

Carnegie Mellon University
Department of Civil and Environmental Engineering

12-725: Fate, Transport, and Physico-chemical Processes of Organic Compounds in Aquatic Systems

Problem Set #8 Spring 2020

Due 4/3/20

1. P19.7 in EOC

PCE – Theoretical v_{PCEaw}

From Appendix C: $K_{PCE,aw} = 10^{-0.08} \gg 10^{-3} = K_{law}^{crit} \rightarrow$ we can assume that $v_{PCE,aw} \approx v_{PCE}$

Assume large-eddy model for river flow:

$$v_{iw}(\bar{u}_f) = \left(\frac{D_{iw} \bar{u}_f}{h} \right)^{\frac{1}{2}}$$

To find D_{PCEw} the follow relationship between molar volume and the diffusion coefficient in water will be used (Eq. 17-24a, EOC):

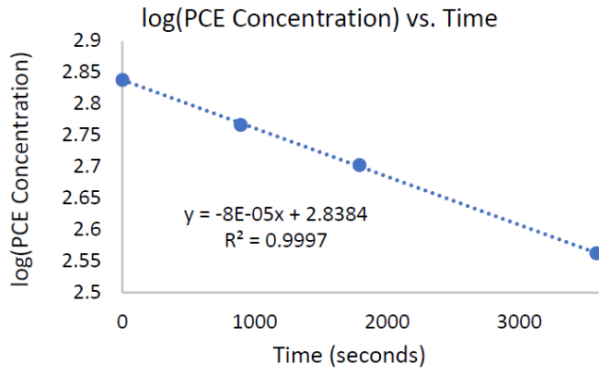
$$D_{iw} = 1.52 \times 10^{-4} \bar{V}^{-0.64}$$

$$D_{PCEw} = 1.52 \times 10^{-4} \left(84 \frac{cm^3}{mol} \right)^{-0.64} = 8.9 \times 10^{-6} \frac{cm^2}{s}$$

$$v_{PCEw} \left(0.67 \frac{m}{s} \right) = \left(\frac{\left(8.9 \times 10^{-6} \frac{cm^2}{s} \right) \left(0.67 \frac{m}{s} \right)}{0.4 m} \right)^{0.5} = 0.0039 \frac{cm}{s} \approx v_{PCEaw} = 10^{-4.41} \frac{m}{s}$$

PCE – Experimental v_{PCEaw}

In Excel, plot the log of the PCE concentration vs. time:



Slope of linear regression line = $-k_v (1/s)$

Where, $k_v = \frac{v_{iaw}}{h} \rightarrow v_{iaw} = k_v \times h$

$$v_{PCEaw} = 8 \times 10^{-5} \times 0.4 = \mathbf{10^{-4.49} \frac{m}{s}}$$

1,4-DCB – Theoretical v_{DCBaw}

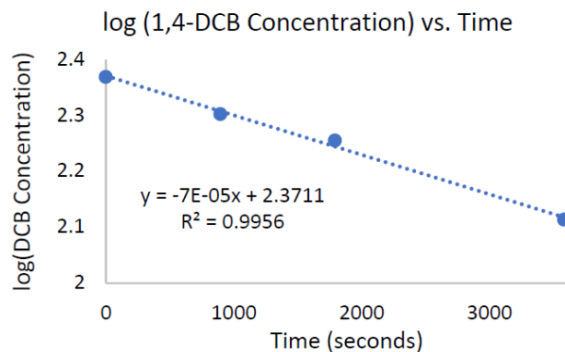
From Appendix C: $K_{1DCB,aw} = 10^{-1.04} \gg 10^{-3} = K_{iaw}^{crit} \rightarrow$ we can assume that $v_{DCB,aw} \approx v_{DCB,w}$

$$D_{DCBw} = 1.52 \times 10^{-4} \left(96 \frac{cm^3}{mol} \right)^{-0.64} = 7.1 \times 10^{-6} \frac{cm^2}{s}$$

$$v_{DCBw} \left(0.67 \frac{m}{s} \right) = \left(\frac{\left(7.1 \times 10^{-6} \frac{cm^2}{s} \right) \left(0.67 \frac{m}{s} \right)}{0.4 m} \right)^{0.5} = 0.0035 \frac{cm}{s} \approx v_{PCEaw} = \mathbf{10^{-4.46} \frac{m}{s}}$$

