PART II

Evaluating and Improving Environmental Performance of Chemical Processes

Overview

Evaluating the environmental impacts of processes and improving environmental performance of process designs are complex task involving a wide variety of analysis tools.

Textbook Framework

1. Specify the product to be manufactured and evaluate potential Environmental fate(Chap. 5), release, and exposure (Chap. 6).
2. Establish the input/output structure of the process, including chemical synthesis pathways and potential byproducts (Chap. 7).
3. Evaluate potential emissions and environmental impacts associated with the conceptual process (Chap. 8).
4. Specify the unit operations and process flows and identify pollution prevention opportunities (Chap. 9).
5. Examine flowsheet to identify environmental improvements and opportunities for energy and mass integration(Chap. 10)
6. Evaluate environmental performance of detailed processes (Chap. 11)
7. Evaluate environmental costs associated with the process (Chap. 12).

CHAPTER 5

Evaluating Environmental Fate: Approach based on Chemical Structure

Goal

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

5.1 Introduction

Screening chemicals for environmental risk: an overview

- Over 9000 chemicals are produced commercially.
- Every year, thousand or more new chemicals are developed

Questions regarding screening chemicals for environmental risk

1. Will its manufacture or use pose environmental & human risks ?
2. If there are risks, what are the exposure pathways ?
3. Will the chemicals degrade if it is released to environment ? or will it persist ?
4. If the chemicals degraded, will the degradation products pose a risk to environmental ?

5.1 Introduction

Screening chemicals for environmental risk: an overview

PMN (Premanufacturing Notice)

Qualitative and quantitative methods for estimating risks when only information available is a chemical structure.

Many of these methods have been developed by the US EPA and its contractors. The methods are routinely used in evaluating ***premanufacturing notices (PMN)*** submitted under the Toxic Substances Control Act (TSCA).

Under the provisions of TSCA, before a new chemical can be manufactured in the USA, a PMN <u>MUST</u> be submitted to the US EPA.

5.1 Introduction

Screening chemicals for environmental risk: an overview

PMN (Premanufacturing Notice)

The PMN specifies the chemical to be manufactured, the quantity to be manufactured, and any known environmental impacts including potential releases from the manufacturing site.

Based on these limited data, the US 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 tool has been developed that relate chem. structure to potential environ. risks.

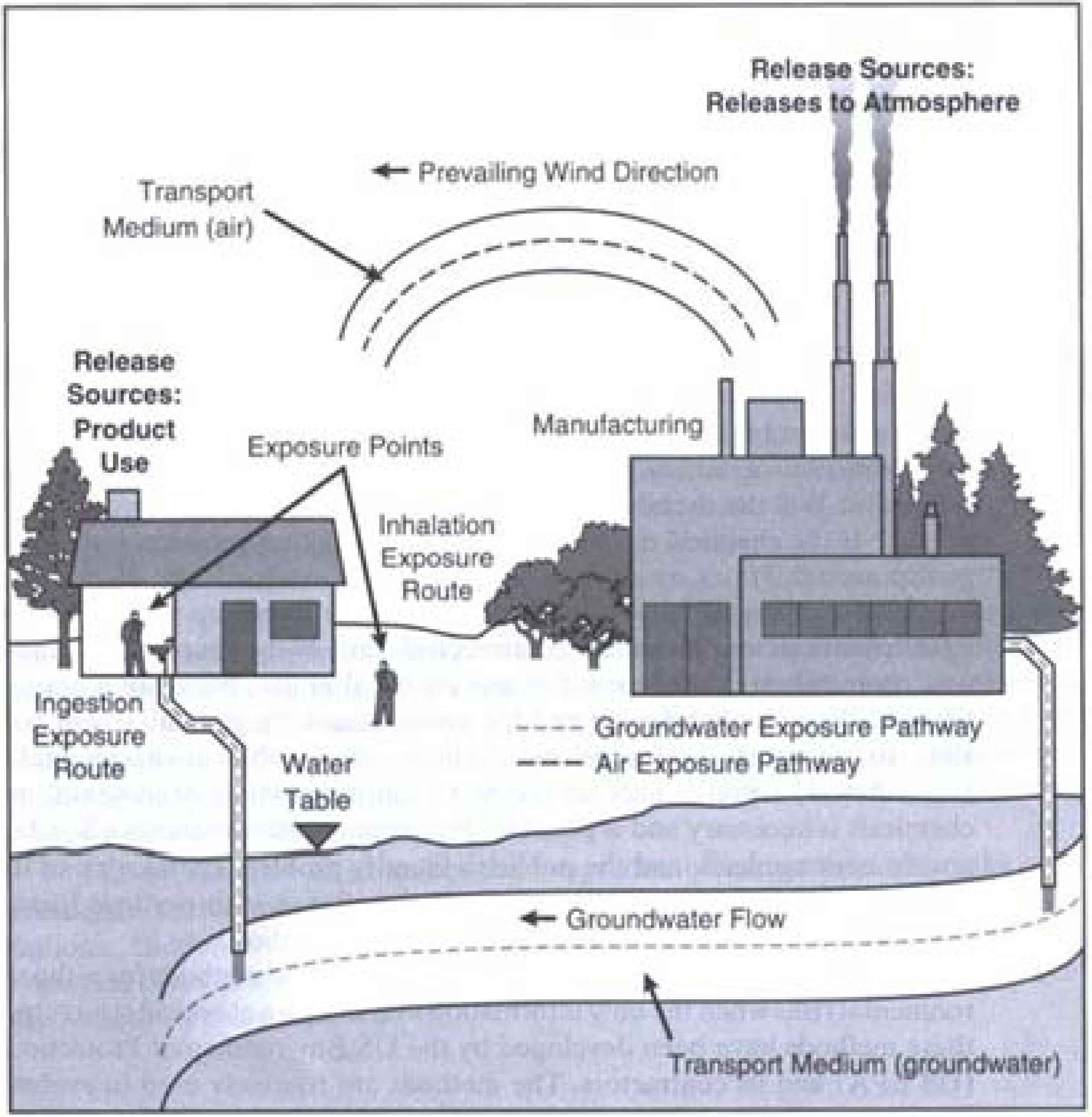


Fig. 5.1-1 The chemical and physical properties that will influence each of the processes that determine environmental exposure and hazard

Chemical Properties Needed to Perform Environmental Risk 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

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*

Property Describe Partitioning *(between solid, liquid and gas phase)*

1. melting point, boiling point, vapor pressure.
2. *(Additional properties)* Henry's law constant, octanol-water partition coefficient, water solubility, soil sorption coefficient, and bio-concentration factors, etc.

Group contribution methods

SARs: Structure activity relationships
QSARs: Quantitative Structure activity relationships

Assume that

molecule is made up of a collection of atoms or bonds

Assume that

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

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

Table 5.2-1

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

Table 5.2-1

Properties that influence environmental phase partitioning

Property	*Definition*	*Significance in estimating environmental fate and risks*
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

Table 5.2-1

Properties that influence environmental phase partitioning

Property	*Definition*	*Significance in estimating environmental fate and risks*
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

Table 5.2-1

Properties that influence environmental phase partitioning

Property	*Definition*	*Significance in estimating environmental fate and risks*
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

Chemical and Physical Property Definitions

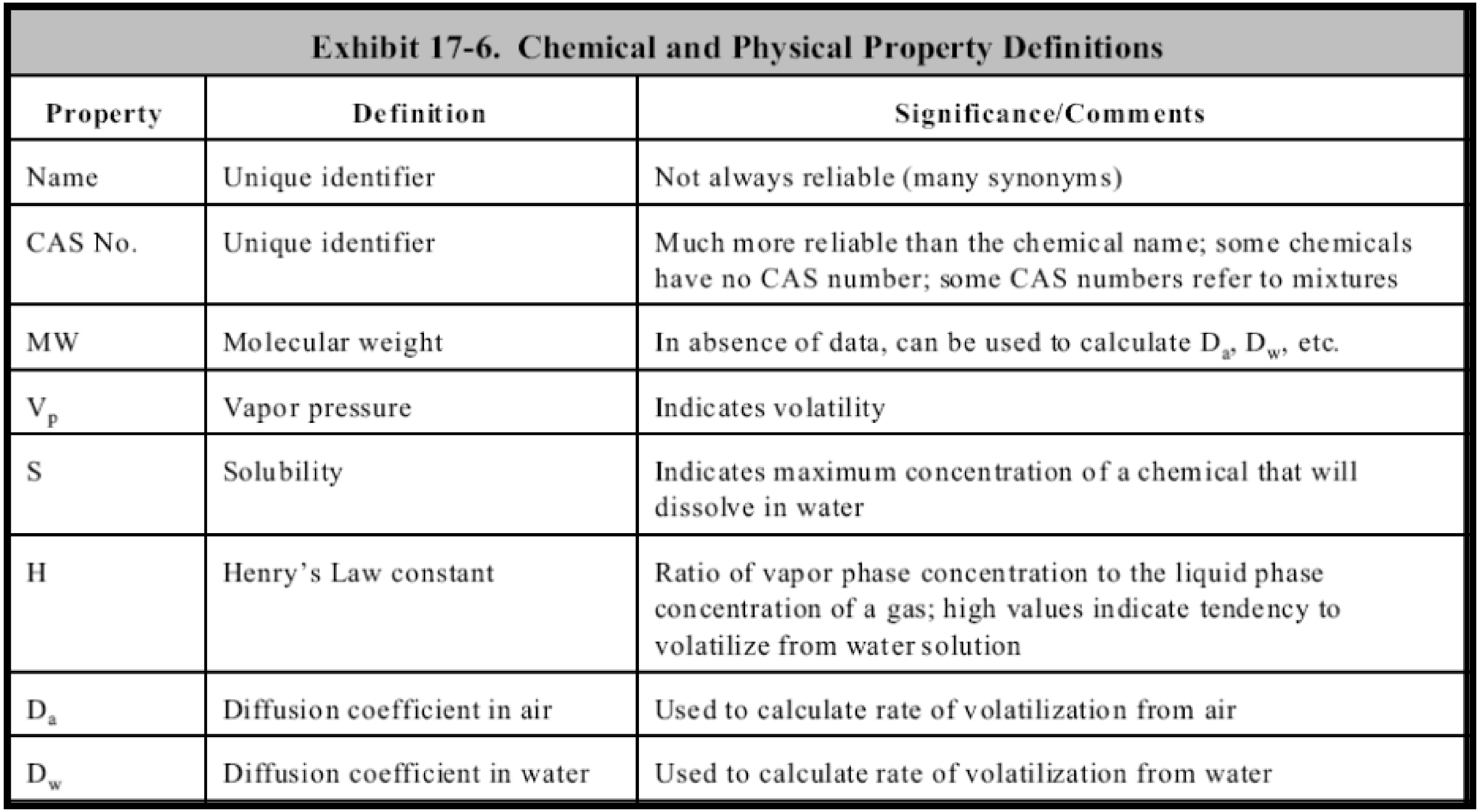


Exhibit 17-6. Chemical and Physical Property Definitions

Property	Definition	Significance/Comments
Name	Unique identifier	Not always reliable (many synonyms)
CAS No.	Unique identifier	Much more reliable than the chemical name; some chemicals have no CAS number; some CAS numbers refer to mixtures
MW	Molecular weight	In absence of data, can be used to calculate D_a, D_w, etc.
V_p	Vapor pressure	Indicates volatility
S	Solubility	Indicates maximum concentration of a chemical that will dissolve in water
H	Henry's Law constant	Ratio of vapor phase concentration to the liquid phase concentration of a gas; high values indicate tendency to volatilize from water solution
D_a	Diffusion coefficient in air	Used to calculate rate of volatilization from air
D_w	Diffusion coefficient in water	Used to calculate rate of volatilization from water

http://www.epa.gov/ttnmain1/fera/data/risk/vol_1/chapter_17.pdf

Chemical and Physical Property Definitions

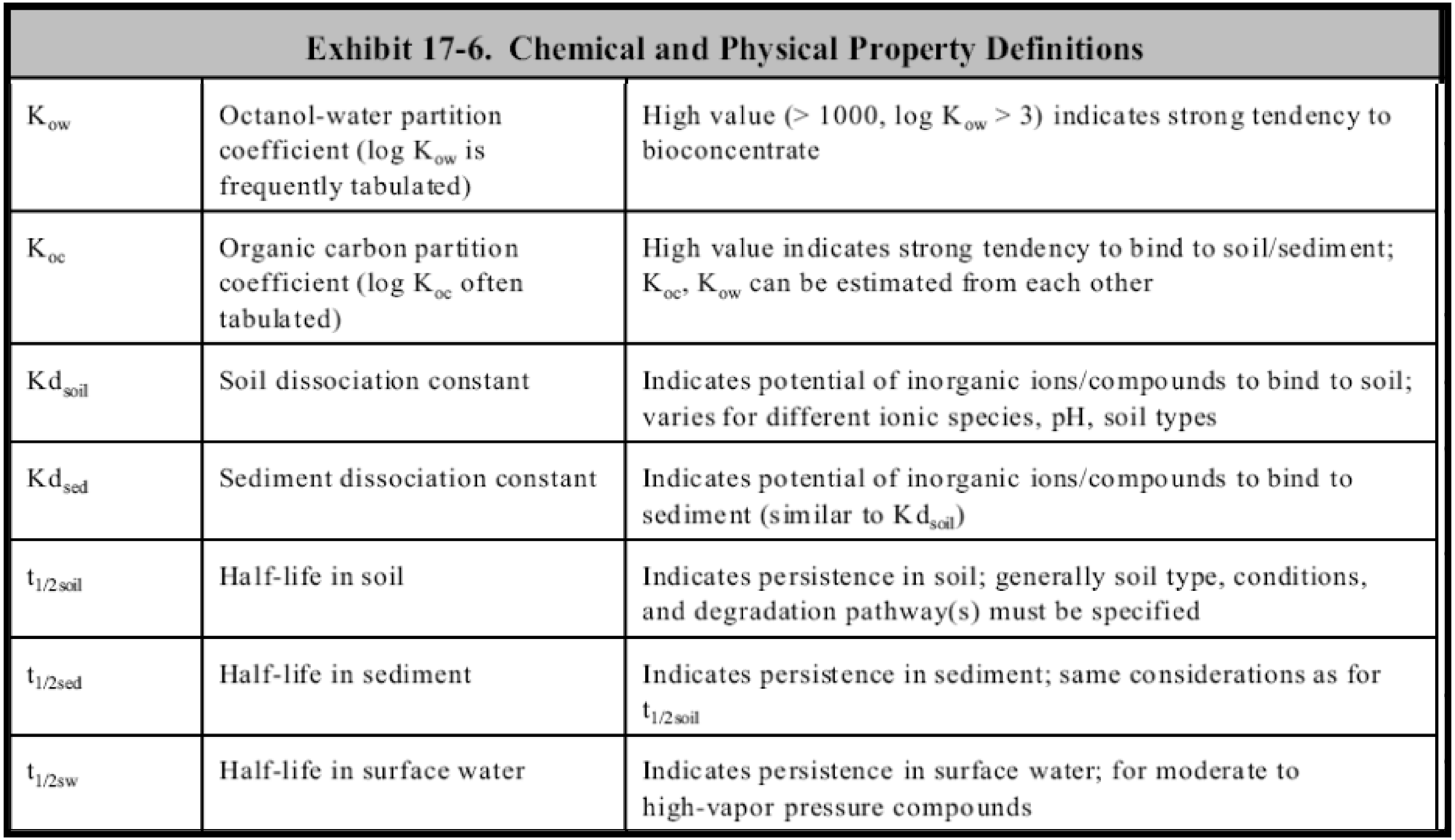


Exhibit 17-6. Chemical and Physical Property Definitions

K_{ow}	Octanol-water partition coefficient (log K_{ow} is frequently tabulated)	High value (> 1000, log K_{ow} > 3) indicates strong tendency to bioconcentrate
K_{oc}	Organic carbon partition coefficient (log K_{oc} often tabulated)	High value indicates strong tendency to bind to soil/sediment; K_{oc}, K_{ow} can be estimated from each other
Kd_{soil}	Soil dissociation constant	Indicates potential of inorganic ions/compounds to bind to soil; varies for different ionic species, pH, soil types
Kd_{sed}	Sediment dissociation constant	Indicates potential of inorganic ions/compounds to bind to sediment (similar to Kd_{soil})
$t_{1/2soil}$	Half-life in soil	Indicates persistence in soil; generally soil type, conditions, and degradation pathway(s) must be specified
$t_{1/2sed}$	Half-life in sediment	Indicates persistence in sediment; same considerations as for $t_{1/2soil}$
$t_{1/2sw}$	Half-life in surface water	Indicates persistence in surface water; for moderate to high-vapor pressure compounds

