Chapter 5: Evaluating Environmental Partitioning and Fate: Approaches based on chemical structure

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Chapter 5: Educational goals and topics covered in this chapter

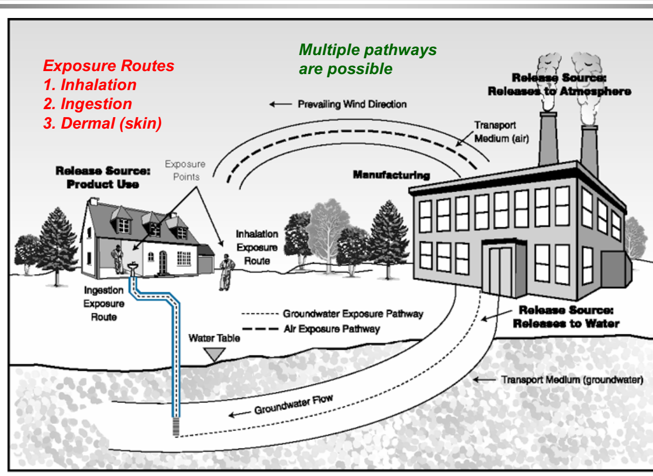
Students will:

- become 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 and fate based on chemical structure
- be able to perform mass balances to estimate environmental partitioning and be able to design chemical structures that have targeted properties
- be aware of the limitations of structure-property estimation methods

Why is this important?

- Over 10,000 chemicals are manufactured and each year 1,000 new chemicals come on the market?
- Is the risk of manufacture of these new chemicals large or small?
- A pre-manufacture notice (PMN) is submitted to the US EPA as part of the Toxics Substances Control Act (TSCA)
- Methods used in Ch. 5 are used to estimate environmental fate and toxicity properties for these new chemicals.

Chapter 5: Exposure assessment



Chapter 5: Chemical properties and corresponding environmental processes

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

Environmental Process	*Relevant Properties*
Estimates of dispersion and fate	Volatility, density, melting point, water solubility, octanol-water partition coefficient, soil sorption coefficient
Persistence in the environment	Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation
Uptake by organisms	Volatility, lipophilicity, molecular size, degradation 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

Chapter 5: Environmental 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
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

Chapter 5: Environmental properties (cont.)

Henry's law constant (H)	**Equilibrium ratio of the concentration of a compound in the gas phase to the concentration of the compound in a dilute aqueous solution (sometimes reported as 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 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**

Chapter 5: Environmental properties (cont.)

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 chemicalÕs 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

Chapter 5 : Property estimation methods based on chemical structure

Assumption:

A molecule is composed of a collection of functional groups or molecular fragments and that each group or fragment contributes in a well-defined manner to the properties of the molecule.

Chapter 5 : Property estimation methods based on chemical structure (cont.)

- Empirical approach based on exp. data
  - Specific to chemical classes
  - Termed structure-activity relationships (SARs)
- Approaches in Ch 5
  - Functional Groups (K_{OW}, k_{OH}, P_{Bio})
  - Bond Types (H)
  - Molecular Connectivity (K_{OC})
  - Linear Free Energy (k_{Hyd})

Chapter 5 : Property estimation methods based on other properties

- Based on K_{OW}, octanol-water partitioning
  - » BCF - bioconcentration factor
  - » LC50 - lethal dose 50% mortality
  - » S - water solubility of organic compounds
  - » K_{OC} - organic carbon/water partitioning

Chapter 5 : Functional groups

- K_{OW} - octanol-water partitioning

  Describes partitioning of organic pollutants between the water phase and octanol – a convenient surrogate system for water-organic matter partitioning in soils and sediments.

$$\log K_{ow} = 0.229 + \Sigma\, n_i\, f_i + \Sigma\, n_j\, c_j$$

n = number of functional groups of types i or j
f_i = contribution to log K_{ow} of group i
c_j = correction factor for functional group j

