Pollution Prevention and Risk Reduction for Chemical Processes

Module 1 (Part 1): Screening Chemicals for Environmental Risks

Background Reading:
D. T. Allen, Chapter 5 "Screening Chemicals for Environmental Risks"

By the end of this section you should:

- **be aware of the chemical and physical properties that govern a chemical's environmental partitioning and fate**
- **be able to estimate properties that govern environmental partitioning based on chemical structure**
- **be able to estimate properties that govern environmental fate based on chemical structure**
- **be aware of the limitations of structure-property estimation methods**

Outline:

I. Screening chemicals for environmental risk: an overview
II. Group contribution methods (structure activity relationships)
III. Properties that govern environmental partitioning
- **A. Boiling point**
- **B. Vapor pressure**
- **C. Octanol Water Partition Coefficient**
- **D. Bioconcentration factor**
- **E. Henry's Law Coefficient**
- **F. Soil sorption**

IV. Properties that govern environmental fate
- **A. Atmospheric lifetimes**
- **B. Biodegradation**

I. Screening chemicals for environmental risk: an overview

A new chemical is to be manufactured. Will its manufacture or use pose significant environmental 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?

Table 5-1 Chemical properties needed to perform environmental hazard screenings

Environmental Process	*Relevant Properties*
Estimates of releases and environmental dispersion	Volatility, density, melting point, water solubility
Persistence in the environment	Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation
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

II. Group contribution methods (structure activity relationships)

Assume that molecule is made up of a collection of atoms or bonds

Example: 1-Propanol

1- propanol functional group characterization:

1- propanol bond characterization:

For each bond or functional group, assume that the building block makes a well defined contribution to the property:

Example: heat capacity

Combine the group contributions in a fundamentally sound but empirically derived manner to estimate molecular properties

III. CHEMICAL AND PHYSICAL PROPERTIES INFLUENCING PHASE PARTITIONING

Table 5-2 Properties that influence environmental phase partitioning

Property	*Definition*	*Significance in estimating environmental fate and risks*
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 coefficient (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 atm-m^3/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 water to the concentration of the compound in octanol	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 μg/g organic carbon) to the concentration of the compound in a liquid phase (in μg/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 L/kg)	Characterizes the magnification of concentrations through the food chain

III A. Boiling point

$$T_b\ (K) = 198.2 + \Sigma\ n_i\ g_i \qquad \text{(Equation 5-1)}$$

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:

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

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

Structural groups and group contributions (g_i) for boiling point estimation are listed in Table 5-3.

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 5-1.

Table 5-3. 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
Carbon groups		*Nitrogen groups*	
$-CH_3$	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
Oxygen groups		-CN	119.16
-OH	106.27	Aromatic-CN	95.43
Primary -OH	88.46		
Secondary –OH	80.63	*Halogen groups*	
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
Carboxyl groups		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	*Sulfur groups*	
$-C(O)NH_2$	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 problem 5-1

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

Solution

a.) Ethanol has the molecular structure CH_3- CH_2-OH. Referring to the groups in Table 5-3, this structure can be represented by one - CH_3 group, one -CH_2 group and one –OH group. The uncorrected normal boiling point, from equation 5-1 is given by:

T_b (K) = = 350.7 K

The corrected value is:

$$T_b \text{ (corrected)} = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 = 356.1 \text{ K}$$

The actual boiling point is 351 K, so the predicted value is in error by +1.5%

b.) Toluene has the molecular structure CH_3- C_6H_5. Referring to the groups in Table 5-3, this structure can be represented by one - CH_3 group, one –*aa*C- group (a substituted carbon bound to two aromatic carbons) and five –*aa*CH groups. The uncorrected normal boiling point, from equation 5-1 is given by:

T_b (K) = = 393.6 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 CH_3-CH=O. Referring to the groups in Table 4-3, this structure can be represented by one - CH_3 group and one -CHO group. The uncorrected normal boiling point, from equation 5-1 is given by:

T_b (K) = = 303.6 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%

II. B Vapor pressure

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

$$\text{Ln } P_{vp} = A + B/(T - C) \quad \text{(Equation 5-5)}$$

Where 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:

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

Using Equation 5-6 allows the three parameters to be changed from A, B, and C to B, C and T_b. Lyman, et al. (1990) provide a derivation of the following equation, starting from the Antoine equation (Eqn. 5-5):

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

where R is the gas constant. The parameters A and C can be estimated from boiling point:

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

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

Example problem 5-2

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

Solution

Toluene has the molecular structure CH_3- C_6H_5 and in Example 5-1, it's 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:

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

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

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

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

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

Table 5.4 Factors (K_F) used in estimating boiling points (Lyman, et al., 1990)

Compound type	***Number of carbon atoms in co***							
	1	2	3	4	5	6	7	8
Hydrocarbons (consider a phenyl group as a single carbon atom)								
n-alkanes	0.97	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
Mono- and diolefins and isomers		1.01	1.01	1.01	1.01	1.01	1.01	1.01
Cyclic saturated hydrocarbons			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
Halides								
Monochlorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02
Monoiodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03
Mixed halides (completely halogenated)	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
Compounds containing a keto group								
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04
Ketones			1.08	1.07	1.06	1.06	1.05	1.04
aldehydes		1.09	1.08	1.08	1.07	1.06	1.05	1.04
Nitrogen compounds								
Primary amines	1.16	1.13	1.12	1.11	1.10	1.10	1.09	1.09
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05
Tertiary amines			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
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04
Sulfur compounds								
Mercaptans	1.05	1.03	1.02	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
Alcohols and Miscellaneous compounds								
Alcohols (single -OH group)	1.22	1.31	1.31	1.31	1.31	1.30	1.29	1.28
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
Aliphatic esters		1.03	1.03	1.02	1.02	1.02	1.01	1.01
Oxides (cyclic ethers)		1.08	1.07	1.06	1.05	1.05	1.04	1.03

Table 5-5 Factors (K_F) used in estimating boiling points for aromatics (Lyman, et al., 1990)

Compound type	**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_6H_5NHR)	1.06
Naphthols (single –OH)	1.09
Naphthylamines (single $–NH_2$)	1.06
N-substituted naphthylamines	1.03

III.C Octanol-water partition coefficient

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.

$$\log K_{ow} = 0.229 + \Sigma\, n_i\, f_i \qquad \text{(Equation 5-11)}$$

where $\log K_{ow}$ is the base 10 logarithm 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 5-6.

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:

$$\log K_{ow} = 0.229 + \Sigma\, n_i\, f_i + \Sigma\, n_j\, c_j \qquad \text{(Equation 5-12)}$$

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 5-7.

On first inspection, these correction factors may seem a bit baffling and arbitrary, however, more careful analysis reveals rationale behind the corrections.

Electronic interactions of substituents

Ring corrections

Hydrogen bonding

Others

Table 5-6. Structural groups and group contributions for estimating octanol-water partition coefficients (Meylan and Howard, 1994).

Structural group	Contribution (f_i) to octanol-water partition coefficient	Structural group	Contribution (f_i) to octanol-water partition coefficient
Aromatic atoms		*Aliphatic nitrogen groups*	
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
Aromatic nitrogen		-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
Aliphatic Carbon		-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	*Aliphatic oxygen*	
		-OH (nitrogen attach.)	-0.0427
Olefinic/acetylenic C		-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
Carbonyls		-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	*Aliphatic sulfur*	
NC(O)O (carbamate)	0.1283	$-SO_2N$ (aliph. attach)	-0.4351
NC(O)S(thiocarbamate)	0.5240	$-SO_2N$ (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	$-SO_2OH$ (sulfonic acid)	-3.1580
-C(O)N (arom. attach)	0.1599		
-C(O)S- (aliph. attach)	-1.100	*Halogen groups*	
-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	-Br (aliph. attach)	0.3997
		-Br (arom. attach)	0.8900

Table 5-7. Correction factors for estimating octanol-water partition coefficients (Meylan and Howard, 1994).