http://www.epa.gov/ttnmain1/fera/data/risk/vol_1/chapter_17.pdf

Chemical and Physical Property Definitions

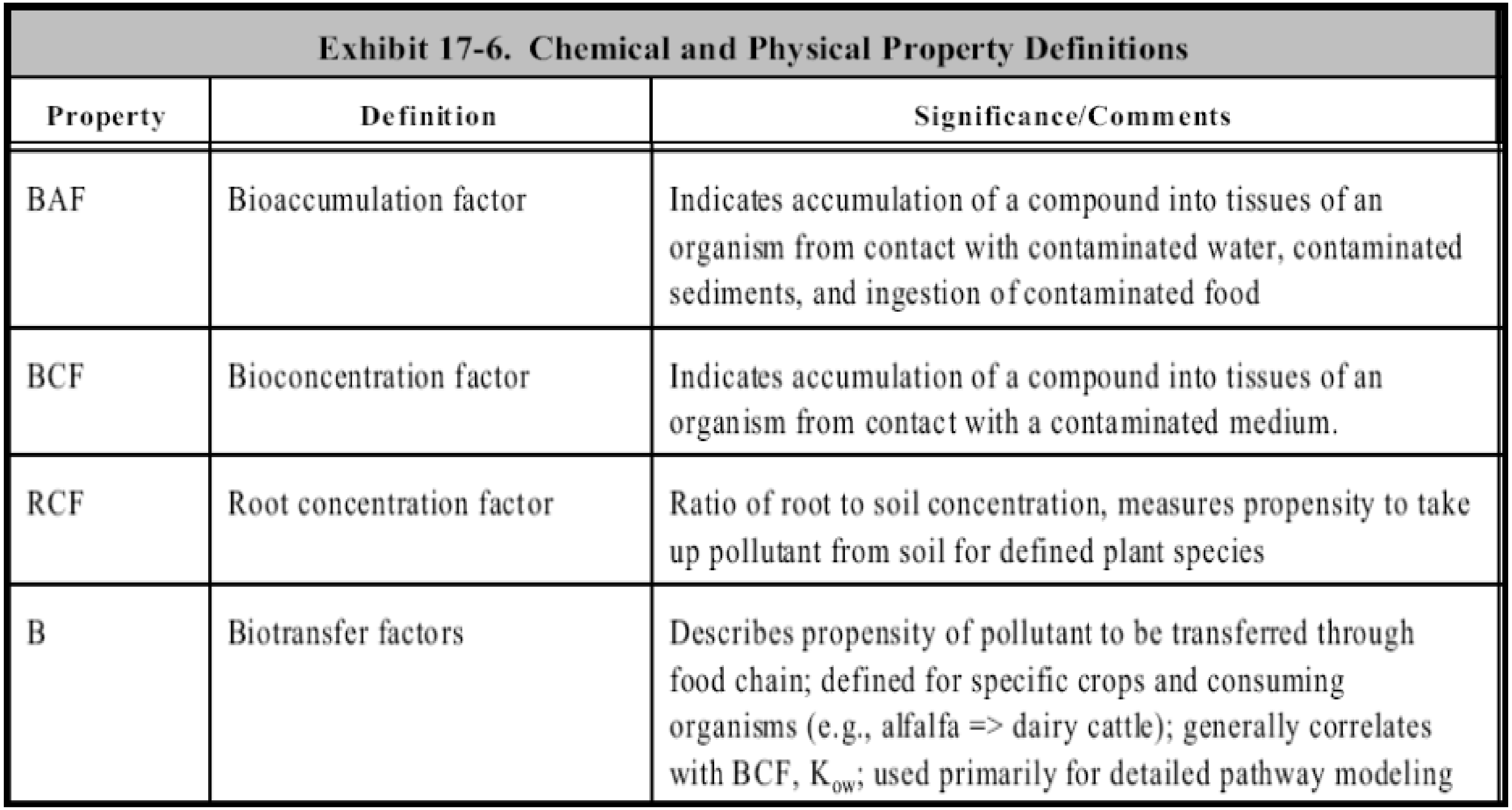


Exhibit 17-6. Chemical and Physical Property Definitions

Property	Definition	Significance/Comments
BAF	Bioaccumulation factor	Indicates accumulation of a compound into tissues of an organism from contact with contaminated water, contaminated sediments, and ingestion of contaminated food
BCF	Bioconcentration factor	Indicates accumulation of a compound into tissues of an organism from contact with a contaminated medium.
RCF	Root concentration factor	Ratio of root to soil concentration, measures propensity to take up pollutant from soil for defined plant species
B	Biotransfer factors	Describes propensity of pollutant to be transferred through food chain; defined for specific crops and consuming organisms (e.g., alfalfa => dairy cattle); generally correlates with BCF, K_{ow}; used primarily for detailed pathway modeling

http://www.epa.gov/ttnmain1/fera/data/risk/vol_1/chapter_17.pdf

Boiling Point and Melting Point

1. Boiling Point

Joback-Reid GC formula (1987) and Stein-Brown, modified(1994)

$$T_b(K) = 198.2 + \sum n_i g_i$$

$$T_b(corrected) = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 \quad [T_b \le 700K]$$

$$T_b(corrected) = T_b + 282.7 - 0.5209T_b \quad [T_b > 700K]$$

T_b : the normal boiling point @ 1 atm [K]
n_i: the number of groups of type i in the molecules
g_i: the contribution of each group to the boiling point

- Structural groups and group contributions (g_i) for b.p. estimation are in Table 5.2-2 and average error is 3.2 % over 4000 compounds.

Boiling Point and Melting Point

2. Melting point

$$T_m(K) = 0.5839\, T_b(K)$$

Melting point is occasionally used in estimating the phase partitioning of solids.

Lyman, W.J., “Estimation of Physical Properties,” Environmental Exposure From Chemicals, volume 1, Neely, W.B. and Blau, G.E., eds. CRC Press Boca Raton, FL 38-44 (1985)

Table 5.2-2

Structural groups & group contributions for boiling point estimation

(Stein & Brown, 1994)

Structural group	Contribution (g_i) to normal boiling point
Carbon groups	
$-CH_3$	21.98
$>CH_2$	24.22
$>C_{ring}H_2$	26.44
$>CH-$	11.86
$>C_{ring}H-$	21.66
$>C<$	4.50
$>C_{ring}<$	11.12
$=CH_2$	16.44
$=CH-$	27.95
$=C_{ring}H-$	28.03
$=C<$	23.58
$=C_{ring}<$	28.19
aaCH*	28.53
aaC-	30.76
aaaC	45.46
$\equiv CH$	21.71
$\equiv C-$	32.99

*The symbol a denotes an aromatic bond

Table 5.2-2

Structural groups & group contributions for boiling point estimation

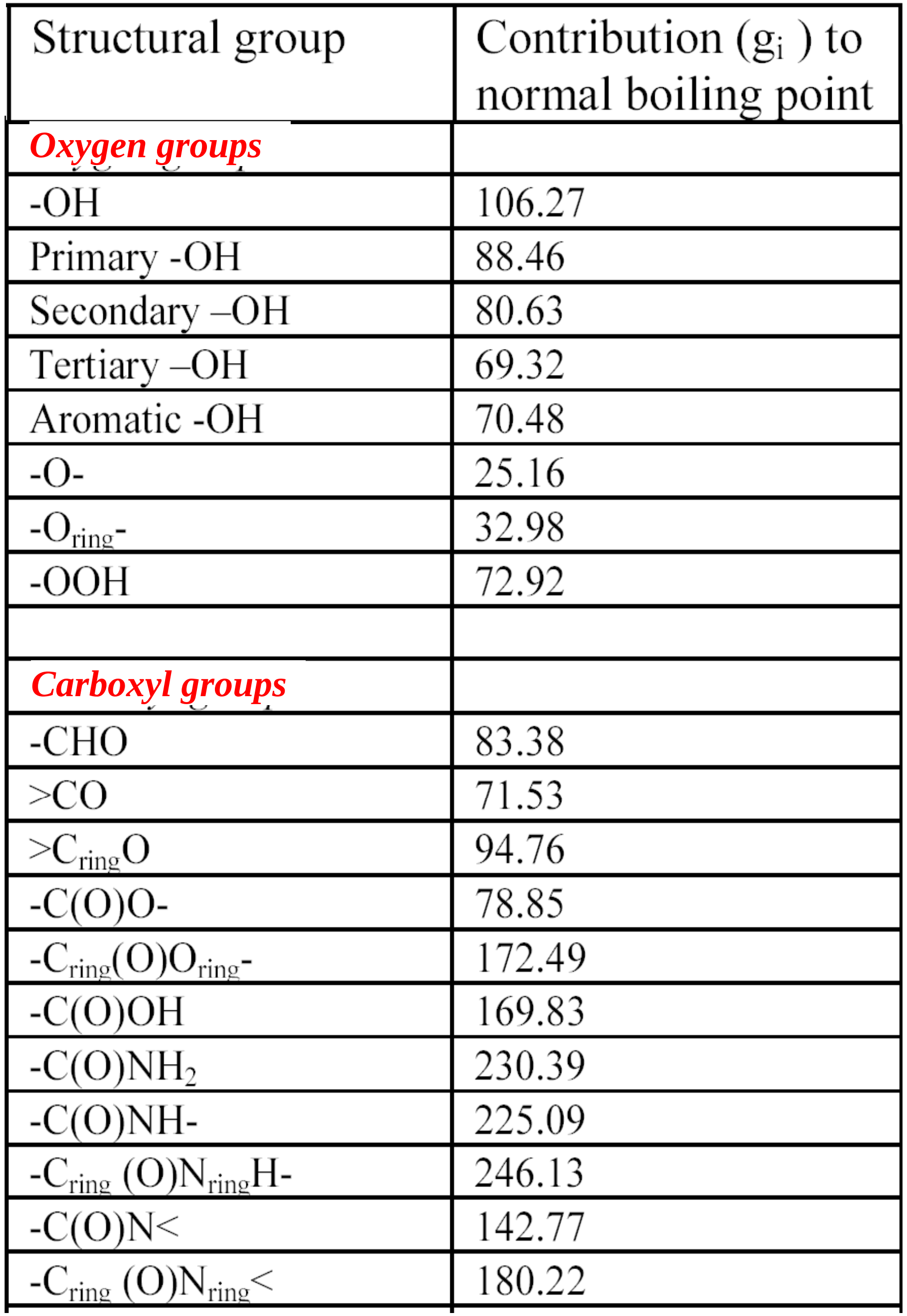
(Stein & Brown, 1994)

Structural group	Contribution (g_i) to normal boiling point
Nitrogen groups	
$-NH_2$	61.98
Aromatic-NH_2	86.63
$>NH$	45.28
$>N_{ring}H$	65.50
$>N-$	25.78
$>N_{ring}-$	32.77
$>NOH$	104.87
$>NNO$	184.68
anN	39.88
$=NH$	73.40
$=N-$	31.32
$=N_{ring}-$	43.54
$=N_{ring}N_{ring}H-$	179.43
$-N_{ring}=C_{ring}N_{ring}H-$	284.16
$-N=NNH-$	257.29
$-N=N-$	90.87
$-NO$	30.91
$-NO_2$	113.99
$-CN$	119.16
Aromatic-CN	95.43

Table 5.2-2

Structural groups & group contributions for boiling point estimation

(Stein & Brown, 1994)



Structural group	Contribution (g_i) to normal boiling point
Oxygen groups	
-OH	106.27
Primary -OH	88.46
Secondary –OH	80.63
Tertiary –OH	69.32
Aromatic -OH	70.48
-O-	25.16
$-O_{ring}-$	32.98
-OOH	72.92
Carboxyl groups	
-CHO	83.38
>CO	71.53
$>C_{ring}O$	94.76
-C(O)O-	78.85
$-C_{ring}(O)O_{ring}-$	172.49
-C(O)OH	169.83
$-C(O)NH_2$	230.39
-C(O)NH-	225.09
$-C_{ring}\ (O)N_{ring}H-$	246.13
-C(O)N<	142.77
$-C_{ring}\ (O)N_{ring}<$	180.22

Table 5.2-2

Structural groups & group contributions for boiling point estimation

(Stein & Brown, 1994)

Structural group	Contribution (g_i) to normal boiling point
Halogen groups	
-F	0.13
Aromatic-F	-7.81
-Cl	34.08
Primary-Cl	62.63
Secondary-Cl	49.41
Tertiary-Cl	36.23
Aromatic-Cl	36.79
-Br	76.28
Aromatic-Br	61.85
-I	111.67
Aromatic-I	99.93
Sulfur groups	
-SH	81.71
Aromatic-SH	77.49
-S-	69.42
$-S_{ring}-$	69.00
$>SO$	154.50
$>SO_2$	171.58
$>CS$	106.20
$>C_{ring}S$	179.26

Example problem 5.2-1

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

Solution

$$T_b(K) = 198.2 + 21.98 + 24.22 + 88.46 = 332.9K$$

b.) Toluene has the molecular structure CH_3- C_6H_5. Referring to the groups in Table 5.2-2, 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:

$$T_b(K) = 198.2 + 21.98 + 30.76 + 5(28.53) = 393.6K$$

The corrected value is:

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

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:

$$T_b(K) = 198.2 + 21.98 + 83.38 = 303.6K$$

The corrected value is:

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

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

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.

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 temperature, will be important in screening chemicals for environmental risk.

Vapor Pressure

Antoine Equation

Halogen groups

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

➔ *at normal boiling point*

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.

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

$$\ln P_{VP}(atm) = \frac{A(T_b - C)^2}{0.97RT_b} \times \left[\frac{1}{T_b - C} - \frac{1}{T - C} \right] \quad (5\text{-}7)$$

Empirical Parameter Correlations

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

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

✸ *Parameter K_F are in Table 5.2–3 and 5.2–4*

Vapor Pressure

Equation (5-7) through (5-9) work well in estimating vapor pressure that range from 10^{-2} to 1 atm, 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.

2. For Solids

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

P = the vapor pressure (atm)
T_b = the normal boiling point (K)
T_m = the melting point (K)

Table 5.2-3 *Factors(K_F) used in estimating boiling points*

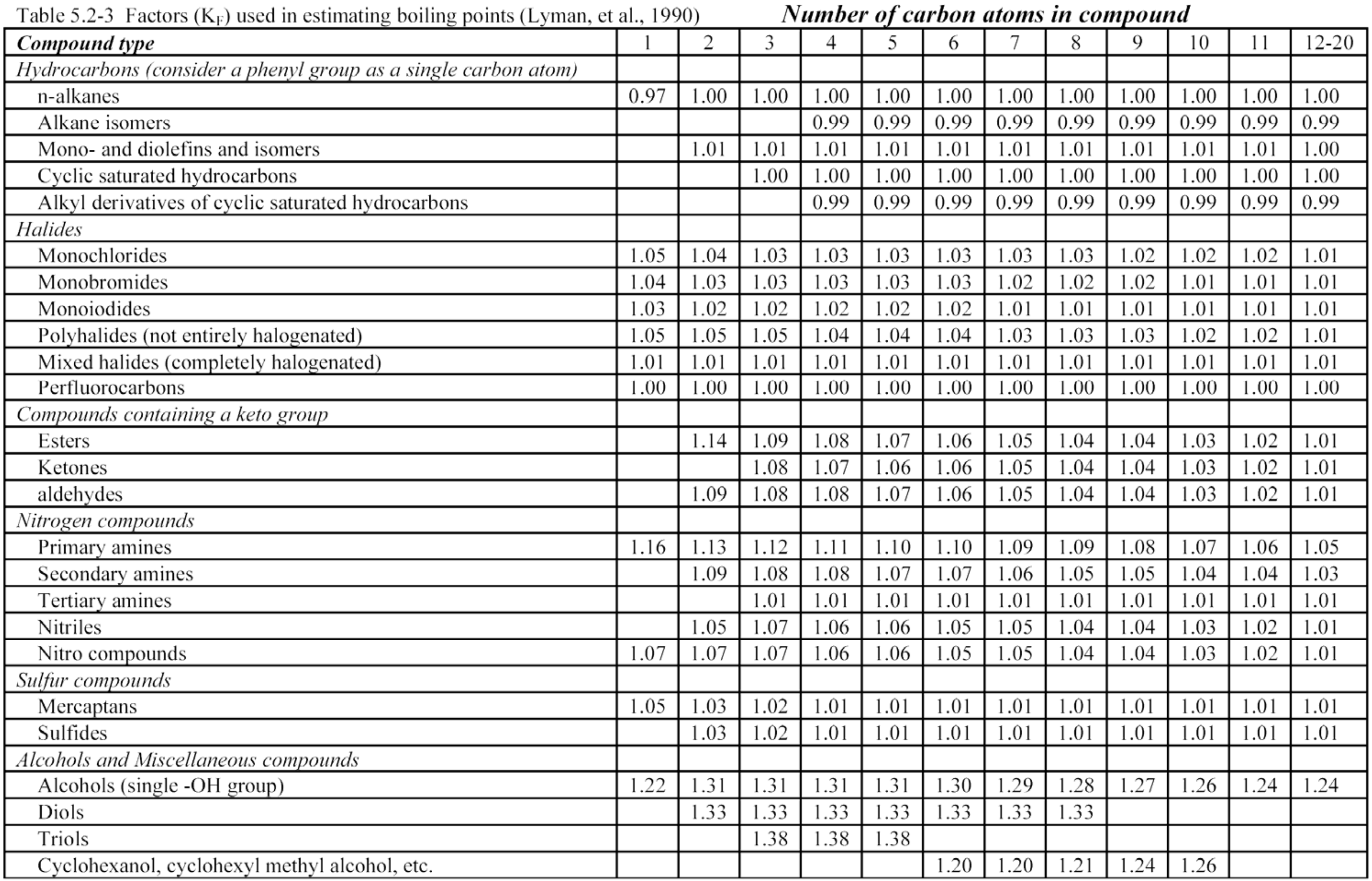


Table 5.2-3 Factors (K_F) used in estimating boiling points (Lyman, et al., 1990)

	Number of carbon atoms in compound											
Compound type	1	2	3	4	5	6	7	8	9	10	11	12-20
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	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
Halides												
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
Monoiodides	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
Compounds containing a keto group												
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
Nitrogen compounds												
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
Sulfur compounds												
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
Alcohols and Miscellaneous compounds												
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		

Table 5.2-4 *Factors(K_F) used in estimating boiling points for aromatics*

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

Example problem 5.2-3

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:

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

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

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

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

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

Octanol-Water Partition Coefficient, Kow

Octanol-Water Partition Coefficient
are used to characterize partitioning of a molecule between
aqueous phase, such as rivers and lakes, and
hydrophobic phases, such as the organic fraction of sediments
suspended in water bodies.

