**Remediation of soil and groundwater**
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**Problem set #6 solution: soil treatment and washing**

Problem 1: Windrow

$V_{soil}$= 40,000 $m^3$
target time for remediation: <365 days
initial concentrations
$C_{TPH, s, avg}$= 10,000 mg/kg $C_{TPH, s, max}$= 98,000 mg/kg
Final concentrations
$C_{TPH, s, avg}$= 100 mg/kg $C_{TPH, s, max}$= 500 mg/kg

$K_D$=0.039 $m^3.kg^{-1}$
$K'_H$=6*$10^{-6}$ [-]
Soil: porosity ε=0.3 [-].
Volumetric water content θ=0.1 [-]
Wet bulk density $\rho_{wb}$=1500 $kg.m^{-3}$

$M_T$= $V_{soil}$* $\rho_{wb}$= 40000 $m^3$ * 1500 $kg.m^{-3}$ = 6.0 * $10^7$ kg
$V_L$= $V_{soil}$* θ= 40000 $m^3$ * 0.1= 4000 $m^3$
$M_{water}$= $V_L$* $\rho_{water}$ = 4000 $m^3$ * 998 $kg.m^{-3}$ = 4.0 * $10^6$ kg
$M_S$= $M_T$- $M_{water}$=6.0 * $10^7$ kg-4.0 * $10^6$ kg= 5.6* $10^7$ kg (gas phase is assumed not to weight anything)
$V_{void}$= $V_{soil}$* ε= 40000 $m^3$ * 0.3= 12000 $m^3$
$V_G$= $V_{void}$- $V_L$=12000 $m^3$-4000 $m^3$=8000 $m^3$

Degradation takes place in the aqueous phase, therefore the first order degradation is based on solution concentrations.

$$\ln\left(\frac{C_{aq,t}}{C_{aq,0}}\right) = -kt$$

We must calculate equivalent aqueous phase concentrations for the above solid-phase associated concentrations.
To do so, we know that

$$C_{i,aq} = \frac{m_{i.tot}}{V_L + K_D M_S + K_H^{'} V_G}$$

So, we must calculate the mass of contaminant, and we must know the characteristics of the contaminant and the soil.

initial

$m_{i.tot,avg}$= 10,000 mg/kg* 5.6* $10^7$ kg * (1kg/$10^6$ mg) = 5.6* $10^5$ kg
$m_{i.tot,max}$= 98,000 mg/kg* 5.6* $10^7$ kg * (1kg/$10^6$ mg) = 5.5* $10^6$ kg

Final
$m_{i.tot,avg}$= 100 mg/kg* 5.6* $10^7$ kg * (1kg/$10^6$ mg) = 5.6* $10^3$ kg
$m_{i.tot,max}$= 500 mg/kg* 5.6* $10^7$ kg * (1kg/$10^6$ mg) = 2.8* $10^4$ kg

We can calculate the $C_{i,aq}$ (and we will here) but those values are proportional to the mass.

Calculate the corresponding $C_{i,aq}$

$V_L + K_D M_S + K'_H V_G = 4000\ m^3 + 0.039 \frac{m^3}{kg} * 5.6 *\ 10^7 kg + 6 * 10^{-6} * 8000\ m^3 = 2.2 * 10^6 m^3$

initial
$C_{i.aq,avg}$= 5.6* $10^5$ kg/$2.2 * 10^6 m^3$=$2.5 * 10^{-1} kg.m^{-3}$
$C_{i.aq,max}$= 5.5* $10^6$ kg/$2.2 * 10^6 m^3$=$2.5\ kg.m^{-3}$

Final
$C_{i.aq,avg}$= 5.6* $10^3$ kg/$2.2 * 10^6 m^3 = 2.5 * 10^{-3} kg.m^{-3}$
$C_{i.aq,max}$= 2.8* $10^4$ kg/$2.2 * 10^6 m^3 = 1.3 * 10^{-2} kg.m^{-3}$

How much time will it take?

For the average concentrations:

$$t = -\frac{1}{0.07} * \ln\left(\frac{2.5 * 10^{-3}}{2.5 * 10^{-1}}\right) = 66\ days$$

For the maximum concentrations:

$$t = -\frac{1}{0.07} * \ln\left(\frac{1.3 * 10^{-2}}{2.5}\right) = 76\ days$$

It should not be a problem to degrade the contaminant within the target time of 1 year.

