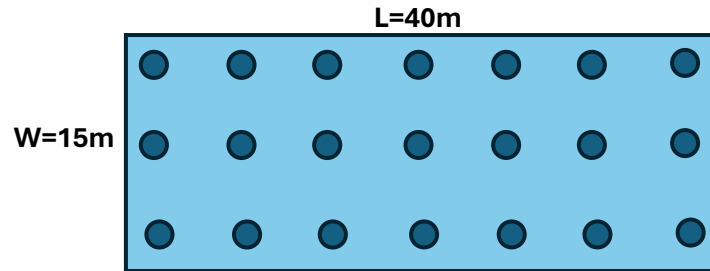


Lecture notes week 7

Example 1: Land treatment of petroleum-contaminated soil



Time (days)	Measured conc (g/kg) ($C_{i,tot}$)
0	20
110	13
229	9
298	2

Total volume of ZOI

$$V_T = 15\text{m} \times 40\text{m} \times 0.1\text{m} = 60 \text{ m}^3$$

$$M_T = V_T \times \rho_{wb} = 60 \text{ m}^3 \times 1540 \text{ kg} \cdot \text{m}^{-3} = 92400 \text{ kg}$$

$$V_L = V_T \times \theta = 60 \text{ m}^3 \times 0.1 = 6 \text{ m}^3$$

$$M_L = V_L \times \rho_w = 6 \text{ m}^3 \times 998 \text{ kg} \cdot \text{m}^{-3} = 5988 \text{ kg}$$

$$M_S = M_T - M_w = 92400 \text{ kg} - 5988 \text{ kg} = 86412 \text{ kg}$$

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

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

$$m_{i,tot} = 20 \text{ g} \cdot \text{kg}^{-1} \times 86412 \text{ kg} \times (1\text{kg} / 1000\text{g}) = 1728 \text{ kg}$$

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.

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

$$e^{-kt} = e^{-0.008 \cdot 298} = 0.092$$

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

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

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 $\varepsilon=0.55$ [-]

$\rho_{wb}= 1200 \text{ kg.m}^{-3}$

Initial and targeted water content $\theta=0.2$ and 0.45 [-](respectively)

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

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

Use heptane C_7H_{16} with a density of 680 kg/me and $MW=100 \text{ g/mol}$

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

O_2 content in air $=0.3 \text{ g/L}$

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

Water density $\rho_{water}=998 \text{ kg.m}^{-3}$

Aim for 98% mass removal of TPH

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

Select units: volume= m³; 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 m²

Volume of wet soil= 7.8 m² * 80m= 624 m³=V_T

Mass of wet soil= 624 m³* 1200 kg.m⁻³=7.5* 10⁵ kg=M_{S, wet}

Soil characteristics

1. Volume of water (initial)= V_T* θ = 624 m³ * 0.2= 125 m³= V_{L, initial}
2. Volume of gas initial= V_T*ε-V_L=624*0.55-125=218 m³=V_G
3. Volume of solid= V_S= V_T-V_L-V_G=624 -125-218= 281 m³= 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 m³ * 0.45= 281 m³= V_{L, final}

4. Volume of water to add= V_{water, add}= V_{L, final}- V_{L, initial}= 281 -125 = 156 m³

We can calculate the mass of dry soil (initial)

M_S= M_{S, wet}- M_{water}=7.5* 10⁵ kg-125 m³*998 kg.m⁻³=6.2 *10⁵ kg= M_S

Mass of contaminant m_{TPH}= M_S * C_{i,tot}=80 g of C₇H₁₆/kg dry soil* 6.2 *10⁵ kg= 5 *10⁴ kg = m_{TPH,tot}

Nutrients needed.

