Movement of Pollutants

- In addition to transferring from one phase to another, pollutants may move in the environment within the phase they are in.

Examples:
- PCBs emitted to the atmosphere will travel with particles along wind currents and deposit in some cases hundreds of km away from source.
- Dissolved pollutants (e.g., gasoline spill) may move through the subsurface with ground water.

There are two main physical processes that transport the contaminants away from the source:
- Advection
- Diffusion and dispersion

Rate of mass accumulation = Rate of mass flow in - Rate of mass flow out ± Rate of transformation

Advection

- Moving along with air in the atmosphere or water in a water body (e.g., rivers, lakes, ocean, groundwater)
- Pollutant tags along at velocity of flowing air or water
- If pollutant transfers to another phase (e.g., aerosols or particulate matter in water) then its direction of movement will be altered

Time required to move a given particle from point 1 to point 2 is:

\[ t_2 - t_1 = \Delta t = \frac{L}{v} \]

- We can also refer to a volumetric flow rate, Q in (m³/s), as the velocity that a given surface moves through the “channel.”
Advection

If the channel gets narrower or shallower (or both), the velocity at which the water flows must increase to conserve mass.

\[ v_{\text{downstream}} > v_{\text{upstream}} \]
\[ Q_{\text{downstream}} = Q_{\text{upstream}} \]

Advection

Advective Flux

\[ F_{\text{adv}} = \nu C \]
\[ \frac{\partial C}{\partial t} = \frac{\partial F_{\text{adv},x}}{\partial x} + \frac{\partial F_{\text{adv},y}}{\partial y} + \frac{\partial F_{\text{adv},z}}{\partial z} \]

If the velocities are constant or zero:

\[ \frac{\partial C}{\partial t} = \nu_x \frac{\partial C}{\partial x} + \nu_y \frac{\partial C}{\partial y} + \nu_z \frac{\partial C}{\partial z} \]

Water moving through soil (or fractured rock) cannot go through the entire area since it is partially blocked by rock.

It can only go through the pore space, which means a rather tortuous path...

Actual area available for flow is:

\[ A_{\text{flow}} = nA_{\text{total}} \]

Why does water flow in the subsurface?

- think of it as a container, which fills in one end by rainfall and empties on the other to a stream, river, lake or ocean

Water (or an organic liquid) flows from a high point to a low point:

\[ h_1 \]
\[ h_2 \]
Advection

- The driving force is the difference in heights:
  \[ \Delta h = h_1 - h_2 \]

- Volumetric flow rate is similar to flow rate for open channels, but with a "correction" factor to account for the reduced path for water in soil:
  \[ Q = -K \frac{\Delta h}{L} A \quad \text{(Darcy's law)} \]

- Slope of water table, i.e. how fast it is dropping per distance traveled, is called gradient in hydraulic head:
  \[ \text{gradient} = \frac{dh}{dx} = \frac{\Delta h}{\Delta x} = \left[ \frac{\text{m}}{\text{m}} \right] \]

- \( K \), the hydraulic conductivity, is a property of soil or rock.
  - It is measured for water flowing through the porous media.

- We can use a more general parameter to evaluate the movement of any type of fluid (air, water, organics, oil) through soil, called the permeability, \( k \), which is related to the hydraulic conductivity:
  \[ K = k \frac{\rho g}{\mu} \]

- \( K \) is a very important factor for determining if an aquifer is suitable to extract water.
  - If \( K > 10 \text{ m/day} \) then a well will produce abundant water.
  - If \( K < 0.1 \text{ m/day} \), the soil or rock is too "tight" to be useful for water extraction.

  This is also a very important for remediation!

- Another common term is "specific discharge", which is related to volumetric flow rate, by simply dividing by area:
  \[ q = \frac{Q}{A} = -\frac{K \Delta h}{L} = [\text{m/s}] \]

- Actual "groundwater velocity", i.e. how fast a particle or a pollutant flowing with water moves is:
  \[ v'_w = \frac{q}{n} = [\text{m/s}] \]
  porosity
Advection

Example:
Place a tracer in the water in one well and see how much time it takes to come out in another well:
- It takes 10 days for the tracer to travel 5 m, from injection well to observation (monitoring) well
- Soil porosity is estimated to be 0.32
- Difference in water level is 0.10 m between wells
- What is the permeability of the soil?

\[ q = v_w n = 0.16 \text{ m/day} \]
\[ K = \frac{q L}{\Delta h} = 8 \text{ m/day} = 9.26 \times 10^{-5} \text{ m/s} \]
\[ k = \frac{\mu K}{\rho g} = 9.43 \times 10^{-12} \text{ m}^2 \]

Diffusion

Diffusion is the process through which pollutant molecules move through air or water (or different organic pollutants in a mixture, e.g. gasoline).
- What causes (molecular) diffusion?
  - At a given temperature (e.g. 20 °C), the molecules have a certain energy which keeps them moving

As the molecules move, they eventually strike other molecules.
- For a pollutant in air or water, the highest probability is that it will strike an air or water molecule, rather than another pollutant molecule
- Striking another molecule changes the path in which pollutant molecule was initially going

Eventually, the pollutant strikes another pollutant molecule, which sends them in opposite ways...
- Diffusion moves pollutants from high concentration to low concentration, spreading them out

Example
- If you put a small amount of dye very carefully into a beaker full of water so that you don’t create currents, the dye will slowly spread out until the water becomes uniformly colored
- Dye must be of same density as water or else it may sink or float, which is an advective process...
Now put a small amount of dye in a moving fluid (e.g. air, river, ocean current) and watch it spread.

