Remediation of soils and groundwater
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Problem set #1: contaminant properties

<u>Problem 1</u>:
Select units: mass in g and volume in m^3

Soil in closed bottle 10 mL gas = 10^{-5} m^3 = V_G
90 mL water = $9 \cdot 10^{-5}$ m^3 = V_L

M_S = 36 mg = $3.6 * 10^{-2}$ g solid

$$\rho_s = 1 \frac{g}{cm^3} * \frac{10^6 cm^3}{m^3} = 10^6 \frac{g}{m^3}$$

(this calculation is not necessary for this exercise)

f_{OC} = 0.1
10 mg PCE= 10^{-2} g
MW_{PCE} = 166 g/mol
K_H' = 0.6 [-]
Log K_{OW} = 2.67 [-]

<u>Calculating K_D</u>

$$\log K_{OC} = 0.989 \cdot \log K_{OW} - 0.346 = 2.29$$

$$K_D = f_{OC} \cdot K_{OC} = 19.7 \frac{m^3}{g}$$

<u>Mass balance:</u>

$$\boxed{m_{PCE,aq} + m_{PCE,g} + m_{PCE,s} = m_{PCE,t} = 10^{-2} g} \qquad (1)$$

<u>Partitioning coefficients:</u>

$$K_H' = \frac{C_{PCE,g}}{C_{PCE,aq}};\ C_{PCE,g} = C_{PCE,aq} * K_H'$$

$$m_{PCE,g} = C_{PCE,g} * V_G;\ m_{PCE,g} = C_{PCE,aq} * K_H' * V_G$$

$$m_{PCE,aq} = C_{PCE,aq} * V_L;\ C_{PCE,aq} = \frac{m_{PCE,aq}}{V_L}$$

$$\boxed{m_{PCE,g} = m_{PCE,aq} * \frac{K_H' * V_G}{V_L}} \qquad (2)$$

Similarly,

$$K_D = \frac{C_{PCE,s}}{C_{PCE,aq}};\ C_{PCE,s} = C_{PCE,aq} * K_D$$

$$m_{PCE,s} = C_{PCE,s} * M_S;\ m_{PCE,s} = C_{PCE,aq} * K_D * M_S$$

$$\boxed{m_{PCE,s} = m_{PCE,aq} * \frac{K_D * M_S}{V_L}} \qquad (3)$$

<u>Three equations (1) through (3) and three unknowns (</u>$m_{PCE,aq}, m_{PCE,s}, m_{PCE,g}$)

From equation (1):

$$m_{PCE,aq} + \frac{K'_H \cdot V_G}{V_L} \cdot m_{PCE,aq} + \frac{K_D \cdot M_S}{V_L} \cdot m_{PCE,aq} = 10^{-2} g = m_{PCE,total}$$

$$m_{PCE,aq} = \frac{10^{-2} g}{\frac{0.6 \cdot 10^{-5} m^3}{9 \cdot 10^{-5} m^3} + \frac{19.7 \frac{m^3}{g} \cdot 36 \cdot 10^{-3} g}{9 \cdot 10^{-5} m^3} + 1} = \frac{10^{-2} g}{0.0666 + 7880 + 1}$$

$$m_{PCE,aq} = 1.27 \cdot 10^{-6} g$$

$$m_{PCE,s} = 1.27 \cdot 10^{-6} g * \frac{19.7 \frac{m^3}{g} * 3.6 * 10^{-2}\ g}{9 * 10^{-5}\ m^3} = 10^{-2} g$$

$$m_{PCE,g} = 1.27 \cdot 10^{-6} g * \frac{6 * 10^{-1} [-] * 10^{-5} m^3}{9 \cdot 10^{-5} m^3} = 8.46 \cdot 10^{-8} g$$

Most of the PCE is associated with the solid phase.

Problem 2:
Decide on the the units. L for volume, g for mass.

$C_{cont,initial} = 100 \frac{\mu g}{L} = 100 \frac{\mu g}{L} * \frac{1 g}{10^6 \mu g} = 10^{-4} \frac{g}{L}$

$$V_{L,initial} = 100\ mL * \frac{1 L}{1000\ mL} = 0.1\ L$$

Overall mass is equal to the volume of the original solution x original concentration
$m_{cont,total} = C_{cont,initial} * V_L = 10^{-4} \frac{g}{L} * 0.1\ L = 10^{-5}$ g

Also, the total mass is equal to what is in the 1L bottle after transfer
$m_{cont,total} = m_{cont,g} + m_{cont,aq}$
$m_{cont,total} = C_{cont,g} . V_G + C_{cont,\ aq} . V_L = C_{cont,aq} * K'_H \cdot V_G + C_{cont,\ aq} . V_L$
$m_{cont,total} = C_{cont,\ aq} * (K'_H \cdot V_G + V_L)$

$$C_{cont,aq} = \frac{m_{cont,total}}{K'_H \cdot V_G + V_L}$$

$C_{benz,\ aq} = 3.42 * 10^{-5}$ g/L

$C_{tol,\ aq} = 3.21 * 10^{-5}$ g/L

$C_{ethylbenz,\ aq} = 2.57 * 10^{-5}$ g/L

$C_{xyl,\ aq} = 2.62 * 10^{-5}$ g/L

The actual concentration in the aqueous phase is much lower than the intended concentration. This solution needs to be stored with minimal headspace to minimize the volatilization of the compounds.