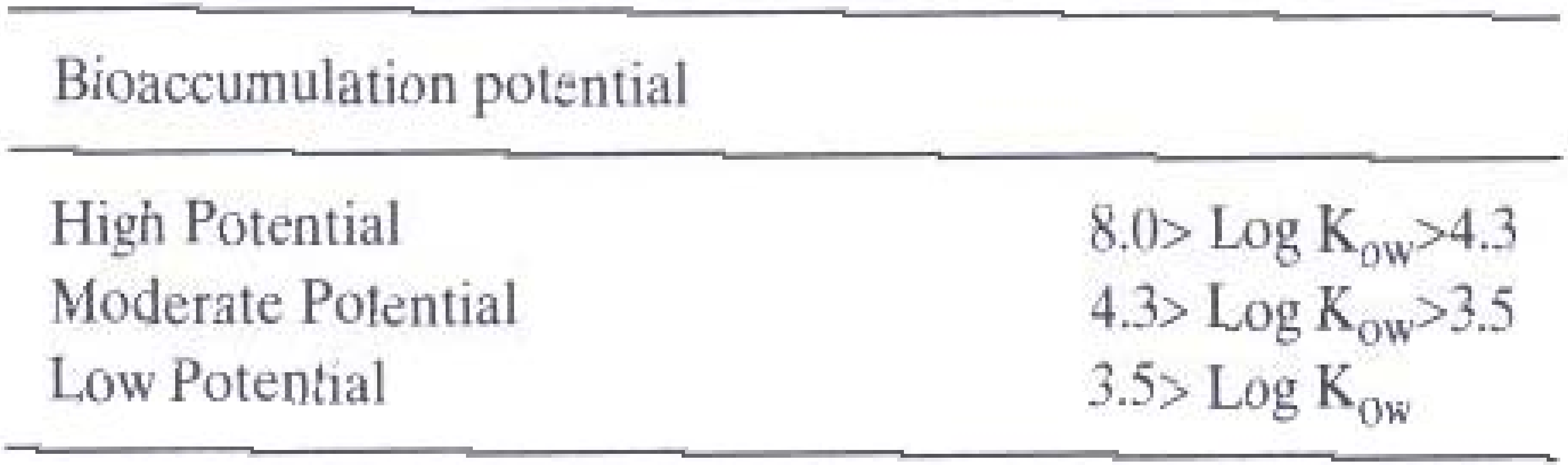
Because K_{ow} characterizes partitioning between aquous and organics, lipid-like phase, it is used to estimate a variety of toxicological and environmental fate parameters.

Use of K_{OW}

✶ gauge for the potential for bioaccumulation
(if a chemical is lipophilic, it can be stored in fatty tissue of fish and will bioaccumulate in animals that eat fish)

Classification criteria for bioaccumulation

Table 5.2-5



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

Octanol-Water Partition Coefficient, Kow

Group contribution methods have been developed for octanol-water partition coefficients (Meylan and Howard, 1995)

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

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 5.2-6.

Octanol-Water Partition Coefficient, Kow

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:

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

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.

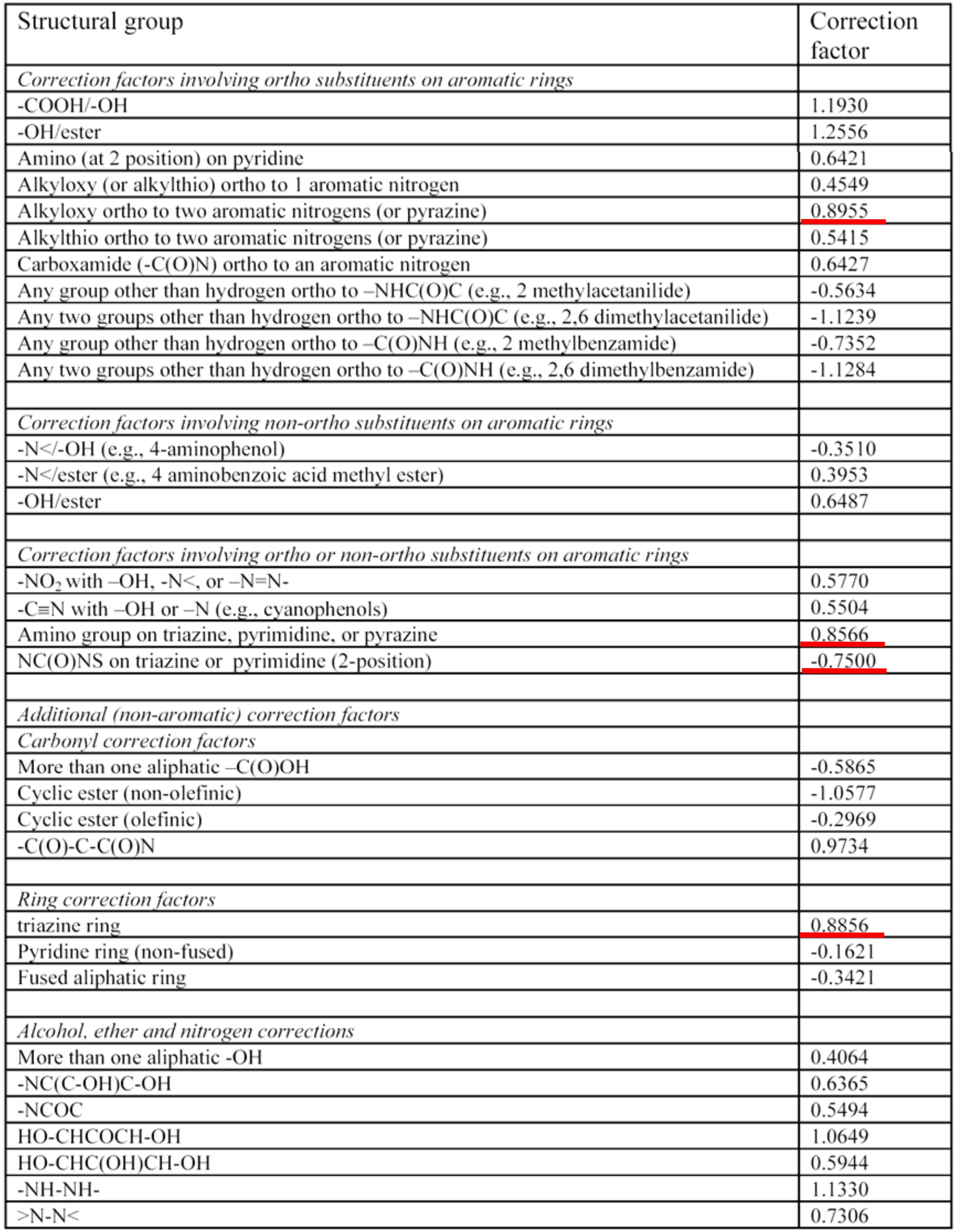
Table 5.2−6

Structural groups and group contributions (f_i) for estimating octanol−water partition coefficients, K_{OW}

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$_2$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	*Halogen groups*	
-C(O)- (aliph. attach)	-1.5586	-F (aliph. attach)	-0.0031
-C(O)- (cyclic, 2 arom. attach)	-0.2063	-Cl (aliph. attach) **-Cl (olefinic attach)**	0.3102 **0.4923**
-C(O)- (olefinic attach)	-1.2700	-Cl (arom. attach)	0.6445
-C(O)- (cyclic, arom., olefinic attach.)	-0.5497	-Br (aliph. attach)	0.3997

Table 5.2-7

Correction factors, c_j, for estimating octanol-water partition coefficient



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 5.2-4

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

Solution

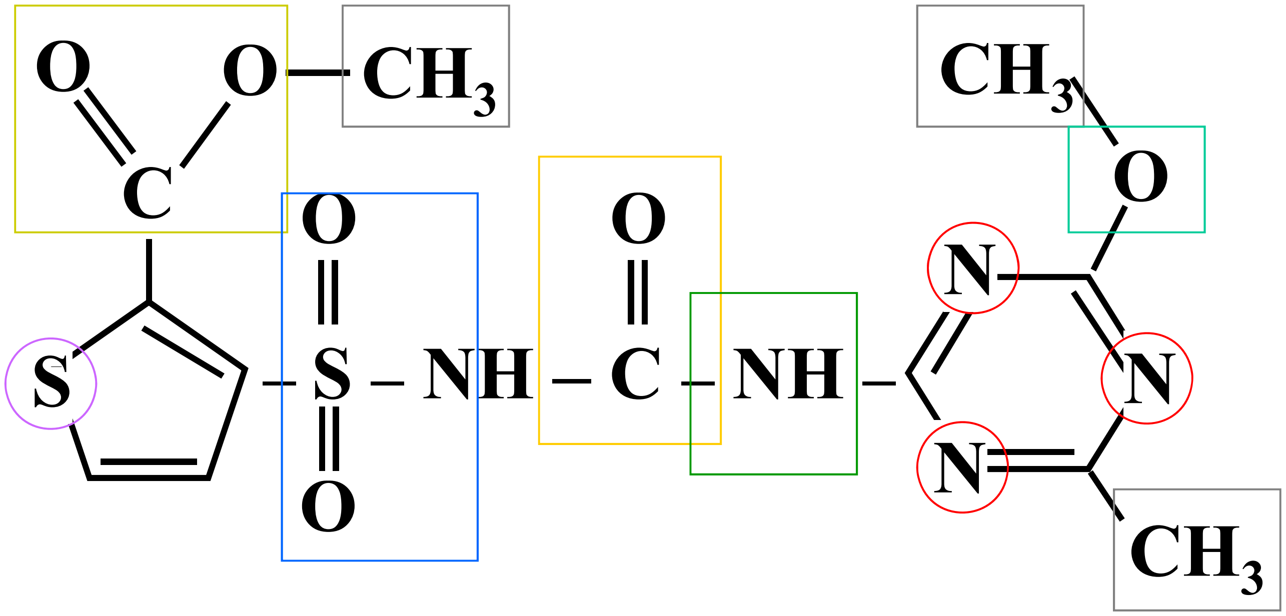
a.) Dichloroethylene has the molecular structure CH_2= CCl_2. Referring to the groups in Table 5.2-6, this structure can be represented by one $=CH_2$ group, one =CH- or =C< group and two –Cl (olefinic attachment) groups. The uncorrected value of K_{ow} from equation 5-11 is given by:

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

$$K_{ow} = 130$$

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%

Structure of herbicide



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 5-11 is given by:

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

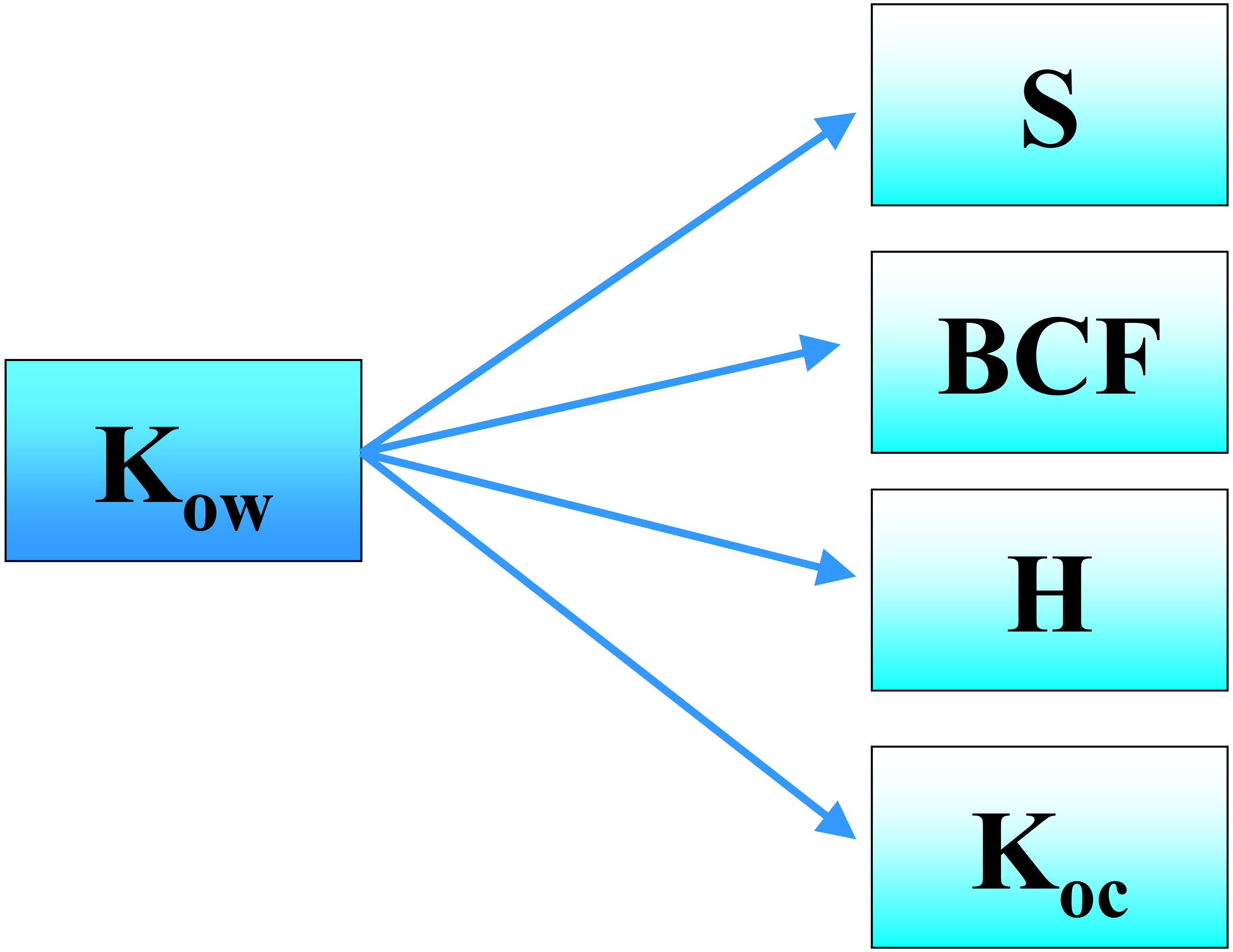
$$0.4082 - 0.7121 - 0.2079 + 1.0453 = -0.614$$

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 –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.

Application of K_{ow}



K_{ow}

S

Water Solubility

BCF

Bioconcentration Factor

H

Henry's Law Constant

K_{oc}

Soil Sorption Coefficients

5.2.4 Bioconcentration Factor, BCF

One of the primary reasons for estimating the octanol-water partition coefficient (K_{OW}) is to assess the partitioning of a chemical between aqueous and lipid phases in living organisms.

▶ 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)*

▶ High BCF value indicate a living organism will extract a material from aqueous phase *(ingested water or blood)*, and concentrate it in lipid tissues *(e.g., fats) : accumulate in fish*

Bioconcentration Factor, BCF

Table 5.2-8 *Classification criteria for bioaccumulation*

Bioaccumulation potential	
High Potential	BCF > 1000
Moderate Potential	1000 > BCF > 250
Low Potential	250 > BCF

Group Contribution Method for BCF

(Veith and Koisan, 1983)

Correlation between octanol-water partition coefficient (K_{OW}) and BCF

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

For Correction for nonionic compounds

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

j_j : correction factor **(Table 5.2-9)**

Bioconcentration Factor, BCF

(Veith and Koisan, 1983)

Table 5.2-9 Correction factors for BCF of nonionic compounds

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.) <u>2,2,4 trimethyl-1,3 pentanediol</u> has the molecular structure HO-CH_2-(C)(CH_3)$_2$-CH(OH)-(CH)(CH_3)-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 -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 5-11 is given by:

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

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.

$$\text{Log BCF} = 0.79(1.49) - 0.40 = 0.7771; \quad \boxed{\text{BCF} = 5.99}$$

Referring to table 5.2-8, it is evident that *2,2,4 trimethyl-1,3 pentanediol* has low potential for bioaccumulation.

Example 5.2-5

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

Solution

b.)trichlorobiphenyl can be represented by 12 aromatic carbons and 3 –Cl (aromatic attachment) groups. The uncorrected value of K_{ow} from equation 5-11 is given by:

$$\text{Log Kow} = 0.229 + 12(0.2940) + 3(0.6445) = 5.69$$

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

$$\text{Log BCF} = 0.77(5.69) - 0.70 + 0.62 = 4.30; \quad \boxed{\text{BCF} = 20000}$$

Referring to table 5.2-8, it is evident that 2, 4',5 trichlorobiphenyl has a very high potential for bioaccumulation.

5.2.5 Water Solubility, S

In assessing environmental transport and partitioning, it is often necessary to predict maximum, or saturation, concentration.

In the gas phase, this is done by estimating vapor pressure. In aqueous phases, saturation concentrations are estimated using water solubility.

Water solubility can be estimate in many ways. Activity coefficients, solubility parameters, and other chemical and structural properties can be used as a basis for estimating water solubility.

