

## CHAPTER 7 - VOLATILIZATION OF PESTICIDES FROM SOIL

Skip pp. 181-186 and Go to section 7-2, Phase Distributions of Pesticides in Soils

The following notes are not in the order presented in the textbook, but will assist you in reading the textbook and in doing the assigned problems.

### Quantitative Evaluation of Mass Balance

- I. Partition Coefficients
- II. Fugacity

#### I. PARTITION COEFFICIENTS - more details in textbook (SSSA)

$$\begin{aligned}
 K_d = C_s/C_w &= \text{Conc. in soil phase/Conc. in water phase} \\
 &= \frac{\text{mg/Kg}}{\text{mg/L}} = \frac{\text{mg} \times \text{L}}{\text{Kg} \text{ mg}} = \text{L/Kg} \\
 &= \frac{\text{mg/Kg soil}}{\text{mg/Kg water}} \text{ (unitless)}
 \end{aligned}$$

$$K_{oc} = K_d/f_{oc} = K_d/\text{fraction of organic carbon in soil}$$

$$\begin{aligned}
 K_o = C_o/C_w &= \text{Conc. in oil phase/Conc. in water phase} \\
 &= \frac{\text{mg/Kg}}{\text{mg/Kg}} \quad \text{or} \quad \frac{\text{mg/L}}{\text{mg/L}}
 \end{aligned}$$

$$\text{Henry's Law: } P/S = \frac{\text{vapor pressure}}{\text{solubility}} = \frac{\text{atm}}{\text{mole/m}^3} = \text{atm-m}^3/\text{mole}$$

$$K_h = C_a/C_w = \text{Conc. in air phase/Conc. in water phase}$$

- (1) H, Henry's Law is often used for  $K_h$
- (2)  $\frac{\text{moles/m}^3 \text{ air}}{\text{moles/m}^3 \text{ water}}$  (unitless)
- (3)  $H/RT = \frac{\text{atm-m}^3/\text{mole}}{(\text{atm-m}^3/\text{mole-}^\circ\text{K}) \circ\text{K}}$  (unitless)

$$\text{Raoult's Law: } C_w = X_o S_w$$

where  $C_w$  is the chemical concentration in the aqueous phase (moles/L) in equilibrium with the organic phase,  $X_o$  is the mole fraction of the chemical in the organic phase, and  $S_w$  is the aqueous solubility of the chemical (moles/L).

## CHAPTER 7-RELATED MATERIAL - PARTITIONING

### Use of Partition Coefficients

1. Determining Partitioning between Water and Air

**Given:** benzene  
Molecular weight (g/mol) = 78  
Solubility (water) (g/m<sup>3</sup>) = 1780  
Vapor Pressure (atm) = 0.127

**Determine:** (1) Henry's Law Constant in units of atm - m<sup>3</sup> / mole  
(2) Unitless air/water partition coefficient (K<sub>h</sub>), given the conversion  
 $\frac{8.206 \times 10^{-5} \text{ atm-m}^3}{\text{deg K} - \text{mole}}$  and a temperature of 25 C (298 K)

### USING RAOULT'S LAW FOR PREDICTING RELEASE CONCENTRATIONS FROM NON-AQUEOUS PHASE LIQUIDS IN RESIDUAL SATURATION

[Reference: EPRI, 1992. Estimating Release of Polycyclic Aromatic Hydrocarbons from Coal Tar at Manufactured-Gas Plant Sites. EPRI TR-101060.]