Structural group	Correction factor
Correction factors involving ortho substituents on aromatic rings	
-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
Correction factors involving non-ortho substituents on aromatic rings	
-N</-OH (e.g., 4-aminophenol)	-0.3510
-N</ester (e.g., 4 aminobenzoic acid methyl ester)	0.3953
-OH/ester	0.6487
Correction factors involving ortho or non-ortho substituents on aromatic rings	
$-NO_2$ 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
Additional (non-aromatic) correction factors	
Carbonyl correction factors	
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
Ring correction factors	
triazine ring	0.8856
Pyridine ring (non-fused)	-0.1621
Fused aliphatic ring	-0.3421
Alcohol, ether and nitrogen corrections	
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 5-3

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

Solution

a.) Dichloroethylene has the molecular structure CH_2= CCl_2. Referring to the groups in Table 5-4, this structure can be represented by one =CH_2 group, one =CH- or =C< group and two –Cl (olefinic attachment) groups. The uncorrected value of K_{ow} from equation 5-4 is given by:

log K_{ow} = = 2.116

K_{ow} = 130.6

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 - CH_3 groups, one –NH- (aliphatic attachment), 7 aromatic carbons, 3 aromatic nitrogens, one –O- (one aromatic attachment) group, one –N (one aromatic attachment) group, one aromatic sulfur group, one –C(=O)O (ester, aromatic attachment) group, one –SO_2N (aromatic attachment) group and one –NC(=O)NS (urea type) group. The uncorrected value of K_{ow} from equation 5-4 is given by:

log K_{ow} =

= -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 –NC(=O)NS on a triazine (-0.7500). The total of these correction facors 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.

III. D *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.

Octanol-water partition coefficients are generally used to estimate BCF. For example, Veith and Kosian (1983) propose:

$$\text{Log BCF} = 0.79\ (\log K_{ow}) - 0.40 \qquad \text{(Equation 5-13)}$$

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:

$$\text{Log BCF} = 0.77\ (\log K_{ow}) - 0.70 + \Sigma\ j_j \qquad \text{(Equation 5-14)}$$

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 5-8.

Note that there are fewer correction factors in Table 5-8 than in Table 5-7. 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 5-8 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 5-8. 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 5-4

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

Solution

a.) <u>2,2,4 trimethyl-1,3 pentanediol</u> has the molecular structure $HO\text{-}CH_2\text{-}(C)(CH_3)_2\text{-}CH(OH)\text{-}(CH)(CH_3)\text{-}CH_3$. Before estimating BCF, it is first necessary to estimate K_{ow}. Referring to the groups in Table 5-4, the structure can be represented by four $-CH_3$ groups, one $-CH_2-$ group, one >C< group, two –CH< groups and two –OH groups (aliphatic attachment). The uncorrected value of K_{ow} from equation 5-4 is given by:

$$\log K_{ow} = \qquad = 1.08$$

$$K_{ow} = 12.1$$

2,2,4 trimethyl-1,3 pentanediol requires a correction for molecules containing two or more aliphatic –OH (0.4064). The corrected value for log K_{ow} is 1.49. The experimental value for log K_{ow} is 1.24.

b.)<u>trichlorobiphenyl</u> can be represented by 12 aromatic carbons and 3 –Cl (aromatic attachment) groups. The uncorrected value of K_{ow} from equation 5-4 is given by:

$$\log K_{ow} = \qquad = 5.69$$

No corrections are required. The experimental value for log K_{ow} is 5.81.