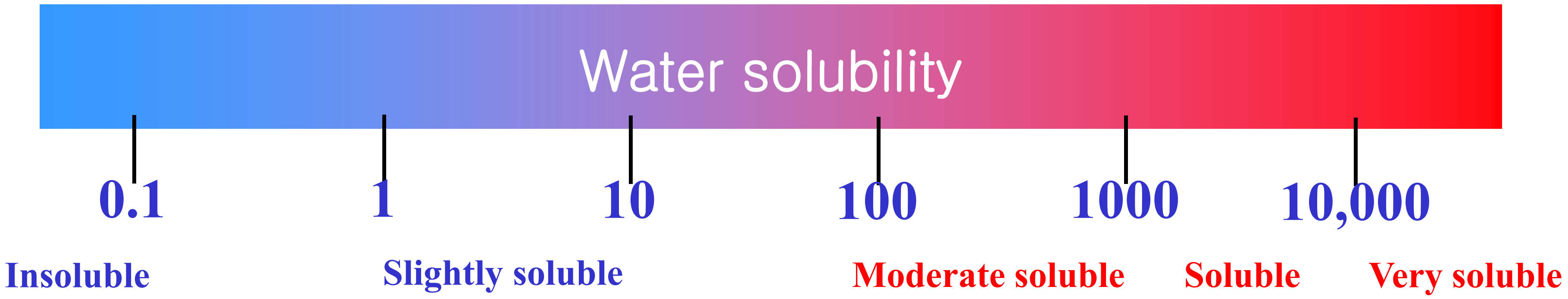
Water Solubility, S

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, which properties such as activity coefficients are not frequently calculated in environmental screening studies.

Classification criteria for water solubility

Water Solubility	
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



Water Solubility, S

(Meylan, et al. 1996)

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

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

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

S = the water solubility [mol/L]

K_{ow} = the octanol-water partition coefficient

T_m = the melting point [°C]

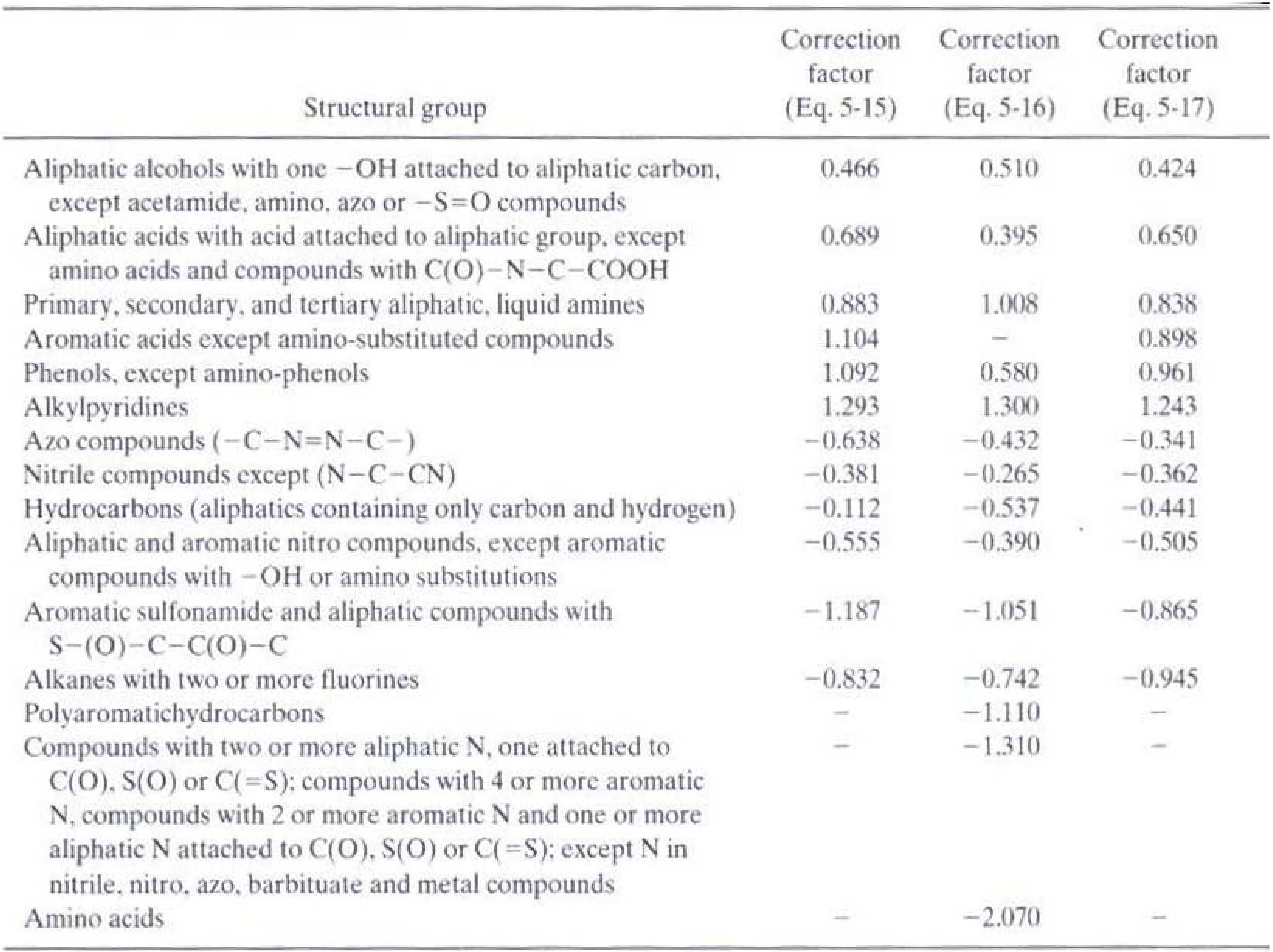
MW = the molecular weight

h_j = the correction factor for each group and the summation is taken over all groups that have correction factor

Water Solubility, S

- Correction factors are different for each equation
- Mean error in the range of 0.3 to 0.4 log units
- Any of these three equations can be used, but, if more information is available for the correction, the estimate is more accurate

Table 5.2-11 Correction factors for estimating water



Structural group	Correction factor (Eq. 5-15)	Correction factor (Eq. 5-16)	Correction factor (Eq. 5-17)
Aliphatic alcohols with one −OH attached to aliphatic carbon, except acetamide, amino, azo or −S=O compounds	0.466	0.510	0.424
Aliphatic acids with acid attached to aliphatic group, except amino acids and compounds with C(O)−N−C−COOH	0.689	0.395	0.650
Primary, secondary, and tertiary aliphatic, liquid amines	0.883	1.008	0.838
Aromatic acids except amino-substituted compounds	1.104	–	0.898
Phenols, except amino-phenols	1.092	0.580	0.961
Alkylpyridines	1.293	1.300	1.243
Azo compounds (−C−N=N−C−)	−0.638	−0.432	−0.341
Nitrile compounds except (N−C−CN)	−0.381	−0.265	−0.362
Hydrocarbons (aliphatics containing only carbon and hydrogen)	−0.112	−0.537	−0.441
Aliphatic and aromatic nitro compounds, except aromatic compounds with −OH or amino substitutions	−0.555	−0.390	−0.505
Aromatic sulfonamide and aliphatic compounds with S−(O)−C−C(O)−C	−1.187	−1.051	−0.865
Alkanes with two or more fluorines	−0.832	−0.742	−0.945
Polyaromatichydrocarbons	–	−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	–

5.2.6 Henry's Law Constant, H

(Meylan and Howard, 1991)

The Henry's law constant

$$\equiv \frac{\text{compound's concentration in air}}{\text{compound's concentration in water}}$$

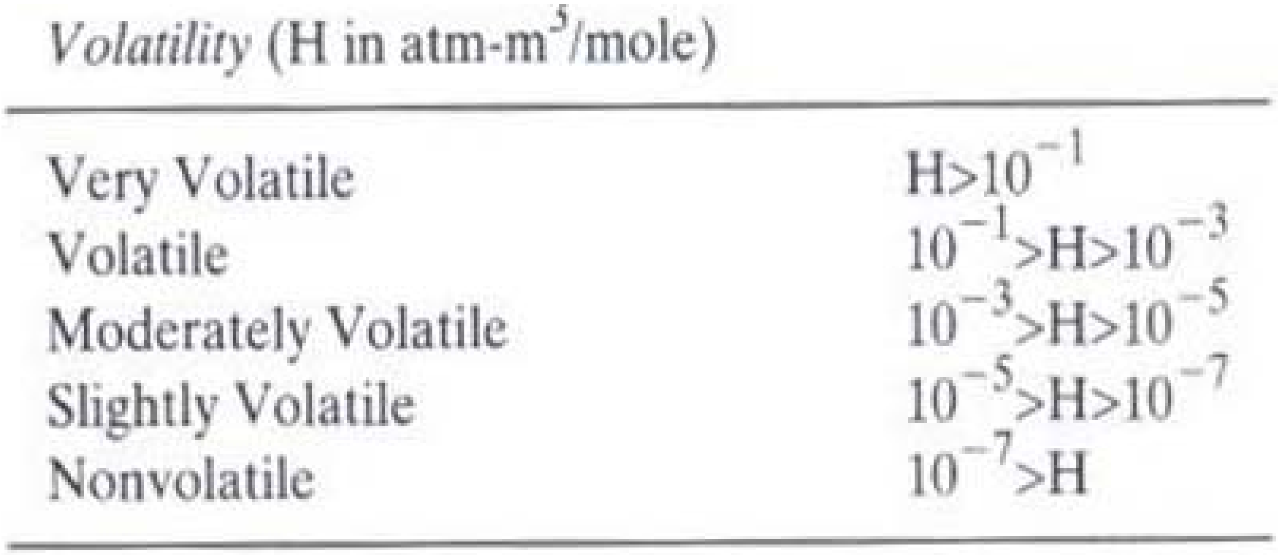
at equilibrium.

5.2.6 Henry's Law Constant, H

(Meylan and Howard, 1991)

- Compound's affinity for air over water
- High H tend to partition into the air,
- Low H into the water

Table 5.2-12 Classification criteria for volatility

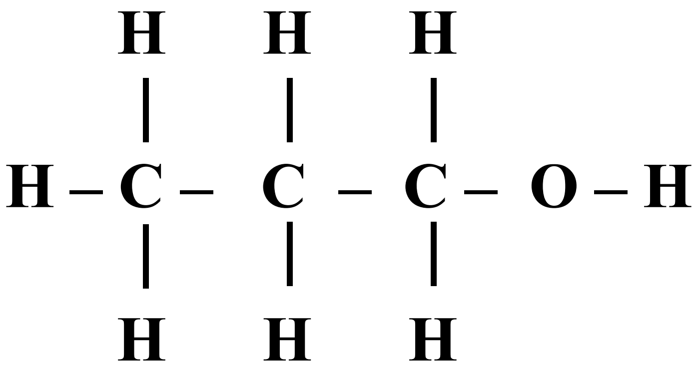


Volatility (H in atm-m^3/mole)	
Very Volatile	$H>10^{-1}$
Volatile	$10^{-1}>H>10^{-3}$
Moderately Volatile	$10^{-3}>H>10^{-5}$
Slightly Volatile	$10^{-5}>H>10^{-7}$
Nonvolatile	$10^{-7}>H$

5.2.6 Henry's Law Constant, H

(Meylan and Howard, 1991)

A group contribution method can also be used to estimated the value of the Henry's Law constant. Group contribution method is structured differently from the previous methods. The structural elements are bonds rather than functional groups.



$CH_3CH_2CH_2OH$

1-propanol

One	**$-CH_3$ group**
Two	**$>CH_2$ groups**
One primary	**$-OH$ group**

Seven	**C-H bonds**
Two	**C-C bonds**
One	**C-O bond**
One	**O-H bond**

Henry’s Law Constant, H

(Meylan and Howard, 1991)

$$-\log H = \log(\text{air/water partition coeff}) = \sum n_i h_i + \sum n_j c_j$$

H : dimensionless Henry’s law constant

$\boldsymbol{h_j}$: bond contribution to the air-water partition coefficient

$\boldsymbol{n_j}$: number of groups of type j in the molecule

$\boldsymbol{c_j}$: correction factor for each group ***(Table 5.2-13, 5.2-14)***

Mean error in log units range

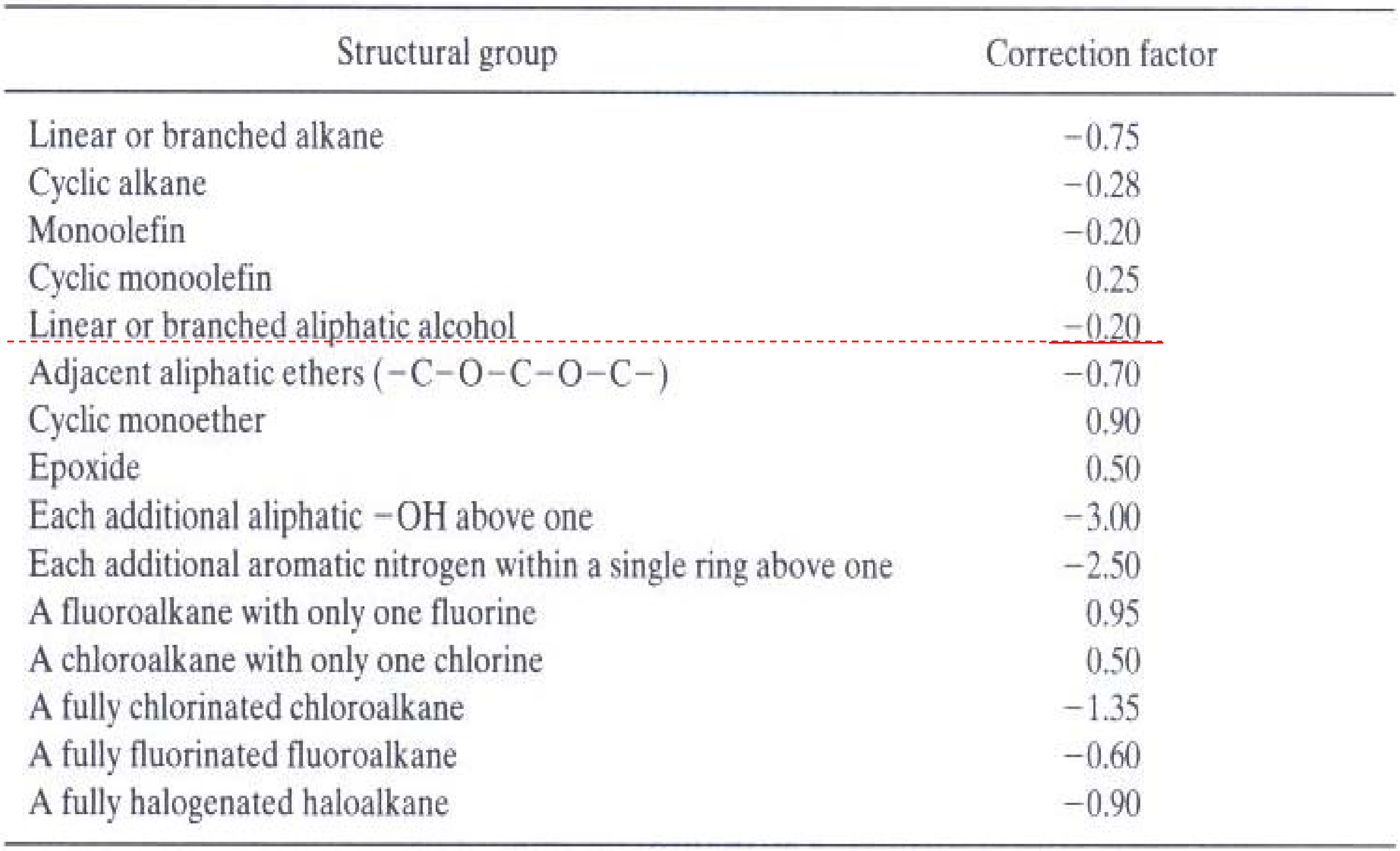
from 0.06 for alkanes and alkylbenzenes

to 0.4 for halo-alkanes

Table 5.2-13 Structural groups and group contributions for estimating Henry’s law constant

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-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
$C_{acetylenic}\equiv C_{acetylenic}$	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



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 5.2-7

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.

