Exercise 1 - solution

In order to increase the activity coefficient of a given compound by a factor of ten, the exponent (K^s_i[salt]) has to be equal to 1.

$$K^s_i[\text{salt}] = 1$$

The K^s_i value of hexane for NaCl is 0.28 M^{-1} (see Table).

Then a total salt concentration of 1/0.28 M^{-1} = 3.57 M is needed, which corresponds to an amount of 208.8 kg/m^3.

Exercise 2 - solution

Given: Maximum Contaminant Level (MCL) of benzene: 0.005 mg/L
Solubility of benzene: 1.8 g/L = 0.02 M
Denisty = 0.87 kg/L

a): LNAPL (density < 1)

b) 1.5 L benzene = 1.305 kg (from: density*volume)
(Total mass) / (soluble mass/L)= 1305 g / 1.8 g/L = 725 L

c) Potential to ruin drinking water:
(Total mass) / (MCL) = 1305 g / 0.000005 g/L = 261’000’000 L

Exercise 3 - solution

Compund	Log K_{ow}
Chloroform	1.97
Dioxine	6.8
DDT	6.19
Naphtalene	3.35
Trichloroethylene	2.42

A high log K_{ow} indicates a low water solubility. So the aqueous concentration will be:

chloroform > TCE > naphtalene > DDT > dioxine

Exercise 4 - solution

a) At first, 100% of the mass of CH_3-CH_2-S-CH_2-CH_3 is in the water. After the addition of octanol, we want 90 % of the mass of CH_3-CH_2-S-CH_2-CH_3 to be in octanol. So we want:

$$V_{octanol} * C_{i, octanol} = 9 * V_{water} * C_{i, water}$$ (the subscript i stands for CH_3-CH_2-S-CH_2-CH_3).

We rearrange to:

$$V_{octanol} / V_{water} = 9 * C_{i, water} / C_{i, octanol} = 9/K_{i,ow}$$

We can estimate $K_{i,ow}$ based on the aqueous solubility ($C_{i,w}^{sat}$) of CH_3-CH_2-S-CH_2-CH_3. We don't know $C_{i,w}^{sat}$, but we can determine it from the activity coefficient $\gamma_{i,w}$ using the relationship:

$$C_{i,w}^{sat} = \frac{1}{\gamma_{i,w} \bar{v}_w} = \frac{1}{\gamma_{i,w} 0.018\ L/mol} = 0.0022\ M$$

Now that we know C_w^{sat}, we can use it to estimate $K_{i,ow}$. Since CH_3-CH_2-S-CH_2-CH_3 behaves similarly to alkanes, we can use the relationship developed for alkanes (see Table in the notes):

$$\log K_{i,ow} = -0.81 * \log C_{i,w}^{sat} - 0.2 = 1.95$$, so $K_{i,ow} = 10^{1.95}$

Now we can calculate $V_{octanol}$ needed for 1L of groundwater:

$$\mathbf{V_{octanol} = 9 * V_{water} / K_{i,ow} = 0.1\ L}$$

b) Recall that $K_{i,ow} = \frac{1}{C_{i,w}^{sat}} \frac{1}{\gamma_{i,o} \bar{v}_o}$.

$K_{i,ow}$ is primarily determined by $C_{i,w}^{sat}$ ($\gamma_{i,o}$ is usually close to 1, and $\bar{v}_o$ does not depend on i). $C_{i,w}^{sat}$ is not very senstive to changes in temperature ($\Delta_{wL}H_i \approx 0$). So $K_{i,ow}$ is not very sensitive to temperature changes either. Increasing the temperature is not a good strategy to improve the extraction.

Exercise 5 - solution

In this situation, we can assume chemical equilibrium between benzene in the pure liquid phase and in the gas phase. Therefore, the partial pressure of benzene in the air in the bottle corresponds to its liquid vapor pressure:

$$p_{benzene} \text{ in the bottle} = p^*_{benzene,\,L}$$

To convert the pressure to concentration, we use the ideal gas law:

$nRT = pV$ or $C_{benzene\ in\ air} = p_{benzene} / RT = p^*_{benzene,\,L} / RT = 10^{4.1}$ Pa /(8314 $M^{-1}\cdot Pa\cdot K^{-1}$*298 K) = **0.005 M**

(Make sure to use R in the correct units of pressure!)