Problem 2: slurry and biopile

$C_6 H_{14} + 9.5\ O_2 \Rightarrow 6\ CO_2 + 7\ H_2O$

On a mass basis:

$$\frac{1\ mole\ C_6H_{14}}{9.5\ moles\ O_2} \times \frac{1\ mole\ O_2}{32\ g\ O_2} \times \frac{86\ g\ C_6H_{14}}{1\ mole\ C_6H_{14}} = \frac{86\ g\ C_6H_{14}}{304\ g\ O_2} = \frac{1\ g\ C_6H_{14}}{3.5\ g\ O_2}$$

Given that air-saturated water contains 8 to 10 mg/L (depending on the temperature), we will consider a concentration of 9 mg/L.
For 1 g of hydrocarbon:

$$\frac{3.5\ g\ O_2\ required}{\frac{9\ mg\ O_2}{1\ L\ H_2O} \times \frac{1g}{1{,}000\ mg}} = 390\ L\ H_2O$$

To determine how much water is needed to treat 90% of the TPH here, let us first calculate the total mass of TPH.

$M_T = V_{soil} * \rho_{wb} = 3300\ m^3 * 1440\ kg.m^{-3} = 4.8 * 10^6\ kg$
$V_L = V_{soil} * \theta = 3300\ m^3 * 0.2 = 660\ m^3$
$M_{water} = V_L * \rho_{water} = 660\ m^3 * 998\ kg.m^{-3} = 6.6 * 10^5\ kg$
$M_S = M_T - M_{water} = 4.8 * 10^6\ kg - 4.8 * 10^6\ kg = 4.1 * 10^6\ kg$

$m_{i,tot} = 30{,}000\ mg/kg * 4.1 * 10^6\ kg * (1kg/10^6\ mg) = 1.2 * 10^5\ kg$

The mass of TPH to degrade is then
$m_{i,tot,deg} = 0.9 * 1.2 * 10^5 kg = 1.1 * 10^5 kg = 1.1 * 10^8 g$

$$\frac{390\ L\ water}{1\ g\ TPH} \times 1.1 * 10^8\ g\ TPH \times \frac{1\ m^3}{1{,}000 L} = 4.3 * 10^7\ m^3\ air\ saturated\ water$$

43 million cubic meters is not feasible in a slurry system. This is not surprising given the high concentration of contaminant. Slurry phase bioremediation is not a good option in that case.
Hence, the plan to use biopiles in which air is delivered.

We can calculate the removal rate per operation phase but first, we need to convert the solid phase concentration into total mass.

$m_{i,tot} = C_{i,s} * M_S$
For instance for OC 1:
initial
$$m_{i,tot} = 30000 \frac{mg}{kg} * 4.1 * 10^6\ \text{kg} * \left(\frac{1\text{kg}}{10^6 g}\right) = 1.2 * 10^5 kg$$
Final
$$m_{i,tot} = 22100 \frac{mg}{kg} * 4.1 * 10^6\ \text{kg} * \left(\frac{1\text{kg}}{10^6 g}\right) = 9.0 * 10^4 kg$$

Because the rate of removal is in $day^{-1}$, we assume a first order process.

$$\text{k} = -\frac{1}{t} * \ln\left(\frac{C_{aq,t}}{C_{aq,0}}\right)$$

Because of the proportionality between $C_{i,aq}$ and $m_{i,tot}$, it is the same as

$$k = -\frac{1}{t} * \ln\left(\frac{m_{i,tot,t}}{m_{i,tot,0}}\right)$$

| OC | Initial concentration (mg/kg) | Final concentration (mg/kg) | initial mass (kg) | final mass (kg) | rate of removal (k in day-1) | time per OC (days) |
|---|---|---|---|---|---|---|
| 1 | 30,000 | 22,100 | 1.2E+05 | 9.0E+04 | 0.005 | 60 |
| 2 | 22,100 | 15,300 | 9.0E+04 | 6.3E+04 | 0.005 | 75 |
| 3 | 15,300 | 15,000 | 6.3E+04 | 6.1E+04 | 0.0003 | 60 |
| 4 | 15,000 | 13,500 | 6.1E+04 | 5.5E+04 | 0.001 | 90 |
| 5 | 13,500 | 5,200 | 5.5E+04 | 2.1E+04 | 0.011 | 90 |

The average removal rate is then 0.004 $d^{-1}$

The percent removal over the entire remediation is
Removal= $\%R = \frac{30{,}000-5{,}200\ mg/kg}{30{,}000\ mg/kg} * 100$ =82.7%.
There is removal in the initial phases (OC1 and OC2) likely due to the degradation of the readily bioavailable compound and the mobilization of volatile compounds.
The best removal rate is achieved with the surfactant. Very little removal is achieved during OC3 and OC4, presumably due to the fact that the contaminants are not available in the aqueous phase. Treatment with a surfactant helped solubilize the contaminants, allowing faster degradation.