We assume the composition of the carbon is C₇H₁₆ (MW= 100 g/mol)

Moles of C₇H₁₆= 80 g of C₇H₁₆/kg dry soil / 100 g/mol= 0.8 mol C₇H₁₆/ kg dry soil

Moles of C= 0.8 mol/ kg dry soil * 7 moles C/ mole of C₇H₁₆= 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

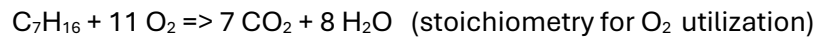
Moles of P needed= 5.6 moles C/kg dry soil * 1 mole P/100 moles C= 0.06 moles P/kg dry soil

This means that we need:

$$5. \text{ Mass of N fertilizer } m_{N, \text{fert}} = 0.56 \frac{\text{moles N}}{\text{kg dry soil}} * \frac{1 \text{ mole } (NH_4)_2SO_4}{2 \text{ moles N}} * \frac{132 \text{ g } (NH_4)_2SO_4}{1 \text{ mole } (NH_4)_2SO_4} * 6.2 * 10^5 \text{ kg dry soil} = 2.3 * 10^4 \text{ kg N fertilizer}$$

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

Air needed.



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

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

$$\text{Mass of } O_2 \text{ needed} = 32 \text{ g/mol } O_2 * 5.5 * 10^6 \text{ moles } O_2 = 1.8 * 10^8 \text{ g } O_2$$

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

$$\text{Air flow rate } Q_{\text{air}} = 0.2 \text{ m}^3 \text{ air}/(\text{m}^3 \text{ wet soil. min}) * 624 \text{ m}^3 \text{ wet soil} = 125 \text{ m}^3 \text{ air/min}$$

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

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.

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

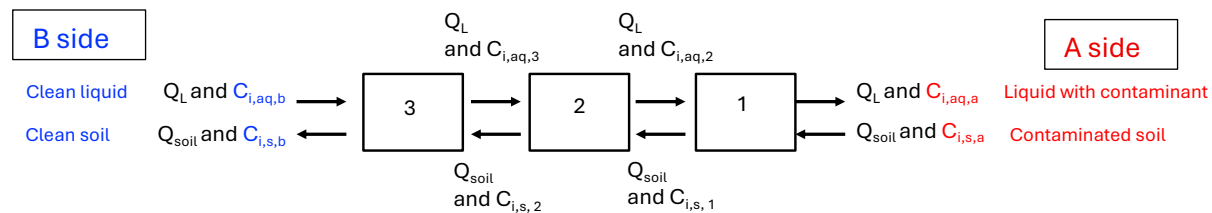
$$\frac{C_{i,aq}(t)}{C_{i,aq}(t_0)} = 0.02$$

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

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 ($K = 2 \text{ L/kg}$):

	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

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

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

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: $C_{i,s,b}^* = K C_{i,aq,b} = 2 * 5 * 10^{-8} \frac{kg}{kg} = 10^{-7} \frac{kg}{kg}$

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

Example 4: Soil slurry biodegradation

Information available

$$\mu_{s,max} = 0.29 \text{ h}^{-1}$$

$$K_s = 2.12 \text{ mg.g}^{-1}$$

$$X_w = 2 \text{ mg.L}^{-1}$$

$$\mu_{aq,max} = 0.23 \text{ h}^{-1}$$

$$K_w = 1.99 \text{ mg.L}^{-1}$$

$$Y = 0.34 \text{ mg cells/mg substrate}$$

$$M_s = 20 \text{ g}$$

$$K_D = 5 \text{ L.g}^{-1}$$

$$K_b = 0.167 \text{ L.g}^{-1}$$

$$V_L = 0.25 \text{ L}$$

$$C_{i,s,0} = 0.5 \text{ mg.g}^{-1}$$

Units:

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

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

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

Therefore

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

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

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

$$C_{i,aq,0} = \frac{C_{i,s,0}}{K_D} = \frac{0.5 \frac{mg \text{ phenol}}{g \text{ soil}}}{5 \frac{g \text{ soil}}{L \text{ water}}} = 0.1 \frac{mg \text{ phenol}}{L \text{ water}}$$

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

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

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

It simplifies to t=24 h