Exercise 6 - solution

Answer (a)

The air–water partition constant, K_{iaw}, of benzene is 0.22 at 25°C (Appendix C), The quotient of the concentrations of benzene in the air and in water is:

$$\frac{C_{ia}}{C_{iw}} = \frac{0.05}{0.4} = 0.125$$

Hence, at 25°C, $C_{ia}/C_{iw} < K_{iaw}$, and therefore, there is a net flux from the water to the air (the system wants to move toward equilibrium).

Answer b)

For T-correction, use table 3.5 or $\ln\frac{K_{12}}{K_{12}} = \frac{\Delta_{12}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Based on table, for ΔH_{12}=30kJ/mol, $K_{i,aw}$ decreases a factor of 1.53 for every 10°C decrease in temperature. So for a temperature decrease of 20°C,

$K_{i,aw}(5°C)=(K_{i,aw}(25°C)/(1.53^2)= 0.093$

Thus, at 5°C the ratio $C_{ia}/C_{iw} > K_{iaw}$; therefore, this time there is a net flux from the air to the water.

This example shows that the direction of gas exchange may be strongly influenced by temperature.

Exercise 7 - solution

First, calculate K_H in pure water.
Convert pressure to units of atm: 1 atm = 101 325 Pascal or approx. 10^5 Pa
So = $p^*_{iL} = 10^{-3.01}$ Pa = $10^{-8.01}$ atm.

$K_{i,H} \approx p^*_{iL}/C_w^{sat} = 10^{-8.01}/10^{-6.6} = 10^{-1.41}$ atm/M = 0.038 atm/M

Now use the relationship $K_{i,H,salt} = K_{i,H} * 10^{+K_i^s[salt]}$ to determine K_H in seawater.

According to table 5.7 (see earlier slide), K^s(anthracene) = 0.3, and [salt]= 0.6 M

K_H(seawater) $=10^{-1.41}*10^{0.3*0.6} = 10^{-1.23}$ atm/M

So K_H in seawater increases by a factor 1.51. Anthracene is “salted out” and escapes more easily into the atmosphere.

Exercise 8 - solution

With 10 ppbv the partial pressure of benzene in the air is $p_i = 10 \times 10^{-9}$ bar $= 10^{-8}$ bar, which corresponds to a concentration of:

$$C_{ia} = \frac{p_i}{RT} = \frac{10^{-8}}{(0.0831)(298)} = 4.0 \times 10^{-10}\ \mathrm{mol \cdot L^{-1}} = 0.03\,\mu\mathrm{g \cdot L^{-1}}$$

For estimating the air–olive oil partition coefficient, calculate first the air–octanol partition constant from the air–water (K_{iaw}) and octanol–water (K_{iow}) partition constants given in Appendix C (Eq. 6-11):

$$K_{iao} = \frac{K_{iaw}}{K_{iow}} = \frac{10^{-0.65}}{10^{+2.17}} = 10^{-2.82}$$

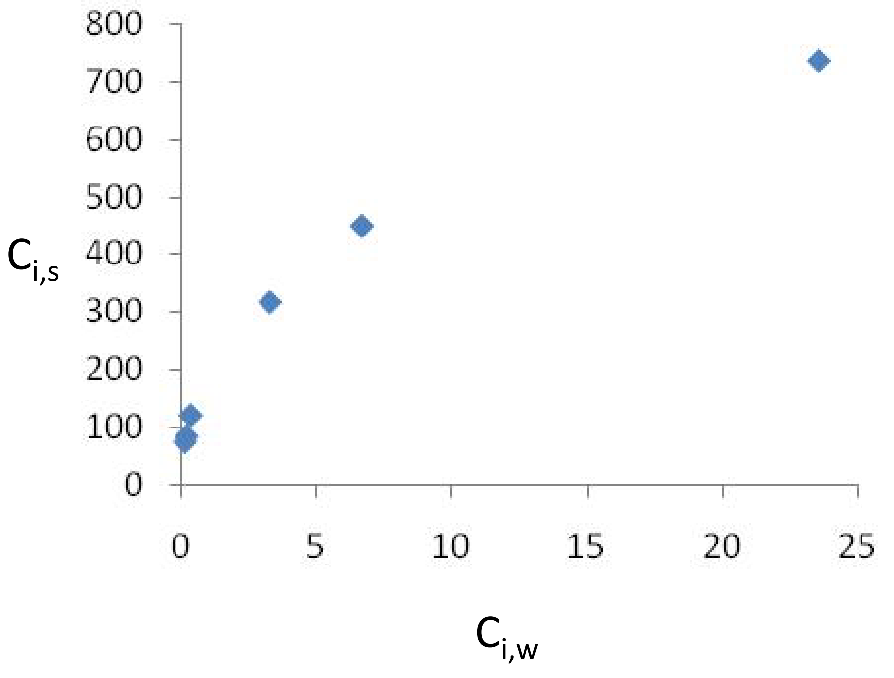
Use the LFER shown in Fig. 6-7 for alkyl aromatic compounds ($\log K_{ia\ \mathrm{olive\ oil}} = 1.08 \log K_{iao} + 0.22$) to estimate the air–olive oil partition coefficient:

$$\log K_{ia\ \mathrm{olive\ oil}} = (1.08)\,(-2.82) + 0.22 = -2.83$$

Hence, the estimate yields *a* $K_{i,\ a\text{-}olive\ oil}$ value of about 10^{-3}, and thus a maximum benzene concentration in the olive oil of 30 µg/L (calculated using the relationship: $K_{i,\ a\text{-}olive\ oil} = C_{i,a}/C_{i,olive\ oil}$).

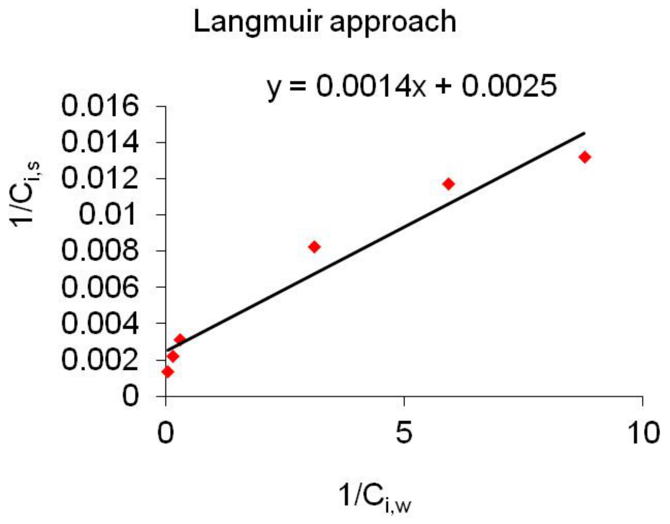
Considering that the drinking water standard for benzene is 5 µg/L, this should not cause a serious health problem, assuming that your daily olive oil intake is much smaller than your daily water intake.

Exercise 9 - solution



Does not look like a linear relationship. Try Langmuir and Freundlich.

Exercise 9 - solution

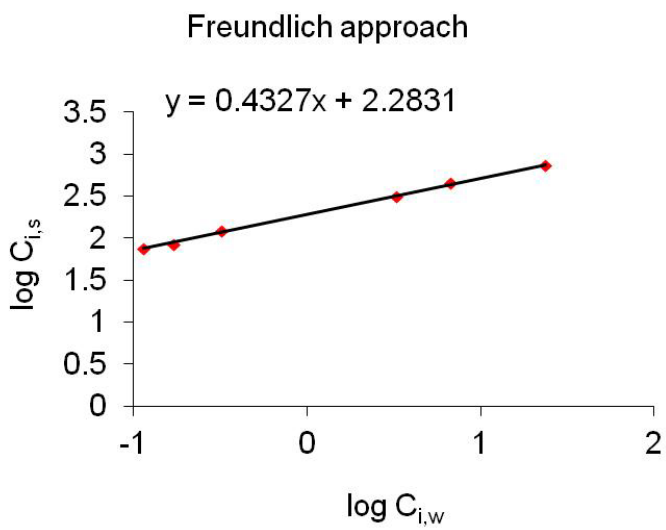


$$C_{i,s} = \frac{K_{i,L}\Gamma_{\max}C_{i,w}}{1+K_{i,L}C_{i,w}}$$

$$\frac{1}{C_{i,s}} = \frac{1}{K_{i,L}\Gamma_{\max}}\frac{1}{C_{i,w}} + \frac{1}{\Gamma_{\max}}$$

Intercept = $1/\Gamma_{max} \rightarrow \Gamma_{max}$ = 400 μg/g

Slope = $1/(\Gamma_{max}*K_{i,L}) \rightarrow K_{i,L}$= 0.003 L/μg



$$C_{i,s} = K_{i,F}C_{i,w}^{n}$$

$$\log C_{i,s} = \log K_{i,F} + n * \log C_{i,w}$$

Slope = n = 0.4327

Intercept =log $K_F \rightarrow K_F$ = 191.9 [μg/g]/([μg/ L]^n)

This seems to fit the data best.

