Problem Set #8  

14. 

\[
\frac{dn}{dx} = 0.001 \quad (N \to S) \\
K = 10^{-4} \text{ m/s} \\
b = 10 \text{ m} \\
\text{find necessary pumping rate to capture all the pollutant}
\]

using capture curves (p. 223):

- dumping area extends ~ 500 m to each side of well A
- this corresponds to \( Q_w = 1200 \text{ m}^3 \) (assuming dispersion can be neglected)

\[
Q_a = K \frac{dn}{dx} = 10^{-4} \text{ m/s} (0.001) = 10^{-7} \text{ m/s}
\]

\[
Q_w = 1200 \text{ m}^3 (bQ_a) = 1200 \text{ m}^3 (10 \text{ m} \times 10^{-7} \text{ m/s}) = \boxed{1.2 \times 10^{-3} \text{ m}^3/\text{s}}
\]

16. a) saturated: \( n = 0.3, \frac{f_{oc}}{f_{cl}} = 1.0, \rho_0 = 2.1 \text{ g/cm}^3 \)

\( \text{C}_\text{HCl}_3, K_{ow} = 10^{1.97} \)

estimate retardation factor

1st equation in table 3-5:

\[
\log K_{oc} = 0.544 \log K_{ow} + 1.377 \\
= 0.544 (1.97) + 1.377 = 2.45
\]

\[
K_d = \frac{f_{oc} \cdot K_{oc}}{f_{cl}} = 0.01 (10^{2.45} \text{ mL/g}) = 2.81 \text{ mL/g}
\]

\[
R = 1 + \frac{K_d \rho_0}{n} = 1 + \frac{(2.81 \text{ mL/g}) \times 2.1 \text{ g/cm}^3}{0.3} = 20.7
\]

\( R = 21 \)
b) unsaturated: \( \theta = 0.15 \) (fraction of water)

Note that the equation given in lecture, \( R = 1 + \frac{K_a \rho_n}{\theta} \), refers to a chemical that is not volatile.

CHCl₃ partitions into organic carbon according to \( K_a \), and into the air according to \( H \). Both of these phases are immobile.

go back to the most basic definition of \( R \):

\[
R = \frac{\text{mobile + immobile}}{\text{mobile}}
\]

mobile = CHCl₃ in water
immobile = CHCl₃ in air, org. carbon

amount in water = \( C_w \theta \)
amount in air = \( C_a(n-\theta) \) \( \theta \) includes air + water; \( \theta \) is water only
amount in org. carbon = \( C_s \rho_n \)

\[
R = \frac{C_w \theta + C_a(n-\theta) + C_s \rho_n}{C_w \theta} = 1 + \frac{C_a(n-\theta)}{C_w \theta} + \frac{C_s \rho_n}{C_w \theta}
\]

using the definitions that \( H = \frac{C_a}{C_w} \) and \( K_a = \frac{C_s}{C_w} \)

\[
R = 1 + \frac{H(n-\theta) + K_a \rho_n}{\theta} = \frac{1 + 0.2(0.15) + 2.81 mL/g (2.1 g/cm³)}{0.15} = 40.5 \quad \boxed{R = 41}
\]
hexane: MW = 86

\[ P = 182 \text{ mmHg (at } 20^\circ \text{C)} \]

\[ \rho = 0.60 \text{ g/cm}^3 \Rightarrow \text{hexane is less dense than water;} \]

it will form a NAPL on top of the water table (and thus be diffusing through air)

a) for maximum flux:

- if hexane is directly under the compressor room

- if Croom = 0, and Cair (right above the NAPL) determined by vapor pressure

\[ J = -D \frac{dC}{dx} \quad \text{Cair} = \frac{C}{V} \frac{P}{RT} = \frac{182 \text{ mmHg (atm)} \times 760 \text{ mmHg}}{0.08206 \text{ atm} \times \text{mol} \times \text{K}} (293 \text{ K}) \]

\[ = 0.0083 \text{ mol/L} = 8.3 \text{ mol/m}^3 \]

\[ \text{Def} = D \cdot \frac{n}{\sqrt{z}} \quad \text{correction for porosity \& tortuosity (p.231);} \]

other approximations are possible

\[ = 0.2 \text{ cm} \times (0.2) = 0.028 \text{ cm/s} \]

\[ J = \frac{0.028 \text{ cm}^2}{s} \times \left( \frac{m}{100 \text{ cm}} \right)^2 \times 8.3 \text{ mol/m}^3 - 0 = \frac{7.7 \times 10^{-7} \text{ mol/m}^2 \cdot \text{sec}}{3.048 \text{ m}} \]

b) We want to find Croom at steady state and compare this to the flammable limit.