- (1) It has often been assumed that organic contaminant concentrations in the aqueous phase migrating from a source including NAPL would be equal to the corresponding pure compound aqueous solubilities. This may be a reasonable estimate if the source is composed of a single contaminant.
- (2) Most complex wastes occurring as NAPLs (coal tar, gasoline, etc.) consist of mixtures of contaminants.
- (3) Use of Raoult's Law:  $C_w = X_o S_w$   
 $C_w$  = concentration in the aqueous phase (moles/L) in equilibrium with the organic phase,  
 $S_w$  = the aqueous solubility of the pure liquid chemical (moles/L), and  
 $X_o$  = the mole fraction of the chemical in the organic (NAPL) phase.
- (4) Prediction using commonly available parameters:  $C_w = (M_i) (MW_{\text{coal tar}}) (S_w)$   
 $M_i$  = concentration in coal tar (mg PAH/ Kg coal tar),  
 $MW_{\text{coal tar}}$  = molecular weight of the coal tar (Kg / mole), and  
 $S_w$  = pure liquid chemical solubility (moles / L).
- (5) Simple application of Raoult's Law for benzene and toluene. The pure compound solubilities of benzene and toluene are 23.1 and 5.6 mmol/L, respectively. Note that the pure compound solubilities are observed only in the absence of the second component, i.e, when  $X_o = 0$  or 1. The excellent agreement between measured results and predicted results from Raoult's Law illustrates the **role of mole fraction** on solubility.
- (6) Application of Raoult's Law for benzene and octanol. Deviation from ideal behavior are observed. The two components are dissimilar in chemical nature. Benzene is an aromatic compound while octanol is an alkane with a polar functional group (-OH).

- (7) Application of Raoult's Law to compositionally-complex mixtures - use partition coefficients for chemicals between organic and water phases.

$$K = C_o / C_w,$$

where  $C_o$  is concentration in organic phase (mole/L) and  $C_w$  in water (mole/L).

Substitute Raoult's Law expression and get:

$$K = C_o / (X_o S_w)$$

Then to eliminate amount of information required, can use average molecular weight ( $MW_o$ ) and density ( $p_o$ ) of the organic mixture, as follows:

$$K = (p_o / MW_o) / S_w$$

where  $MW_o$  is in g / mole, and  $p_o$  is in g / L.

Therefore, linearize equation to the form:

$$\log K = -\log S_w - \log (MW_o / p_o) \quad \text{where}$$

slope is negative one and intercept is dependent on the  $p_o$  and  $MW_o$  of the organic mixture.

- (8) Examples:

- (a) Gasoline
- (b) Diesel fuel
- (c) Coal tar

### EXAMPLE OF RAOULT'S LAW FOR PREDICTING AQUEOUS-PHASE CONCENTRATIONS FOR COAL TAR CONTAMINATION

1. Prediction of PAHs in groundwater ( $C_w$ ) in contact with a coal-tar source.

$$C_w = (M_i) (MW_{\text{coal tar}}) (S_w) (10^{-3})$$

gives groundwater concentration,  $C_w$ , in mg / L

where  $M_i$  is the concentration of the PAH of concern (i) in the coal tar (mg/kg),

$MW_{\text{ct}}$  is the average molecular weight of the coal tar (g / mole), and

$S_w$  is the pure liquid chemical solubility (moles / L).

2. PAH = naphthalene leaving a coal tar source at an MGP site.  
 $M_i = 20,000 \text{ mg / kg}$   
 $MW_{\text{ct}} = 300 \text{ g / mole}$   
 $S_w$  becomes  $S_{\text{scl}}$  (for crystalline compounds) =  $7.943\text{E-}4 \text{ moles/L}$

(1) What is the aqueous concentration of naphthalene leaving the coal tar source?

(2) What is the fraction in the aqueous phase of the aqueous solubility of naphthalene? The aqueous solubility of naphthalene is 32 mg/L.

#### TABLE OF MEAN MOLECULAR WEIGHTS FOR NAPLs

<u>NAPL</u>	<u>Molecular Weight (gm/mole)</u>
Gasoline	100 - 120
Diesel Fuel	160 - 230
Coal Tar	150 - 480
JP-4	150 - 170 (average 160) unweathered

$$C_w = (M_i / MW) S_w$$

$$= \frac{\text{mg PAH}}{\text{Kg}} \times \frac{\text{g}}{\text{mole}} \times \frac{\text{mole}}{\text{L}_{\text{water}}} \times \frac{10^{-3} \text{ Kg}}{\text{g}}$$

$$= \frac{\text{mg PAH}}{\text{L water}}$$

See chart from EPRI reference. "Comparison of measured and calculated (Raoult's law) aqueous solubilities in binary mixtures of □ benzene-toluene (A), and benzene-octanol (B).

