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

Problem 1:

pyrene in sludge 20'000 ppm
(compost + sludge) pile 2'500 kg = M_T
sludge is 25% by mass of pile
active = 40 d (mass reduced by 30%)
curing = 90 d

$t_{1/2}$ = 30 d - active
$t_{1/2}$ = 55 d - curing

What is the final pyrene concentration?

Initial pyrene concentration in the pile:
$C_0 = C_{pyrene,sludge} * C_{sludge\ in\ pile} = 20'000\ ppm * 0.25 = 5'000\ ppm$

1) First stage (active)

First order degradation: $\ln\left(\frac{C_0}{C_t}\right) = -kt_{\frac{1}{2}}$ → $k_1 = 0.023\ d^{-1}$

$$\boxed{C_{40} = e^{-0.023*40} C_0 \rightarrow C_{40} = 0.4\ C_0}$$

2) Second stage (curing)

First order degradation: $\ln\left(\frac{C_0}{C_t}\right) = -kt_{\frac{1}{2}}$ → $k_2 = 0.013\ d^{-1}$

$$\boxed{C_{130} = e^{-0.013*90} C_{40} = 0.31\ C_{40} = 0.12\ C_0}$$

Numerical application: $C_{130} = 0.12 * 5'000 = 600$ ppm

If we consider that 30% of the compost mass was lost:
At which this happens is not important because we consider that it does not affect the rate constants previously determined.

$$C'_{130} = \frac{(M_{compost}+M_{sludge})C_{130}}{0.7*M_{compost}+M_{sludge}} = \frac{C_{130}}{\underbrace{0.7*0.75+0.25}_{C_{sludge\ in\ pile} = 0.25\frac{kg_{sludge}}{kg_{pile}}}} = 774 \text{ ppm}$$

Problem 2:

V_{soil}= 40,000 m^3

target time for remediation: <365 days

$C_{TPH, i, avg}$= 10,000 mg/kg

$C_{TPH, f, avg}$= 100 mg/kg

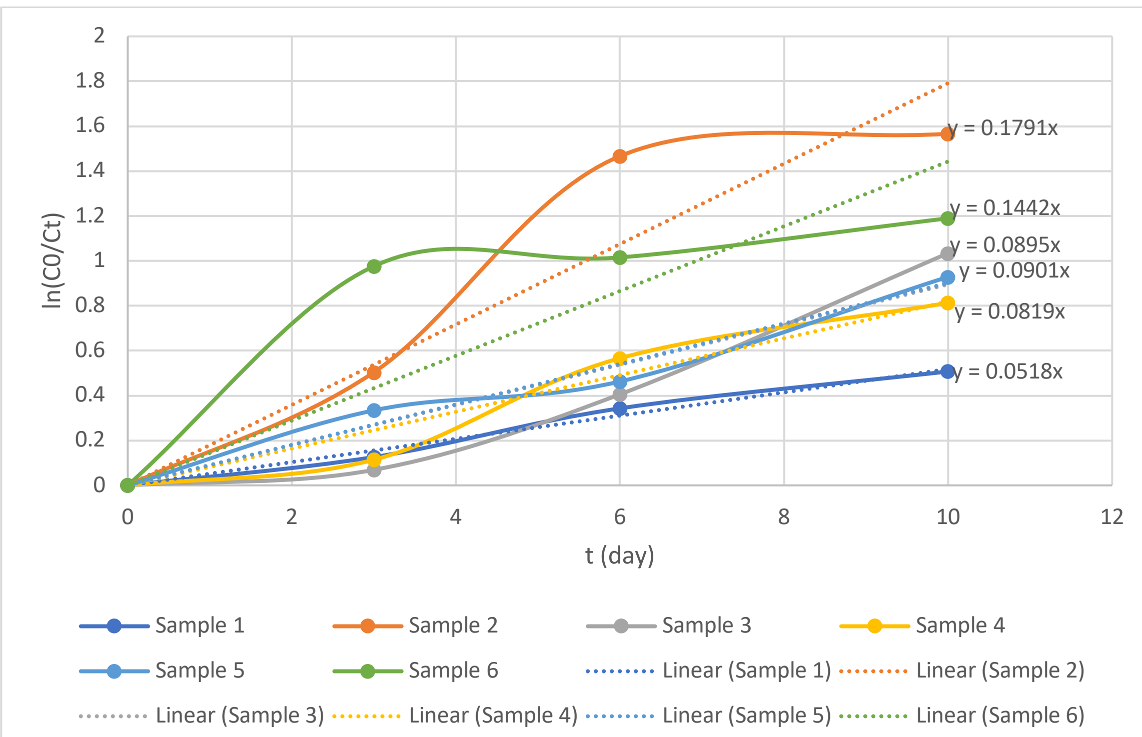
$C_{TPH, i, max}$= 98,000 mg/kg

$C_{TPH, f, max}$= 500 mg/kg

$$k = \frac{\ln(C_0) - \ln(C)}{t}$$

From the different sampling points, calculate the slowest degradation rate, which corresponds to the worst-case scenario. Hence, we can calculate how quickly we can expect the degradation to occur at the slowest rate and whether the one-year target can be met (conservative approach).

