to a 10^8 liter pond. Estimate the amount of hexachlorobenzene that would be ingested if a person were to eat a 0.5 kg fish from the pond. Assume that the pond is well mixed and that the organic sediment content is 10 ppm and the total fish loading is 100 g per 100 cubic meter.

6. The Great Lakes Basin is one of the largest freshwater ecosystems in the world. Recently there has been some concern that persistent, bioaccumulative and toxic compounds have been accumulating in the basin, possibly compromising this valuable natural resource. Of particular concern are the chlorinated organics. In 1993 (the most recent year for which data are available) the chlorinated organic released in greatest quantity in the Great Lakes Basin was tetrachloroethylene. The emission rates to air, land and water for the basin were 1.8×10^7 pounds per year, 2.6×10^6 pounds per year and 8.4×10^2 pounds per year, respectively.

- a.) Calculate the equilibrium partitioning of tetrachloroethylene in the air, water, soil and sediment of the Great Lakes Basin. Use one year of emissions as your basis. Assume no degradation, initial concentrations are zero, and that the Great Lakes Basin has the properties listed below.

<i>Property</i>	<i>air</i>	<i>water</i>	<i>soil</i>	<i>sediment</i>
Volume (m ³)	7.6×10^{14}	2.3×10^{13}	2.6×10^{10}	4.8×10^8
Area (m ²)	7.6×10^{11}	2.4×10^{11}	5.2×10^{11}	2.4×10^{11}
Organic fraction			0.02	0.04
Density (kg/m ³)	1.2	1000	1500	1280
Residence time (hr)	130	272,000	550	1700

- b.) Will the system that you modeled in part a.) ever reach a steady state? Explain your reasoning.
- c.) Estimate the atmospheric residence time and the biodegradability of tetrachloroethylene. Based on these values, estimate the steady state concentration of tetrachloroethylene in each environmental compartment.

(Hint: for steady state to be reached, the total mass input to the systems must equal the total mass lost due to reaction. Assume that biodegradation occurs in water, sediment and soils and that degradation occurs in the atmosphere. Set up a mass balance where you have only one concentration as an independent variable and solve for that concentration)

- d.) In parts a-c you assumed that the environmental compartments were closed (e.g., you effectively assumed that the atmosphere was not ventilated by winds from other regions). Now assume that you want to account for advection in your calculation of steady state concentrations. Describe qualitatively how you would include the atmospheric, water, soil and sediment residence time information provided in the Table for Part a.) into your analysis. Use equations in your explanation if you wish, but do not attempt a quantitative analysis.

7. Design a solvent molecule that has a vapor pressure greater than 1 mm Hg, a molecular weight between 75 and 150, and will biodegrade in less than one month.

8. Design a solvent molecule that has a vapor pressure less than 1 mm Hg (at 300 K), a molecular weight between 75 and 150, and will biodegrade in less than one month.

9. The group contribution equation for estimating boiling point is:

$$T_b = 198.2 + \sum n_i g_i$$

Without consulting the tables in Chapter 5, estimate the relative magnitude of the group contributions for the following three functional groups: -OH, -CH₃, -Cl (aliphatic). Report your answer as x<y<z, where x,y, and z are the three functional groups. For example if you believed that the values of the three group contributions for -OH, -CH₃, -Cl were -1, 0 and 1, respectively, your answer would be -OH< -CH₃< -Cl. Explain your reasoning.

10. Without consulting the tables in Chapter 5, estimate the relative magnitude of the group contributions for octanol-water partition coefficient for the following three functional groups: -OH, -CH₃, -Cl (aliphatic). Report your answer as x<y<z, where x,y, and z are the three functional groups. For example if you believed that the values of the three group contributions for -OH, -CH₃, -Cl were -1, 0 and 1, respectively, your answer would be -OH< -CH₃< -Cl. Explain your reasoning.