III.E Henry's Law Coefficient

A useful parameter in estimating water-gas partitioning is the Henry's Law coefficient. The Henry's Law coefficient, as commonly used in describing environmental fate, is the ratio of a compounds concentration in water to its concentration in air, at equilibrium. It is generally expressed either as a dimensionless ratio, or in units of atm-m^3/mole-^{o}K. Once again, a group contribution method can be used to estimate the value of this property. 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.

```
      H   H   H
      ú   ú   ú
H – C – C – C – O - H
      ú   ú   ú
      H   H   H
```

Using the groups from Table 4-3, 1-propanol would consist of one –CH_3 group, two >CH_2 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 coefficient is obtained by summing each of the bond contributions. This preliminary estimate is then adjusted by correction factors for selected functional groups.

$$-\log H = \log(\text{water to air partition coefficient}) = \Sigma\, n_i\, h_i + \Sigma\, n_j\, c_j$$

(Equation 5-18)

where n_j is the number of bonds or groups of type j in the molecule, h_i is the bond contribution to the water to air partition coefficient, 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) and correction factors (c_j) are listed in Tables 5-10 and 5-11.

Table 5-10. Structural groups and group contributions for estimating octanol-water partition coefficients (Meylan and Howard, 1991).

Bond type	Contribution (h_i) to Henry's law coefficient	Bond type	Contribution (h_i) to Henry's law coefficient
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-NO2	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 5-11. Correction factors for Henry's law coefficients (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 5-6
Estimate the Henry's law coefficient 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 (water to air partition coefficient) is given by:

$$-\log H = \log(\text{water to air partition coefficient}) =$$

$$= 3.7112$$

The correction is for linear or branched alcohols (-0.20) giving a net value of 3.5112. The experimental value is 3.55, an error of -1.1% in the logarithm of the water to air partition coefficient.

III. F Soil sorption Coefficients

The soil sorption coefficient describes the physical adsorption and chemical absorption of a compound onto a surface, and 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.

$$\text{Log } K_{oc} = 0.53\,{}^{1}\chi + 0.62 + \Sigma\, n_j P_j \quad \text{(Equation 5-21)}$$

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 μg/g organic carbon) to the concentration of the compound in a liquid phase (in μg/ml); ${}^{1}\chi$ is the first order molecular connectivity index, as described in the Appendix to this chapter; n_i is the number of groups of type i 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 5-12.

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:

$$\begin{array}{c} CH_3 \\ | \\ H_3C\text{-}CH\text{-}CH_2\text{-}CH_3 \end{array}$$

The next step is to count the number of bonds carbons 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.

$$\begin{array}{c} \textbf{(1)} \\ CH_3 \\ | \\ H_3C\text{-}CH\text{-}CH_2\text{-}CH_3 \\ \textbf{(1)}\ \ \textbf{(3)}\ \ \textbf{(2)}\ \ \ \textbf{(1)} \end{array}$$

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

(1,3), (1,3), (3,2), (2,1)

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

$$^1\chi = \Sigma(\delta_I * \delta_j)^{-0.5}$$

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

$^1\chi =$ $= 3.787$

Table 5-12. Correction factors for soil sorption coefficients (Meylan and Howard, 1992).

Structural group	Correction factor
N containing groups	
azo	-1.028
N, C containing groups	
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
N, O containing groups	
nitro	-0.632
N, C, O containing groups	
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
C, O containing groups	
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
P, O containing groups	
Aliphatic organophosphorus, P=O	-1.698
Aromatic organophosphorus, P=O	-2.878
P, S containing groups	
P=S	-1.263
C, S containing groups	
Thiocarbonyl	-1.100
S, O containing groups	
sulfone	-0.995

Example problem 5-7

Estimate the soil sorption coefficient of 2-hexanol.

Solution

a.) As shown in Example problem 5-5, 2-hexanol has the molecular structure CH_3-(CH-OH)-C_4H_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):

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

Where the value of ${}^{1}\chi$ is 3.414 gives an uncorrected value of 2.429. Adding in the correction term for an aliphatic alcohol (-1.519) yields an estimate of 0.91.

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 propogate through the entire environmental assessment.

Section 4.2: 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 coefficient for the herbicide listed in Example 4-2)?**
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?**