1,4-DCB – Experimental v_{DCBaw}

In Excel, plot the concentration of 1,4-DCB vs. time:

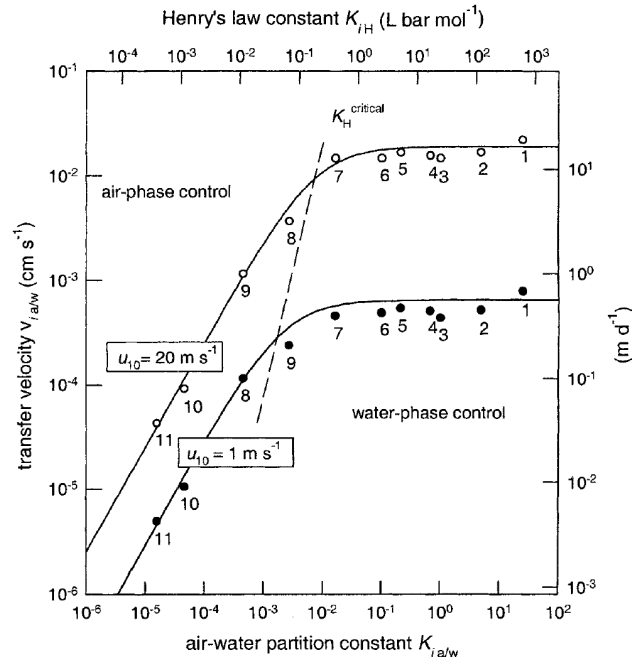


Slope of linear regression line = $-k_v (1/s)$

$$v_{iaw} = k_v \times h$$

$$v_{DCBaw} = 7 \times 10^{-5} \times 0.4 = \mathbf{10^{-4.55} \frac{m}{s}}$$

- The following chart shows the water-side transfer velocity (v_w) vs. $K_{ia/w}$. Explain the trends observed in the graph.



Solution.

The overall mass transfer velocity $V_{i,a/w}$ depends on both the air side MT coefficient and the water side MT coefficient. However, $V_{ia} \sim 1000 V_{iw}$ so for very volatile compounds the resistance to MT lies primarily on the water side and no longer depends $K_{i,a/w}$. Thus, the plots tend to level out for $K_{i,a/w} > 10^{-3}$. At value of $K_{i,a/w} < 10^{-3}$, the overall MT velocity $v_{i,a/w}$ increases with increasing $K_{i,a/w}$. This value of $K_{i,a/w}$ where this transition occurs depends a bit on the wind speed because v_{iw} depends on wind speed.

3. A company using large quantities of trichloroethene (TCE) as a reagent resides on the Ohio River. An accidental release results in a slug of TCE in the river. After mixing, the average TCE concentration in the river is 6 mg/L. The summer flow rate in the Ohio is approximately 56 m³/s, which corresponds to an average velocity of 0.27 m/s, and is 2 m deep. Assume that large eddies dominate, and that the wind speed is low enough ($u_{10}=3$ m/s) such that bubble enhancement is negligible.