at steady state, flux in = flux out

\[ \text{Flux in} = \text{Def} (\text{Cair} - \text{Croom}) = \frac{2.8 \times 10^{-4} \text{ m}^2 \text{s}}{3.048 \text{ m}} (8.3 \text{ mol/m}^3 - \text{Croom}) \]

\[ = 7.6 \times 10^{-5} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Croom} \]

\[ - 9.2 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \]

(multiply by area to get flux instead of flux density; taking A=1m^2 is simplest)
flux out = volume \cdot Croom \cdot air changes \quad (\text{notice this is mol/time also})

for \( A = 1 \text{ m}^2, \ V = 1.8 \text{ m}^3 \)

\[
\left( 7.6 \times 10^{-4} \text{ mol} \cdot 9.2 \times 10^{-7} \text{ m}^3 \cdot \text{Croom} \times 1 \text{ m}^3 \right) = 1.8 \text{ m}^3 \cdot \text{Croom} \cdot \left( 0.1 \right) \times \frac{\text{d}}{\text{day}} = 8.64 \text{ g/L}
\]

\[ 7.6 \times 10^{-4} - 9.2 \times 10^{-7} \text{Croom} = 2.1 \times 10^{-4} \text{Croom} \]

\[ \text{Croom} = 2.6 \text{ mol/m}^3 \]

Convert to partial pressure:

\[ P = \frac{nRT}{V} = \frac{2.6 \times 10^{-3} \text{ mol/L}}{0.08206 \text{ atm L} \cdot \text{mol K}} = 0.061 \text{ atm} \]

Since ambient air pressure is 1 atm, the concentration of hexane is 0.1% = flammable limit is reached

\( \text{a).} \quad \) 1.5 travel times have elapsed but the well is still pumping clean water...

this means the contaminant has either been degraded or is being slowed down. Since BTEX are fairly hydrophobic (which means they have relatively high \( K_d \) values) and the aquifer contains organic carbon, retardation is a definite possibility.

\[
\begin{align*}
\text{benzene} & \quad \text{toluene} & \quad \text{ethylbenzene} & \quad \text{xylene} \\
\end{align*}
\]

(3 arrangements possible)

for benzene, log \( K_d = 2.13 \)

Since these are aromatic compounds (aromatic = containing 6-carbon rings), we can use this equation:

\[ \log K_ac = 0.937 \log K_d - 0.006 = 1.99 \]

\[ K_d = \frac{K_ac}{0.937} = 0.006 \times 10^{1.99} = 0.293 \text{ mL/g} \]

\[ R = \frac{1 + K_d \rho_s}{\rho_c} = 1 + 0.293 \text{ mL/g} \times 1.8 \text{ g/mL} = 2.8 \]

We assume \( n = 0.3 \)

\[ \rho_c = (1 - n) \rho_s = 0.1 \times 2.0 \text{ g/mL} = 1.8 \text{ g/mL} \]

Retardation can definitely account for the delay. The BTEX could also have been degraded, most likely through biodegradation (photolysis isn't going to be too likely underground, and aromatic compounds aren't really susceptible to hydrolysis).
b) Biodegradation can account for the drop in pH. BTEX gets oxidized to CO₂, which is acidic (as H₂CO₃).

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>Change</th>
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<tbody>
<tr>
<td>pH = 9</td>
<td>pH = 7</td>
<td>ΔC₇ = 10⁻⁴ M</td>
</tr>
<tr>
<td>Alk = 5x10⁻⁴ eq/L</td>
<td>Alk = 5x10⁻⁴ eq/L</td>
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</tr>
<tr>
<td>C₇ = 5x10⁻⁴ M</td>
<td>C₇ = 5x10⁻⁴ M</td>
<td></td>
</tr>
</tbody>
</table>

31. a) This is just a matter of balancing redox equations:

- Assume complete oxidation to CO₂

\[ \text{C₇H₈} \rightarrow 7\text{CO₂} \]
\[ \text{C₇H₈} + 14\text{H}_2\text{O} \rightarrow 7\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \]
\[ \frac{1}{44} \text{mol C₇H₈ per e}^- \]

- Denitrification expected to occur: N₂ is product

\[ 2\text{N}_3^- \rightarrow \text{N}_2 + 3\text{H}_2\text{O} \]
\[ 2\text{N}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 3\text{H}_2\text{O} \]
\[ \frac{1}{6} \text{N}_3^- \text{per e}^- \]

\[ 25,000 \text{ g C₇H₈} \times \frac{\text{mol C₇H₈}}{100 \text{ g}} \times \frac{\frac{1}{44} \text{ mol N}_3^-}{1 \text{ mol C₇H₈}} \times \frac{1 \text{ mol NaNO₃}}{1 \text{ mol N}_3^-} \times \frac{85 \text{ g NaNO₃}}{1 \text{ mol}} \]
\[ = 187 \text{ kg NaNO₃} \]

b) From p.132 we see that while denitrification is occurring, \( p_e \approx 12 \).