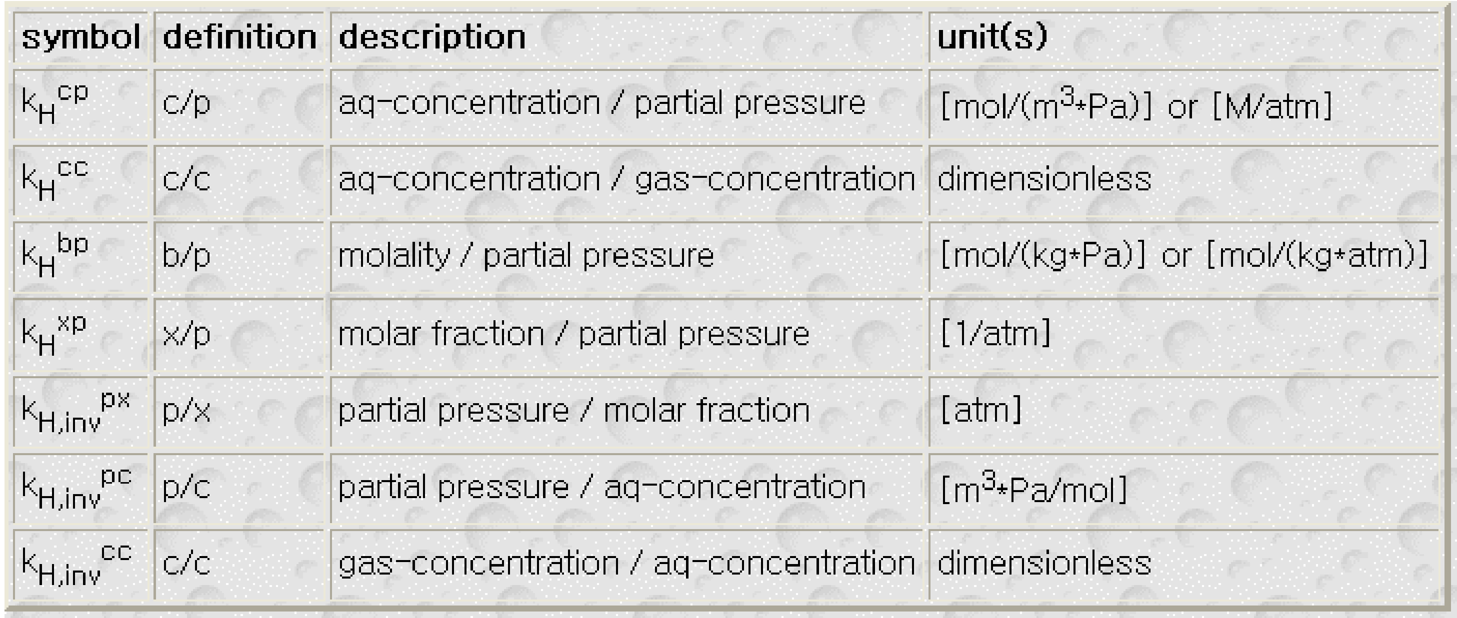
The uncorrected value of log (water to air partition coefficient) is given by:

$$-\log H = \log(air / water \;\; partition\ coeff\,)$$

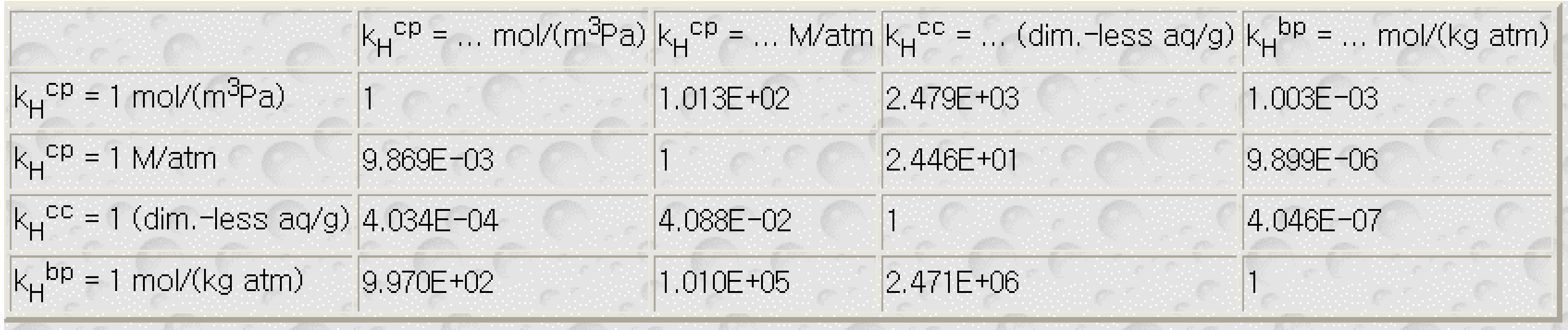
$$= \underbrace{7(-0.1197)}_{\textbf{Seven C-H bonds}} + \underbrace{2(0.1163)}_{\textbf{Two C-C bonds}} + \underbrace{1.0855}_{\textbf{One C-O bond}} + \underbrace{3.2318}_{\textbf{One O-H bond}} = 3.7112$$

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

Converting Henry's Law Constants



symbol	definition	description	unit(s)
k_H^{cp}	c/p	aq-concentration / partial pressure	[mol/(m^3*Pa)] or [M/atm]
k_H^{cc}	c/c	aq-concentration / gas-concentration	dimensionless
k_H^{bp}	b/p	molality / partial pressure	[mol/(kg*Pa)] or [mol/(kg*atm)]
k_H^{xp}	x/p	molar fraction / partial pressure	[1/atm]
$k_{H,inv}^{px}$	p/x	partial pressure / molar fraction	[atm]
$k_{H,inv}^{pc}$	p/c	partial pressure / aq-concentration	[m^3*Pa/mol]
$k_{H,inv}^{cc}$	c/c	gas-concentration / aq-concentration	dimensionless



	k_H^{cp} = ... mol/(m^{3}Pa)	k_H^{cp} = ... M/atm	k_H^{cc} = ... (dim.-less aq/g)	k_H^{bp} = ... mol/(kg atm)
k_H^{cp} = 1 mol/(m^{3}Pa)	1	1.013E+02	2.479E+03	1.003E-03
k_H^{cp} = 1 M/atm	9.869E-03	1	2.446E+01	9.899E-06
k_H^{cc} = 1 (dim.-less aq/g)	4.034E-04	4.088E-02	1	4.046E-07
k_H^{bp} = 1 mol/(kg atm)	9.970E+02	1.010E+05	2.471E+06	1

k_H = Henry's law coefficients representing solubility (i.e. aqueous-phase composition divided by gas-phase composition)
$k_{H,inv}$ = Henry's law coefficients representing volatility (i.e. gas-phase composition divided by aqueous-phase composition)

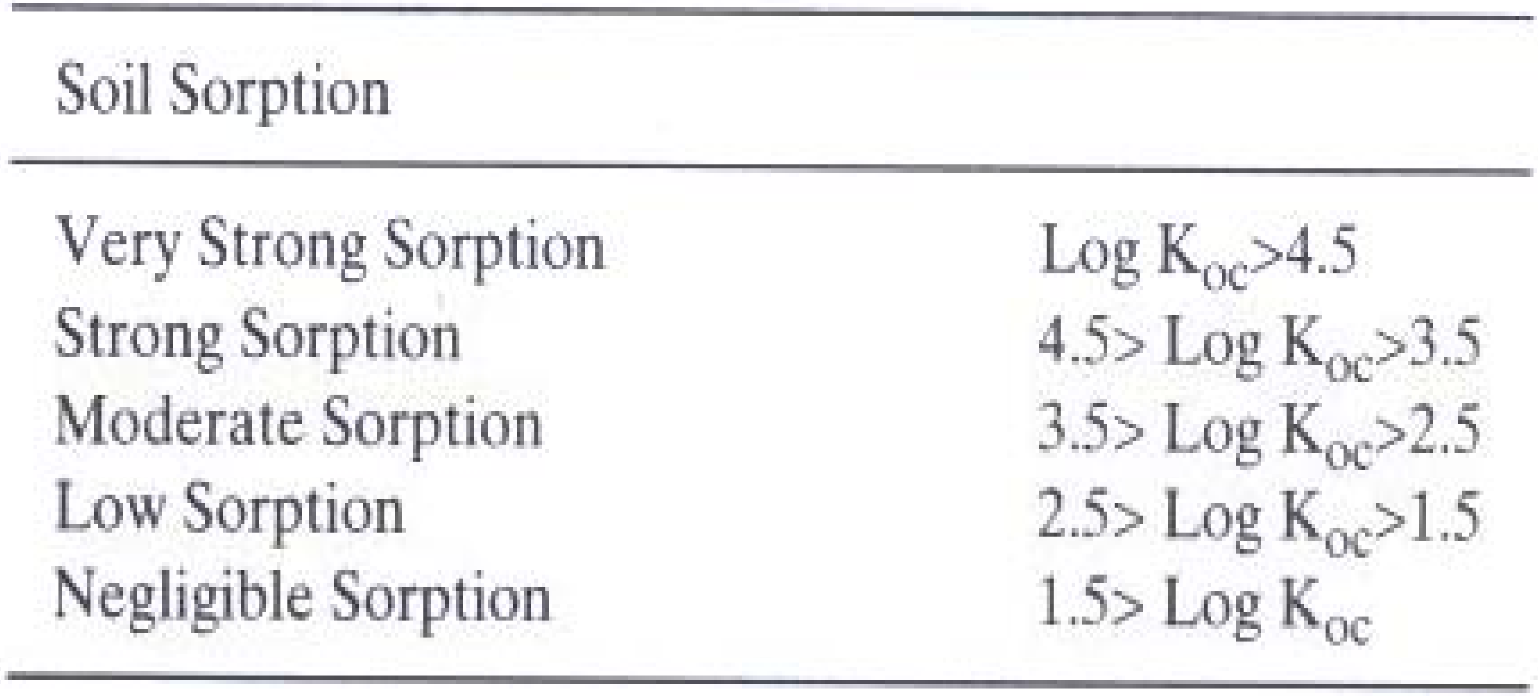
www.henrys-law.org

5.2.7 Soil Sorption Coefficient, K_{OC}

$$K_{OC} = \frac{\text{Mass of a compound absorbed/unit weight of organic carbon in a soil } (\mu g/g \text{ organic carbon})}{\text{the concentration of the compound in a liquid phase } [\mu g/ml]}$$

5.2.7 Soil Sorption Coefficient, K_{OC}

Table 5.2-15 Classification criteria for soil sorption



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	$1.5 > \text{Log } K_{oc}$

Soil Sorption Coefficient, K_{OC}

(Lyman et al., 1990)

$$\log K_{OC} = 0.544 \log K_{OW} + 1.366 \qquad (5\text{-}19)$$

$$\log K_{OC} = -0.55 \log S + 3.64 \qquad (5\text{-}20)$$

These eqs are restricted to quit specific classes of compounds. The soil sorption coeff. describes the physical adsorption and chemical adsorption of a compound onto a surface. Therefore, the coefficient depends not only on bulk properties, but also on steric properties that influence the interaction of a molecule with a surface.

Soil Sorption Coefficient, K_{OC}

(Meylan et al., 1990)

Simple correction

$$\log K_{OC} = 0.53\,{}^{1}\chi + 0.62 + \sum n_j P_j \qquad (5\text{-}21)$$

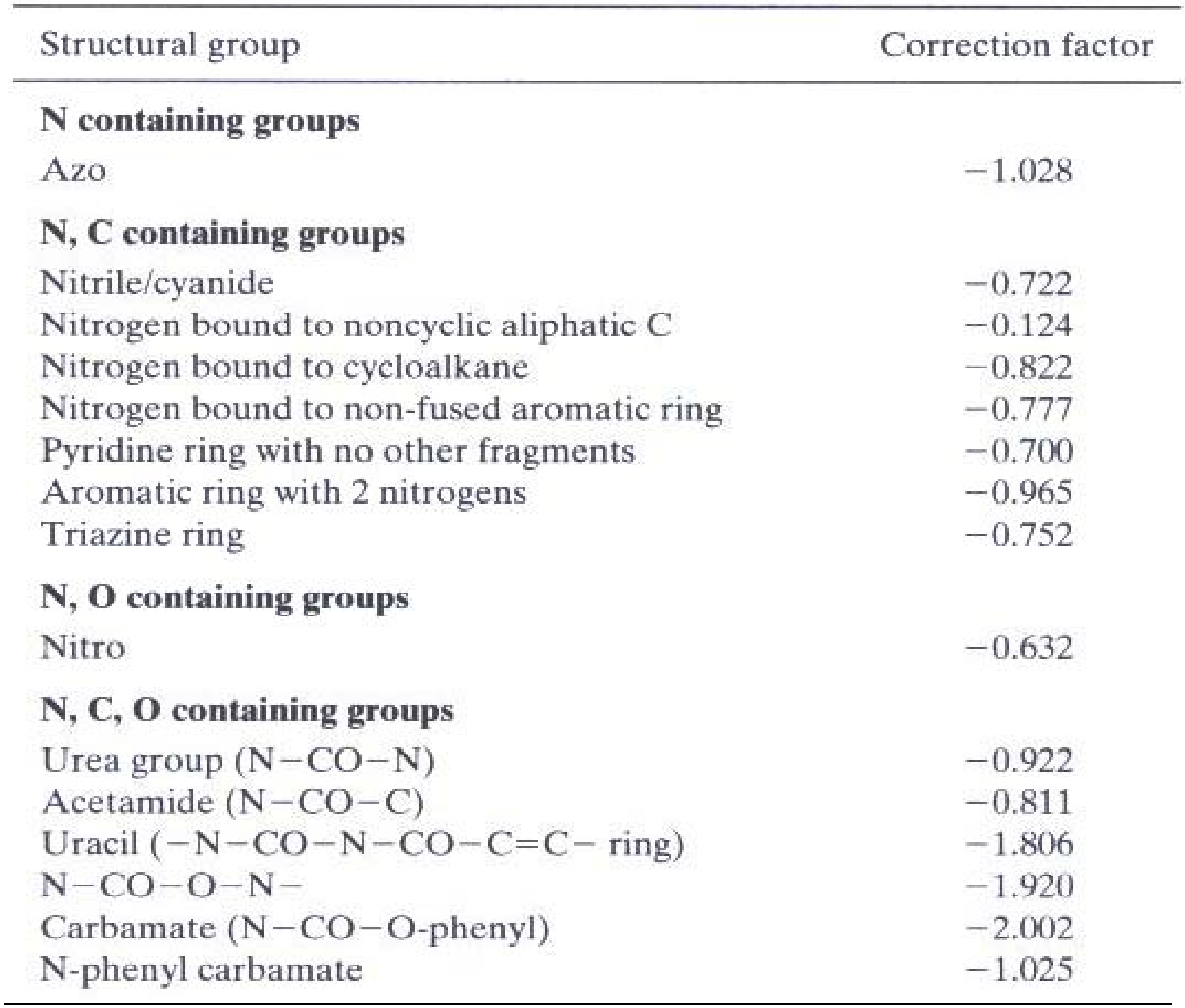
${}^{1}\chi$: first order molecular connectivity index as described in appendix

n_j : number of groups of type j in the molecule

P_j : correction factor for each group

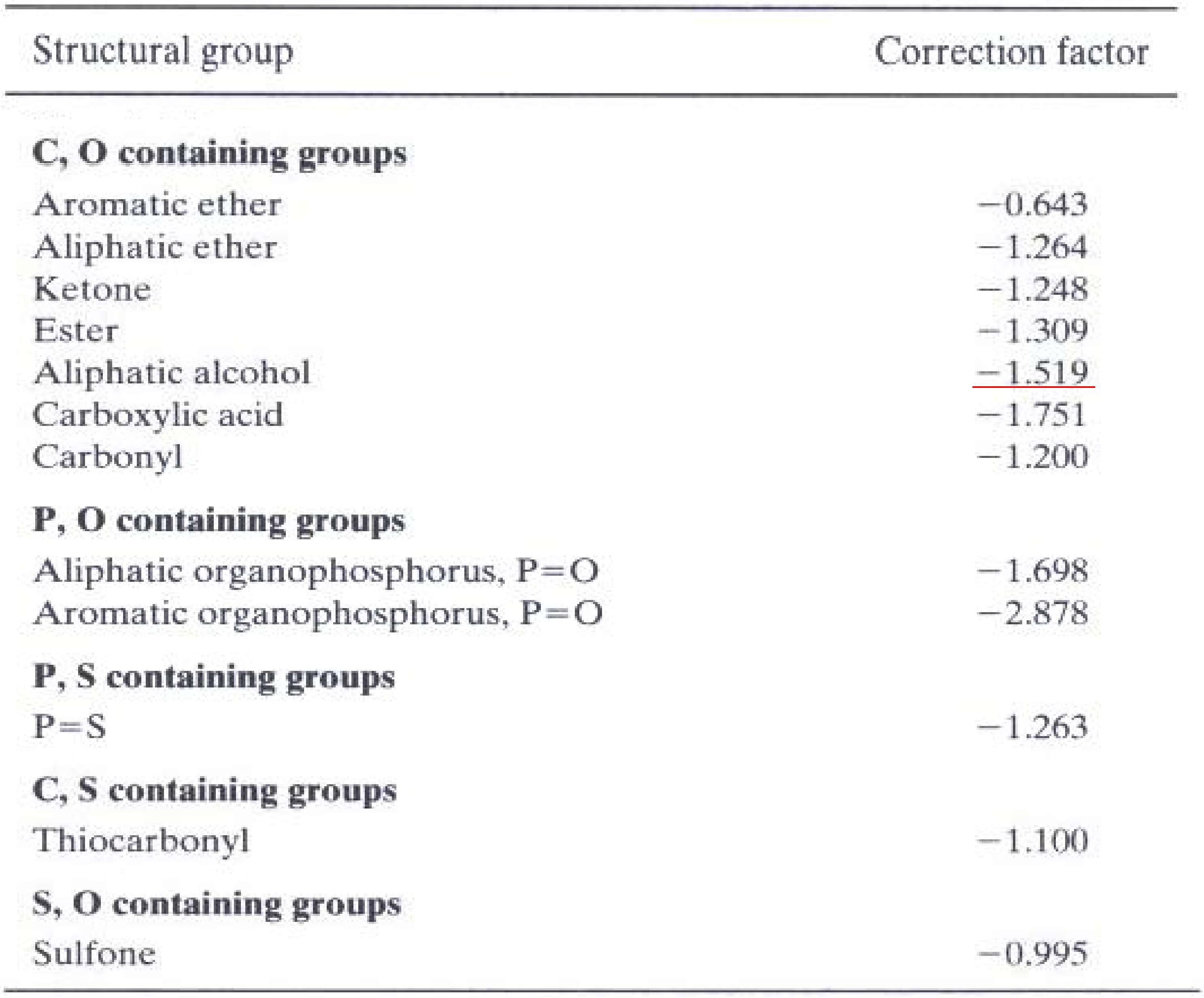
Mean errors of approximately 0.6 log units can be expected

Table 5.2-16 Correction factors for soil sorption coefficients



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

Table 5.2-16 Correction factors for soil sorption coefficients



Structural group	Correction factor
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

Molecular Connectivity

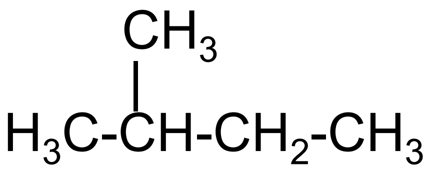
The correlating variables, used in the equations described in this chapter, were primarily bulk properties such as boiling point and octanol-water partition coefficient. While these variables are adequate correlating parameters for many properties, they will not be adequate for properties that *depend 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 first order molecular connectivity ($^1\chi$)

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 $^1\chi$.

