

Lecture Packet #11: Solute Transport in Groundwater

Importance of Solute Transport in Groundwater

- Geologic questions: ion migration, ore deposition.
- Environmental problems: contamination of drinking water by organic compounds and metals, radioactive waste disposal, saltwater intrusion.

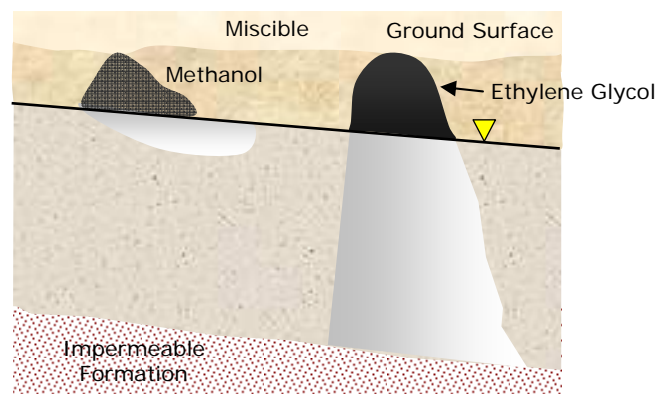
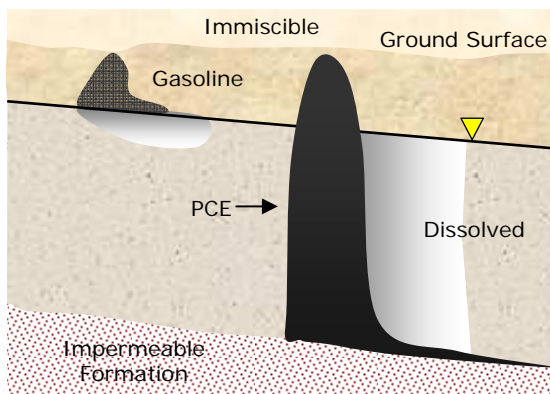
Drinking water standards

- **Dissolved compounds** can be toxic and carcinogenic.
- Safe Drinking Water Act directed EPA to establish MCLs (maximum levels)

Typical values:

Contaminant	MCL
Trichloroethylene (TCE)	5 µg/L
Tetrachloroethylene (PCE)	5 µg/L
Vinyl Chloride	2 µg/L
Benzene	5 µg/L
Carbon Tetrachloride	5 µg/L
Copper	1 mg/L
Lead	0.05 mg/L
Mercury	2 µg/L
Arsenic	10 µg/L

- **Immiscible compounds** serve as a source of dissolved groundwater contamination.



NAPLs – non-aqueous phase liquids

LNAPL – lighter-than-water NAPL (floaters)

- For example, fuels: gasoline, diesel fuel
- Plume forms on surface of water table
- Migrates in direction of water table
- Must be skimmed

DNAPL – denser-than-water NAPL (sinkers)

- For example: chlorinated hydrocarbons – TCE (1.46 sg), TCA (1.34), carbon tet (1.59)

- Can sink to bottom of aquifer to form pool
- Can migrate down dip on aquifer bottom
- Recovery difficult to impossible

The problem:

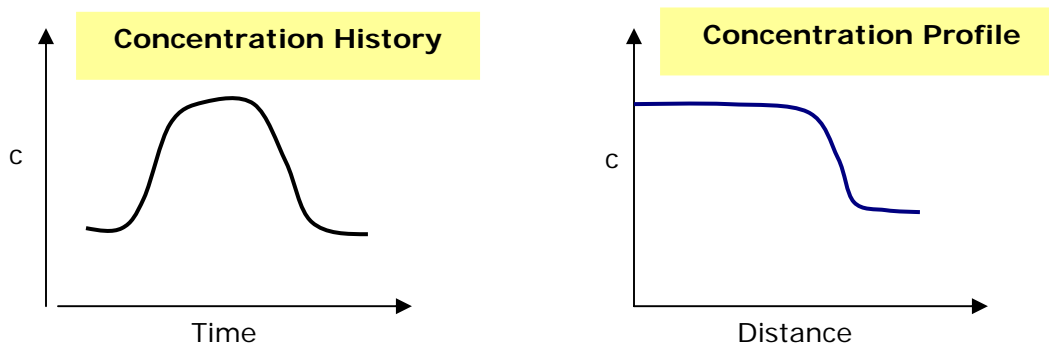
- Easy to contaminate
- Low concentrations are bad
- Substances can migrate with flowing groundwater
- Hard to remove

Dissolved Substances

A **solute** is a substance dissolved in a liquid

- Example: Chloride is a **solute** and water is the **solvent**
- Concentrations measure in [Mass/Length³] (mg/L)