- Average particle (dye or pollutant) moves along with flow, while some go a bit faster and others go slower.
- The "pulse" gets spread out.

If instead of a small pulse we add a continuous amount of dye (or pollutant from a UST or a smokestack), then we see a "plume" moving with the flow.

- If there was no diffusion, the plume would be a "sharp front", but instead we get a "diffuse" front.

---

**Source:** Pepper et al., 1996
When a pollutant moves dissolved in water or volatilized in air, the interaction with solid obstacles results in additional spreading.

- Buildings, rocks in river, sand grains in aquifer
- Wind and water currents also contribute to spreading

Similar effect to diffusion: it is typical to lump them together into a parameter called the “total dispersion coefficient”, $D$.

To differentiate, molecular diffusion is given the symbol, $D_m$, and dispersion (which is due to fluid movement or hydrodynamic forces) is $D_h$.

Experimental and field evidence indicates that dispersion is a linear function of velocity:

$$D_h = \alpha \cdot v$$

$\alpha = \text{dispersivity}$
Dispersion

- Dispersivity is measured in field by running tracer experiments.
- Dispersivity along the direction of flow (longitudinal dispersivity) is typically ~10 times greater than across the flow (lateral or vertical dispersivity)
- Velocities in those directions are smaller.

Dispersion in Fractured Rock

- Flow through fractured rocks is essentially through the fractures, which represent great paths for the pollutants to travel through.
- Some fractures may be filled by later deposits or sediments and thus have a low conductivity.
- There are also some “dead-end” fractures which result in a large difference in travel times among pollutant molecules.

Dispersion in Fractured Rock

Distance, x (m)

Concentration (kg/m³)

soil

fractured rock

observation point

Advection-Diffusion

We can use a simple mathematical model to explain how fast a spill or emission to the environment will spread.

We look at how the concentration of pollutant changes with time:

\[ \text{Change in concentration} = \text{Movement due to advection} - \text{Spreading due to Diffusion/dispersion} \]

Advection-Diffusion

We can express it in two forms:

\[ \frac{dC}{dt} = -v \frac{dC}{dx} + D \frac{d^2C}{dx^2} \]

\[ \frac{\Delta C}{\Delta t} = -v \frac{\Delta C}{\Delta x} + D \frac{\Delta^2C}{\Delta x^2} \]

This is called the advection-diffusion equation.

Advection-Diffusion

In 3 dimensions

\[ \frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} - v_y \frac{\partial C}{\partial y} - v_z \frac{\partial C}{\partial z} \]

\[ + \left[ D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right] \]
Gaussian model for pulse (puff) release assuming all flow is along x-axis

\[ C_i(x,y,z,t) = \left[ \frac{M_i}{\sqrt{2\pi}^{3/2} D_x D_y D_z} \right] \times \exp \left( -\frac{1}{2} \left( \frac{x-v_x t}{D_x} \right)^2 + \left( \frac{y}{D_y} \right)^2 + \left( \frac{z}{D_z} \right)^2 \right) \]

Gaussian model for continuous (plume) release

\[ C_i(x,y,z) = \left( \frac{Q_i}{4\pi D_x D_y D_z} \right) \exp \left( -\frac{1}{2} \left( \frac{y}{D_y} - \left( \frac{x}{D_x} \right) \right)^2 \right) \]
Groundwater Transport

- Starting from the advection-dispersion equation, use Darcy’s law for the velocity.
- For a pulse release (short spill):

  \[ C_i(x,y,z,t) = \frac{M_i}{8\pi D_x D_y D_z} \left[ \frac{1}{\sqrt{4\pi D_x t}} \right] \left[ \frac{1}{\sqrt{4\pi D_y t}} \right] \left[ \frac{1}{\sqrt{4\pi D_z t}} \right] \left[ 1 - \text{erfc} \left( \frac{x - v_x' t}{\sqrt{4D_x t}} \right) \right] \left[ 1 - \text{erfc} \left( \frac{y - v_y' t}{\sqrt{4D_y t}} \right) \right] \left[ 1 - \text{erfc} \left( \frac{z - v_z' t}{\sqrt{4D_z t}} \right) \right] \]

After a long time,

\[ C_i(x,t) = \frac{C_{oi}}{2} \left[ \text{erfc} \left( \frac{x - v_x' t}{\sqrt{2D_x t}} \right) \right] \]

where \( C_{oi} \) is the initial concentration at the source.

