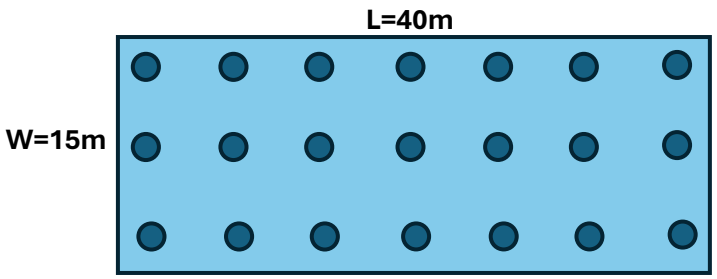
Lecture notes week 7

Example 1: Land treatment of petroleum-contaminated soil



Time (days)	Measured conc (g/kg) (Ci,tot)
0	20
110	13
229	9
298	2

Total volume of ZOI

V_T=15m*40m*0.1m= 60 m^3

M_T= V_T*ρ_{wb}= 60 m^3 *1540 $kg.m^{-3}$= 92400 kg

V_L=V_T*θ=60 m^3 * 0.1=6 m^3

M_L= V_L *ρ_w =6 m^3 * 998 $kg.m^{-3}$= 5988 kg

M_S = M_T-M_w=92400 kg-5988 kg= 86412 kg

At time zero, the average concentration in the ZOI is 20 $g.kg^{-1}$

This means that the total mass of contaminant in the ZOI soil is:

$m_{i,tot}$=20 $g.kg^{-1}$* 86412 kg* (1kg/ 1000g) = 1728 kg

First rate degradation:

$$C_{i,aq}(t) = C_{i,aq,0}e^{-kt}$$

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

Aqueous concentration and mass are proportional.

$$\frac{C_{i,aq}(t)}{C_{i,aq,0}} = e^{-kt} = \frac{m_{i,tot}(t)}{m_{i,tot}(0)}$$

$$e^{-kt} = e^{-0.008*298} = 0.092$$

$$\frac{m_{i,tot}(t)}{m_{i,tot}(0)} = 0.092$$

$$m_{i,tot}(298\ d) = 0.092 * \ m_{i,tot}(0) = 0.0092 * 1728\ kg = 159\ kg$$

Percent removal:

$$\frac{(1728-159)}{1728} \times 100 = 91\%$$

Example 2: Design a biopile

Calculate:

1. Water volume
2. Air volume
3. Solid volume
4. Volume of water needed
5. Mass of nutrients needed
6. Volume of air needed
7. Expression for $C_{i,aq}$
8. How much time to reach 98% removal?

Information available:

Size of the biopile (h=2.5; l=1.24m; L=5m; d=80 m)

Porosity ε=0.55 [-]

ρ_{wb}= 1200 kg.m^{-3}

Initial and targeted water content θ=0.2 and 0.45 [-](respectively)

TPH concentration $C_{i,tot}$=80 g.kg^{-1} wet soil

Rate of degradation (first order) k=0.05 d^{-1}

Use heptane C7H16 with a density of 680 kg/me and MW=100 g/mol

C:N:P (molar ratio)= 100:10:1

O_2 content in air =0.3 g/L

Air flow rate: Q=0.2 m^3 air.m^{-3} soil.min^{-1}

Water density ρ_{water}=998 kg.m^{-3}

Aim for 98% mass removal of TPH

Use $(NH_4)_2SO_4$ and $Na_3PO_4.12H_2O$ as fertilizers

Select units: volume= m^3; mass of soil= kg; mass of contaminant= g; time= days

Calculate values characterizing the system:

Volume of soil; mass of wet soil; mass of dry soil; volume of water; volume of air;

Volume of soil= area of trapeze* length of biopile

Area of trapeze= (1.24m+5m)/2*1.5m= 7.8 m^2

Volume of wet soil= 7.8 m^2 * 80m= 624 m^3=V_T

Mass of wet soil= 624 m^3* 1200 $kg.m^{-3}$=7.5* 10^5 kg=$M_{S,\ wet}$

Soil characteristics

1. Volume of water (initial)= V_T* θ = 624 m^3 * 0.2= 125 m^3= $V_{L,\ initial}$
2. Volume of gas initial= V_T*ε-V_L=624*0.55-125=218 m^3=V_G
3. Volume of solid= V_S= V_T-V_L-V_G=624 -125-218= 281 m^3= V_S

We assume that the contaminant is contained within the solid phase, aqueous and gas phase so it does not have its own volume.