Use excel to plot $\ln\left(\frac{C_0}{C_t}\right) = kt$ for each sample. Then plot the linear regression equations. With this method, the slowest rate is: k = 0.052 d^{-1}.



$$t = \frac{\ln(C_0) - \ln(C)}{k} = \frac{\ln(10{,}000) - \ln(100)}{0.051} \Rightarrow \text{t=90 days}$$

$$t = \frac{\ln(C_0) - \ln(C)}{k} = \frac{\ln(98{,}000) - \ln(500)}{0.051} \Rightarrow \text{t=103 days}$$

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

Problem 3:

$C_{0,}$= 900 ppm
C_{46d}= 300 ppm

a- Assuming 1st order kinetics, we obtain a k of

$$k = \frac{\ln(C_0) - \ln(C)}{t} \Rightarrow k=0.024\ d^{-1}$$

b- The half-life is given by

$$t_{1/2} = \frac{\ln 2}{k} \Rightarrow t_{1/2}= 29 \text{ days}$$

c- $k_T = k_{22}\Theta^{T-22}$ where Θ=1.02

k_T=0.026 d^{-1}

d- $$t_{1/2} = \frac{\ln 2}{k} \Rightarrow t_{1/2}= 26 \text{ days}$$

Problem 4:

$C_6H_{14} + 9.5\ O_2 \Rightarrow 6\ CO_2 + 7\ H_2O$

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 to degrade.

$$3{,}300\ m^3\ soil\ \times\ 1{,}440 \frac{kg\ soil}{m^3 soil} \times 30{,}000 \frac{mg\ TPH}{kg\ soil} \times \frac{1\ metric\ ton}{10^9 mg} = 142\ .5\ metric\ tons\ of\ TPH$$

$$\frac{390\ L\ water}{1\ g\ TPH} \times 142.5\ tons\ TPH \times 0.9 \times \frac{10^6 g}{1\ ton} \times \frac{1\ m^3}{1{,}000L} = 50{,}038{,}560\ m^3\ air\ saturated\ water$$

This is not really feasible in a flow-through slurry system. Hence, the plan to use biopiles with which air is delivered.

TPH concentration (mg/kg)	total TPH (mg)	total TPH (metric tons)	phase	removal (% of initial)	duration (days)	removal rate (day-1)	
30,000	1.43E+11	142.6					
22,100	1.05E+11	105.0	OC1	26.3	60	0.0051	
15,300	7.27E+10	72.7	OC2	22.7	75	0.0049	
15,000	7.13E+10	71.3	OC3	1.0	60	0.0003	
13,500	6.42E+10	64.2	OC4	5.0	90	0.0012	
5,200	2.47E+10	24.7	OC5	27.7	90	0.0106	
				82.7		0.0044	average removal rate (day-1)
				total removed (% of initial)			

Because the rate of removal is in day^{-1}, we assume a first order process.
K= ln(C/Co)/t
The total removal is 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.
There is also good removal with the surfactant. Very little removal is achieved during OC3 and OC4, presumably due to the fact that the contaminants were not bioavailable. Treatment with a surfactant helped solubilize the contaminants, allowing degradation.

Problem5:

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

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

Batch reactor first order kinetics (aqueous concentrations!):

$$t = -\frac{\ln\left(\frac{C_t}{C_0}\right)}{k}$$

C_0 is the aqueous concentration in the water in equilibrium $C_{aq,eq,0}$ with the solid phase:

$$m_{tot} = m_s + m_{aq} = C_{s,eq,0}M_S + C_{aq,eq,0}V_L$$

This results in: $C_0 = C_{aq,eq,0} = \frac{m_{tot}}{K_D M_S + V_L} = \frac{C_{s,0}M_S}{K_D M_S + V_L} = \frac{C_{s,0}}{K_D + \frac{V_L}{M_S}}$

We need to determine $\frac{V_L}{M_S}$ (no gas phase in a reactor):

$$\frac{V_L}{M_S} = \frac{1}{C_{SS}} - \frac{V_S}{M_S} = \frac{1}{C_{SS}} - \frac{1}{\rho_S} = \frac{1}{10} - \frac{1}{2600} = 0.1\,\frac{m^3}{kg}$$

$$C_0 = \frac{800\,\frac{mg}{kg}}{0.2\,\frac{m^3}{kg} + 0.1\,\frac{m^3}{kg}} = 2{,}665\,\frac{mg}{m^3}$$

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

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

We have all the elements to calculate the residence time needed to reach the target concentration:

First order degradation rate

$$t = -\frac{\ln\left(\frac{C_t}{C_0}\right)}{k} = -\frac{\ln\left(\frac{200}{2665}\right)}{0.05} = 52\ days$$