- (a) Estimate the overall mass transfer coefficient, $v_{i,a/w}$, and the mass transfer rate constant, k_v , for TCE in the river. State any assumptions that you make.

$$\frac{1}{V_{i,a/w}} = \frac{1}{v_{i,w}} + \frac{1}{K_{i,a/w} v_{i,a}}$$

We need $K_{i,a/w}$ (dimensionless Henry's constant), $v_{i,a}$, and $v_{i,w}$ for the system. This is flowing river and if we assume that large eddies dominate, we can use the O'Connor-Dobbins estimate for $v_{i,w}$. Note that you can calculate u_{crit} for the river and prove that this assumption is indeed true.

$$v_{i,w} = \sqrt{\frac{D_{i,w}}{H}} \sqrt{u}$$

In this river, $u=0.27\text{m/s}$ and $H=2\text{ m}$

The diffusion coefficients can be estimated or looked up. Assume $25\text{ }^{\circ}\text{C}$.

$$D_{i,w} = \frac{2.7 \times 10^{-4}}{M_i^{0.71}}$$

For TCE, $M_w=131.4\text{ g/mol}$,

$$D_{\text{TCE}}=8.5 \times 10^{-6}\text{ cm}^2/\text{s}$$

$$V_{iw\text{ TCE}} = \sqrt{\frac{8.5 \times 10^{-6} \times 0.27}{2}} = 1.07 \times 10^{-3}\text{ cm/s}$$

Assume $V_{ia} \approx 1000 V_{iw}$

$$V_{ia,\text{TCE}}=1.07\text{ cm/s}$$

$\log K_{ia/w, \text{TCE}} = -0.31$, $K_{ia/w, \text{TCE}}=0.49$ (appendix C)

$$\frac{1}{V_{i,a/w}} = \frac{1}{1.07 \times 10^{-3}\text{ cm/s}} + \frac{1}{0.49 \times 1.07\text{ cm/s}}$$

$$V_{i,a/w} \approx 1.07 \times 10^{-3}\text{ cm/s}$$

$$V_{i,a/w} * a = 1.07 \times 10^{-3}\text{ cm/s} * 1/2\text{m} = 5.35 \times 10^{-6}/\text{s}$$

- (b) Verify that liquid phase resistance controls the mass transfer of TCE from the river into the atmosphere. What fraction of the overall mass transfer resistance is attributed to the gas phase resistance? Calculate a revised estimate for the overall mass transfer coefficient, $V_{i,a/w}$, this time accounting for the gas phase resistance. Can the gas-phase resistance safely be ignored in this case?

$$\frac{R_w}{R_T} = \frac{\frac{1}{v_{i,w}}}{\frac{1}{v_{i,w}} + \frac{1}{K_{i,a/w} v_{i,a}}}$$

$$\frac{R_a}{R_T} = \frac{\frac{1}{K_{i,a/w} v_{i,a}}}{\frac{1}{v_{i,w}} + \frac{1}{K_{i,a/w} v_{i,a}}}$$

For TCE, resistance in the water phase R_w is nearly 100%, thus it is largely controlled by its water-side resistance to mass transfer. Gas phase resistance can be safely ignored. If we ignore it, we still get $V_{i,a/w}=1.07 \times 10^{-3}\text{ cm/s}$

- (c) Assume that chlorophenol was released instead of TCE. Calculate $v_{i,w}$, $v_{i,a}$, $v_{i,a/w}$, and k_v for chlorophenol in the same river. Is the assumption that liquid-phase resistance controls the mass transfer of ethanol from the river to the atmosphere valid?

For chlorophenol, $k_{iaw}=5.8 \times 10^{-4}$ (Appendix C) and $M_w=129$

Thus $D_{iw}=8.6 \times 10^{-6} \text{ cm}^2/\text{s}$

$$v_{i,w,\text{Chlorophenol}}=1.1 \times 10^{-3} \text{ cm/s}$$

$$v_{i,a,\text{Chlorophenol}}=1.1 \text{ cm/s}$$

$$\frac{1}{v_{i,a/w}} = \frac{1}{1.1 \times 10^{-3} \text{ cm/s}} + \frac{1}{5.8 \times 10^{-4} \times 1.1 \text{ cm/s}}$$

$$v_{iaw} = 4 \times 10^{-4} \text{ cm/s}$$

In this case, clearly it is not a water-side controlled transfer. In this case, air phase is more important ($R=1567$), but water side also has a contribution ($R=909$)

- (d) Repeat part (a) but assume that the river bottom is fine-grained sand, and that large eddies do not dominate mass transfer from air to water.