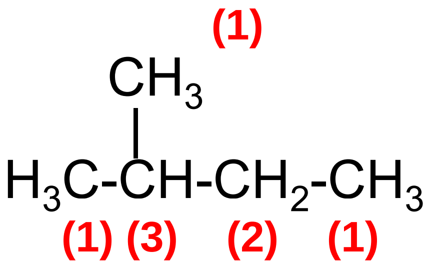
Molecular Connectivity

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



$$H_3C\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}CH_3$$

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.



$$H_3C\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}CH_3$$

Molecular Connectivity

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: $\boxed{^1\chi = \Sigma\ (\delta_i \times \delta_j)^{-0.5}}$

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

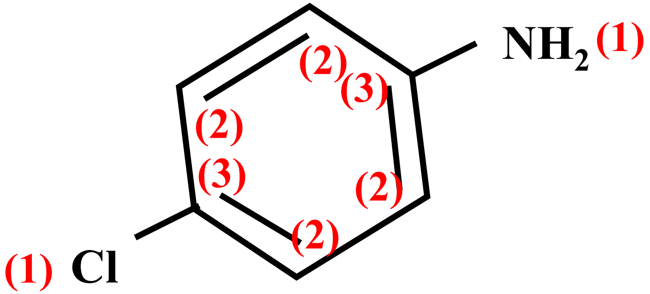
Clearly, this calculation yields a simplistic characterization of complex structural features. Note that isopentene would yield exactly the same value as isopentane, as would 1-chloro, 2 methyl propane. Nevertheless, this simple characterization of molecular topology is often used, as described in Section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

Example

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)

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

Example problem 5.2-8

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 $\boxed{1.01}$. 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 3.27 gives an uncorrected value of 2.35. Adding in the correction term for an aliphatic alcohol (-1.519) yields an estimate of $\boxed{0.83}$.

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 coefficient 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

(Semi-quantitative screening tools for ranking relative persistence)

Estimating Atmospheric Lifetime

▶ chemicals emitted to atmosphere undergo oxidation through a wide range of processes

▶ most important oxidation for organic compounds is the rate of reaction with the hydroxyl radical

(extremely reactive, abstract hydrogen from saturated organics)

5.3 Estimating Environmental Persistence

(Semi-quantitative screening tools for ranking relative persistence)

- *Hydroxyl radical reactions are the semi-quantitative indicator of how long the compound will persist in the atmosphere*

- Hydrogen abstraction from saturated organic compounds

  $C_3H_8 + OH\bullet \Rightarrow CH_3\text{-}\dot{C}H\text{-}CH_3 + H_2O$ $-r_A = 1.2\times 10^{12}$ cm³/molecule-sec

  ↳ *oxidized products*

- Hydroxyl radical addition to double bond

  $C_3H_6 + OH\bullet \Rightarrow CH_3\text{-}\dot{C}H\text{-}CH_2OH$ $-r_A = 26\times 10^{12}$ cm³/molecule-sec

  ↳ *oxidized products*

- Hydroxyl radical addition to an aromatic ring

  $C_6H_6 + OH\bullet \Rightarrow \dot{C}_6H_6\text{-}OH$ $-r_A = 2\times 10^{12}$ cm³/molecule-sec

  ↳ *oxidized products*

Estimating Atmospheric Life time

1. Rate of Reaction with – OH

- These reactions (previous page) are first step in a series of reactions lead to the oxidation of organics in the atmosphere

- 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.

- The rate of reactions are 1.2×10^{12} , 26.0×10^{12} and 2.0×10^{12} cm^3/molecule-sec, respectively.

- *Rate of disappearance be in the ratio of 1.2 : 26 : 2*
  (ratio of atmospheric lifetimes of 106 hrs : 5 hrs : 64 hrs)
  (Ex 5.3-1)

Estimating Atmospheric Life time

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.

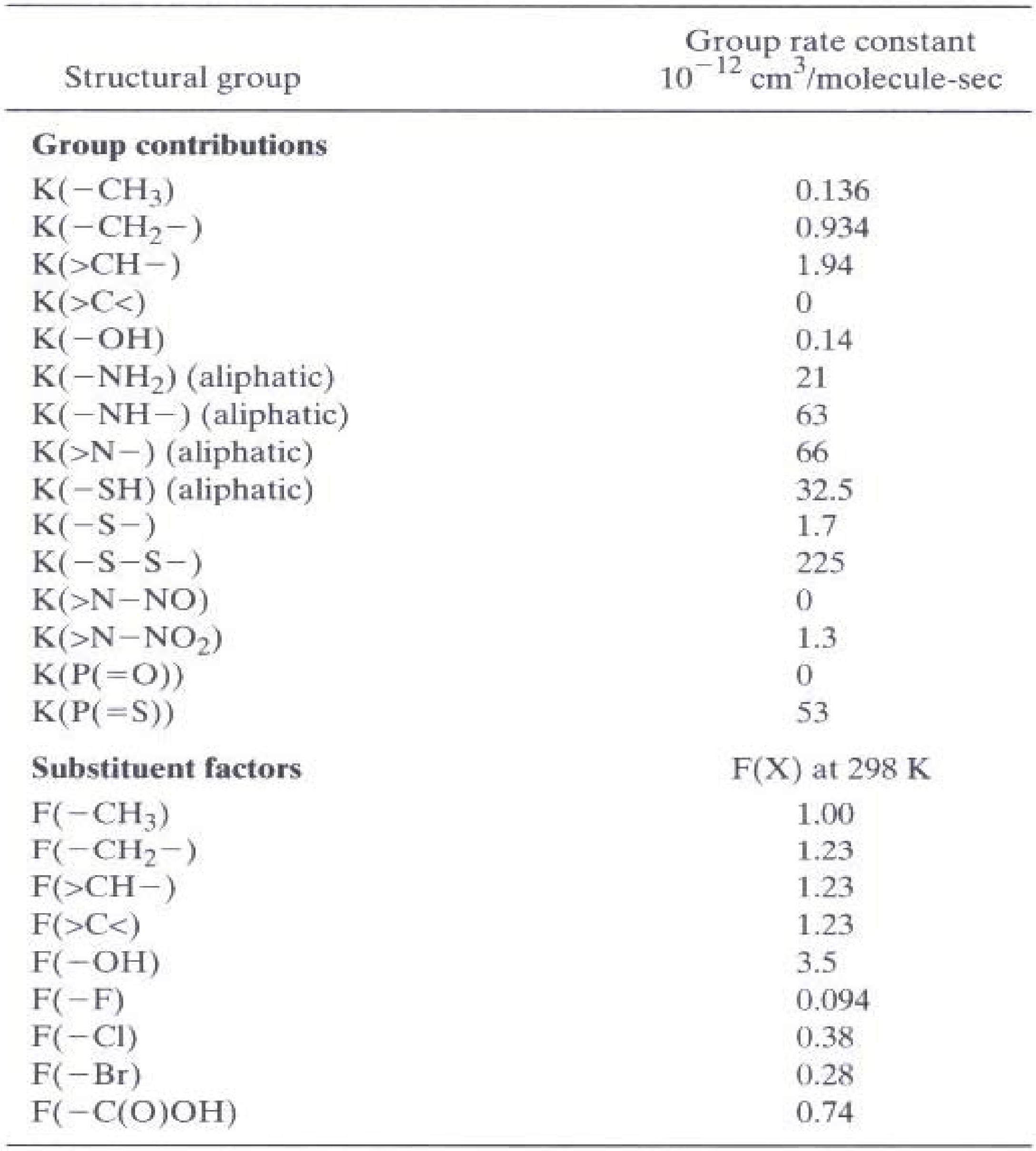
2. Group Contribution method

(Tables 5.3-1~3)

A molecule is divided into a collection of functional groups and each group makes a defined contribution to the overall rate of reaction.

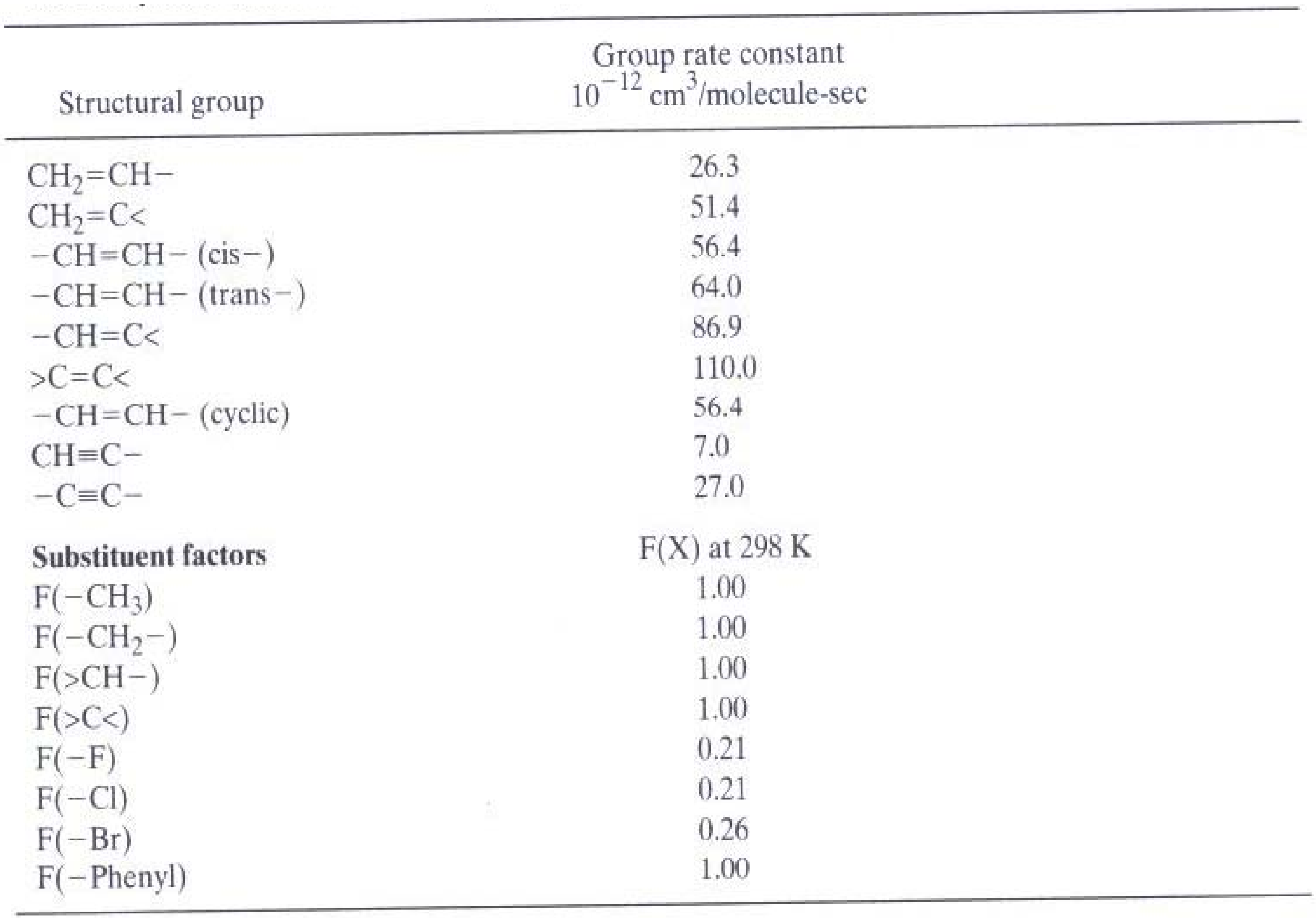
(Examples 5.3-1, 5.3-2, 5.3-3)

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



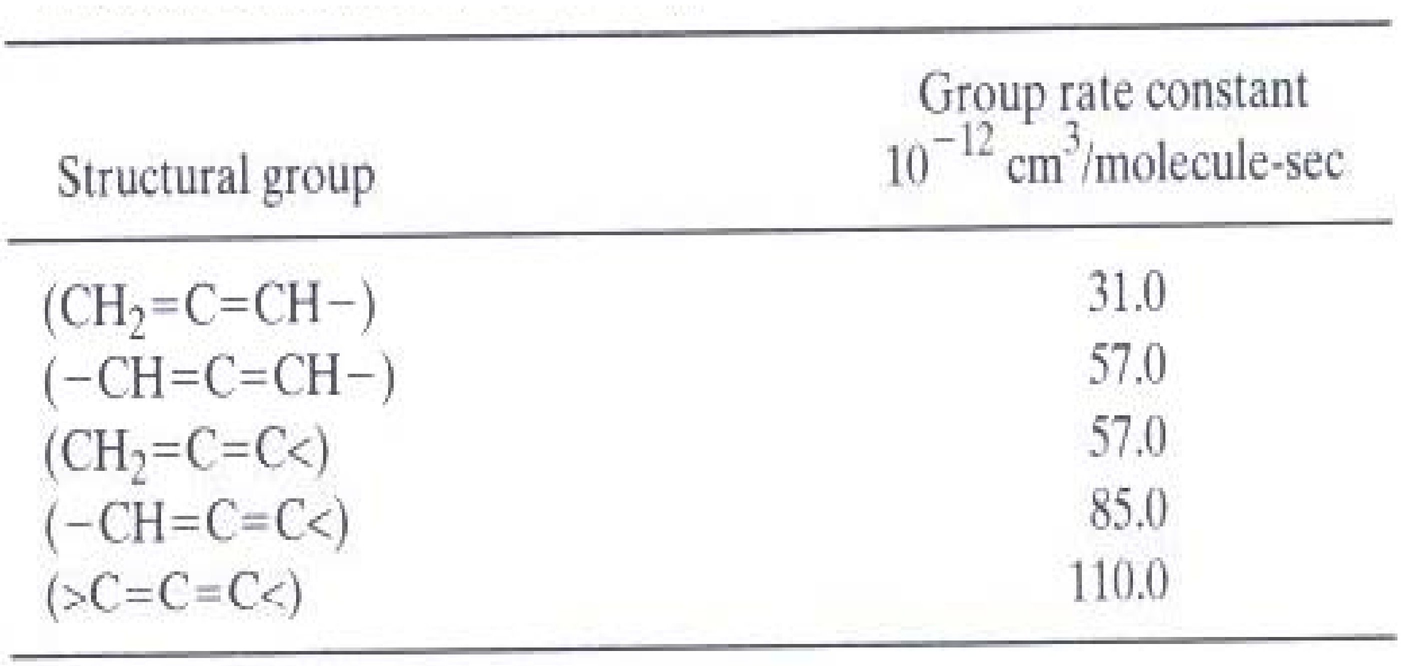
Structural group	Group rate constant 10^{-12} cm^3/molecule-sec
Group contributions	
K($-CH_3$)	0.136
K($-CH_2-$)	0.934
K($>CH-$)	1.94
K($>C<$)	0
K($-OH$)	0.14
K($-NH_2$) (aliphatic)	21
K($-NH-$) (aliphatic)	63
K($>N-$) (aliphatic)	66
K($-SH$) (aliphatic)	32.5
K($-S-$)	1.7
K($-S-S-$)	225
K($>N-NO$)	0
K($>N-NO_2$)	1.3
K($P(=O)$)	0
K($P(=S)$)	53
Substituent factors	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**



Structural group	Group rate constant 10^{-12} cm^3/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
$CH{\equiv}C-$	7.0
$-C{\equiv}C-$	27.0
Substituent factors	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-)**



Structural group	Group rate constant 10^{-12} cm^3/molecule-sec
$(CH_2{=}C{=}CH-)$	31.0
$(-CH{=}C{=}CH-)$	57.0
$(CH_2{=}C{=}C<)$	57.0
$(-CH{=}C{=}C<)$	85.0
$(>C{=}C{=}C<)$	110.0

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:

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

where [OH•] is the concentration of the hydroxyl radical and $[C_{propene}\ ]$ 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:

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

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

Since ($[C_{\text{propene}}]/[C_{0\text{-propene}}]$) = ½ when the concentration has reached one half of its original value, the half life is given by:

$$t_{1/2} = \ln(2) / (\boldsymbol{k}\,[\mathrm{OH}\bullet])$$

Assuming a value of 1.5×10^{6} molecules/cm^3 for the concentration of the hydroxyl radical (while 1.5×10^{6} molecules/cm^3 is a typical value – summertime concentrations in Houston can reach 10^{7} molecules/cm^3) and a value of 26×10^{-12} cm^3/molecule-sec for ***k***:

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

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

$$\boxed{t_{1/2} = 5.0\ \mathrm{hr}}$$

Repeating this calculation for *propane* and *benzene*, with reaction rates of 1.2×10^{-12} and 2.0×10^{-12} cm^3/molecule-sec, leads to atmospheric half lives of 106 and 64 hours, respectively.

