“Fugacity”

Module 1: Basic Concepts, Lecture 4

Chemical Fate and Transport in the Environment, 2nd edition. H.F. Hemond and E.J. Fechner-Levy. Academic Press. London. 2000.

Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. D. Mackay, W.Y. Shiu, and K.C. Ma. Lewis/CRC Press. Boca Raton. 1992

1.8.4 Equilibrium Partitioning Among all Phases: Fugacity

- Fugacity literally means the “tendency to flee” and is used to determine to the relative concentrations of a chemical in air, water, and soil phases at equilibrium (can also be used to include other environmental phases, such as fish, bottom sediments, dissolved gases, suspended sediment, etc.).
- Fugacity has units of pressure and is related to concentrations through a fugacity capacity constant (in units of mol/atm-m^3)
- $C_i = Z_i f$

where C_i is the chemical concentration in phase i [M/L^3]

Z_i is the fugacity capacity [T^2/L^2]

f is the fugacity [M/LT^2]

$$Z_{air} = \frac{1}{RT}$$

$$Z_{water} = \frac{1}{H}$$

$$Z_{sediment} = \frac{r_s \bullet K_d}{H}$$

$$Z_{fish} = \frac{r_{fish} \bullet BCF}{H}$$

Where BCF is the bioconcentration factor (or the partition coefficient) between fish and water.

Example Problem 1-15

- Assume air volume of 10^{10} m^3, water volume of $7x10^6$ m^3, and 3.5 m^3 of fish
- 10 kg of methylene chloride is released into the water
- Predict the equilibrium partitioning into each phase.
- Assume BCF of 4.4 L/kg, a fish density of 1 g/cm^3, and a temperature of 25^{o}C.

Convert mass of methylene chloride into moles:

$$10kg \bullet \frac{1{,}000g}{1kg} \bullet \frac{1mol}{84.93g} = 118mol$$

Calculate fugacity capacity for each phase:

$$Z_{air} = \frac{1}{RT} = \frac{1}{0.0821L-atm/(mol-K) \bullet 298K} \bullet \frac{1{,}000L}{1m^3}$$

$$Z_{air} = 40.9mol/(atm-m^3)$$

$$Z_{water} = \frac{1}{H} = \frac{1}{3x10^{-3}\, atm - m^3/mol} = 333\, mol/(atm-m^3)$$

$$Z_{fish} = \frac{r_{fish} \bullet BCF}{H} = \frac{1{,}000g/m^3 \bullet 4.4L/kg}{3x10^{-3}\, atm - m^3/mol} \bullet \frac{1kg}{1{,}000g} \bullet \frac{1m^3}{1{,}000L} = 1.5mol/(atm-m^3)$$

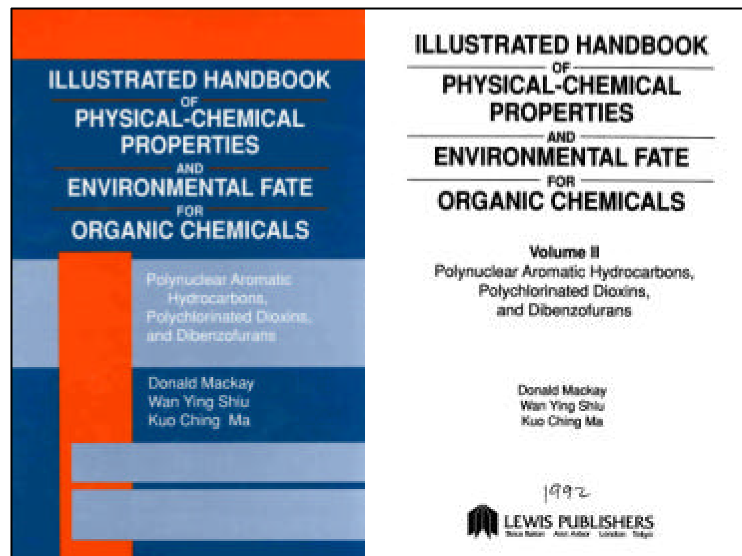
The fugacity of the entire system:

$$f = \frac{M_{tot}}{\sum_i (Z_i \bullet V_i)}$$

$$f = \frac{118\, mol}{40.9 \bullet 10^{10} + 333.7 \bullet 10^6 + 1.5 \bullet 3.5} = 2.9x10^{-10}\, atm$$

- M_{air} = (2.9 x 10^{-10})(10^{10})(40.9) = 117 mol
- M_{water} = (2.9 x 10^{-10})(7x10^6)(333) = 0.7 mol
- M_{fish} = (2.9 x 10^{-10})(3.5)(1.5) = 1.5 x 10^{-9} mol

- At equilibrium, the methylene chloride will overwhelmingly be in the air, compared to the other two phases.
- However, the concentration will be highest in the water (the phase with the highest fugacity capacity).



Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals is a comprehensive series in five volumes that focuses on environmental fate prediction and quantitative structure property relationship analysis. Volume II examines the properties and environmental fate of three classes of an important series of chemicals: polycyclic aromatic hydrocarbons (about 50 chemical compounds), highly toxic chlorinated "dioxins," and equally toxic chlorinated dibenzofurans, which are similar to dioxins in structure and toxicity.

WHAT IS DIFFERENT ABOUT THESE BOOKS?

These books are like no others in that they tackle environmental fate calculations and QSPR Plots. Environmental partitioning and persistence are calculated in a generic "unit world" using standard fugacity models. This shows where the chemicals will go, relative concentrations, persistence, and important intermedia transport processes. From this information, a behavior profile emerges that can be presented in a standard format.

For the series of chemicals presented, QSPR Plots can be prepared by plotting these properties against molecular descriptors (e.g., carbon number, chlorine number, molar volume), and relationships between properties can be explored. This helps validate the data, and estimates of properties for other chemicals can be made from these plots.

The chemicals included in these volumes will contain the following information:

Chemical Name	Octanol-Water Partition Coefficient
CAS Number	Vapor Pressure
Structure	Organic Carbon-Water Partition Coefficient
Molecular Mass	Bioconcentration Factor
Molar Volume	Henry's Law Constant
Melting and Boiling Points	Dissociation Constant
Water Solubility	Estimated Half-Lives in Air, Water, Soil, Sediments

Full references and methods of measurement will be given. Multiple values will be cited and a recommendation made for a "best" value.

This exciting new work is an essential reference guide for environmental scientists, environmental engineers, laboratories, regulators, industrial hygienists, consultants, and environmental toxicologists.

Mackay's Fugacity Calculations

- 3 levels of fugacity calculations are presented by Mackay, *et al*, with increasing complexity.
- These calculations are based on set volumes for each media compartment.
- Computer code is given to allow calculations for other volumes.

Compartment Dimensions for Levels I and II Calculations

Compartment	Air	Water	Soil	Sediment	Suspended Sediment	Fish
Volume, V (m^3)	10^{14}	$2x10^{11}$	$9x10^9$	10^8	10^6	$2x10^5$
Depth, h (m)	1000	20	0.1	0.01	-	-
Area, A (m^2)	$100x10^9$	$10x10^9$	$90x10^9$	$10x10^9$	-	-
Org. Fraction (ϕ_{OC})	-	-	0.02	0.04	0.2	-
Density, ρ (kg/m^3)	1.2	1000	2400	2400	1500	1000
Adv. Residence Time, t (hours)	100	1000	-	50,000	-	-
Adv. flow, G (m^3/h)	10^{12}	$2x10^8$	-	2000	-	-

Mackay, *et al*. 1992, Table 1.2a

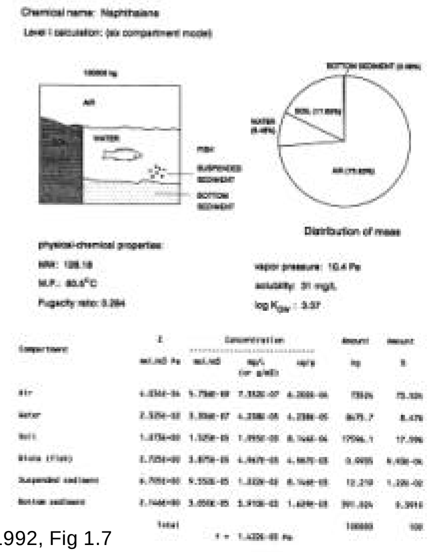
Compartment Dimensions for Level III Calculations

Air	Total volume	10^{14} m^3 (as above)
	Air phase	10^{14} m^3
	Aerosol phase	2000 m^3 ($v = 2x10^{-11}$)
Water	Total volume	$2x10^{11}$ m^3
	Water phase	$2x10^{11}$ m^3 (as above)
	Suspended sediment phase	10^6 m^3 ($v = 5x10^{-6}$)
	Fish phase	$2x10^5$ m^3 ($v = 1x10^{-6}$)
Soil	Total volume	$18x10^9$ m^3
	Air phase	$3.6x10^9$ m^3 ($v = 0.2$)
	Water phase	$5.4x10^9$ m^3 ($v = 0.3$)
	Solid phase	$9.0x10^9$ m^3 ($v = 0.5$) (as above)
Sediment	Total volume	$500x10^6$ m^3
	Water phase	$400x10^6$ m^3 ($v = 0.8$)
	Solid phase	$100x10^6$ m^3 ($v = 0.2$) (as above)

Mackay, *et al*. 1992, Table 1.2a

Level I Fugacity Calculations

- Level 1: describes how a given amount of chemical partitions at equilibrium between six media (air, water, soil, bottom sediment, suspended sediment, and fish).
  - Slug discharge (one time loss).
  - Reactivity is ignored.
  - Soil and sediment are treated as simple solid phases (presence of air and water in the pores is ignored).