Here we will just apply a small eddy model

We use equation 19-24 to calculate v_{iw} .

$$v_{iw} \left(\frac{\text{cm}}{\text{s}} \right) = 3.26 \times 10^{-3} \left(\frac{\bar{u}_F (\text{m/s})}{h (\text{m})} \right)^{1/4} = 2.2 \times 10^{-3} \text{ cm/s}$$

Assume $V_{ia}=1000V_{iw}$, $V_{ia}=2.2 \text{ cm/s}$

$$\frac{1}{v_{i,a/w}} = \frac{1}{2.2 \times 10^{-3} \text{ cm/s}} + \frac{1}{0.22 \times 0.49 \text{ cm/s}}$$

$$v_{i,a/w} \approx 2.2 \times 10^{-3} \text{ cm/s}$$

$$v_{i,a/w} * a = 2.2 \times 10^{-3} \text{ cm/s} * 1/2 \text{ m} = 1.1 \times 10^{-6} / \text{s}$$

This is roughly a factor of 5 lower. This makes sense given that the small eddy model has less mixing.

4. Sediment caps comprised of granular material such as clean sand are sometimes used to isolate contaminated sediments from the overlying water column. The cap provides an additional length (L) the contaminants must diffuse through before they enter the water column. Consider a 30-cm sediment cap of quartz sand placed over a PAH contaminated sediment. The cap porosity is measured at 37% and the tortuosity is determined to be 1.4. The sand bulk density is measured at 1.52 g/cm^3 .

- Estimate the effective diffusivity of fluorene (a model PAH) in the sand sediment cap assuming there is no sorption to the cap material.
- Assuming that the PAH concentration in the sediment remains constant, determine the time required for the fluorene concentration at $x=10\text{cm}$ in the cap to reach 10% of the concentration in the sediment.
- Repeat this calculation, but assume that the fluorene concentration in the sediment is depleting. How different are your estimates for the time required to reach 10% of C_0 at $x=10\text{cm}$ in the cap?

- (d) Determine the time required for the fluorene concentration at $x=10\text{cm}$ in the sediment cap to reach 10% of the concentration in sediment for a sediment cap containing 0.3% organic carbon. You can assume that the concentration in the sediment remains constant.
- (e) Repeat this calculation, but now incorporate 5% activated carbon on the sand cap. Does this improve the performance of the cap? By how much?
- (f) Do you think capping with organic rich sands or with activated carbon can be an effective sediment remediation strategy? What are the potential problems with this approach?

Draw a picture of the system:

water

cap $\phi=0.37$ $\tau=1.4$ $\rho_b=1.52 \text{ g/cm}^3$ $\updownarrow 10\text{-cm}$

sediment $C=C_o=\text{constant or depleting}$

- (a) Estimate the effective diffusivity of fluorene in the sand layer assuming there is no sorption of pentachlorophenol to the cap material.

$$D_{eff} = \frac{\phi D_{iw}}{\tau(1 + r_{sw}K_{id})}$$

For fluorene, $D_{iw}=7.9 \times 10^{-6} \text{ cm}^2/\text{s}$

Without sorption, $K_d=0$ so:

$$D_{ieff}=0.37(7.9 \times 10^{-6} \text{ cm}^2/\text{s})/1.4=2.1 \times 10^{-6} \text{ cm}^2/\text{s}$$

- (b) Determine the time required for the fluorene to reach 10% of the concentration in the sediment at a distance of 10-cm in the cap.

