Fate and Transport: Bringing together all the pieces

We now have the pieces to put together a conceptual and a simple numerical model of fate and transport of a pollutant in the environment:
- what moves it through the environment
- where is it going to end up
- how fast will it get there
- how long will it last in the environment

We go back to our advection/dispersion equation, which considers the change in mass of a pollutant in the environment:
\[
\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - F_{\text{gas}} - F_{\text{solid}} \pm F_{\text{react}} + (I - O)
\]
(assuming the pollutant is dissolved in water)

F*gas = Flux from water to gas, controlled by the concentration gradient, the diffusivity, the equilibrium ratio ($K_{h}$) and the thickness of the layers = [kg/d]. (We know the contact area)
Same idea for other fluxes
F*react = reaction or sum of reactions, including biodegradation, in [kg/d]
I = input of pollutant to the system, [kg/d]
O = output of pollutant from the system, [kg/d]
V = volume of system [m3]

Pulse Release in Groundwater
\[
C_t(x,t) = \left[ M_t \right] \exp \left( \frac{(x-v'_x t)^2}{4D'_t} \right) \exp(-k'_\text{deg} t)
\]
To account for retardation:
- $D'_t = D_t / R$
- $v'_x = v_x / R$
- $k'_\text{deg} = k_{\text{deg}} / R$

Example: PCE into a lake (Greifensee)
Fate and Transport

- Example: PCE into a lake (Greifensee)

\[ V = \text{total volume} = 150 \times 10^6 \text{ m}^3 \]
\[ A = \text{surface area} = 8.6 \times 10^6 \text{ m}^2 \]
\[ h = \text{mean depth} = \frac{V}{A} = 17.4 \text{ m} \]
\[ Q = \text{throughflow of water} = 0.34 \times 10^6 \text{ m}^3/\text{d} \]
\[ t_w = \text{mean water residence time} = \frac{V}{Q} = 440 \text{ d} \]

- From direct measurements we obtain the additional information:

\[ C_w = \text{conc. of PCE in lake} = 91 \times 10^{-6} \text{ g/m}^3 \]
\[ I = \text{River input} = 0.149 \text{ kg/d} \]
\[ O = \text{Loss at outlet} = 0.030 \text{ kg/d} \]

- From a simple calculation, if the amount of water flowing through is about constant:
  - no losses due to
    - Reaction
    - Sorption
  - Why is \( I \neq O \)?

- If we assume that the mass of PCE in the lake is constant, then:

\[
\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - F^*_{\text{gas}} - F^*_{\text{solid}} - F^*_{\text{react}} + (I - O)
\]

Well-mixed

\[ F^*_{\text{gas}} = I - O = 0.119 \text{ kg/d} \]

- Further analysis indicates that the PCE concentration in the lake is not constant...
- Calculate \( F^*_{\text{gas}} \) using our two-film model:

\[ F^*_{\text{gas}} = A v_{\text{tot}} \left( C_w - \frac{C_a}{K_H} \right) \]

- From experimental measurements:

\[ C_a \approx 1.66 \times 10^{-6} \text{ g/m}^3 \]
\[ K_H = 0.727 \]
\[ C_w = 91 \times 10^{-6} \Rightarrow C_a/K_H = 2.3 \times 10^{-6} \]
\[ v_{\text{tot}} = 3 \times 10^{-6} \text{ m/s, considering a mean wind speed of 1 m/s} \]
Fate and Transport

\[ F_{\text{gas}} = A \nu_{\text{tot}} C_w = 0.20 \text{ kg/d} \]

\[
\frac{dM}{dt} = - F_{\text{gas}} + I - O = - 0.200 + 0.149 - 0.030 = - 0.08 \text{ kg/d}
\]

The initial mass in the lake was \( M_0 = C_w V = 13.8 \text{ kg} \), so it will take > 200 days to reduce the concentrations significantly in the lake.

### Example: Indoor Radon

- **F_{\text{air}} = 1000 \text{ m}^3**
- **A = 200 \text{ m}^2**

The flux of Radon (\(^{222}\text{Rn}\)) into the house is

\[ I = (17,500 \text{ atoms/ m}^2 \text{ s})(200 \text{ m}^2) = 3.5 \times 10^6 \text{ atoms/s} = 1.26 \times 10^{10} \text{ atoms/hr} \]

- **The house has a ventilation rate of 1 complete exchange of air every 10 hours**
- **We assume that the air is well mixed...**

If \( N = \) number of atoms of \(^{222}\text{Rn}\) in the house, then:

\[
O = 0.1 N = [\text{atoms removed/hr}]
\]

\(^{222}\text{Rn}\) has a half-life of 3.85 days, or a decay rate of 0.00756/hr. The atoms in the house decay at a rate of:

\[ F_{\text{decay}} = - k_{\text{decay}} N = - 0.00756 N \]

What is the concentration of Rn in the house if we assume a steady-state?

\[
\frac{dN}{dt} = I - O - F_{\text{decay}} = 0
\]

\[
= 1.26 \times 10^{10} \text{ atoms/hr} - (0.1/\text{hr} + 0.00756/\text{hr}) N
\]

\[
N = 1.17 \times 10^{11} \text{ atoms}
\]

\[
C = \frac{N}{V} = 1.17 \times 10^8 \text{ atoms/m}^3
\]

Average person exposed to this concentration will receive \(5.8 \times 10^{-6} \text{ rads/yr}\)

- **almost negligible when compared to the normal exposure to all sources of radiation ~ 0.2 rads/yr**
When can we neglect a process?