5.3.3. Estimating Lifetimes in Aqueous Environment

- Most important reaction is ***hydrolysis***, which can be catalyzed by acids and bases

- Hydrolysis rate can be estimated by structural analysis based on linear free energy relationship.

5.3.3. Estimating Lifetimes in Aqueous Environment

Mill's equation (1987)

log (hydrolysis rate)

= log (hydrolysis rate of a reference compound) + Constant × σ

log (hydrolysis rate) = A + B σ

σ : Hammet structural parameter

- constants A and B are must be determined individual class of reactants

  - A : depends on the reference reaction chosen
  - B : depends on rate on structural feature

Estimating Overall Biodegradability

(rate at which compounds are metabolized by living organisms, basically difficult to assess)

- Due to the scarcity of related data, group contribution is not available to date.
- Model by Boethling (1994) provides biodegradation index (I):

whether aerobic biodegradation occurs over hours, days, weeks months, or longer

$$\boxed{I = 3.199 + a_1 f_1 + a_2 f_2 + \ldots + a_n f_n + a_m MW} \qquad (5\text{-}23)$$

I : indicator of the aerobic biodegradation rate

f_n : number of groups of type n in the molecule

a_n : contribution of group n to degradation rate (table 5.3-4)

a_m : -0.00221

Estimating Overall Biodegradability

(rate at which compounds are metabolized by living organisms, basically difficult to assess)

Relative ranking of the biodegradability

5 : degrade over hours;
4 : lifetime of days;
3 : weeks
2 : months
1 : longer than months

Table 5.3-4

Group contributions to ultimate aerobic biodegradation index, Boethling (1994)

Structural group	Group contribution (a_n)
Molecular weight	-0.00221
Functional groups	
Unsubstituted mono-, di-, or tri-aromatic ring	-0.586
Unsubstituted phenyl group	0.022
Aromatic acid (-COOH)	0.088
Linear 4 carbon terminal chain (-CH2-CH2-CH2-CH3)	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 5.3-4

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:

$$\mathbf{I} = 3.199 + 0.160 - 0.00221(60) = \boxed{3.22}$$

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:

$$\mathbf{I} = 3.199 + 2(0.022) - 0.058 - 0.00221(170) = \boxed{2.81}$$

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

5.4 Estimating Ecosystem Risks

(http://www.epa.gov)

Structure activity relationships may also be used to assess ecosystem and human health impacts. In assessing ecosystem hazard, the standard practice is to estimate toxicity for a variety of species.

Mortality of guppy (fish) by octanol-water partition coefficient

$$\boxed{\text{Log}\,(1/LC_{50}) = 0.871\,\log K_{ow} - 4.87} \qquad (5\text{-}24)$$

LC_{50} : concentration that is lethal to 50% of the population of a 14-day exposure (expressed in μmol/L)

This equation was developed using data from a variety of chlorobenzenes, chlorotoluenes, chloroalkanes, diethyl ether, acetone (Konemann, 1981)

5.4 Estimating Ecosystem Risks

(http://www.epa.gov)

Other equations are specific to certain compound classes

(Ex) *correlations for acrylates are*

$$\log (LC_{50}) = 0.00886 - 0.51136 \log K_{OW} \qquad (5\text{-}25)$$

(daphnids, mortality after 48 hrs exposure)

$$\log (LC_{50}) = -1.46 - 0.18 \log K_{OW} \qquad (5\text{-}26)$$

(fish, mortality after 96 hrs exposure)

LC_{50} = [milli-moles/L]

Example 5.4-1

Compared to the fish, guppy and daphnid mortalities for an acrylate with log K_{ow} = 1.28 (e.g. methyl methacylate).

Solution:

The concentration yielding 50% mortality are:

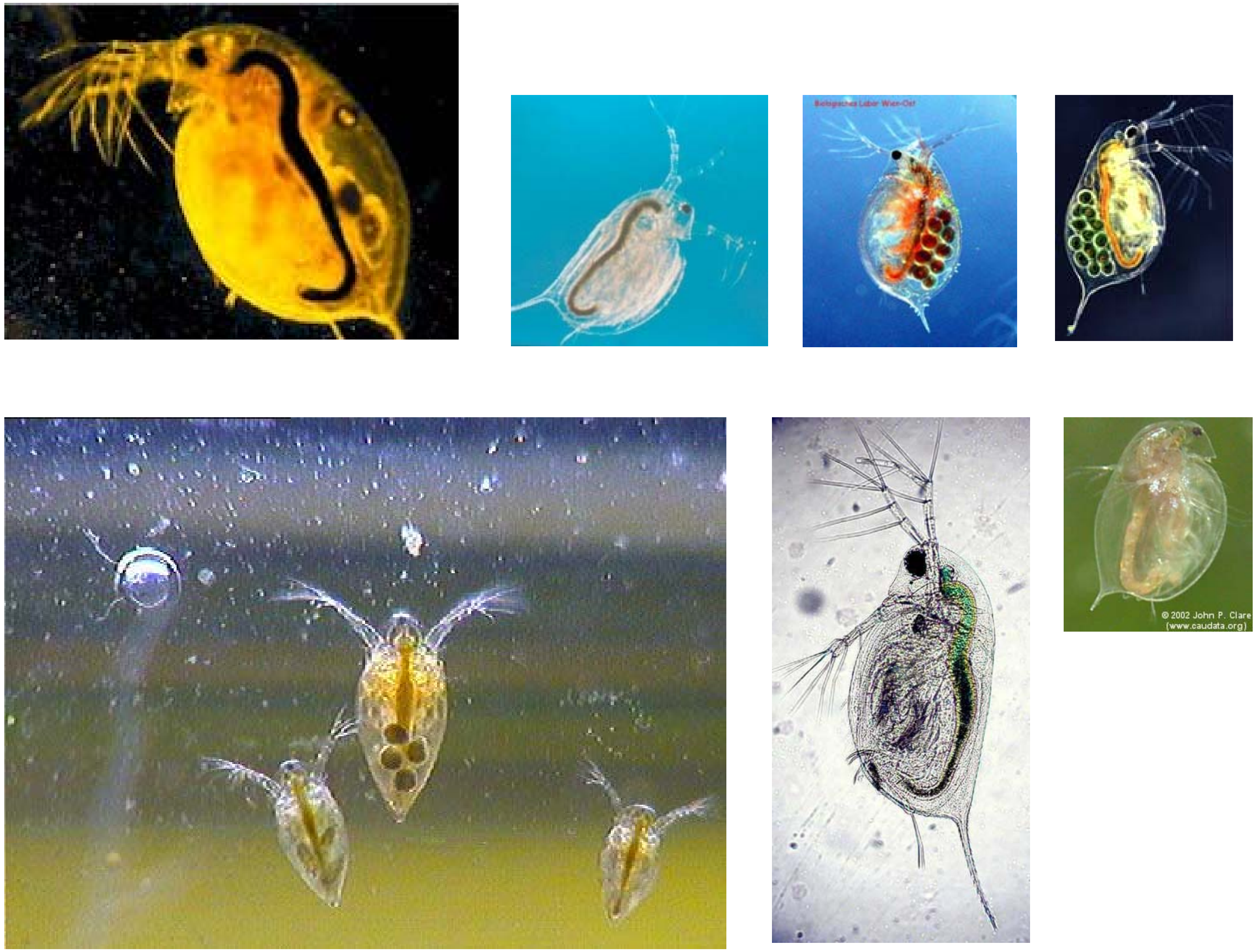
Guppy	(14 day)	5690 mmol/L
Daphnids	(48 hour)	0.226 mmol/L = 226 mmol/L
Fish	(96 hour)	0.020 mmol/L = 20 mmol/L

5.4 Estimating Ecosystem Risks

(http://www.epa.gov)

Daphnids

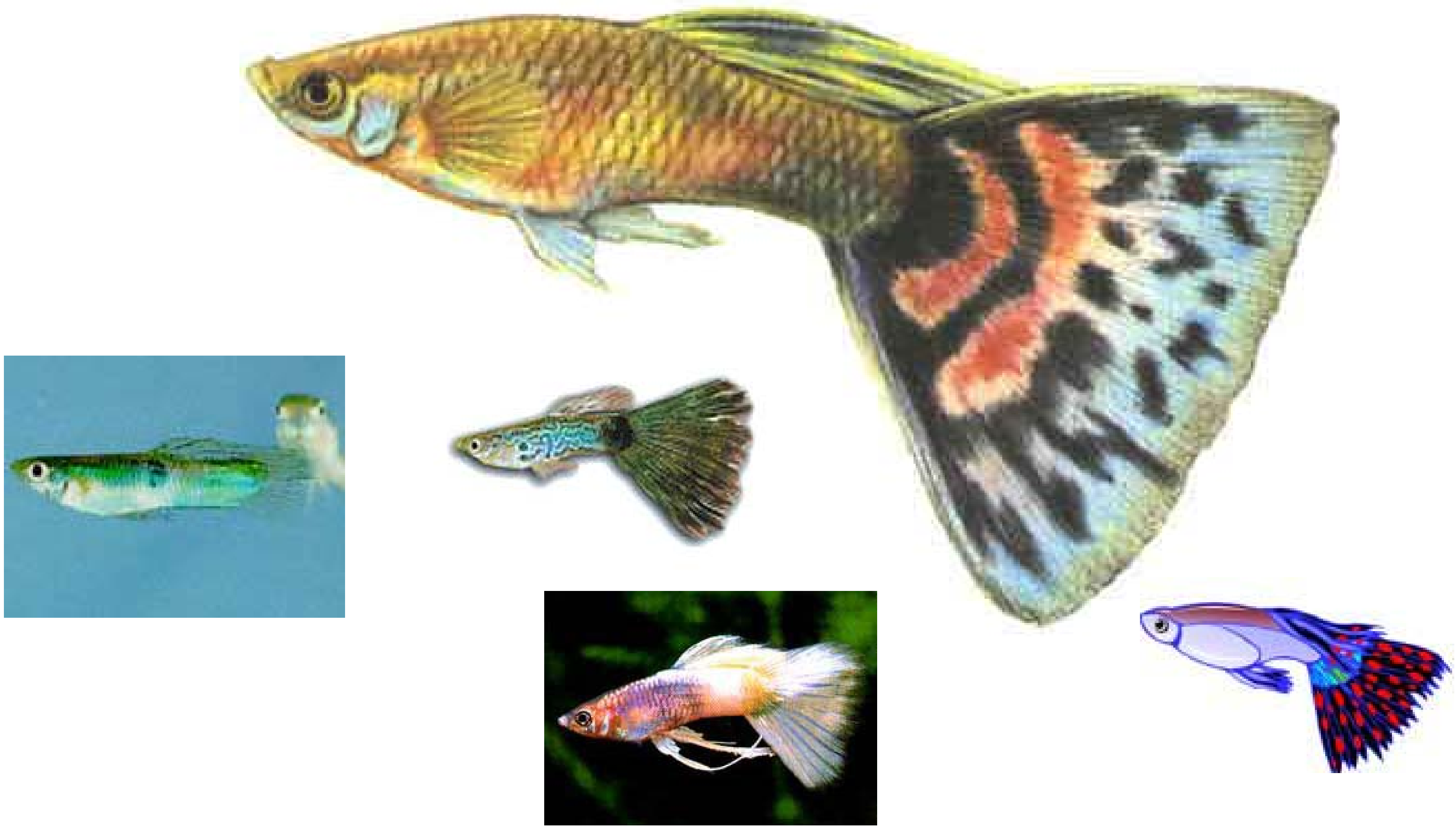
물벼룩



5.4 Estimating Ecosystem Risks

(http://www.epa.gov)

guppy (fish)



5.4 Estimating Ecosystem Risks

(http://www.epa.gov)

guppy (NASA, NAVY)

5.5 Estimating Environmental Fate and Exposure

How those properties can be employed to estimate partitioning and fate

Examples 5.5-1~5.5-4.

Ex. 5.5-1. Calculate atmospheric chemical concentration
(depends on emission rate, mixing rate, and lifetime)

Ex. 5.5-2. Calculate initial partitioning of a chemical in water, sediment and biota

Ex. 5.5-3. Calculate volatilization from river

Ex. 5.5-4. Chemical concentration in drinking water

Ex. 5.5-1. Calculate atmospheric chemical concentration (depends on emission rate, mixing rate, and lifetime)

Propylene is emitted at a rate of 10 ton/yr into an airshed that has a volume of 10^4 km^3. Assume that the airshed has a residence time of one day and is well mixed. Calculate the steady state concentration of propylene($C_{C3H6,SS}$), accounting for chemical reaction. Calculate an inhalation exposure for an adult, assuming an inhalation rate of 20 l/min.

air·shed: n. 한 지역의 대기(大氣);(지역별로 구분한) 대기 분수계

Ex. 5.5-1. Calculate atmospheric chemical concentration

Solution:

In – Out –Disappearance due to reaction = 0

In = 10^4 kg/yr = $7.5\text{x}10^{-3}$ gmol/s (MW=42)

Out = flow rate x steady state

= 10^4 km^3/day x $C_{C3H6,SS}$ = 1.16 x 10^{14} cm^3/s x $C_{C3H6,SS}$

Disappearance due to reaction = volume x rate

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

= 10^4 km^3 x 26 x 10^{-12} cm^3/molecule-sec

x 1.5 x 10^6 molecule/cm^3 x $C_{C3H6,SS}$

= 10^{19} cm^3 x 39 x 10^{-6}/s x $C_{C3H6,SS}$

$C_{C3H6,SS}$ = 1.5 x 10^{-17} moles/cm^3

Assuming 1 mole = 22,400 cm^3 @ambient conditions

$C_{C3H6,SS}$ = 3.3 x 10^{-33} moles propylene/mole air = 3.3 ppt

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

Exposure = 20,000 cm^3/min x 1.5 x 10^{-17} mole/cm^3

= $30\text{x}10^{-14}$ moles/min = 6.6 $\text{x}10^{-6}$g/yr

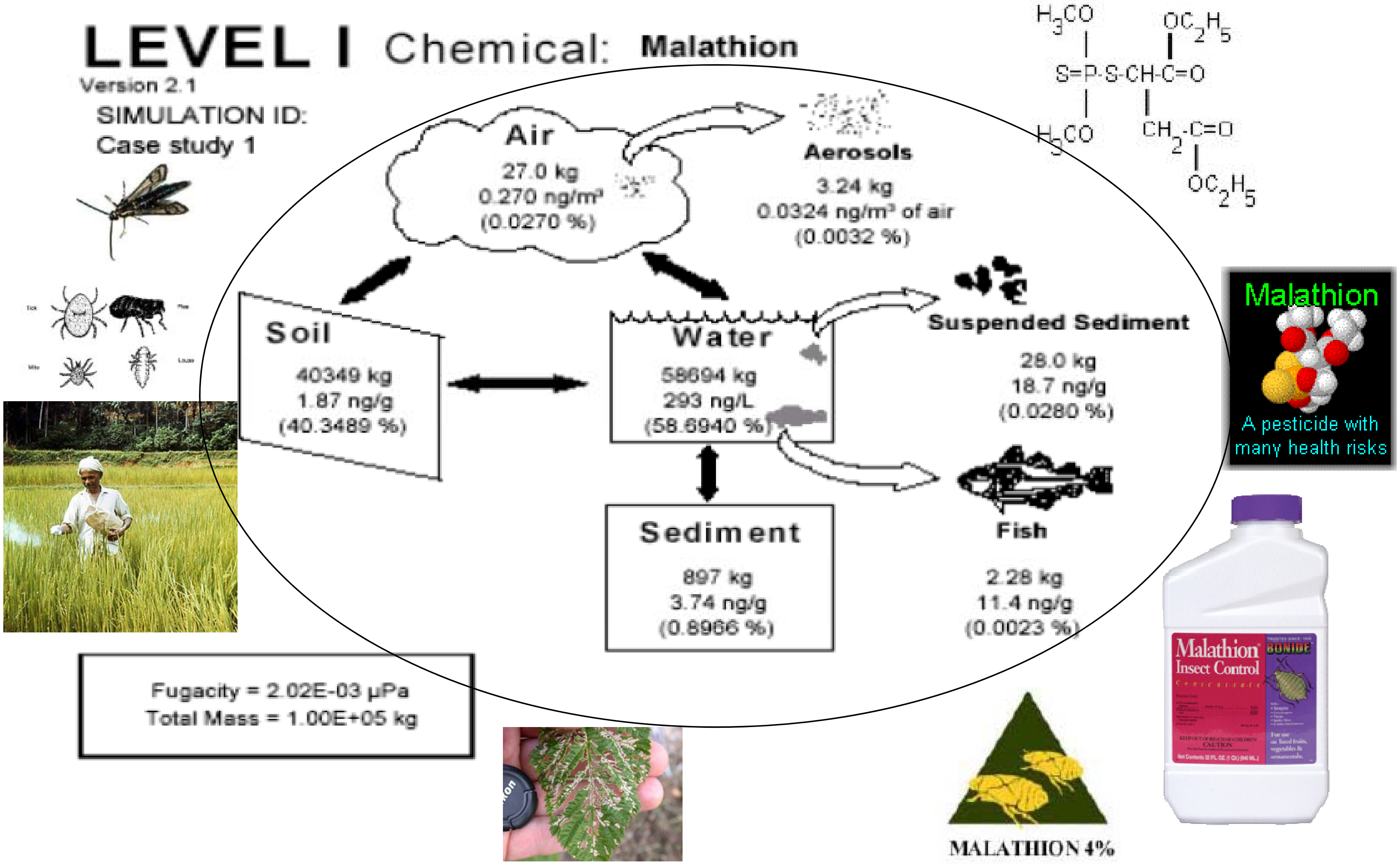
Calculating exposure through drinking contaminated surface water

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?
- volatilized to the atmosphere?
- taken up by living organisms?
- biodegraded or was lost through other reaction?
- removed by the treatment processes in the public water system?