Groundwater plume evolving over time, in one dimension:

\[ C_i(x,t) = \frac{C_{oi}}{2} \left[ \text{erfc} \left( \frac{x - v_x' t}{\sqrt{2D_x t}} \right) - \text{erfc} \left( \frac{x + v_x' t}{\sqrt{2D_x t}} \right) \right] \]

Error Function

\[ \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt \]

\[ \text{erfc}(z) = 1 - \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-t^2} dt \]

Table 9.3: Values for the Error Function

<table>
<thead>
<tr>
<th>z</th>
<th>erf(z)</th>
<th>erfc(z)</th>
</tr>
</thead>
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<tr>
<td>0.9</td>
<td>0.6418</td>
<td>0.3582</td>
</tr>
</tbody>
</table>
**Groundwater Transport**

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**EXAMPLE 8.5 One-Dimensional Contaminant Transport with No Transformation**

A surface impoundment containing cyanide leaches into a groundwater system of high permeability that behaves as a one-dimensional aquifer with a hydraulic conductivity of 4 m/day, effective porosity of 0.3, and a hydraulic gradient of 0.03 m/m. If the initial concentration of cyanide is 42 mg/L, with a longitudinal dispersion coefficient \(D_x\) of 2.1 m/day and sorption and transformation processes are negligible, determine the time required for the concentration to reach 1 mg/L at a well 1000 m (3,281 ft) away.

**Solution**

1. Use Equation 8.25 to determine the pseudo-water velocity.

\[
\frac{x}{v} = \frac{L}{v}
\]

where:

- \(x\) = 1000 m
- \(v\) = 0.4 m/day
- \(L\) = 2.1 m/day

2. Using Equation 8.25, develop an expression for time. Note that the last term can be ignored because the 1L will be zero for this case:

\[
C(x, t) = \frac{C_0}{1 + \left( \frac{x}{D_x} \right)}
\]

where:

- \(C_0\) = 42 mg/L
- \(x\) = 1000 m
- \(v\) = 0.4 m/day
- \(D_x\) = 2.1 m/day

3. An expression for \(t\) may be determined by interpolating between values in Table 8.3, converted to 1L.

\[
1000 = \frac{0.4t}{2 \times 2.1} \Rightarrow t = 400 \text{ days} = 1.1 \text{ years}
\]

---

**Dispersivity**

\[
D_x = \alpha_x v_x
\]

\(\alpha_x = 0.1 \text{ L}\)

\(D_y \sim 0.1 D_x\)

\(D_z \sim 0.1 D_x\)

---

**Advection-Dispersion Examples**

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**Figure 9.28** Plume of leachate migrating from a sanitary landfill on a sandy aquifer. Concentration zone is represented by contours of CT concentration in groundwater.
A pollutant that sorbs onto soil is slowed down with respect to the velocity of the water or air phase. It takes longer for the pollutant to travel a given distance than water does. We call the effect of sorption on transport a "retardation." The retardation factor is related to K_d:

$$R = \left[ 1 + \frac{\rho_s K_d}{n} \right]$$

The velocity of the pollutant, $v_p$, with respect to the water velocity, $v_w$, is:

$$v_p = \frac{v_w}{R}$$

Tracers (e.g., chlorine, bromine) do not typically sorb and thus have $R = 1$. Under certain circumstances, they may have $R < 1$ (e.g., anion exclusion in clays). If $R = 10$, then the pollutant moves at 1/10th the velocity of water.

Retardation can help to contain the extent of contamination, but it also implies that typical remediation alternatives will take a long time to remove all the pollutant from the soil.

To account for sorption, the advection-dispersion equation is written as:

$$R \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2}$$

or:

$$\frac{\partial C}{\partial t} = -\frac{v}{R} \frac{\partial C}{\partial x} + \frac{D}{R} \frac{\partial^2 C}{\partial x^2}$$
Retardation

\[ C_i(x,t) = \frac{C_{0i}}{2} \left\{ \exp \left[ \frac{x}{2D_x^*} \left( \sqrt{v_x^*} - \sqrt{\frac{v_x^*}{2} + 4D_x^*} \right) \right] \text{erfc} \left( \frac{x - t\sqrt{v_x^* + 4D_x^*}}{2\sqrt{D_x^*}t} \right) + \exp \left[ \frac{x}{2D_x^*} \left( \sqrt{v_x^*} + \sqrt{\frac{v_x^*}{2} + 4D_x^*} \right) \right] \text{erfc} \left( \frac{x + t\sqrt{v_x^* + 4D_x^*}}{2\sqrt{D_x^*}t} \right) \right\} \]

where:

\[ v_x^* = \frac{v_x}{R}, \quad D_x^* = \frac{D_x}{R} \]

Heterogeneity in Soils

- Why are soils so heterogeneous?
  - Layers formed through sedimentation have different composition and packing
  - Layer orientation may be quite different from horizontal due to tectonic processes posterior to the sedimentation process
  - Weathering, chemical and biological processes may also affect properties

How do we deal with heterogeneity?

- Instead of using an average value for permeability or dispersivity, we describe them using their statistics (e.g. mean and standard deviation) to characterize the uncertainty
- Using measurements at different points, plus geological information, we generate maps of permeability, porosity, etc. and apply the numerical models using these maps.