Problem 3: Slurry

800 $mg/kg_{dry\ soil}$ = $C_{s,0}$
40 $mg/kg_{dry\ soil}$ = $C_{s,f}$
$K_D$ = 0.2 $m^3/kg$
k = 0.05 $d^{-1}$
Css = 10 $kg_{dry\ soil}/m^3_{slurry}$
$\rho_S$ = 2'600 $kg/m^3$

This is a slurry reactor, no gas phase.

**How long should the soil stay in the reactor to be remediated?**

$m_{tot} = m_s + m_{aq} = C_s M_S + C_{aq} V_L$
This results in: $C_{aq} = \frac{m_{tot}}{K_D M_S + V_L} = \frac{C_s M_S}{K_D M_S + V_L} = \frac{C_S}{K_D + \frac{V_L}{M_S}}$
We need to determine $\frac{V_L}{M_S}$ but we know that $C_{SS} = \frac{M_S}{V_L}$
Therefore,
$\frac{V_L}{M_S} = \frac{1}{C_{ss}}$

The initial aqueous concentration is:

$$C_{aq} = \frac{C_s}{K_D + \frac{1}{C_{ss}}} = \frac{800\frac{mg}{kg}}{0.2\frac{m^3}{kg} + 0.1\frac{m^3}{kg}} = 2{,}667\frac{mg}{m^3} = 2.667\ \frac{mg}{L}$$

The final aqueous concentration is calculated in equilibrium with the soil concentration.

$$C_t = C_{aq,eq,f} = \frac{C_{s,eq,f}}{K_D} = 200\frac{mg}{m^3} = 0.2\frac{mg}{L}$$

We use the simplified analytical solution (although in real life, we would use compute a numerical solution)

$$K_S ln\left(\frac{C_{i,aq}}{C_{i,aq,0}}\right) + K_D\left(C_{i,aq} - C_{i,aq,0}\right) = -\frac{X_w M_S K_b \mu_{s,max} K_D}{Y(V_L + M_S K_D)} t$$

Therefore

$$t = -\left[K_S ln\left(\frac{C_{i,aq}}{C_{i,aq,0}}\right) + K_D\left(C_{i,aq} - C_{i,aq,0}\right)\right]\left[\frac{Y(V_L + M_S K_D)}{X_w M_S K_b \mu_{s,max} K_D}\right]$$

We use the same values as for the class example except for values we know:

| | | |
|---|---|---|
| $\mu_{s,max}$ = 0.29 $h^{-1}$ | $K_s$ = 2.12 $mg.g^{-1}$ | $X_w$ = 2 $mg.L^{-1}$ |
| $\mu_{aq,max}$ = 0.23 $h^{-1}$ | $K_w$ = 1.99 $mg.L^{-1}$ | Y= 0.34 mg cells/mg substrate |
| $M_S$= 10 g | $K_D$=0.2 $L.g^{-1}$ | $K_b$= 0.167 $L.g^{-1}$ |
| $V_L$= 1 L | | |

$$t = -\left[2.12\ \frac{mg}{g\ soil} \cdot \ln\left(\frac{0.2}{2.667}\right) + 0.2\ \frac{L\ water}{g\ soil} \cdot (0.2 - 2.667)\ \frac{mg}{L\ water}\right] \cdot$$

$$\left[\frac{0.34\ \frac{mg\ cells}{mg} \cdot \left(1\ L\ water\ + 10\ g\ soil\ \cdot 0.2\ \frac{L\ water}{g\ soil}\right)}{2\ \frac{mg\ cells}{L\ water} \cdot 10\ g\ soil\ \cdot\ 0.167\ \frac{L\ water}{g\ soil} \cdot 0.29\ \frac{1}{h} \cdot 0.2\ \frac{L\ water}{g\ soil}}\right]$$

t=9.1 hours