Partitioning of Malathion



LEVEL I Chemical: **Malathion**

Version 2.1

SIMULATION ID:
Case study 1

Air
27.0 kg
0.270 ng/m³
(0.0270 %)

Aerosols
3.24 kg
0.0324 ng/m³ of air
(0.0032 %)

Soil
40349 kg
1.87 ng/g
(40.3489 %)

Water
58694 kg
293 ng/L
(58.6940 %)

Suspended Sediment
28.0 kg
18.7 ng/g
(0.0280 %)

Sediment
897 kg
3.74 ng/g
(0.8966 %)

Fish
2.28 kg
11.4 ng/g
(0.0023 %)

Fugacity = 2.02E-03 µPa
Total Mass = 1.00E+05 kg

Information for Exposure Estimating

- Soil sorption coefficient
- Vapor pressure
- Water solubility
- Bioconcentration factor
- Biodegradability
- River flow rate
- Surface area
- Sediment concentration

Ex. 5.5-2 Estimate the initial partitioning of the chemical in the water, sediment, and biota

Assume that a chemical, with a molecular weight of 150, is released at a rate of 300kg/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 : 100g per 1000 cubic meter

Ex. 5.5-2 Estimate the initial partitioning of the chemical in the water, sediment, and biota

Solution

The ratio of concentration 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 L/day x 1 kg/L = 500 million kg/day
Sediment = 500 million L/day x 15kg sediment/million kg water (15ppm)
= 7500 kg sediment/day
Biota = 500 million L/day x 0.1 kg biota/million kg water
= 50kg biota/day

Ex. 5.5-2 Estimate the initial partitioning of the chemical in the water, sediment, and biota

Solution

Performing a mass balance:

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

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

C_{water} is = 0.5 x 10^{-6} kg chemical/kg water = 0.5 ppm

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

500,000,000 : 75,000,000 : 5,000,000 (86 : 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.

Ex. 5.5-3 Is volatilization from the river likely to be significant?

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

Data

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

Ex. 5.5-3 Is volatilization from the river likely to be significant?

Solution

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

$$\frac{0.5\times10^{-6}\, g\ chemical}{g\ water}\times\frac{1\ mole\ chemical}{150g}\times\frac{18g}{1\ mole\ water}\times10^{-1}\, mmHg$$
$$=0.6\times10^{-9}\, mmHg=8.0\times10^{-12}\, atm$$

To determine if the loss rate is significant, assume that a volume 10m above the river reached this concentration for the length of the river to the public water system inlet (a total volume of 100,000 x 10 x 30 m3). Nothing that 1 gram-mole of air at standard conditions occupies 22.4 liters:

$$30\times10^{6}\, m^{3}\times\frac{1\ mole\ air}{0.0224m^{3}}\times\frac{8.0\times10^{-12}\, moles\ chemical}{mole\ air}\times\frac{150g}{mole}=1.6g$$

Ex. 5.5-3 Is volatilization from the river likely to be significant?

Solution

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.

Ex. 5.5-4

what would be the concentration in drinking water?

For the discharge described in Example 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

Ex. 5.5-4 Is volatilization from the river likely to be significant?

Solution

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

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

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

$$\ln \frac{[C]}{[C_0]} = -\frac{\ln 2}{300 \text{ hours}} \times t = -\frac{\ln 2}{300 \text{ hours}} \times 55 \text{ hours}$$

$$\frac{[C]}{[C_0]} = 0.88$$

The concentration entering the treatment plant is 0.88 x 0.5 ppm. The concentration in the drinking water is 0.05 x 0.88 x 0.5ppm = 20 ppb.

5.6 Classifying Environmental Risks
Based on Chemical Structure

Criteria in risk-based evaluation

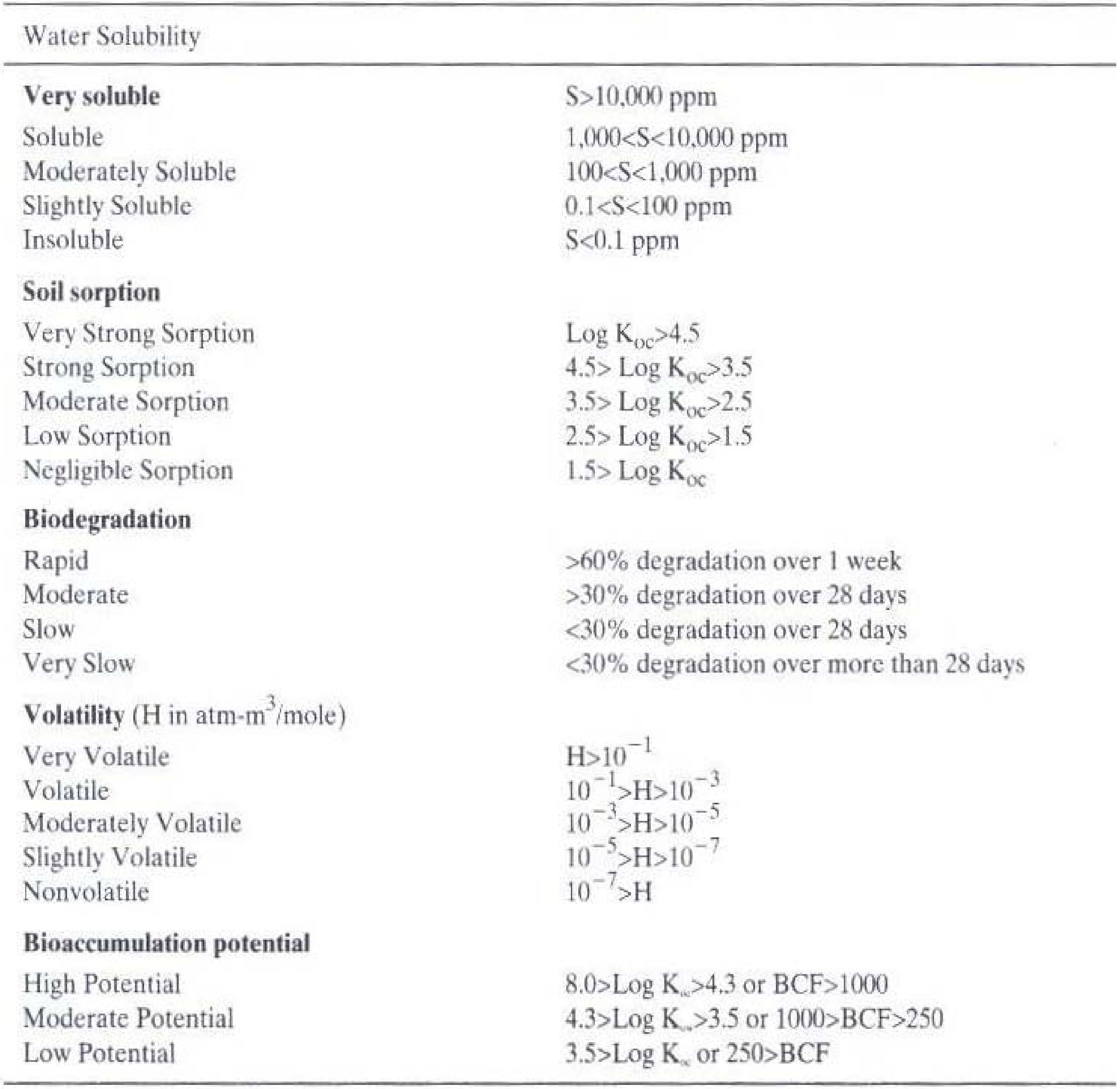
- persistence *(need to consider atmospheric half-lives,*
  biodegradation half-lives)
- bioaccumulation
- toxicity *(eco-toxicity measures. human toxicity measures)*

There is no single evaluation methodology that is universally accepted for evaluating the environmental hazards of chemicals

(Ex) ***Table 5.6-1***

classifications will group chemicals into categories of high, moderate and low concern using values established by EPA TSCA (Toxic Substances Control Act)

Table 5.6-1 Classification criteria for persistence and bioaccumulation



Water Solubility	
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	Log $K_{oc}>4.5$
Strong Sorption	$4.5>$ Log $K_{oc}>3.5$
Moderate Sorption	$3.5>$ Log $K_{oc}>2.5$
Low Sorption	$2.5>$ Log $K_{oc}>1.5$
Negligible Sorption	$1.5>$ 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	$8.0>$Log $K_{ow}>4.3$ or BCF>1000
Moderate Potential	$4.3>$Log $K_{ow}>3.5$ or 1000>BCF>250
Low Potential	$3.5>$Log K_{ow} or 250>BCF

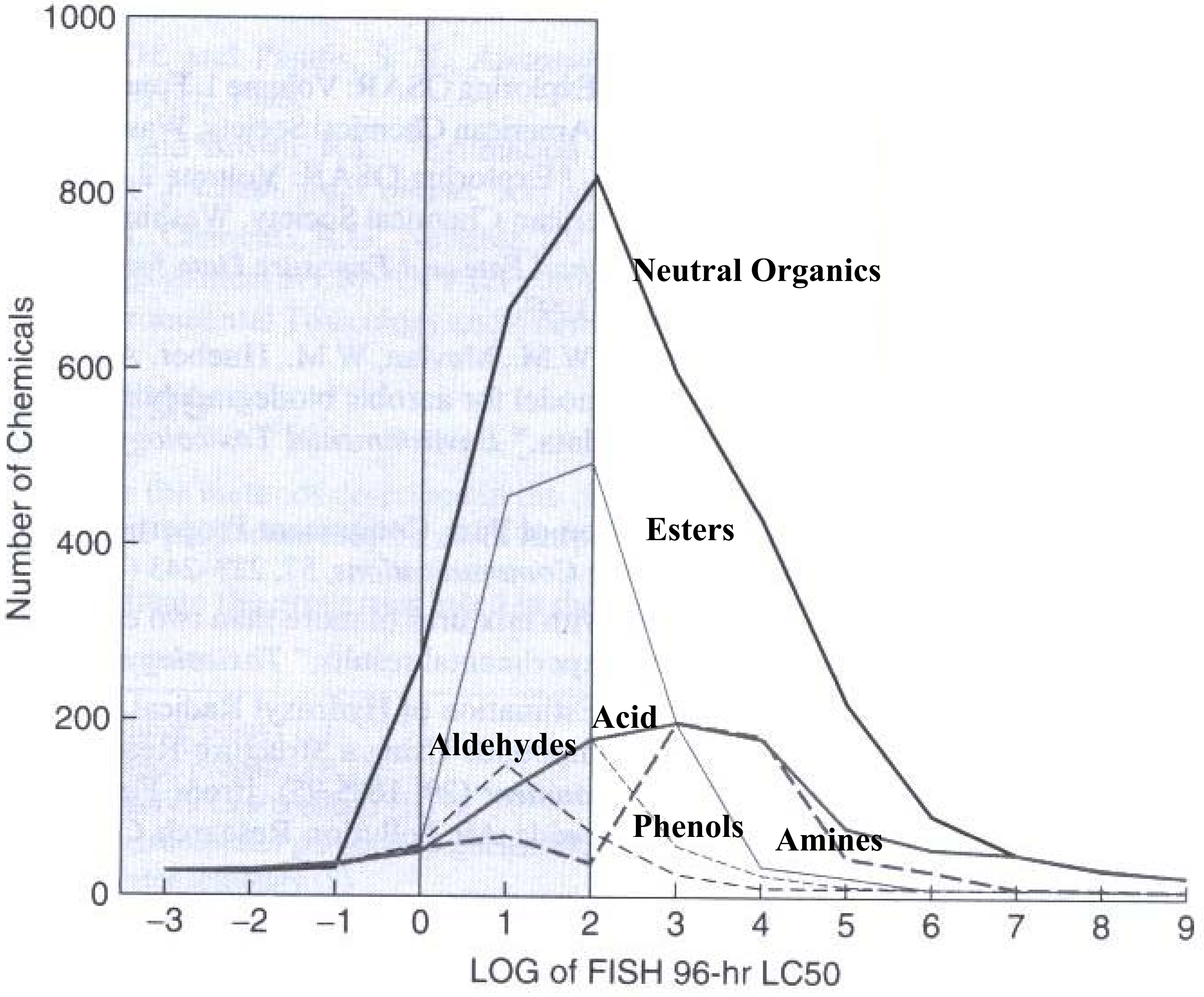


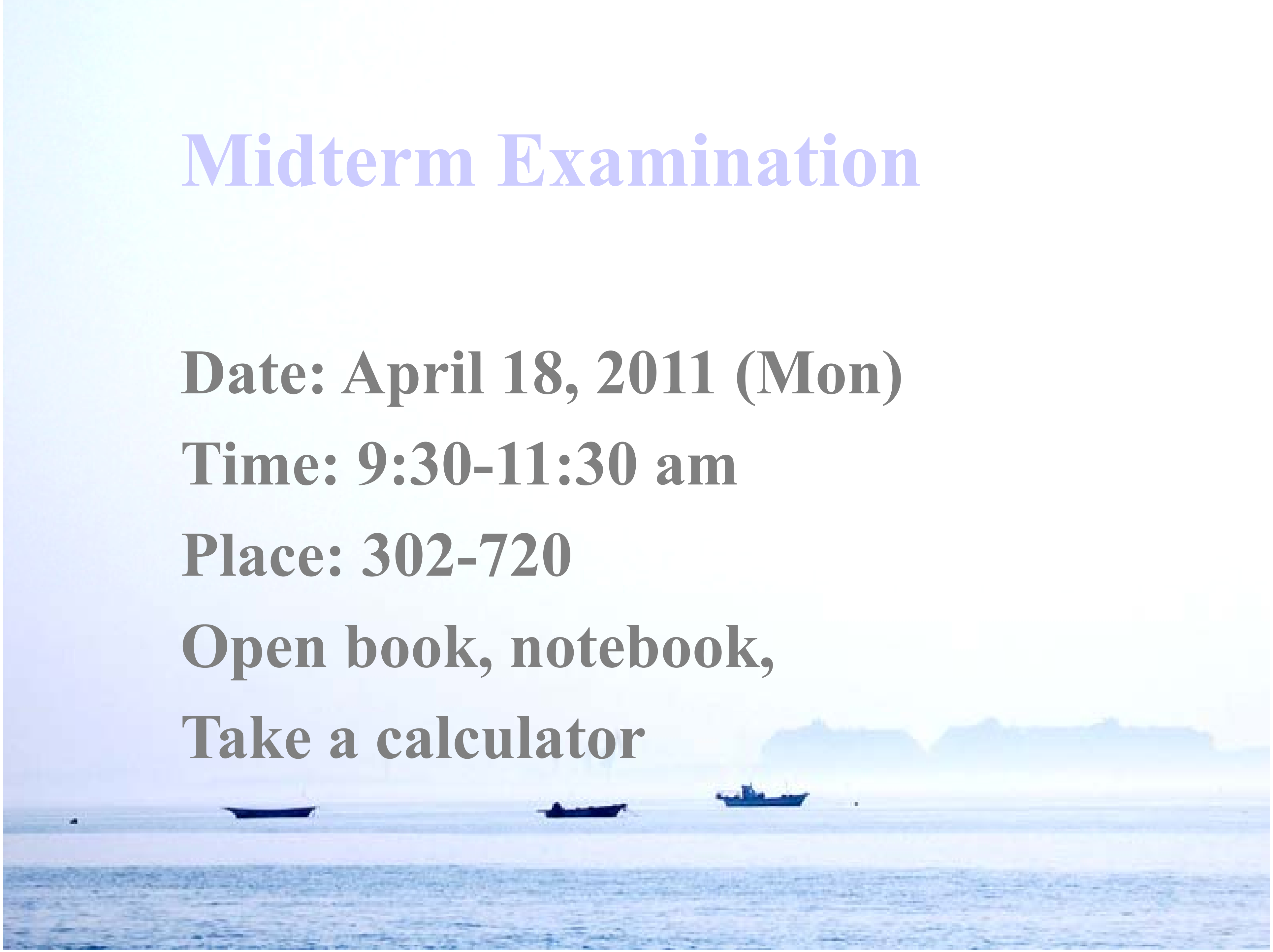
Fig. 5.6-1 Distributions of measures of eco-toxicity for several thousand compounds

Homework #5

Problems

5-1.
5-4.

Due date: April 21, 2011



Midterm Examination

Date: April 18, 2011 (Mon)

Time: 9:30-11:30 am

Place: 302-720

Open book, notebook,

Take a calculator