5. USING SIMPLE PARTITIONING MODELS

Simple air-water-soil partitioning models can be used to answer important questions about the: 1) transport vs. attenuation, 2) mass distribution, 3) monitoring, and 4) remediation strategy for organic contaminants in surface and ground waters. For example, in a soil or groundwater system, one very basic type of question that can be readily answered is that of contaminant-mass distribution in the solid, aqueous and gaseous phases. Two principles, or types of equations are involved: mass law and material balance.

A reaction for partitioning of chemical species A between aqueous (*w*) and organic-carbon (*s*) phases in soil:

$$A(w) \rightleftharpoons A(s) \tag{5.1}$$

has the equilibrium, or mass-law expression:

$$K_d = \frac{\left[A(s)\right]}{\left[A(w)\right]} \tag{5.2}$$

where $\left[A(s)\right]$ and $\left[A(w)\right]$ are the sorbed and aqueous concentrations, respectively, of species A. K_d is the equilibrium distribution constant. Note that (5.1) is a chemical reaction and (5.2) is a mass law expression.

In the sorption literature, equation (5.2) is often written as:

$$C_s = K_d C_w \tag{5.3}$$

where C_s is the sorbed concentration and C_w is the aqueous concentration. C_s has units of micrograms of contaminant per gram of solids $\mu\text{g g}_s^{-1}$. C_w typically has units of micrograms per cm^3 of water $\mu\text{g g}_w^{-3}$. For smaller concentrations, one would use ng g_s^{-1} and ng cm_w^{-3} for C_s and C_w, respectively. K_d has units of $\text{cm}_w^3\ \text{g}_s^{-1}$. Note that it is important to keep in mind the phase associated with the units - i.e. cm^3 of water and grams of soil.

A statement of material balance on the same system is: total contaminant mass is the sum of the mass in the aqueous phase and the mass sorbed. In equation form:

$$m_T = C_s M_s + C_w V_w \tag{5.4}$$

where m_T is the total contaminant mass in the system, M_s is the mass of solids in the system, and V_w is the volume of water in the system.

M_s and V_w must be measured. They are often expressed as mass or volume relative to the total volume of the system $\left(V_T\right)$. The ratio $\frac{M_s}{V_T}$ is simply the bulk density of the system $\left(\rho_b\right)$, with units of $\mathrm{g}_s\ \mathrm{cm}_T^{-3}$, grams solid per total cm^3. The ratio $\frac{V_w}{V_T}$ is equal to the porosity (θ) in a water-saturated soil, and has units of $\left(\mathrm{cm}_w^3\ \mathrm{cm}_T^{-3}\right)$. In unsaturated media one can define θ_s to be the fraction of the void volume filled with water $\left(\mathrm{cm}_w^3\ \mathrm{cm}_v^{-3}\right)$. So the ratio $\frac{V_w}{V_T}$ is $\theta\theta_s$; and the relative volume of air in the system is $\theta\left(1-\theta_s\right)$, or $\frac{V_A}{V_T}$.

Example 5.1:

In a water-saturated soil contaminated with trichloroethylene (TCE), a concentration of 200 ppb is measured in the water. How much total TCE is in the soil, per unit volume? What fraction of the TCE is in the water versus sorbed onto the solids? What is the sorbed concentration? Estimated properties of the media are: $\theta = 0.30\ \mathrm{cm}_w^3\ \mathrm{cm}_T^{-3}$, $\rho_b = 1.85\ \mathrm{g}_s\ \mathrm{cm}_T^{-3}$ and $f_{om} = 0.03$. The total mass per unit volume is:

$$\frac{m_t}{V_T} = C_w\theta + C_s\rho_b = C_w\left(\theta + \rho_b K_d\right) \qquad \text{(i)}$$