Water needed

Volume of water need to add:

Volume of water (final)= V_T* θ_f = 624 m^3 * 0.45= 281 m^3= $V_{L,\ final}$

4. Volume of water to add= $V_{water,\ add}$= $V_{L,\ final}$- $V_{L,\ initial}$= 281 -125 = 156 m^3

We can calculate the mass of dry soil (initial)

M_S= $M_{S,\ wet}$- M_{water}=7.5* 10^5 kg-125 m^3*998 $kg.m^{-3}$=6.2 *10^5 kg= M_S

Mass of contaminant m_{TPH}= Ms * $C_{i,tot}$=80 g of C_7H_{16}/kg dry soil* 6.2 *10^5 kg= 5 *10^4 kg = $m_{TPH,tot}$

Nutrients needed.

We assume the composition of the carbon is C_7H_{16} (MW= 100 g/mol)

Moles of C_7H_{16}= 80 g of C_7H_{16}/kg dry soil / 100 g/mol= 0.8 mol C_7H_{16}/ kg dry soil

Moles of C= 0.8 mol/ kg dry soil * 7 moles C/ mole of C_7H_{16}= 5.6 moles C/kg dry soil

Moles of N needed= 5.6 moles C/kg dry soil * 1 mole N/10 moles= 0.56 moles N/kg dry soil

Moles of P needed= 5.6 moles C/kg dry soil * 1 mole P/100 moles C= 0.06 moles P/kg dry soil

This means that we need:

5. Mass of N fertilizer $m_{N,\,fert}$=0.56 $\frac{moles\ N}{kg\ dry\ soil} * \frac{1\ mole\ (NH4)2SO4}{2\ moles\ N} * \frac{132\ g\ (NH4)2SO4}{1\ mole\ (NH4)2SO4}$* 6.2 *$10^5$ kg dry soil= 2.3 *10^4 kg N fertilizer

   Mass of P fertilizer $m_{N,\,fert}$=0.06 moles P/kg dry soil* 6.2 *10^5 kg dry soil* 380 g fert./mol P = 1.3 *10^4 kg P fertilizer

Air needed.

C_7H_{16} + 11 O_2 => 7 CO_2 + 8 H_2O (stoichiometry for O_2 utilization)

Moles O_2 needed per mole of C_7H_{16} = 11 moles O_2/mole C_7H_{16}

Moles of O_2 needed n_{O2}= 11 moles O_2/mole C_7H_{16} * 0.8 mol C_7H_{16}/ kg dry soil * 6.2 *10^5 kg= 5.5 *10^6 moles O_2

Mass of O_2 needed= 32 g/mol O_2 * 5.5 *10^6 moles O_2= 1.8 *10^8 g O_2

Volume of air needed V_{air}= 1.8 *10^8 g O_2 * 1L air/0.3 g O_2 * 1m^3/1000L= 5.9 * 10^5 m^3

Air flow rate Qair= 0.2 m^3 air/ (m^3 wet soil. min)* 624 m^3 wet soil= 125 m^3 air/min

Time to deliver the O_2 needed t_{air}= 5.9 * 10^5 m^3/125 m^3 air/min * 1 day/ (1440 min)= 3.3 days

Removal rate

We have a first order degradation rate. This means that

$$\frac{dC_{i,aq}}{dt} = -kC_{i,aq}(t)$$

And that

$$C_{i,aq}(t) = C_{i,aq,0}e^{-kt}$$

And that

$$t = -\frac{1}{k} ln\left(\frac{C_{i,aq}(t)}{C_{i,aq}(t_0)}\right)$$

We are looking for the time t corresponding to a 98% mass removal.

How does that correspond to removal of aqueous contaminant concentration?

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

Therefore, $C_{i,aq}$ is proportional to $m_{i.tot}$ and a decrease of 98% in mass is also a decrease of 98% in aqueous concentration.

$C_{i,aq}(t)=0.02* C_{i,aq}(t_0)$ so

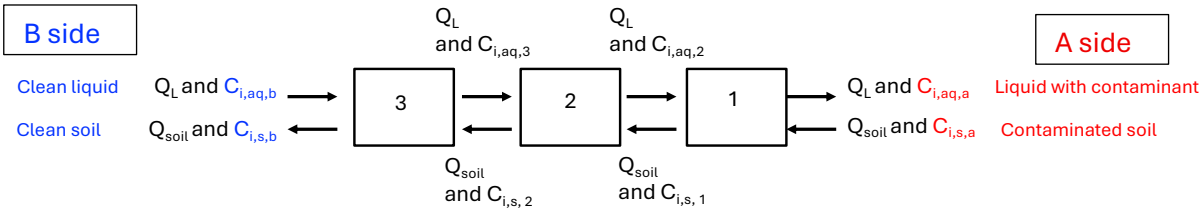
$$\frac{C_{i,aq}(t)}{C_{i,aq}(t_0)} = 0.02$$

$$t = -\frac{1}{0.05\ d^{-1}}\ln(0.02) = 78.2\ d$$

There is plenty of time to deliver more than enough O_2 to the soil to allow for 98% removal of the TPH.