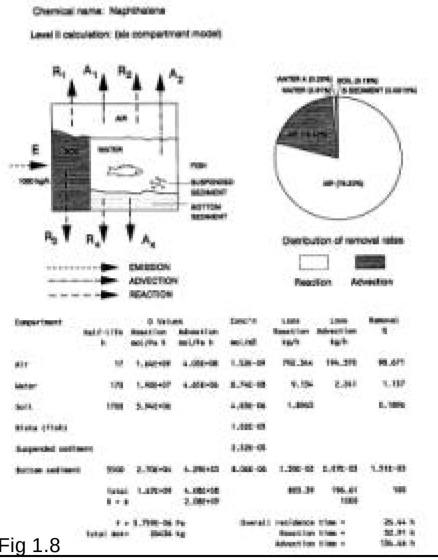
Mackay, *et al*. 1992, Fig 1.7

Results of Level I Analysis for Napthalene

- Air will contain about 74% of the napthalene at equilibrium, with a concentration of about 0.7μg/m^3.
- Water will contain about 8.5%, at about 42ng/L.
- Soils will contain about 18%, at about 8x10^{-4} μg/g (barely detectable, even though a large fraction).
- Sediments will contain about 0.4%, at about 16x10^{-4} μg/g (barely detectable).
- Little evidence for bioaccumulation of napthalene in fish (5x10^{-3} μg/g).
- The more hydrophobic and less volatile PAHs tend to partition less into air and more into soil and sediment.

Level II Fugacity Calculations

- Level II: Simulates continuous chemical discharge into the environment.
  - Achieves a steady-state equilibrium condition at which input and output rates are equal for the four primary media (not for fish or suspended sediment).
  - The rates of loss by reaction are based on selected reactivity class.
  - Advection loss flow rates are based on residence times for each medium.



Mackay, *et al*. 1992, Fig 1.8

Results of Level II Analysis for Napthalene

- The overall fugacity is about 26% of the value obtained in the level I analysis. The amounts and concentrations for each medium will therefore be reduced to this level.
- The primary loss mechanism is the reaction in air (79% of the input).
- Most of the remainder is lost of advective outflow.
- The overall residence time is 26.4 hours (there is an overall inventory of napthalene in the system of 26.4 hours x 1,000 kg/hr, or 26,400 kg).
- Water, soil, and sediment losses are unimportant because they contain so little of the napthalene and because of slower reaction and advection rates.
- The water reaction rate constant would have to increase by 20-fold to become significant, while the soil rate would have to increase by 100 and the sediment by 10,000 (these rates could therefore be known with less accuracy than the atmospheric reaction rate, the most important).

Level III Fugacity Calculations

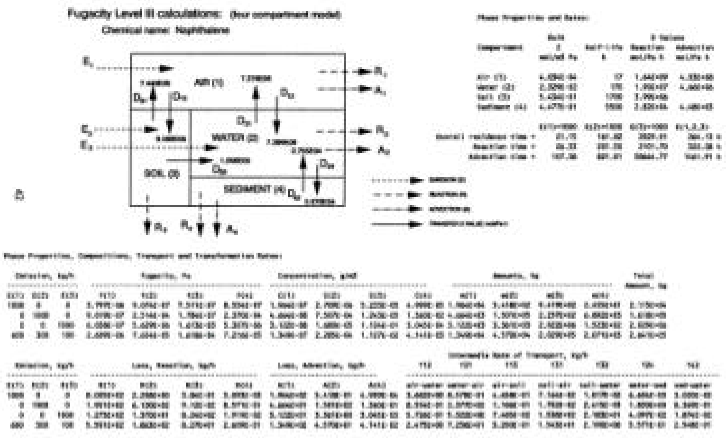
- Level III: Intermedia transport is considered.
  - Determines values for 12 intermedia transport velocity parameters, which are used to calculate the 7 intermedia reaction and advection D values
  - The rate of reactive loss is:

    $D_{Ri}f$ [mol/h]
  - As and example, for air to water intermedia transport, the four processes considered are diffusion (adsorption), dissolution in rain of gaseous chemical, and wet and dry deposition or particle-associated chemical.