Representing data involving dissolved substances, $C(x,y,z,t)$



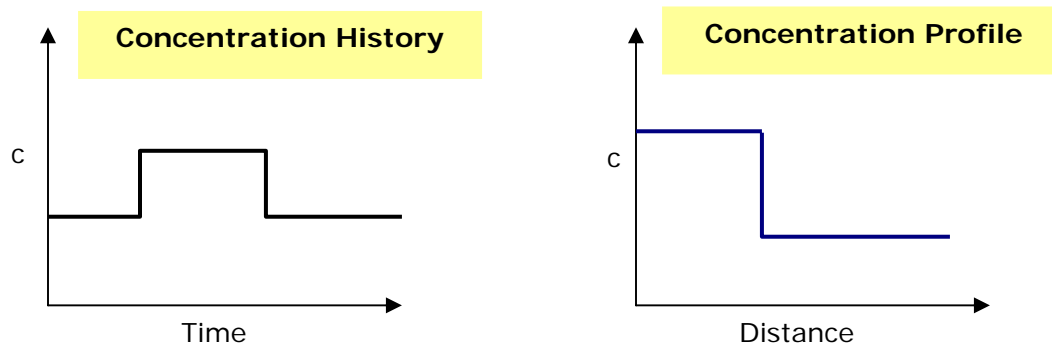
Processes of Solute Migration

1) **Advection** – movement of the solute with the bulk fluid where it moves with the average velocity of the water (alone it is plug flow)

- Recall from Darcy's law we have linear average velocity:

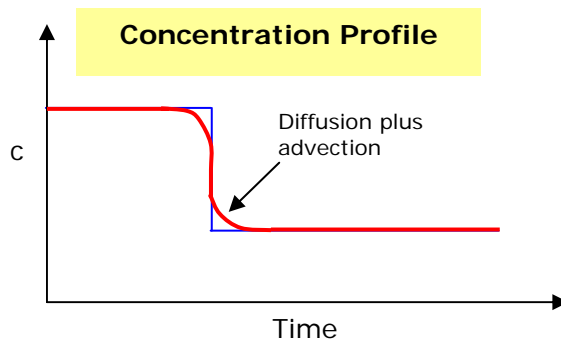
$$V = -\frac{K}{n_e} \frac{dh}{dL}$$

- Advective flux is simply velocity of water times the solute concentration $F_{advec} = VC$



2) **Hydrodynamic dispersion** – spread of a solute plume involving the mixing of solute with native groundwater

- Molecular diffusion – spread of solute molecules due to thermal motion (function of temperature)
- Given by Fick's Law $F_{diff} = -D_{molec} \frac{dc}{dx}$
 - Where D_{molec} is the diffusion coefficient in porous media (value less than that in water); D units $[L^2/T]$
 - dc/dx is the concentration gradient



Get a narrow mixing zone where concentrations are smeared out.

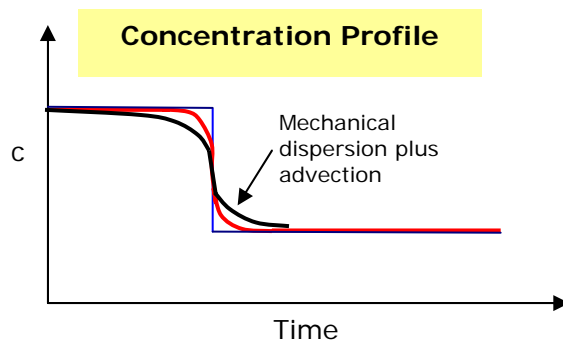
Important Observation – mixing zone seen in lab or field is much, much, much bigger than can be explained by diffusion alone.

Lab experiments show:

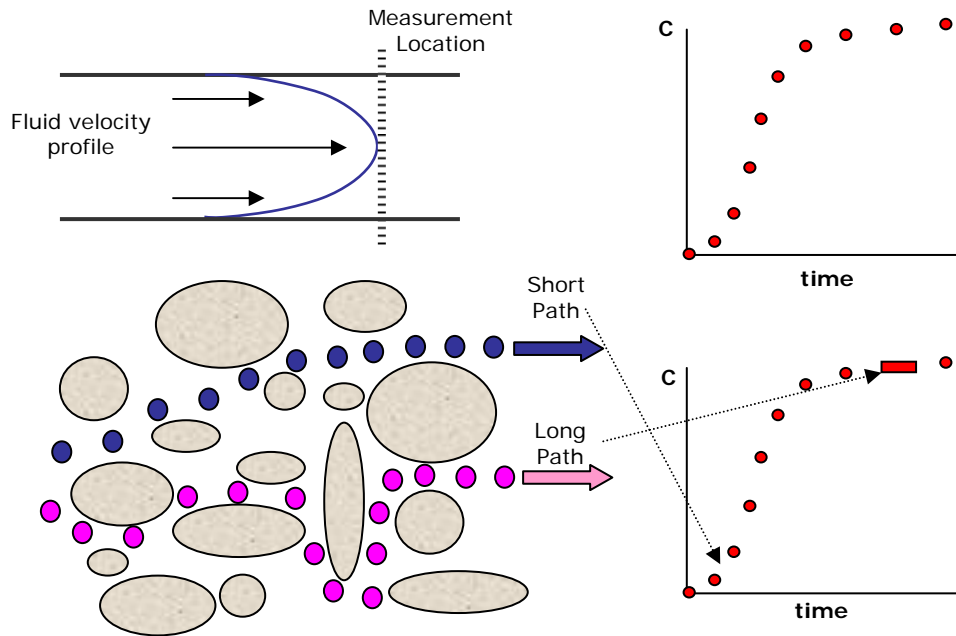
- Spreading exists
- Spreading is more intense than due to diffusion
- Spreading depends on groundwater velocity
- Fick's law applies, but the "D" is much bigger

$$F_{mech} = -D_{mech} \frac{dc}{dx}$$

This is due to Mechanical Dispersion – the mixing that occurs because the porous media forces some solute molecules to move faster than others while following a tortuous path through pores of different sizes



Velocity variations due to: for example –



Mechanical dispersion from lab fits: $D_{mech} = \alpha|V|$
 Where α is the **dispersivity** with units of length [L]

The **Hydrodynamic Dispersion Coefficient** consists of

$$D_h = D_{hydrodynamic} = D_{mechanical} + D_{molecular}$$

NOT to be confused are:

Dispersion – the spreading or mixing process

Dispersion Coefficient – the D with units of $[L^2/T]$

Dispersivity – spreading or mixing parameter, a length, [L]

The flux of solute is due to:

- Advection (the main process)
- Dispersion (hydrodynamic dispersion)

$$F_{total} = VC + (-D_{mech}) \frac{dc}{dx}$$

Solute Transport Equation

Recall development of flow equation:

Conservation of mass + some empirical law

For transport of a nonreactive solute we use the above definition for flux as the empirical law giving in 1D:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}$$

Change in concentration with time dispersion advection

in uniform steady flow (one direction) the 2D transport equation is:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - V_x \frac{\partial C}{\partial x}$$

Where the longitudinal hydrodynamic dispersion coefficient is:

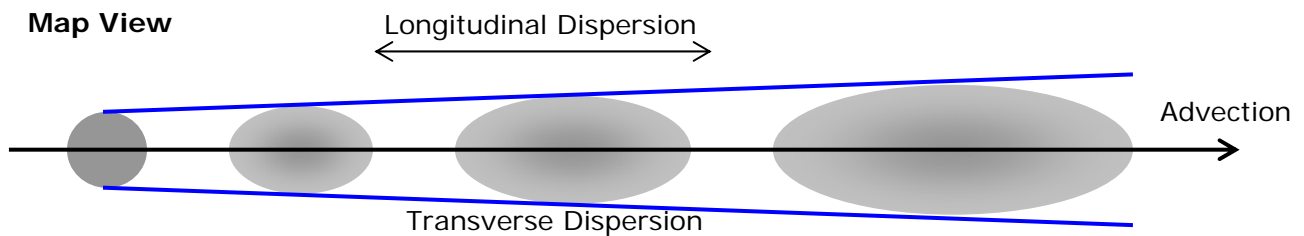
$$D_L = \alpha_L |V| \text{ and } \alpha_L \text{ is the longitudinal dispersivity}$$

The transverse hydrodynamic dispersion coefficient is:

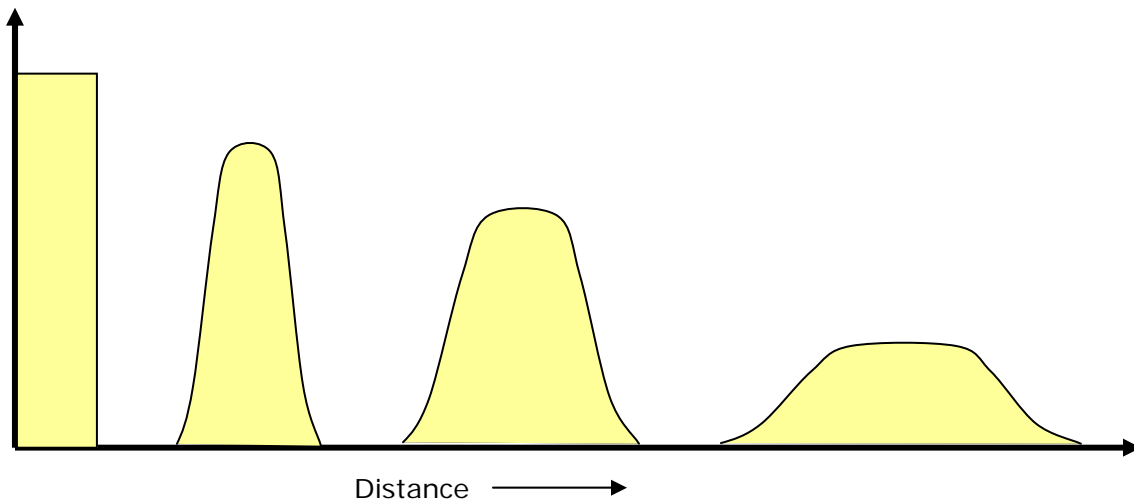
$$D_T = \alpha_T |V| \text{ and } \alpha_T \text{ is the transverse dispersivity (much smaller than longitudinal dispersivity)}$$

Note: In 2D if flow is in two directions then you get 4 dispersion terms and two advective terms and the form of the "D"s is more complex)

From a pulse injection you get a plume (a cloud) of solute that migrates via advection and spreads longitudinally (mostly) and transversely (a bit) – Mass is conserved.

