Chapter 6 - Solute Transport

- fertilizer movement
- leaching of salt (reclamation)
- pollutant movement

Transport depends on

- $\text{H}_2\text{O}$ flow velocity
- Water content
- Soil characteristics
- Solute species
- Solute reactions

Examples

- Solute in soil originally
- Applied as a pulse by fertilizer application or contaminant spill
- Applied continuously with irrigation water
Miscible Displacement

Definition: Displacing solution is miscible (mixes) with displaced solution
- Mixing occurs at boundary
- Mixing due to diffusion and dispersion
- Dispersion due to mass flow of H₂O

For No Mixing at Boundary (Immiscible)

Cₜ (or C), the concentration of the material of interest as it exists from the column
C₀, the initial concentration of the material of interest that enters the column
# of Pore Volumes = \frac{\text{Volume Effluent}}{\text{Total Volume Solution in Media}}

For soil, total volume of solution in media \( (V_t) \) is

\[ V_t = \theta_v V \]

Water content (cm\(^3\)/cm\(^3\)) Volume of Soil

Solute is the material we are trying to measure.

**Solute in soil initially**

**Pulse of solute**

**Solute applied continuously**

**Effect of flow velocity**

\[ C/C_0 \]

\[ 0 \] Pore Volume

\[ 1.0 \]

\[ 0.04 \text{ cm/h} \]

\[ 1.9 \text{ cm/h} \]
Desaturation eliminates larger flow channels (larger pores) and increases the proportion of the volume of water that does not readily move. These almost stagnant zones (soil micropores) act as sinks to ionic diffusion.

Desaturating the soil causes an incomplete displacement of the initial solution by the solute, thus a more rapid appearance of solute is observed.
Effect of soil texture (Pore size distribution)

- Wider pore size distribution allows for more relatively stagnant zones in loam.

Effect of solute

Cl⁻ excluded by surface of the colloid (assumes the soil has a high C.E.C.)

Tritium (radioactive water) has some proton exchange.

✍️ For a soil with a significant CEC, where would you expect the breakthrough curves for cations to appear? How about pesticides?
**Capillary Model for Solute Transport**

Velocity inside tube at any radius, \( r \), is given by equation below. The total radius of the tube is \( a \).

\[
v = 2 v_o \left[ 1 - \frac{r^2}{a^2} \right]
\]

average velocity

**Mass flow inside tube**

\[
\text{flux } J_x = 2 v_o \left[ 1 - \frac{r^2}{a^2} \right] C
\]

A “cube” of soil depicting solute moving through the cube

Storage of solute inside cube = flux out minus the flux in
Continuity Equation for capillary tube

\[ \frac{\partial C}{\partial t} = -2v_0 \left[ 1 - \frac{r^2}{a^2} \right] \frac{\partial C}{\partial x} \]

Pore Volume

Problems with the capillary model
1. Soil not capillary tubes
2. Longitudinal diffusion occurs
3. Average pore size - Won’t work because pores irregular and diffusion complicated

**Convection-Dispersion Model**

Bulk flow (mass flow) flux of dissolved solute

\[ J_{lc} = J_w C_l \]

Where \( J_{lc} \) is bulk flow flux
\( J_w \) is the water flux
\( C_l \) is the dissolved solute concentration

Hydrodynamic dispersion flux

\[ J_{lh} = -D_{lh} \frac{\partial C_l}{\partial z} \]

where \( J_{lh} \) is the hydrodynamic dispersion flux
\( D_{lh} \) is the hydrodynamic dispersion coefficient
This equation looks like Fick's Law for diffusion.

**Liquid diffusion flux**

\[ J_{ld} = -D_l \frac{\partial C_l}{\partial z} \]

where \( J_{ld} \) is the liquid diffusion flux

\( D_l \) is the soil liquid diffusion coefficient.

This is Fick's Law for solute diffusion in soil.

**Total flux of dissolved solute**

\[ J_l = J_{lc} + J_{nh} + J_{ld} \]

\[ = J_w C_l - D_{nh} \frac{\partial C_l}{\partial z} - D_l \frac{\partial C_l}{\partial z} \]

Or, by combining the last two terms

\[ J_l = -D_e \frac{\partial C_l}{\partial z} + J_w C_l \]

where \( D_e = D_{nh} + D_l \) and

\( D_e \) is the effective diffusion-dispersion coefficient.

**Continuity Equation (Conservation of mass)**

1. For nonsorbing, nonreactive solutes

\[ \frac{\partial C_l}{\partial t} = -D_e \frac{\partial J_l}{\partial z} \]

\[ \frac{\partial C_l}{\partial t} = \frac{D_e \frac{\partial C_l}{\partial z}}{D_e} + \frac{J_w}{D_e} \]

If \( D_e \) and \( J_w \) are constant with \( Z \)
\[
\frac{\partial C_t}{\partial t} = D \frac{\partial^2 C_t}{\partial z^2} \cdot V \frac{\partial C_t}{\partial z}
\]

where \( D = \frac{D_v}{\theta_v} \) and \( V = \frac{J_w}{\theta_v} \)

\( V \) is an average pore water velocity since pores not all the same size.
Dispersion as affected by pore-water velocity

- It has been shown from many experiments that $D$ (or $D_e$) increases as the pore-water velocity increases.

\[ D \text{ (or } D_e) \]

\[ D^l \]

\[ 0 \]

\[ v \]

\[ D_e = D_{lh} + D^l \]

- Since $D^l$ is not expected to change with velocity, $D_{lh}$ is the term changing with velocity.

