Environmental Chemistry, Homework set

Partitioning, part 2 - Solutions

1. Activated carbon for water treatment

TCA sorbs onto AC according to the Freundlich relationship $C_{i,s} = 2.5 * C_{i,w}^{2.94}$ where:

$C_{i,w}$: concentration in water (mg i/L water)

$C_{i,s}$: concentration in or on sorbent (mg i/g AC)

To lower the TCA concentration from 1 mg/L to 0.2 mg/L, we must absorb 0.8 mg TCA in every L of water. Futhermore, if $C_{i,w}$ = 0.2 mg/L, then at equilibrium, the TCA content of the AC is:

$$C_{i,s} = 2.5 * C_{i,w}^{2.94} = 0.022 \text{ mg/g AC}$$

So if each g of AC contains 0.022 mg of TCA, we need $\frac{0.8 \text{ mg TCA/L}}{0.022 \text{ mg TCA/g AC}} = 36.4 \text{ g AC/L}$ to sorb the necessary quantity of TCA.

2. Antibiotics in soil

The recommended limits are:

$C_{i,w}$ = 10 mg/m^3 = 0.01 mg/L

$C_{i,s}$ = 0.01 mg/kg

The aqueous solubility in units of mol/L is 0.078 M

Wanted: f_{oc} such that the limits are not exceeded.

Recall for the partitioning to organic matter: $K_{i,oc} = \frac{C_{i,oc}}{C_{i,w}} = \frac{C_{i,s}/f_{oc}}{C_{i,w}}$ Therefore: $f_{oc} = \frac{C_{i,s}}{C_{i,w}K_{i,oc}}$

So we first need to find $K_{i,oc}$. To do so, we first estimate K_{ow} of cipro, e.g., using the general relationship for pesticides:

$\log K_{i,ow} = -0.84 * \log C_{i,w}^{sat} + 0.12 = 1.05$ (Note that C_w^{sat} must be in units of mol/L)

From $K_{i,ow}$, we can estimate $K_{i,oc}$ using the relationship for halogenated phenylureas :

$\log K_{i,oc} = 0.62 * \log K_{i,ow} + 0.84 = 1.49$ (units of $K_{i,oc}$ are L / kg oc)

Finally, inserting into the equation for f_{oc} above we find: $f_{oc} = \frac{0.01 \, mg/kg}{0.01 \, mg/L * 10^{1.49}} = 0.032$

So the organic carbon content of the soil needs to be **at least 3.2%.** This is a fairly typical organic carbon content for soils.

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3. EDB groundwater spill

a) Given a density of 2.18 g/mL or kg/L, 0.2 L EDB correspond to 0.436 kg EDB. Dividing by the MCL of 0.00005 mg/L gives us the volume that EDB can contaminate: (0.436 kg)/(0.00005 mg/L) = **$8.72*10^9$ L**.

In all of the following, I left away the index "i" for simplicity. All variables "C_x" relate to the concentration of EDB in a phase x, where x can be water, solid, organic carbon or air.

b) The fraction of a compound in groundwater corresponds to:

$$f_w = \frac{C_w V_w}{C_w V_w + C_S M_s} = \frac{1}{1 + K_{oc} f_{oc} r_{sw}}$$

We can calculate r_{sw} based on the porosity and solid density:

$$r_{sw} = \frac{M_s}{V_w} = \rho_s \left(\frac{1-\Phi}{\Phi} \right) = 0.8 \text{ kg/L}$$

K_{oc} can be estimated based on K_{ow}. Because EDB (or dibromoethane) is a halogenated alkane with 2 carbons, we use the equation for C1 and C2 halocarbons:

$$\log K_{oc} = 0.57*\log K_{ow} + 0.66 = 1.78$$

Now we have all parameters we need to determine **f_w, which corresponds to 0.049**. So about 5% of EDB are in the groundwater.

c) Now we replace all the water by air, so EDB partitions between the solid and the air (whereas there is no more water in the system). The fraction of EDB in air can be expressed as:

$$f_a = \frac{C_a V_a}{C_a V_a + C_S M_s} = \frac{1}{1 + \frac{C_s}{C_a}\frac{M_s}{V_a}} = \frac{1}{1 + K_{sa} r_{sa}}$$

K_{sa} corresponds to C_s/C_a, and can be calculated as $(C_s/C_w)/(C_a/C_w) = K_{oc}f_{oc} / K_{aw}$ = 855 L/kg.

r_{sa} corresponds to the ratio of the mass of solid to the volume of air. As all the water from exercise b was replace by air, while the mass of solid is the same, r_{sa} corresponds to r_{sw} from exercise b, and is 0.8 kg/L.