# FUGACITY AND CHEMICAL MASS BALANCE

- (1) Don Mackay introduced the concept of fugacity to express the distribution of a pesticide between various phases of the environment.
- (2) Fugacity has the units of pressure (Pa), and has been called the escaping tendency of a chemical from a particular phase.

$$C_i = f_i Z_i \quad [1]$$

$C_i$  = concentration in phase i,  
 $f_i$  = fugacity in phase i,  
 $Z_i$  = fugacity capacity of phase i

$$\begin{aligned} Z_a &= 1/RT \\ Z_a &= 4(10^{-4}) \text{ mole/ m}^3\text{-Pa} \end{aligned} \quad [2]$$

$Z_a$  = fugacity capacity of air phase

$$Z_w = 1/H$$

$Z_w$  = fugacity capacity of the water phase

$$Z_s = K_{pp_s} Z_w \quad [3]$$

$Z_s$  = fugacity capacity of the soil phase

$$Z_o = Z_w K_{ow}$$

$Z_o$  = fugacity capacity of the oil phase

- (3) If the amount moles (m) in each phase is

$$m_i = C_i V_i = f_i Z_i V_i \quad [4]$$

- (4) At equilibrium (since  $f_1 = f_2 = \dots = f$ ), then

$$f = M / \sum Z_i V_i \quad [5]$$

- (5) Thus, the equilibrium fugacity can be calculated from a knowledge of the volumes and fugacity capacities of the various phases and the total mass of chemical in the system.

- (6) The final distribution of the pesticide or other organic chemical:

1) Concentration in each phase;

2) Amount in each phase;

can be calculated from equations [1] and [4]

## EXAMPLE OF EVALUATING CHEMICAL DISTRIBUTION USING FUGACITY

### Problem 5. Given:

Calculate the relative distribution of naphthalene among air, water, soil, and oil (NAPL) components of a soil system using fugacity and the following site and chemical characteristics. The amount of naphthalene present in the subsurface is not known.

1. Naphthalene characteristics
  - (1) Henry's Law Constant =  $1.27 \times 10^{-3}$  atm-m<sup>3</sup>/mole
  - (2)  $K_{ow}$  = 1995 (dimensionless)
  - (3)  $K_{oc}$  = 1288 L/Kg
  
2. Site characteristics
  - (1) Relative volumes of air, water, soil, and oil = 20%, 30%, 48%, and 2%, respectively
  - (2) Soil dry bulk density = 1.4 g/cc = 1.4 Kg/L
  - (3) Soil organic carbon content = 2% (by weight, gm/gm) (dimensionless)

### Determine:

- (1) Determine the % of naphthalene associated with each phase (air, water, soil, and oil) in the contaminated system.
  
- (2) Construct a mass balance "pie chart" indicating the % mass of each chemical in each phase.

## **Fugacity approach for Characterization, Problem Definition, Treatment Selection, and Monitoring**

**1. Given:** Calculate and compare the percent distribution of 100 moles of each of the following two chemicals that have been accidentally added to vadose zone soil: (1) benzene, and (2) 1,2-dichlorobenzene, in a four compartment vadose zone environment at 20 C. The total volume of all phases = 1,000,000 m<sup>3</sup>. The volumes of air, water, and soil phases are 20%, 30%, and 48%, respectively. A value of 2% is given for the volume of the NAPL phase. Assume an organic carbon content of 4% in the soil phase. (Density of soil = 1500 Kg/m<sup>3</sup>).

### **Analysis:**

- a. Construct a mass balance "pie chart" for each chemical, and indicate the % mass of chemical in each compartment of the pie chart;
- b. Based upon your analysis, is the concentration of each chemical in the water phase above the MCL for that chemical?
- c. Is Pump and Treat (P&T) Technology applicable for these chemicals at this site for remediation? Defend your answer with logic, information, and reasoning.
- d. Is Soil Vacuum Extraction (SVE) Technology applicable for these chemicals at this site for remediation? Defend your answer with logic, information, reasoning.