- This extra spreading due to hydrodynamic dispersion is due to complicated flow paths around soil particles, to differences in water velocity within single pores, and to differences in water velocity in adjacent pores.

2. Equation for adsorbing chemicals

\[
\frac{\rho_b}{\theta_v} \frac{\partial C_a}{\partial t} + \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial z^2} - V \frac{\partial C_i}{\partial z}
\]

where $C_a$ is adsorbed concentration.
Ca is often given by a linear adsorption isotherm

\[ C_a = K_d C_l \]

where \( K_d \) is the distribution or partition coefficient.

If the linear isotherm is substituted into the transport equation above, the following equation is obtained:

\[ R = 1 + \rho_b \frac{K_d}{\theta_v} \]

where \( R = 1 + \rho_b K_d/\theta_v \) is the retardation factor. Dividing the above equation by \( R \)

\[ R \frac{\partial C_l}{\partial t} = D \frac{\partial^2 C_l}{\partial z^2} - V \frac{\partial C_l}{\partial z} \]

gives

\[ \frac{\partial C_l}{\partial t} = D_R \frac{\partial^2 C_l}{\partial z^2} - V_R \frac{\partial C_l}{\partial z} \]

where \( D_R = D/R \) and \( V_R = V/R \) are the retarded dispersion coefficient and retarded velocity, respectively.

3. Equation for reactive chemicals

If the chemical being transported through soil is reactive meaning that it "breaks down", either chemically or biologically, to some other chemicals, the following equation must be used

\[ \theta_v \frac{\partial C_l}{\partial t} = D_x \frac{\partial^2 C_l}{\partial z^2} - J_w \frac{\partial C_l}{\partial z} \]

where \( S \) is some kind of sink term. This term may be a kinetic-type relationship such as zero order, first order, Michaelis-Menten, Monod, etc. For an example of first-order
decay, see the text (Jury et al., 1991).

For chemicals that are biodegraded, how would biodegradation affect the shape of the breakthrough curve for that chemical?

The following figures show experimental apparatus and data from experiments with different porous materials, flow rates, and chemicals:

A cross-sectional sketch of an apparatus used to measure the displacement of the solution from soil columns. (Nielsen and Biggar, 1961)
Displacement of water by a chloride solution in a 10-cm column of glass beads under steady saturated and unsaturated conditions. From Krupp and Elrick (1968).
Chloride and tritium breakthrough curves for Columbia silt loam at soil water contents $a. 0.482 \text{ cm}^3\cdot\text{cm}^{-3}$ and $b. 0.472 \text{ cm}^3\cdot\text{cm}^{-3}$. The vertical broken lines designate 1 pore volume.

From Kutilek and Nielsen (1994)
From Biggar and Nielsen (1962).

-Chloride breakthrough curves from three aggregate size fractions of Aiken clay loam for an average flow velocity of 2.0 cm/hr. at saturation. The volumetric water capacity $V_w$ is indicated by the arrow.

-Chloride and tritium breakthrough curves from three aggregate size fractions of Aiken clay loam for an average flow velocity of 0.04 cm/hr. at saturation. The volumetric water capacity $V_w$ is indicated by the arrow.
Chloride breakthrough curves from saturated 390μ glass beads for two average flow velocities $v$.

-Chloride breakthrough curves from saturated Aiken clay loam aggregates (0.25 to 0.50 mm.) for two average flow velocities $v$.

From Biggar and Nielsen (1962).
From Rolston et al. (1979).
From Castro and Rolston (1977)
Chloride and magnesium breakthrough curves for initially Ca-saturated Oakley sand at soil water contents a. 0.327 cm$^3$·cm$^{-3}$ and b. 0.235 cm$^3$·cm$^{-3}$. The two vertical, broken lines designate 1 pore volume for the chloride and the cation exchange capacity, respectively.

From Kutilek and Nielsen (1994)
Relative concentrations of chloride, tritium, and 1,2-dibromo-3-chloropropane (DBCP) added at the soil surface and measured at the 30- and 150-cm depths in Panoche clay loam during continuous ponding versus depth of water applied. (Nielsen and Jackson, 1968)
Exclusion or immobile water

Diffusion and dispersion

Solute breakthrough curves illustrating several patterns of solute elution

Field-measured chloride concentration distributions from a surface
application of potassium chloride being leached through the profile as a
result of four different water application treatments. Values associated
with each curve correspond to cumulative amounts of water infiltrated

From Kutilek and Nielsen (1994).

Apparatus for sampling the soil solution

Pore liquid sampling with porous cup vacuum sampler (lysimeter) Note: Capillary tube is only inserted to recover the water sample. (From Parkin and Lane, 1970. With permission.)
Soil solution sampling porous cup, pressure-vacuum samplers showing: (A) installation in a backfilled borehole, (B) installation in a backfilled trench, and (C) sampler construction. (Courtesy of Soilmoisture Equipment Corp.)