Chapter 5: Functional groups
1,1-Dichloroethylene example

the molecular structure, $CH_2= CCl_2$

one $=CH_2$ group
one =CH- or =C< group
two –Cl (olefinic attachment) groups

From Table 5.2-6

$\log K_{ow} = 0.229 + 0.5184 + 0.3836 + 2(0.4923) = \boxed{2.11}$
(no correction groups)

Experimental $\log K_{ow} = \boxed{2.13}$

Chapter 5: Bond Types

- H - Henry's law constant

  Describes partitioning of organic pollutants between the water phase and air in the environment

$$-\log H = \Sigma\, n_i\, h_i + \Sigma\, n_j\, c_j$$

n = number of bonds of types i or j
h_i = contribution to H of bond type i
c_j = functional group correction factor

Chapter 5: Bond Types
1-propanol example

the molecular structure,

```
     H   H   H
     |   |   |
H – C – C – C – O - H
     |   |   |
     H   H   H
```

From Table 5.2-13

7 C-H bonds, 2 C-C bonds, 1 C-O bond, and 1 O-H bond

$-\log H = 7(-0.1197) + 2(0.1163) + 1.0855 + 3.2318 = \boxed{3.7112}$

w correction; $-\log H = 3.7112 - 0.20 \boxed{= 3.5112}$ *Table 5.2-14*

linear or branched alcohols

Experimental $-\log H \boxed{= 3.55}$

Chapter 5: Molecular connectivity

- K_{OC} - Organic carbon-water partition coeff.
  Describes partitioning of organic pollutants between the water phase and natural organic matter in soils / sediments

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

${}^{1}\chi$ = 1st order molecular connectivity index
n_j = number of groups of type j
P_j = correction factor for group j

Chapter 5: Molecular connectivity
1-hexanol example

the molecular structure, *see Appendix B for details*

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - O - H$$

δ	(1)	(2)	(2)	(2)	(2)	(2)	(1)	- C atom connectivity
(δ_i,δ_j)	(1,2)	(2,2)	(2,2)	(2,2)	(2,2)	(2,1)		- bond connectivity

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

$$^1\chi = (1/\sqrt{2}) + (1/\sqrt{4}) + (1/\sqrt{4}) + (1/\sqrt{4}) + (1/\sqrt{4}) + (1/\sqrt{2}) = 3.41$$

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

$$\log K_{oc} = 0.53\,(3.41) + 0.62 + (-1.519) = 0.91$$

Experimental $\log K_{oc} = 1.01$

aliphatic alcohol

Chapter 5: Correction Factors

Chemical structure provides an incomplete description of molecular interactions leading to observable properties

Correction Factors for intermolecular forces

» Electronic interactions

» Multiple hydrogen bonding

» Substituent effects

Chapter 5: Software

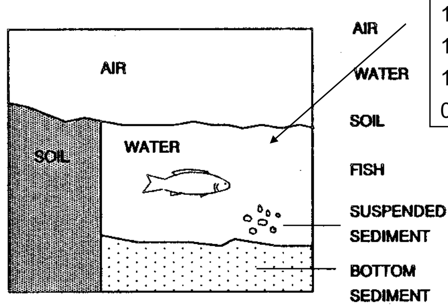
EPIWIN collection of software programs - Properties covered:

- Properties used to estimate partitioning: boiling point, vapor pressure, octanol-water partition coefficient, bioconcentration factor, Henry's law coefficient, soil sorption

- Properties that govern environmental fate: atmospheric lifetimes, biodegradation rates

Downloadable Version, http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm

Chapter 5: Case study 1: Environmental partitioning case study



Water Compartment Only

1 kg Hexachlorobenzene (Hx)