**Fugacity approach for characterization, problem definition, treatment selection, and monitoring. (solution)**

1. 100 moles - distribution in 4-phase soil system

a) Mass balance (pie chart)

Table 1. Benzene

Phase	Volume V (m <sup>3</sup> )	Fugacity Capacity, Z (mol/m <sup>3</sup> -Pa)	VZ (mol/Pa)	Conc. C Z*f (mol/m <sup>3</sup> )	Mass V*C (mol)	Distribution (%)
Air	200,000	0.0004	80	4.6E-6	0.9	0.9
Water	300,000	0.0018	540	2.0E-5	6	6
Soil	480,000	0.0070	3360	8.0E-5	38.4	38.4
NAPL	20,000	0.24	4800	2.74E-3	54.7	54.7
			Σ 8780		Σ 100	Σ 100

Henry's Law Constant = 5.43E-3 atm-m<sup>3</sup>/mol; Log K<sub>oc</sub>=1.81; LogK<sub>ow</sub>=2.13

Volumes: air (10<sup>6</sup>) (20%); water (10<sup>6</sup>) (30%); soil 10<sup>6</sup> (48%); NAPL 10<sup>6</sup> (2%)

Fugacity capacity (Z):

$$Z_{\text{air}} = 1/RT = 0.0004 \text{ (SSSA p.188);}$$

$$Z_{\text{water}} = 1/H = 1/(5.43E-3 \text{ atm-m}^3/\text{mol})/(101325 \text{ Pa/atm})$$

$$Z_{\text{soil}} = (K_{\text{oc}}) (\% \text{OC}) (\rho_b) (Z_{\text{water}}) = 10^{1.81} (0.04)(1500 \text{ Kg/m}^3)/(10^3 \text{ L/m}^3) Z_{\text{water}}$$

$$Z_{\text{NAPL}} = K_{\text{ow}} Z_{\text{water}} = 10^{2.13} Z_{\text{water}}$$

$$f = (\text{total mass, moles}) / \sum_{i=1}^4 (Z_i V_i) \text{ as (mol/Pa)} = 100 / [(80)+(540)+(3360)+(4800)]$$

$$= 100 \text{ moles}/8780 \text{ mol/Pa} = 0.0114 \text{ Pa}$$

b) MCL = 5ug/L

$$(2.0E-5 \text{ mol/m}^3) (78 \text{ g/mol}) (m^3/10^3 \text{ L}) (10^3 \text{ mg/g}) = 0.00156 \text{ mg/L} = 1.56 \text{ ug/L} < \text{MCL}$$

c) P&T Technology applicable? Log K<sub>ow</sub>=2.13 < 3.5, therefore P&T is not ruled out on the basis of chemical property.

d) SVE Technology applicable? H = 5.43 x 10<sup>-3</sup> atm-m<sup>3</sup>/mol > 1 x 10<sup>-3</sup> atm-m<sup>3</sup>/mol, therefore SVE is not ruled out on the basis of chemical property.

## CHAPTER 7. VOLATILIZATION OF PESTICIDES FROM SOIL

1. Skip Section 7-1 - go to p. 187.

2. 7-2 Phase Distributions of Pesticides in Soil:

7-2.1 (1) p.188. In partitioning between phases, matter flows from high chemical potential to low chemical potential. At equilibrium, the chemical potential is the same in all phases.

(2) Don Mackay introduced the concept of fugacity to express the distribution of a pesticide between various phases of the environment.

(3) Fugacity has the units of pressure (Pa), and has been called the **escaping tendency** of a chemical from a particular phase.

$$C_i = f_i Z_i \quad [10]$$

$$Z_a = 1/RT \quad [11]$$

$$Z_w = 1/H$$

$$Z_s = K_{pp_s} Z_w \quad [13]$$

(4) If the amount moles (m) in each phase is

$$m_i = C_i V_i = f_i Z_i V_i \quad [14]$$

(5) At equilibrium (since  $f_1 = f_2 = \dots = f$ ), then

$$f = M / \sum Z_i V_i \quad [15]$$

Thus, the equilibrium fugacity can be calculated from a knowledge of the volumes and fugacity capacities of the various phases and the total mass of pesticide in the system.

(6) The final distribution of the pesticide:

1) Concentration in each phase;

2) Amount in each phase;

can be calculate from equations [10] and [14]

(7) Study Table 7-1 (p. 190), and calculate values in the table.