- We compare the rates of the various processes to determine which one(s) are much greater than the others - which process(es) dominate(s).
- For example, advection vs. diffusion/dispersion:

  \[ \frac{L_v}{D} \gg 1 \]  
  then advection is dominant

  Ratio called Peclet number

Reaction vs. Advection/Diffusion:

\[ \frac{D_k_r}{v^2} \gg 1 \]  
then reaction is dominant

\[ k_r = \text{rate of reaction} = [s^{-1}] \]

We can also compare the fluxes to the air, solid and biota to determine if one of these is the dominant process.

The dominant flux can then be compared to reaction, advection and diffusion.

In general we may have more than one important process taking place.

Sometimes it is quite difficult to determine a particular flux with precision.

- Contact area may not be measurable.
- Some concentrations are only known as a very rough estimate.

Do a mass balance using the known fluxes and reaction rates to determine the unknown flux.

Example: Naphthalene in Ground Water

- Gasification of coal and crude oil was a common method of producing medium- and high-Btu gas for two centuries until early 1900s.
- Many of these plants disposed of process wastes and less-valuable by-products onsite, contaminating soil with coal-tar waste, light oils, naphthalene, and other similar materials.
Polynuclear aromatic hydrocarbons (PAHs) are components of coal-tar wastes and other wastes that remain at many of these manufactured-gas plants sites.

We will study the migration of naphthalene in ground water from a coal gasification plant.

A well at the site had a high concentration of naphthalene (500 µg/L) ... and I suspect other PAHs.

The site was now paved over.

The questions here were:
- What was the concentration at the site boundary?
- When would it migrate off-site?

An old drawing indicated there was a waste burial site near the well.
- Waste was almost all under the water table, except for the top 1 m.
- Aquifer is a shallow, sandy formation.
- Ground water flows to NE at ~70 m/yr.
Naphthalene in Ground Water

Physicochemical data:
- $C_{wsat} = 31$ mg/L
- $K_d = 0.0198$
- $K_{ow} = 10^{3.3} = 2,000$
- $pK_a > 15$
- $\rho = 1,162$ kg/m$^3$

Soil properties:
- $\rho_s = 1,700$ kg/m$^3$
- $n = 0.3$
- $K = 3 \times 10^4$ m/yr
- $f_{src} = 0.1\% = 0.001$
- $D_x = 1050$ m$^2$/yr
- $D_y = 105$ m$^2$/yr

Process Data for Naphthalene

- $\lambda_0 =$ assumed to equal zero (groundwater)
- VOLATILIZATION: $K_v = 0$ underground, paved site conservative assumption
- HYDROLYSIS: $K_h = 0$, BTEX = fr
- $K_h = 0$, tfr
- $C_{react} = 0.08 (0.03) = 1.3$
- $P_f = 1$, naphthalene
- $\alpha = 0$

Biodegradation:
- $\lambda_h = 2$ (yr)$^{-1}$, (soil)
- $\lambda_f = 0.26/yr$

Based on amount of naphthalene present in waste pit and current aqueous concentration (500 µg/L)
- source is expected to last 300 years...
- Site boundary in this direction is 150 m downgradient

We use the advection-dispersion equation with a reaction term and an input:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + F_{react} + I$$

- $I = f(x, y, t)$, is the continuous leaching of naphthalene from the disposal pit into the ground water, which is a source for 300 years

If only dispersion occurs, then maximum concentration would be 390 µg/L
- Due to biodegradation, maximum concentration is 16 µg/L
- Biodegradation is much more important in this case (33:1)
- This concentration is well below chronic criteria for fresh water (620 µg/L)
Naphthalene in Ground Water

- $v_w = 70 \text{ m/yr}$
- $R = 8$
- $v_p = \frac{v_w}{R} = 8.75 \text{ m/yr}$
- $D_p = \frac{D}{R} = 131 \text{ m}^2/\text{yr}$
- $k_r = 0.26 /\text{yr}$

Test #1: $k_r = 0.26 /\text{yr} \gg \sqrt{\frac{v}{D}} = 0.073 /\text{yr}$
Test #2: $k_r = 0.26 /\text{yr} \gg \frac{D}{L^2} = 0.047 /\text{yr}$