Example 3: Soil washing

Simplified scheme with three stages



First, we consider pH = 2 (K = 2 L/kg):

	Soil outlet / liquid influent (B side)	**Soil inlet / liquid effluent** (A side)	
final solid conc.	$C_{i,s,b} = 1.2 * 10^{-7}\frac{kg}{kg}$	$C_{i,s,a} = 3.54 * 10^{-4}\frac{kg}{kg}$	initial solid conc.
initial aqueous	$C_{i,aq,b} = 5 * 10^{-8}\frac{kg}{L}$	$C_{i,aq,a} = 10^{-5}\frac{kg}{L}$	final aqueous

$$N = \frac{ln\left[\left(C_{i,s,a} - C^*_{i,s,a}\right)/\left(C_{i,s,b} - C^*_{i,s,b}\right)\right]}{ln[1/K * Q_L/Q_{soil}]}$$

$$\frac{Q_{soil}}{Q_L} = 0.025 \frac{kg}{L}$$

Equilibrium on the soil inlet (A) side: $C^*_{i,s,a} = K * C_{i,aq,a} = 2 * 10^{-5} = 2 * 10^{-5} \frac{kg}{kg}$

Equilibrium on the soil outlet (B) side: $C^*_{i,s,b} = K * C_{i,aq,b} = 2 * 5 * 10^{-8} \frac{kg}{kg} = 10^{-7} \frac{kg}{kg}$

$$N = \frac{\ln\left(\frac{C_{i,s,a} - C^*_{i,s,a}}{C_{i,s,b} - C^*_{i,s,b}}\right)}{\ln\left(\frac{1}{K} * \frac{Q_L}{Q_{soil}}\right)} = 3.246 => 4\ units$$

Example 4: Soil slurry biodegradation

Information available

$\mu_{s,max} = 0.29\ h^{-1}$	$K_s = 2.12\ mg.g^{-1}$	$X_w = 2\ mg.L^{-1}$
$\mu_{aq,max} = 0.23\ h^{-1}$	$K_w = 1.99\ mg.L^{-1}$	Y= 0.34 mg cells/mg substrate
$M_S = 20\ g$	$K_D = 5\ L.g^{-1}$	$K_b = 0.167\ L.g^{-1}$
$V_L = 0.25\ L$	$C_{i,s,0} = 0.5\ mg.g^{-1}$	

Units:

mg for cells and substrate; L for volume; g for soil;

We use the simplified analytical solution (although in real life, we would 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

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

First, we need to calculate $C_{i,aq,0}$, given that there is no gas phase,

$C_{i,s} = K_D C_{i,aq}$

But, the initial concentration of phenol in the aqueous phase is not that in equilibrium with the initial solid phase concentration.

$m_{i,tot} = m_{i,aq} + m_{i,s}$

$$m_{i,tot} = C_{i,aq} * V_L + C_{i,s} * M_S$$

$$m_{i,tot} = C_{i,aq} * (V_L + C_{i,aq} * K_D * M_S)$$

$$C_{i,aq} = \frac{m_{i,tot}}{V_L + K_D * M_S}$$

$$C_{i,aq,0} = \frac{m_{i,tot}}{V_L + K_D * M_S} = \frac{20g\ of\ dry\ soil * \frac{0.5\ mg\ phenol}{g\ dry\ soil}}{0.25\ L\ water + 5\frac{L\ water}{g\ dry\ soil} * 20\ g\ dry\ soil} = 0.1\ \frac{mg\ phenol}{L\ water}$$

$$C_{i,aq,t} = C_{i,aq,0} * 5\% = 0.1\ \frac{mg\ phenol}{L\ water} * 0.05 = 0.005\ \frac{mg\ phenol}{L\ water}$$

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

$$t = -\left[2.12\ \frac{mg\ phenol}{g\ soil} ln\left(\frac{0.005}{0.1}\right) + 5\frac{L\ water}{g\ soil} * (0.005 - 0.1)\frac{mg\ phenol}{L\ water}\right] *$$

$$\left[\frac{0.34\ \frac{mg\ cells}{mg\ phenol}\left(0.25\ L\ water + 20\ g\ soil * 5\ \frac{L\ water}{g\ soil}\right)}{2\frac{mg\ cells}{L\ water} * 20\ g\ soil * 0.167\frac{L\ water}{g\ soil} * 0.29\frac{1}{h} * 5\frac{L\ water}{g\ soil}}\right]$$

It simplifies to t=24 h