3. 7-2.2 Partitioning in Soil

(1) Batch equilibration method (study) procedure as described

(2) use Freundlich isotherm:  $x/w = K_p C_e^{1/n}$  [16]

(3) High correlation between partitioning in soil and soil organic matter  
 $K_{oc} = K_p / f_{oc}$  [18]

(4) A correlation of  $K_{oc}$  and  $K_{ow}$  values by Rao and Davidson:  
 $\log K_{oc} = 1.029 \log K_{ow} - 0.18$  [19]

(5) p. 193 - Partitioning in soil valid only for moist soil. For dry soil, mineral surfaces are exposed and play a role.

4. p. 193. 7-3 Effects of Residue Distribution and Soil Transport Processes  
7-3.1 Diffusion and Mass Flow - Class Read

- (1) p.194 - Gas-phase diffusion is approximately  $10^4$  times greater than liquid-phase diffusion.

5. p. 195. 7-3.2 - Soil Management Effects: Surface Application vs. Incorporation

- (1) p.196. Dry soils adsorb pesticides strongly. Volatilization loss of pesticides to soil surface is susceptible to changes in surface moisture content.
- (2) p. 197. Shallow soil incorporation at the time of application is an effective management technique in preventing pesticide volatilization.

6. p.197. 7-3.3 - Effect of Tillage Practices on Pesticide Volatilization

- (1) Conservation tillage - emphasizes reduced frequency and intensity of tilling the soil and the preservation of some type of vegetative cover on the soil surface (mulch).
- (2) Factors that control pesticide volatilization from soil:
  - 1) vapor pressure and solubility
  - 2) application method (surface vs. incorporation)
  - 3) soil moisture distribution
  - 4) soil OM content
  - 5) soil temperature
  - 6) soil transport properties
- (3) Consider the effect of conservation tillage on the factors that control pesticide volatilization in (2) listed above.

p.198 (4) Surface application - more prominent in conservation tillage than in conventional tillage

(5) Effect of tillage practices on moisture content of the surface layer.

p.198 (6) Soil OM distribution is different in NT and CT soils.

p.199 (7) Tillage practice also affects the soil temperature.

(8) Tillage practice will also affect pesticide transport through soil by diffusion and convective flow.

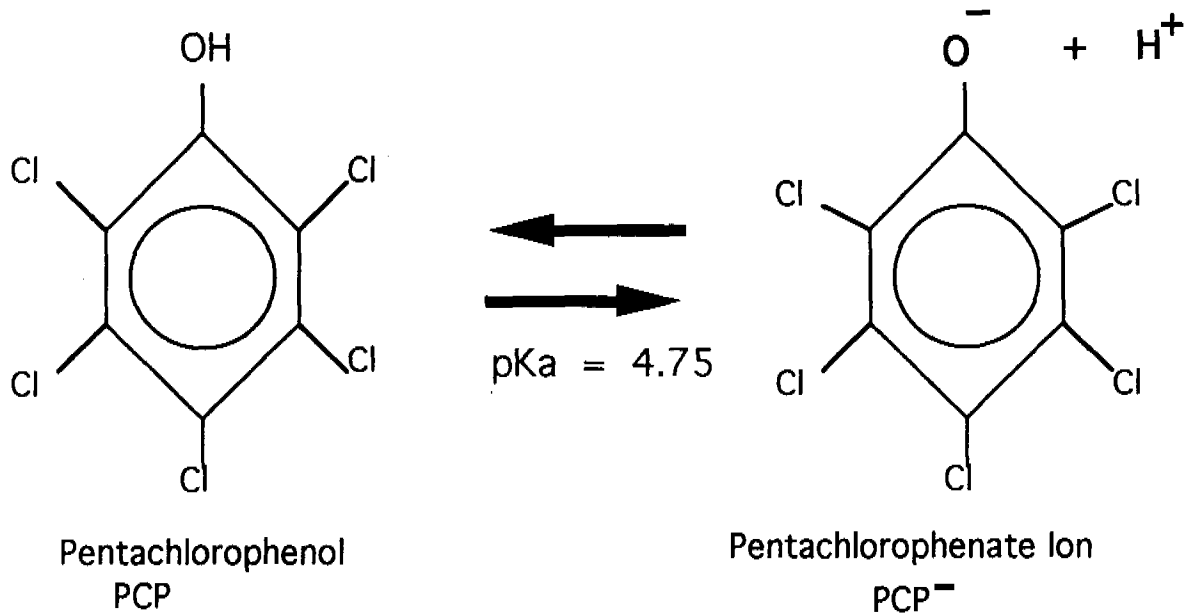
7. 7-4 - Skip  
End of Chapter

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Review pgs. 188-200 in Glotfelty & Schomburg