Now we can determine f_a, which corresponds to **0.0015**.

d) To compare the price of the remediation method, determine how much EDB can be removed at the same price for each technology. For the price of one g of activated carbon, we can buy 10000 L or air. Then lets compare the residual fractions of EDB in water if the EDB is stripped into 10000 L of air, or if the EDB is adsorbed onto 1 g of carbon.

If we add 10000 L of air per L of water, the fraction of EDB remaining in water will be (K_{aw} is given in exercise 1, and r_{aw} corresponds to 10000/1):

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$$f_w = \frac{C_w V_w}{C_w V_w + C_a V_a} = \frac{1}{1 + \frac{C_a V_a}{C_w V_w}} = \frac{1}{1 + K_{aw} r_{aw}} = 0.0035$$

For activated carbon, we can assume a linear adsorption model. We can therefore write for the distribution coefficient of EDB between solid and water, $K_{i,d}$ (or $K_{i,\,sw}$):

$K_{i,d} = K_{i,sw} = C_s/C_w$

Because all of the solid is organic carbon ($f_{oc} = 1$), we can say that $C_s = f_{oc}\, C_{oc} = C_{oc}$

We can re-write the distribution coefficient between water and solid as: $K_{i,d} = C_{ioc}/C_w = K_{i,oc}$

$K_{i,oc}$ can be estimated based on $K_{i,ow}$, as was done in the first exercise. Because dibromoethane is a halogenated alkane with 2 carbons, we use the equation for C1 and C2 halocarbons:

$\text{Log } K_{i,oc} = 0.57 * \log K_{i,ow} + 0.66 = 1.78$

If we add 1 g of activated carbon to 1 L of water, the fraction of EDB in water corresponds to:

$$f_w = \frac{C_w V_w}{C_w V_w + C_{oc} M_{oc}} = \frac{1}{1 + \frac{C_{oc} M_{oc}}{C_w V_w}} = \frac{1}{1 + K_{oc} * 0.001 \frac{kg}{L}} = 0.94$$

So in this case, **air stripping is a more economical method,** it is much more efficient at reducing the residual fraction in water at same price. (Note that the difference in efficiency depends on how much air and carbon is ultimately used, but air is always a better option).

4. Inhalation of chloroform

To answer this question, we need to know the distribution of chloroform between air and water. For this, we need to determine the K_H. K_H can be estimated as p^*_L / C_w^{sat}. We have p^*_L, but not C_w^{sat}. However, we can estimated it from the activity:

$$C_{i,w}^{sat} = \frac{1}{\gamma_{i,w} 0.018 \, L/mol} = 0.0067M$$

Now we can estimate K_H at 25 C:

p^*_L / C_w^{sat} = 0.257/0.0067 = 38.4 atm/M

From this, we can estimate K_H at 35 °C. We use the Antoine equation, or the "shortcut" table given in the partitioning lecture notes. From the table, we find that – given an enthalpy of 30 kJ/mol - for each increase of 10 degrees in temperature, K increases by a factor 1.53. So

K_H (35 C) = 1.53*38.4 = 58.8 atm/M.

The total mass of chloroform in your bathroom all comes from the water, so we have 100 L * 10^{-6} M = 10^{-4} mol. After distributing between air and water, the fraction of chloroform in air is:

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$$f_a = \frac{C_a V_a}{C_a V_a + C_w V_w} = \frac{1}{1 + \frac{RT}{K_H}\frac{V_w}{V_a}} = 0.997$$

This means that basically all chloroform is in air. This means that we have about 10^{-4} mol / 20000 L air = $5*10^{-9}$ mol/L air.

Over the course of 10 minutes you breathe 120 L of air. Overall, you will inhale 120 *($5*10^{-9}$) = **$6*10^{-7}$mol during your bath**.