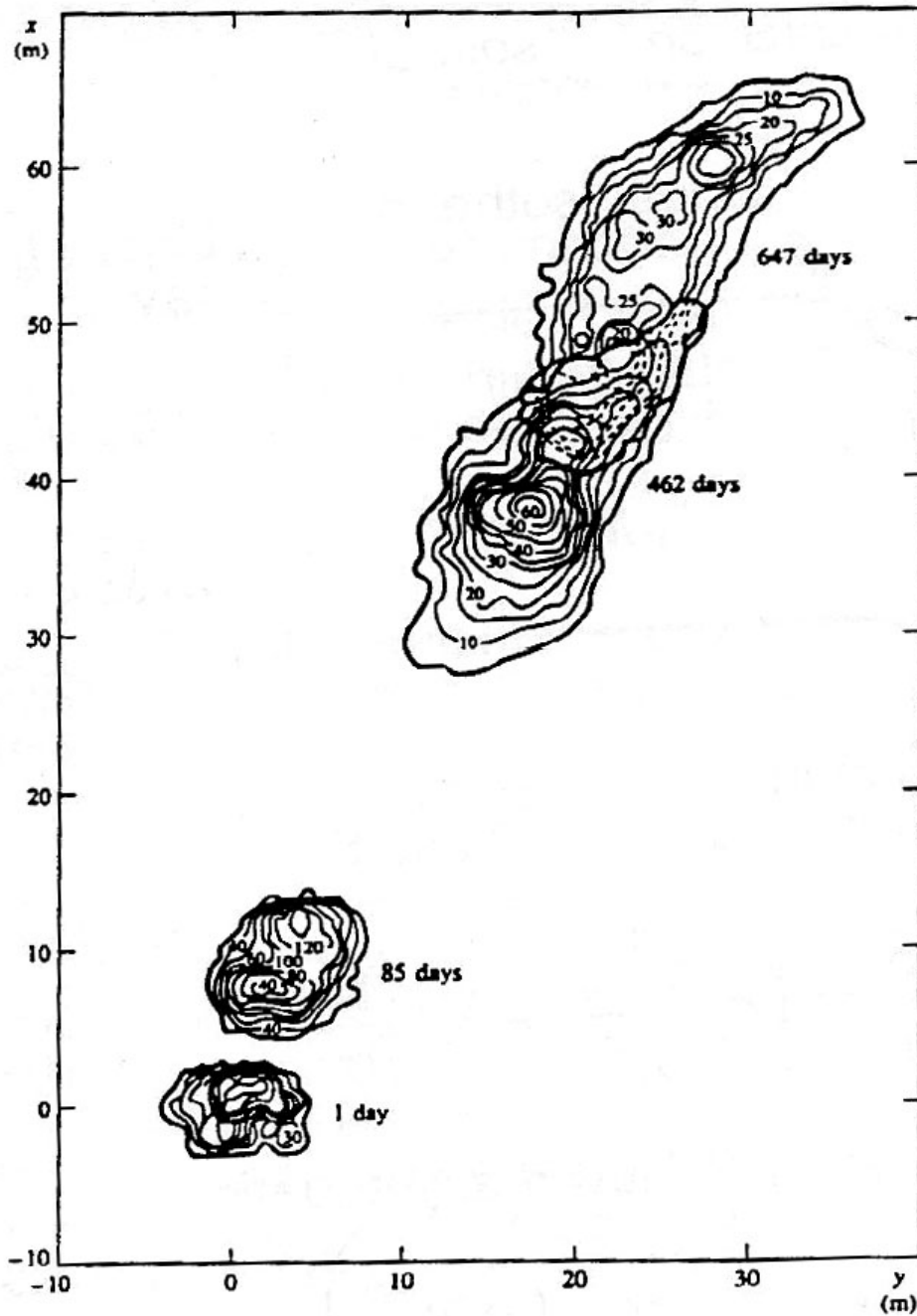


Concentration Profile



In reality:

- Plumes are not so perfectly shaped
- Even in homogeneous media they are distorted
- In heterogeneous media plumes can be complex, following high conductivity lenses and even split into more than one plume
- There is a scale effect in which dispersivity is greater with greater travel distance

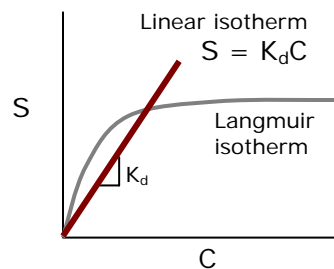


Chemical Reaction During Transport

- Homogeneous reactions – occurring in the aqueous phase
- Heterogeneous reactions – those involving a solid surface or a phase conversion

Sorption – a type of surface reaction in which the solute spends some of its time stuck to solid surfaces thereby delaying its arrival in a process known as retardation.

Equilibrium Isotherm – a relationship that is not a function of time showing the concentration in solution (C) versus that absorbed (S) on the solid surface.



Transport equation has two dependent variables, C and S

$$\frac{\partial C}{\partial t} + \beta \frac{\partial S}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}$$

Two unknowns and only one equation???

But we have a relation, the isotherm...

$S = K_d C \rightarrow$ need to get into a form showing $\frac{\partial S}{\partial t}$

Take derivative $\frac{\partial S}{\partial t} = \frac{\partial K_d C}{\partial t}$

$$\frac{\partial C}{\partial t} + \beta \frac{\partial S}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}$$

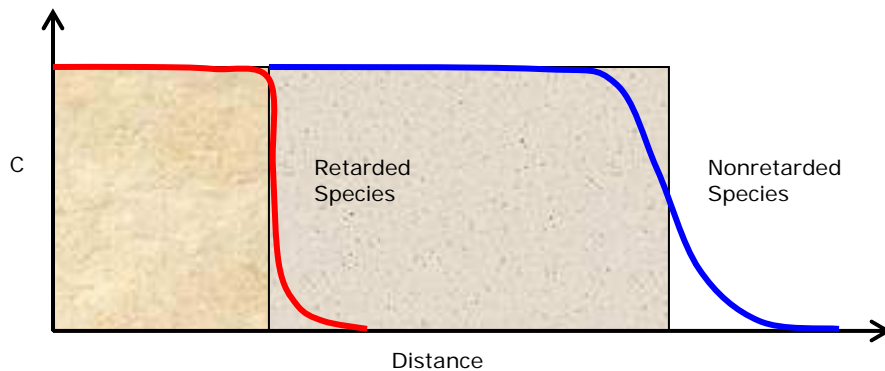
$$\frac{\partial C}{\partial t} + \beta \frac{\partial K_d C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}$$

$$(1 + \beta K_d) \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}$$

$(1 + \beta K_d) =$ retardation factor

Retardation factor \rightarrow the factor by which the non-reactive (nonsorbing) solute migrates compared to the sorbing solute which is delayed.

$$R = \frac{\text{Velocity}_{\text{nonreactive}}}{\text{Velocity}_{\text{sorbing}}}$$



One good thing about sorption

Some hazardous species haven't migrated. Some spills involving plutonium indicate that it hasn't migrated but a few meters at most (in unsaturated zone)

One bad thing about sorption

Even if you pump out a contaminant plume, there will still be stuff stuck to the solids that will make its way back to the liquid. Therefore, it takes a long time to cleanup a contaminant plume if there is sorbed solute.

Hot topics in Transport

- Complex chemical reaction modeling
- Coupled process models (T, Chemistry, High Conc.)
- Theory of dispersion
- Rate Limited Mass Transfer
- Microbial activity to degrade VOCs
- Optimal design of remedial systems