From section 4:

$$\log K_d = \log f_{om} + \log K_{om} \qquad \text{(ii)}$$

$$\log K_{om} = 0.88\log K_{ow} - 0.27 = 1.82 \qquad \text{(iii)}$$

For TCE, $\log K_{ow} = 2.42$. Thus $\log K_{om} = 1.86$ and $\log K_d = 0.3$ for this system. So $C_s = K_d C_w = 0.4\ \mu\mathrm{g}\ \mathrm{g}_s^{-1}$ and $\frac{m_T}{V_T} = C_w\theta + C_s\rho_b = 0.8\mu\mathrm{g}\ \mathrm{cm}_T^{-3}$. The fraction in the water is:

$$f_w = \frac{C_w\theta}{\frac{m_T}{V_T}} = \frac{C_w\theta}{C_w\left(\theta + \rho_b K_d\right)} = \frac{1}{1 + \frac{\rho_b}{\theta}K_d} \qquad \text{(iv)}$$

and the fraction sorbed is:

$$f_s = 1 - f_w = 1 - \frac{1}{\frac{1+\rho_b}{\theta K_d}} = \frac{\frac{\rho_b}{\theta} K_d}{1 + \frac{\rho_b}{\theta} K_d} \tag{v}$$

For the case given, $f_w = 0.075$ and $f_s = 0.925$. Most of the TCE is sorbed onto the soil.

Example 5.2

In an unsaturated soil a concentration of 200 ppm$_v$ of vinyl chloride is measured in the soil gas. How much total vinyl chloride is in the soil, per unit volume? What fraction of the vinyl chloride is in the air versus in the water versus sorbed onto the solids? What are the concentrations of vinyl chloride in the water and sorbed? Estimated media properties at the site are: $\theta = 0.3\ \text{cm}^3\ \text{cm}_T^{-3}$, $\theta_s = 0.7, \rho_b = 1.85\ \text{g cm}_T^{-3}$ and $f_{om} = 0.010$. The total mass per unit volume is:

$$\frac{m_T}{V_T} = C_a\left(1-\theta_s\right)\theta + C_w \theta\,\theta_s + C_s \rho_b \tag{i}$$

where C_a is the concentration in the air $\left(\mu\text{g cm}_a^{-3}\right)$. C_a and C_w are related by Henry's law:

$$C_w = \frac{C_a}{K_H'}$$

where K_H' for vinyl chloride is $0.92\ \text{cm}_w^3\ \text{cm}_a^{-3}$. In terms of C_w, the total mass per unit volume is:

$$\frac{m_T}{V_T} = C_w\left\{\left(1-\theta_s\right)\theta K_H' + \theta\,\theta_s + \rho_b K_d\right\} \tag{iii}$$

K_{ow} for vinyl chloride is 3.98; using (ii) and (iii) from Example 5.1 and equation 4.1b from Table 4.1 gives $\log K_d = -1.74$. Now the measured concentration was given as a volume fraction in air; to convert to C_a, use the ideal-gas law:

$$C_a = 10^6 \frac{n}{V_a} M_w = \frac{10^6 P M_w}{RT} \tag{iv}$$

where $\frac{n}{V_a}$ is the moles of vinyl chloride per volume of air, M_w is the molecular weight of vinyl chloride, P is the partial pressure of vinyl chloride, R is the gas constant and T is temperature ($RT = 24,450 \text{ cm}^3 \text{ atm mol}^{-1}$ for 298 °K). Thus $10^6 P$ is the volume fraction of vinyl chloride in air in ppm$_v$. M_w for vinyl chloride $\left(C_2H_3Cl\right)$ is 63 g mol^{-1}. A calculation gives $C_a = 0.51 \text{ mg cm}_a^{-3}$, $C_w = 0.56 \text{ mg cm}_w^{-3}$, $C_s = 0.010 \text{ mg g}_s^{-1}$, and $\frac{m_T}{V_T} = 0.011 \text{ mg cm}^{-3}$. The fractions in the air, water and sorbed are:

$$f_a = \frac{K_H'\left(1-\theta_s\right)\theta}{K_H'\left(1-\theta_s\right)\theta + \theta\theta_s + \rho_b K_p} = \frac{K_H' \frac{1-\theta_s}{\theta_s}}{K_H' \frac{1-\theta_s}{\theta_s} + 1 + \frac{\rho_b}{\theta\theta_s} K_d} = 0.44 \qquad \text{(v)}$$

$$f_w = \frac{\theta\theta_s}{K_H'\left(1-\theta_s\right)\theta + \theta\theta_s + \rho_b K_d} = \frac{1}{K_H' \frac{1-\theta_s}{\theta_s} + 1 + \frac{\rho_b}{\theta\theta_s} K_d} = 0.48 \qquad \text{(vi)}$$

$$f_s = \frac{\rho_b K_p}{K_H'\left(1-\theta_s\right)\theta + \theta\theta_s + \rho_b K_p} = \frac{\frac{\rho_b}{\theta\theta_s} K_d}{K_H' \frac{1-\theta_s}{\theta_s} + 1 + \frac{\rho_b}{\theta\theta_s} K_d} = 0.08 \qquad \text{(vii)}$$

For the case given, $f_a = 0.44$, $f_w = 0.48$ and $f_s = 0.08$. The vinyl chloride is primarily in the air and water phases.

Questions:

1. Derive expressions for the soil-to-water ratio $\left(\text{g}_s \text{ cm}_w^{-3}\right)$ for saturated and unsaturated cases, and the air-to-water ratio $\left(\text{cm}_a^3 \text{ cm}_w^{-3}\right)$ for the unsaturated case. Calculate the soil-to-water ratios $\left(r_{sw}\right)$ and air-to-water ratio $\left(r_{aw}\right)$ for examples 1 and 2.

2. A 5 5 10 m^3 volume of soil is thought to be contaminated with a mixture of methylene chloride $\left(\text{CH}_2\text{Cl}_2\right)$ and 1,4-dichlorobenzene (DCB). Log K_{ow} values for the two compounds are 1.15 and 3.38 respectively. Observed aqueous concentrations of CH_2Cl_2 and DCB are 100 ppb and 200 ppb, respectively, throughout the soil profile. Soil properties are $\theta = 0.30 \text{ cm}^3 \text{ cm}_T^{-3}$ and $\rho_b = 1.85 \text{ g}_s \text{ cm}_T^{-3}$, $f_{om} = 0.030$ in the top 2 m and $f_{om} = 0.002$ in the bottom 8 m. How much of each contaminant is present in each soil layer and at the whole site? What are the sorbed concentrations

of each contaminant in each layer? What fraction of each contaminant is sorbed versus in the water in each layer?

3. Immediately following a rain DDT is discovered at concentrations of 1.5 ppb in water in an agricultural soil $\left(f_{om} = 0.14\right)$. It is thought to be at this level in the top 20 cm of a 1.5 ha field. Assuming water saturated conditions and uniform soil properties and concentrations, how much DDT is present in the field? What fraction is sorbed vs in the water? What is the sorbed concentration? $\log K_{ow}$ for DDT is 6.36. Assume that $\theta = 0.3 \text{ cm}^3 \text{ cm}_T^{-3}$ and $\rho_b = 1.85 \text{ g}_s \text{ cm}_T^{-3}$.

4. Two compounds, naphthalene and tetrachloroethene (PCE) are found to be in an unsaturated soil. The aqueous naphthalene concentration is 50 ng cm^{-3} and the gas-phase PCE concentration is 20 ppm_V. How much of each is present per unit volume of soil? What are the air, water, and sorbed concentrations of each? What are the mass fractions of each contaminant in each of the three phases? Assume that $\theta = 0.3 \text{ cm}^3 \text{ cm}_T^{-3}$, $\theta_s = 0.75$, $\rho_b = 1.85 \text{ g}_s \text{ cm}_T^{-3}$ and $f_{oc} = 0.020$. $\log K_{ow}$'s are 3.36 and 2.88 and $\log K_H \left(\text{L atm mol}^{-1}\right)$ are –0.37 and 1.44 for naphthalene and PCE, respectively.