## Partitioning of Ionizable Chemicals



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$-\log K_a = -\log [\text{H}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pKa} = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

When  $\text{pH} = \text{pKa}$

$$0 = -\log \frac{[\text{A}^-]}{[\text{HA}]}$$

This occurs when  $[\text{A}^-] = [\text{HA}]$

See Fig. 17 Aqueous solubility of PCP as a function of pH with regression equation. source: Ramaprasad, A. 1994. □  
Limitations on biotransformation of pentachlorophenol in soil. MS Thesis, Dept. of Civil and Environmental □  
Engineering, Utah State University, Logan, UT.

## COURSE NOTES

### CHAPTER 9. HYDROLYTIC TRANSFORMATIONS OF ORGANIC CHEMICALS IN THE ENVIRONMENT

1. p.229. Transformation processes including hydrolysis, oxidation-reduction, and photodegradation lead to decomposition of pollutants.
2. Hydrolysis - can be dominant pathway; often required of functional groups before microbial degradation can be initiated.
3. p.230. Functional Groups susceptible to hydrolysis:

Amides	Esters (aromatic, aliphatic)	Phosphorus esters
Carbamates	Alkyl and aryl halides	
Epoxides	Nitriles	
4. Biotic hydrolysis - rate proportional to bacterial biomass and/or specific enzyme concentration.
5. Abiotic hydrolysis - rate a function of chemical parameters (pH, DOM, dissolved metal ions).



7. 9-1.1 Kinetics: first order in the concentration of the organic species (RX)

$$d[\text{RX}] / dt = -k_{\text{obs}} [\text{RX}] \quad [2]$$

$$\text{half-life } t_{1/2} = 0.693 / k_{\text{obs}} \quad [3]$$

$$k_{\text{obs}} = k_{\text{H}}[\text{H}^+] + k_{\text{OH}}[\text{OH}^-] + k_{\text{w}} + \Sigma (k_{\text{HA}}[\text{HA}] + k_{\text{A}}[\text{A}^-]) \quad [4]$$

8. p.231. Biotic hydrolysis - distinguishing factor is a lag period; conversely abiotic hydrolysis does not exhibit a lag phase.
9. Halogenated hydrocarbons - first step in degradation of these compounds in abiotic hydrolysis, followed by biological degradation.
10. p.232 9-1.2 Role of pH: most common is acid or base-mediated hydrolysis study figures 9-1 and 9-2 on page 233.
11. p.234 9-1.3 Effect of Temperature:  $k_{\text{obs}} = A e^{-E_a / RT}$  [5]
12. Dissolved metal catalysis: Ca, Mg, Fe, Co, and Ni were shown to catalyze hydrolysis of organophosphorus pesticides.
13. Soluble metal ions at concentrations in natural waters will NOT play a significant role.
14. p. 236-237: 9-2.3 Reactions of Organic Compounds:

p. 237: Ability of clay minerals to catalyze hydrolysis and rearrangement of alkenes is well known.
15. 9-3.1 Soil Type: proportion of sand, silt, and clay plays a significant role in hydrolysis of organic compounds. Greater clay fraction ----> greater hydrolysis rates.
16. p.239. Soil Temperature: For most abiotic hydrolysis reactions, hydrolysis rate constants increase with increasing temperature.
17. 9-3.6 Soil Water Content: degradation rates of pesticides often increase with increasing soil moisture content.
18. p.240. Enhanced acidity at soil surface may enhanced acid catalyzed hydrolysis of organic chemicals.
19. p. 240. Table 9-2. Study.