10^5 m^3 volume of water

10^{-3} kg organic carbon / m^3 water

0.1 kg fish / 100 m^3 water

Human Exposure : Fish Ingestion

0.5 kg of fish consumed

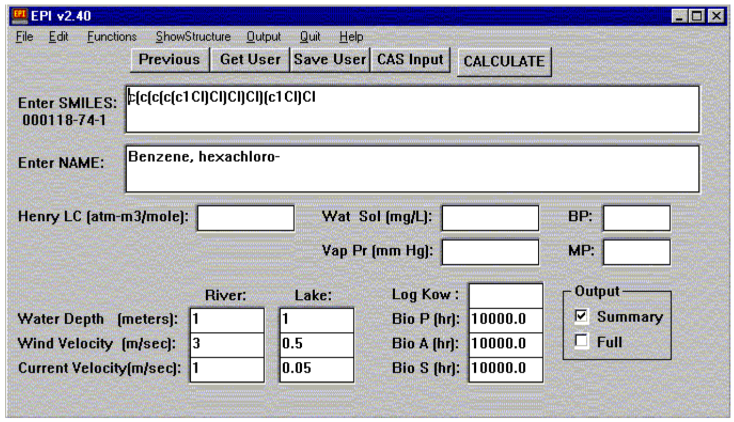
Dose due to ingestion?

Concentration in the Fish (mg/kg)?

Mackay et al., "Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals", Lewis Publishers, 1992

Chapter 5: Case study 1: Mass balance equation for Hx 118-74-1

$$M_{Hx} = M_{Hx,W} + M_{Hx,S} + M_{Hx,F} = V_W C_W + V_W \rho_{oc} K_{oc} C_W + V_W \rho_F BCF\, C_W$$



Chapter 5: Mass balance calculations for Hx 118-74-1

Concentration in Water

$$C_W = \frac{M_{Hx}}{(V_W + V_W \rho_{oc} K_{oc} 10^{-3} + V_W \rho_F\, BCF\, 10^{-3})} = 9.92 \times 10^{-6} \approx 10^{-5} \frac{kg\ Hx}{m^3\, Water}$$

10^5 m^3 | 10^{-3} kg$_{OC}$/m^3 | 3,388 L/ kg$_{OC}$ | 10^{-1} kg$_F$/ 10^2 m^3 | 5,152 L/ kg$_F$ | 10^{-3} m^3/L

Concentration in Fish

$$C_F = BCF \times C_W = (5152 \frac{L}{kg\, Fish})(10^{-5} \frac{kg\, Hx}{m^3 Water})(10^{-3} \frac{m^3 Water}{L}) = 5.2 \times 10^{-5} \frac{kg\, Hx}{kg\, Fish}$$

Dose to Humans

$$Dose = M_F \times C_F = (0.5\ kg\, Fish)(5.2 \times 10^{-5} \frac{kg\, Hx}{kg\, Fish}) = 0.026\ g\ Hx$$

Chapter 5: Benzene 71-43-2
EPIWIN (estimates) vs ChemFate (data)

Properties	EPIWIN	ChemFate
Bioling Pt. (˚C)	102.24	80.09
Melting Pt. (˚C)	-77.92	5.53
Vapor Press. @25˚C (mm Hg)	34	95
log K_{OW}	1.99	2.13
Water Solubility (mg/L)	2000	1790
H (atm•m^3/mole)	5.39×10^{-3}	5.55×10^{-3}
Biodegradation half life	weeks-months	week
Hydrolysis half life	-----	-----
Atmos. Oxidation half life (d)	5.5	10
log K_{OC}	2.22	1.69
Bioconcentration Factor	0.94	1.0

Chapter 5: maleic anhydride 108-31-6
EPIWIN (estimates) vs ChemFate (data)

Properties	EPIWIN	ChemFate
Bioling Pt. (˚C)	156.4	202
Melting Pt. (˚C)	-51.6	52.8
Vapor Press. @25˚C (mm Hg)	2.97	.25
log K_{OW}	1.62	-----
Water Solubility (mg/L)	4912	-----
H (atm•m^3/mole)	1.9×10^{-6}	-----
Biodegradation half life	weeks	-----
Hydrolysis half life	-----	1 minute
Atmos. Oxidation half life (d)	4.71	0.7
log K_{OC}	0	-----
Bioconcentration Factor	0.546	-----

No data because MA hydrolyzes in 1 minute in water

Syracuse Research Corporation, http://www.syrres.com/efdb.htm

Chapter 5: Recap

- Educational goals and topics covered in the module
- Potential uses of the module in chemical engineering courses
- Overview of property estimation methods
- Software demonstration
- Case studies