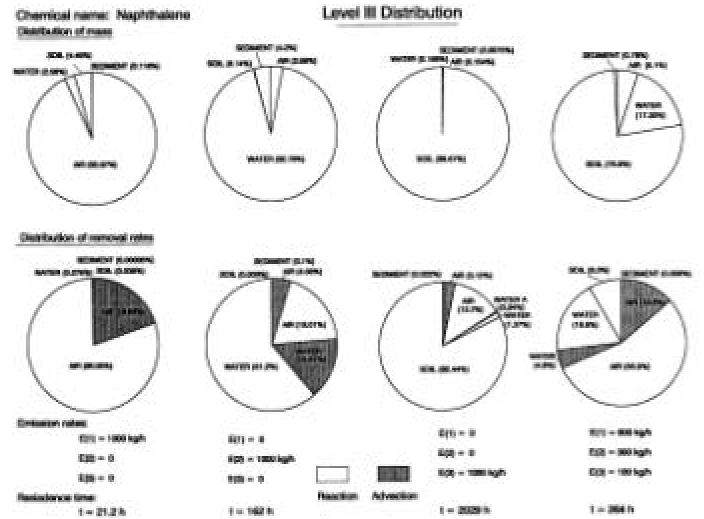
Intermedia Transport Parameters

U		m/h	m/year
1	Air side, air-water MTC*, k_A	5	43800
2	Water side, air-water MTC, k_W	0.05	438
3	Rain rate, U_R	10^{-4}	0.876
4	Aerosol deposition	$6x10^{-10}$	$5.256x10^{-6}$
5	Soil-air phase diffusion MTC, k_{SA}	0.02	175.2
6	Soil-water phase diffusion MTC	$10x10^{-6}$	0.0876
7	Soil-air boundary layer MTC, k_S	5	43800
8	Sediment-water MTC	10^{-4}	0.876
9	Sediment deposition	$5.0x10^{-7}$	0.00438
10	Sediment resuspension	$2.0x10^{-7}$	0.00175
11	Soil-water run-off	$5x10^{-5}$	0.438
12	Soil-solids run-off	10^{-8}	0.0000876

Mackay, *et al*. 1992, Table 1.4



Mackay, *et al*. 1992, Fig 1.9



Mackay, *et al*. 1992, Fig 1.10

Results of Level III Analysis for Napthalene

- The air-water and air-soil exchange are the most important, with the water-sediment and the soil-water transport being slower.
- The magnitude of intermedia transport D values (10^7 mol.Pa-h) compared to the atmospheric reaction and advection values (10^8 to 10^9 mol.Pa-h) suggest that the reaction and advection values will be very fast relative to transport.
- The bulk Z values (the fugacity capacities) are similar for air and water as shown for "pure" phases in the Level I and II analyses, but are lower for soil and sediment because of "dilution" of the solid phase with air or water.

Results of Level III Analysis (cont.)

- The first row of values in the large tables describe the condition if 1,000 kg/h is emitted to the air and is similar to the Level II results. Napthalene discharged to the atmosphere has very little potential to enter other media (due to the mass transfer coefficients). The overall residence time is 21 hours, similar to Level II.
- The second row of values shows the results if 1,000 kg/h is discharged to the water. Obviously, the water concentration is greater (by about 300X, at about 750 ng/L). The overall residence time is longer (at 162 hours). The key processes are the reaction in water (half-life of 170 h), evaporation (half-life of 440 h), and advective outflow (residence time of 1,000 h). The competition between the reaction and evaporation in the water determines the overall fate: 93% of discharged naphthalene is in the water.

Results of Level III Analysis (cont.)

- The 3rd row is for 1,000 kg/h discharged to the soil. The amount in the soil is $2x10^6$ kg, and the overall residence time is 2,000 hours. The rate of reaction in soil is low and there is no advection. The soil concentration (0.11 g/m^3) is controlled almost entirely by the rate at which the napthalene reacts.
- The 4th row is a combination of discharges to each of the 3 media. The results are nearly a linearly combined version of the previous 3 scenarios.
- These 4 scenarios show the when napthalene is discharged into a specific medium, most of the chemical remains in that medium. These results are not the same for all chemicals, of course.

Problem Assignment

- Conduct the fugacity evaluation for napthalene (using the information and method outlined in Hemond and Fechner-Levy), using the same compartment values used by Mackay, and verify their results.
- Select a more hydrophobic and less volatile PAH and show that it partitions less into air and more into soil and sediment.