Problem 3:
Decide on the units: kg for mass of soil, g for mass of contaminant, m^3 for volume.

$C_{benz,s,initial}$ = 900 mg/kg dry soil= 0.9 g/kg dry soil
K_D = 0.02 m^3/kg
Solids concentration = 40 kg dry soil/m^3 slurry
V_T = volume of slurry = 500 m^3
ρ_s = 2,000 kg/m^3
assume no headspace

a- What is V_L?
$M_S = \frac{40kg}{m^3 slurry} \cdot 500\ m^3$ slurry= 20,000 kg soil
$V_S = \frac{M_S}{\rho_S}$ = 20,000 kg $\cdot \frac{1m^3}{2{,}000kg}$ = 10 m^3
$V_L = V_T - V_S$ = 490 m^3

b - what is $C_{benz, aq}$?
Soil was added to the reactor and had an initial concentration of benzene. Therefore,
$m_{benz,total} = C_{benz,s,initial} * M_S == 0.9 \frac{g}{kg\ soil} *$ 20,000 kg soil= 18,000 g

$m_{benz,total} = m_{benz,s} + m_{benz,aq}$
$m_{benz,total} = C_{benz,\ s} \cdot M_S + C_{benz,\ aq} \cdot V_L = C_{benz,\ aq} K_D M_S + C_{benz,\ aq} V_L$

$$C_{benz,\,aq} = \frac{mbenz,total}{K_D \cdot M_s + V_L} = \frac{18{,}000g}{0.02\frac{m^3}{kg} \cdot 20{,}000\ kg + 490m^3} = 20.2\frac{g}{m^3}$$

Problem 4:
Choose units for the problem.
mg for contaminant mass; g for soil mass; m^3 for volume

A – In a river
C_{SS} = 10 mg/L= $10\ \frac{mg}{L} * \frac{1000\ L}{m^3} * \frac{g}{1000\ mg} = 10\frac{g}{m^3}$
$K_{OW} = 10^6$ (PCB) [-]
ρ_S = 1 g solid/cm^3 solid
f_{OC} = 0.1 [-]

What is the distribution of PCB between water and suspended solids?

$$K_D = 0.63 \cdot 10^{-6} \cdot f_{OC} \cdot K_{OW} = 6.3 \cdot 10^{-2} \frac{m^3}{g}$$

Fraction in the solid phase:

$$f_{PCB,s} = \frac{m_{PCB,s}}{m_{PCB,s} + m_{PCB,aq}} = \frac{\frac{m_{PCB,s}}{m_{PCB,aq}}}{\frac{m_{PCB,s}}{m_{PCB,aq}} + 1}$$

$$\frac{m_{PCB,s}}{m_{PCB,aq}} = K_D \cdot C_{SS} = 6.3 \cdot 10^{-2} \frac{m^3 solution}{g\ dry\ solid} \cdot 10 \frac{g\ dry\ solid}{m^3 solution} = 0.63 \frac{g\ PCB\ on\ solid}{g\ PCB\ in\ solution}$$

$$f_{PCB,s} = \frac{0.63}{1.63} = 0.39$$

Comment: over 1/3 of the PCB is on solids even if the solids represent 0.001 % of the total volume

B - For carbon tetrachloride CCl_4 (CT)

$K_{OW} = 440$

$\rho_S = 1.1\ g/cm^3 = 1.1 \frac{g}{cm^3} * \frac{10^6 cm^3}{m^3} == 1.1 * 10^6 \frac{g}{m^3}$

$f_{OC} = 0.02$

$$K_D = 0.63 \cdot 10^{-6} \cdot f_{OC} \cdot K_{OW} = 5.54 \cdot 10^{-6} \frac{m^3}{g}$$

Dimensionless partitioning coefficient:

$$K_p = \frac{C_{CT,s}\ in \frac{g}{m_S^3}}{C_{CT,aq}\ in \frac{g}{m_{aq}^3}}$$

$$K_p = K_D . \rho_s = 5.54 \cdot 10^{-6} \frac{m^3}{g} * \ 1.1 * 10^6 \frac{g}{m^3} = \ 6.1\ [-]$$

C - Mass distribution

$V_S/V_T = 10^{-4}$; an approximation is that $V_S/V_L \sim 10^{-4}$

$$\frac{m_{CT,s}}{m_{CT,aq}} = \frac{C_{CT,s,vol} * V_S}{C_{CT,aq} * V_L} = K_p \frac{V_S}{V_L} = 6.1\ 10^{-4}$$

For CT, the distribution between solid and aqueous phase is very different as compared to PCBs. This is due to the difference in K_{OW}. PCBs have a high K_{OW} because they are hydrophobic and tend to associate with organic matter.