Exercise 10 - solution

To lower the concentration to 0.05 mM H_2S, we must absorb 0.05 mmol of H_2S from every L.

Using the sorption isotherm, determine how much H_2S can be on the carbon if $C_{i,w}$ = 0.05 mM.

$$C_{i,s} = K_{i,F} C_{i,w}^{n}$$

We find that $C_{i,s}$ is 0.633 mmol/g. So if we add 0.1 g of activated carbon to each L of water, we can remove 0.063 mmol/L, which is enough (need to remove at least 0.05 mmol per L).

Exercise 11 - solution

First recognize that 25 mm/m^2 of rain corresponds to 25 L. This is the volume of water.
The volume of air is 5000 m*1m^2.

In summary:
V_a = 5000 m^3
V_w= 0.025 m^3
V_a/V_w= 2*10^5

The fraction of Lindane in the water phase is given by:

$$f_w = \frac{[L]_w V_w}{[L]_w V_w + [L]_a V_a} = \frac{1}{1+\frac{K_H}{RT}\frac{V_a}{V_w}} = \frac{1}{1+\frac{3.2*10^{-3}\, atm/M}{24.46\, atm/M}*2*10^5} = 0.0365$$

Again pay attention to use the correct units of R. Here, R = 0.082 L·atm·K^{-1}·mol^{-1}.

So even though Lindane is (relatively speaking) quite soluble, only 3.65% is washed out by rain.

Exercise 12 - solution

We again need to calculate the fraction of lindane in water, but this time in equilibrium with the aquifer:

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

Note that the sorbed concentration C_s is in units of mass of i/mass of sorbent. To obtain the total mass of i, we must multiply with the <u>mass</u> of the sorbent, not the volume!

We can estimate $K_{lindane,\ oc}$ using the relationship for chloroalkanes (see table some slides back):

$$log\ K_{oc} = 0.42 * log\ K_{ow} + 0.93 = 2.52$$

What is r_{sw}? r_{sw} in lakes and rivers corresponds to the particle concentration, and is about 10^{-6} kg_s/L. In porous material (groundwater), r_{sw} is higher, about 0.1 -10 kg_s/L. It is determined by the porosity Φ and the density of the solid ρ_s (kg_s/L_s):

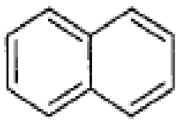
$$r_{sw} = \frac{M_s}{V_w} = \rho_s \left(\frac{1 - \Phi}{\Phi} \right) \qquad \rho_s = \frac{M_s}{V_s} \qquad \Phi = \frac{V_w}{V_{tot}}$$

Assuming r_{sw} = 1 kg_s/L and f_{oc} = 0.5, we find:

$$f_w = 0.01$$

So almost all lindane is adsorbed in the aquifer, and only 1 in 100 molecules will be moving with the groundwater. This phenomenon of diminished chemical transport compared to water transport is called <u>retardation</u>, and the <u>retardation factor</u> corresponds to $1/f_w$.

Exercise 13 - solution



i=naphthalene

$K_{iaw} = 10^{-1.76}$

$K_{ifw} \approx K_{iow} = 10^{3.36}$

$r_{fw} = 10^{-3}$

$r_{fa} = 10^{-3}$

In the Appendix C you find the air–water partition constant (K_{iaw}) of naphthalene and its octanol–water partition coefficient (K_{iow}) that you use as surrogate for the fat–water partition coefficient, K_{ifw}). Note that these entities are given as ratios of molar concentrations. Use the fat (octanol) as phase 1 and calculate the fat–air (octanol–air) partition constant, K_{ifa}:

$$K_{ifa} = \frac{K_{ifw}}{K_{iaw}} = \frac{10^{3.36}}{10^{-1.76}} = 10^{5.12}$$

Insertion of K_{ifw}, K_{ifa}, r_{fw}, r_{fa} into Eq. 3-65 yields the fraction in the fat blob:

$$f_{if} = \frac{1}{1 + \frac{1}{10^{3.36}} \cdot \frac{1}{10^{-3}} + \frac{1}{10^{5.12}} \cdot \frac{1}{10^{-3}}} \cong 0.7$$

Hence, you would take up *0.7* mg of the 1mg total naphthalene if only eating the fat blob, or you would take up only *0.3* mg when leaving the fat blob, and just eating the soup (the part in the air can more or less be neglected).