This is a simple diffusion model holding $C=\text{constant}$ in the sediment layer. The solution is given by eqn 18-20.

$$C_{(x,t)} = C_o \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{eff}t}}\right)$$

For $x=10 \text{ cm}$, the time to reach $C/C_o=0.1$ is $\sim 100\text{d}$ (calculated using excel solver).

- (c) For a depleting boundary, the solution to the equation becomes:

$$C_{(x,t)} = \frac{C_o}{2} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{eff}t}}\right)$$

For $x=10$ cm, the time to reach $C/C_0=0.1$ is ~ 170 d (calculated using excel solver). The longer time reflects the loss of mass at the interface that leads to a longer diffusion path and longer time for diffusion.

- (d) Determine the time required for the pentachlorophenol concentration to reach 10% of the concentration in sediment for a barrier containing sand with 0.3% organic carbon.

The presence of OC increases the sorption capacity of the barrier, which in turn decreased D_{eff} , and increases the time to breakthrough. Given the solution is an erfc, the relationship between D_{eff} and C/C_0 is not inherently obvious and must be calculated.

For $f_{oc}=0.003$ we need to calculate $K_d=K_{oc}*f_{oc}$. Use eqn 9-26b to calculate K_{oc}

$$\log K_{ioc}=0.98*\log K_{ow}-0.32=0.98*4.02-0.32=3.62 \text{ L/kgOC.}$$

$$\text{So } K_d=10^{3.62}*0.003=12.5 \text{ L/kg soil}$$

$$R_{sw}=1.52 \text{ kg soil/L}/0.37=4.1 \text{ (note that 1.52 kg/L is the BULK density which is } \rho_s(1-\phi)$$

$$R_{sw}*K_d=12.5 \text{ L/kg soil}*4.1 \text{ kg soil/L}=51$$

$$D_{eff}=0.37(7.9 \times 10^{-6} \text{ cm}^2/\text{s})/((1+51)(1.4))=1 \times 10^{-8} \text{ cm}^2/\text{s}$$

For this D_{eff} , the time to reach 10% breakthrough at $x=10$ cm is ~ 60 years. This assumes a non-depleting boundary.

- (e) We can repeat this calculation but this time adding activated carbon to the barrier to achieve 5 wt% in the barrier. Assume that you can predict K_d from K_{bc} and assume that the partitioning is linear.

$$\log K_{ibc}=1.6*\log K_{ow}-1.4=1.6*4.02-1.4=5.03 \text{ L/kgbc.}$$

$$\text{So } K_d=10^{5.03}*0.05=5380 \text{ L/kg soil}$$

$$R_{sw}=1.52 \text{ kg soil/L}/0.37=4.1 \text{ (note that 1.52 kg/L is the BULK density which is } \rho_s(1-\phi)$$

$$R_{sw}*K_d=5380 \text{ L/kg soil}*4.1 \text{ kg soil/L}=2.2 \times 10^4$$

$$D_{eff}=0.37(7.9 \times 10^{-6} \text{ cm}^2/\text{s})/((1+2.2 \times 10^4)(1.4))=9.5 \times 10^{-11} \text{ cm}^2/\text{s}$$

For this D_{eff} , the time to reach 10% breakthrough at $x=10$ cm is ~ 6000 years. This assumes a non-depleting boundary.

- (e) Do layers with organic rich sands or activated carbon provide good diffusion barriers for pentachlorophenol? What are the potential problems with this barrier approach?

Sorbent layers over sediments indeed act as very good diffusion barriers, especially for hydrophobic compounds like PAHs or PCBs. Activated carbon is a stronger sorbent than organic carbon, higher K_d , so it would improve this even further. One problem with this “capping” approach is that groundwater seepage through the cap can speed up transport tremendously since now advection dominates the movement rather than diffusion. Also, continued inputs of contamination, e.g. from CSOs will contaminate the top of the cap and this defeats the purpose of the cap. So sources of the contaminant must be shut off for this to be effective.