Lecture 3

Contaminant Transport Mechanisms and Principles
**BASIC DEFINITIONS**

- **Ground surface**
- **Vadose zone, unsaturated zone**
- **Capillary fringe**
- **Water table**
- **Saturated zone**
- **Confining bed**
- **Below ground surface (BGS)**
- **Confined aquifer or artesian aquifer**
- **Water-table, phreatic, or unconfined aquifer**

Capillary fringe may be >200 cm in fine silt
In capillary fringe water is nearly saturated, but held in tension in soil pores
Contaminant concentrations:

- $C_w$, mg/L
  - concentration in water
- $C_g$, mg/L or ppmv
  - concentration in gas
- $C_s$, gm/kg
  - concentration in solids
PARTITIONING RELATIONSHIPS

Solid ↔ water

\[
\frac{C_s}{C_w} = K_d = \frac{\text{mg/kg solid}}{\text{mg/L water}}
\]

\(K_d = \text{partition coefficient}\)

Water ↔ vapor

\[
\frac{C_g}{C_w} = H = \frac{\text{mol/m}^3 \text{ air}}{\text{mg/m}^3 \text{ water}}
\]

\(H = \text{Henry’s Law constant}\)
HENRY’S LAW CONSTANT

H has dimensions: \( \text{atm m}^3 / \text{mol} \)

\( H' \) is dimensionless

\( H' = \frac{H}{RT} \)

\( R = \text{gas constant} = 8.20575 \times 10^{-5} \text{ atm m}^3/\text{mol °K} \)

\( T = \text{temperature in °K} \)
NOTE ON SOIL GAS CONCENTRATION

Soil gas is usually reported as:
ppmv = parts per million by volume

\[ C_g \text{ (ppmv)} = \frac{C_g \text{ (mg/L)} \times 24,000 \text{ mL/mole}}{\text{molecular weight g/mole}} \]
VOLUME REPRESENTATION

Void volume, $V_v$

\[
\begin{align*}
\text{Gas volume, } V_g \\
\text{Water volume, } V_w \\
\text{Solid volume, } V_s
\end{align*}
\]

Total volume, $V_T$
VOLUME-RELATED PROPERTIES

Bulk density \( \rho_b = \frac{\text{mass of solids}}{\text{total volume}} \)

Porosity = \( n = \theta = \frac{V_V}{V_T} \)

Volumetric water content or water-filled porosity = \( \theta_w = \frac{V_W}{V_T} \)

Saturation = \( S = \frac{V_W}{V_V} \)

Gas-filled porosity = \( \theta_g \) (or \( \theta_a \)) = \( \frac{V_g}{V_T} \)

\( \theta_w + \theta_g = n \)
CONTAMINANT CONCENTRATION IN SOIL

Total mass in unit volume of soil:

\[ C_T = \rho_b C_s + \theta_w C_W + \theta_g C_g \]

If soil is saturated, \( \theta_g = 0 \) and \( \theta_w = n \)

\[ C_T = \rho_b C_s + n C_W \]
NOMENCLATURE FOR DARCY’S LAW

\[ Q = K \ i \ A \]

- \( K \) = hydraulic conductivity
- \( i \) = hydraulic gradient = \( \frac{dh}{dL} \)
- \( A \) = cross-sectional area

Velocity of ground-water movement

\[ u = \frac{Q}{n \ A} = \frac{q}{n} = \frac{K \ i}{n} = \text{average linear velocity} \]

\( n \ A \) = area through which ground water flows

\( q = \frac{Q}{A} = \text{Darcy seepage velocity} = \text{Specific discharge} \)

For transport, \( n \) is \( n_e \), effective porosity
Flowing ground water carries any dissolved material with it → Advective Flux

\[ J_A = n \cdot u \cdot C \quad \text{mass / area / time} \]

= mass flux through unit cross section due to ground-water advection

n is needed since no flow except in pores
DIFFUSIVE FLUX

Movement of mass by molecular diffusion (Brownian motion) – proportional to concentration gradient

\[ J_D = -D_0 \frac{\partial C}{\partial x} \]

in surface water

\( D_0 \) is molecular diffusion coefficient [L^2/T]
In porous medium, geometry imposes constraints:

\[ J_D = -\tau \ D_0 \ n \ \frac{\partial C}{\partial x} = -D^* \ n \ \frac{\partial C}{\partial x} \]

\( \tau \) = tortuosity factor

\( D^* \) = effective diffusion coefficient

Factor \( n \) must be included since diffusion is only in pores.
TORTUOSITY

Solute must travel a tortuous path, winding through pores and around solid grains

Common empirical expression: \[ \tau = \left( \frac{L}{L_e} \right)^2 \]

\( L \) = straight-line distance
\( L_e \) = actual (effective) path

\( \tau \approx 0.7 \) for sand
NOTES ON DIFFUSION

Diffusion is not a big factor in saturated groundwater flow – dispersion dominates diffusion.

Diffusion can be important (even dominant) in vapor transport in unsaturated zone.
MECHANICAL DISPERSION

A arrives first, then B, then C → mechanical dispersion
MECHANICAL DISPERSION

Viewed at micro-scale (i.e., pore scale) arrival times A, B, and C can be predicted.

Averaging travel paths A, B, and C leads to apparent spreading of contaminant about the mean.

Spatial averaging $\rightarrow$ dispersion.
MECHANICAL DISPERSION

Dispersion can be effectively approximated by the same relationship as diffusion—i.e., that flux is proportional to concentration gradient:

\[ J_M = -D_M n \frac{\partial C}{\partial x} \]

Dispersion coefficient, \( D_M = \alpha_L u \)

\( \alpha_L \) = longitudinal dispersivity (units of length)
TRADITIONAL VIEW OF HYDRODYNAMIC DISPERSION

ACTUAL OBSERVATIONS OF PLUMES

USGS Cape Cod Research Site


MONITORING WELL ARRAY
USGS MONITORING NETWORK

OBSERVED BROMIDE PLUME – HORIZONTAL VIEW

Significant longitudinal dispersion, but limited lateral dispersion
OBSERVED BROMIDE PLUME – VERTICAL VIEW

Vertical location of bromide tracer cloud at 33, 237, and 461 days after injection. Cloud locations defined by zones in which bromide concentration exceeded 1 mg/L.

Limited vertical dispersion
LONGITUDINAL DISPERSION VS. LENGTH SCALE

Lateral and vertical dispersivity

TRANSPORT EQUATION

Combined transport from advection, diffusion, and dispersion (in one dimension):

\[ J = J_A + J_D + J_M \]

\[ J = nuC - D \cdot n \frac{\partial C}{\partial x} - D_M n \frac{\partial C}{\partial x} \]

\[ J = nuC - D_H \frac{\partial C}{\partial x} \]

\[ D_H = D^* + D_M = \tau D_O + \alpha_L u \]

= hydrodynamic dispersion
Consider conservation of mass over control volume (REV) of aquifer.

REV = Representative Elementary Volume
REV must contain enough pores to get a meaningful representation (statistical average or model)
TRANSPORT EQUATION

Change in contaminant mass with time

\[ \frac{\partial C_T}{\partial t} = -\nabla \cdot J \pm S / S \]  

Flux in less flux out of REV

Sources and sinks due to reactions

\[ \frac{\partial C_T}{\partial t} = -\frac{\partial J}{\partial x} \pm S / S \]  

(1)  

(2)
TRANSPORT EQUATION

\[ C_T = \text{total mass (dissolved mass plus mass adsorbed to solid) per unit volume} = \rho_b C_S + n C \]

Note: \( W \) subscript dropped for convenience and for Consistency with conventional notation.

Substitute Equation 3 into Equation 2:

\[ \frac{\partial}{\partial t} (\rho_b C_S) + \frac{\partial}{\partial t} (nC) = - \frac{\partial}{\partial x} \left( nuC - D_H n \frac{\partial C}{\partial x} \right) \pm \frac{S}{S} \]

↑ no solid phase in flux term
\[ C_S = K_d \, C \text{ by definition of } K_d \]

Assume spatially uniform \( n, \rho_b, K_d, u, \text{ and } D_H \) and no S/S

\[
\left(\rho_b K_d + n\right) \frac{\partial C}{\partial t} = -nu \frac{\partial C}{\partial x} + nD_H \frac{\partial^2 C}{\partial x^2} \quad (5)
\]

\[
\frac{\partial C}{\partial t} = -\left(\frac{\rho_b K_d + n}{n}\right) \frac{\partial C}{\partial x} + \left(\frac{\rho_b K_d + n}{n}\right) \frac{\partial^2 C}{\partial x^2} \quad (6)
\]
"Retardation factor", $R_d$

$$\frac{\rho_b K_d + n}{n} = 1 + \frac{\rho_b K_d}{n} = R_d$$  \hspace{1cm} (7)

Substituting Equation 7 into Equation 6:

$$\frac{\partial C}{\partial t} = - \frac{u}{R_d} \frac{\partial C}{\partial x} + \frac{D_H}{R_d} \frac{\partial^2 C}{\partial x^2}$$  \hspace{1cm} (8)

Effect of adsorption to solids is an apparent slowing of transport of dissolved contaminants
Both $u$ and $D_H$ are slowed
Equation 8 can be solved with a variety of boundary conditions.

In general, equation predicts a spreading Gaussian cloud.
Spreading of a solute slug with time due to diffusion. A slug of solute was injected into the aquifer at time $t_0$ with a resulting initial concentration of $C_0$.

1-D SOLUTION OF TRANSPORT EQUATION

For instantaneous placement of a long-lasting source (for example, a spill that leaves a residual in the soil), solution is:

\[ C(x, t) = \frac{C_0}{2} \text{erfc} \left( \frac{R_d x - ut}{\sqrt{4R_d D_H t}} \right) \]

Where \( C_0 = C(x=0, t) = \) constant concentration at source location \( x = 0 \)

Solution is a front moving with velocity \( u/R_d \)
The profile of a diffusing front as predicted by the complementary error function.

$x = \frac{ut}{R_d}$

Adapted from Fetter, C. W. *Contaminant Hydrogeology.*
Moving front of contaminant from constant source

\[ C_0 = 10 \]
\[ u = 1 \]
\[ D_H = 0.1 \]
\[ R_d = 1 \]
Effect of $D_H$ on moving front of contaminant

- $t = 3$
- $u_t = 3$
- $D_H = 0.1$
- $D_H = 1$
- $C_0 = 10$
- $u = 1$
- $R_d = 1$

Concentration, $C(x,t)$

Distance, $x$
Effect of $R_d$ on moving front of contaminant

- $t = 3$
- $u = 1$
- $D_H = 0.1$
- $C_0 = 10$
- $R_d = 2$
- $R_d = 1$

Concentration, $C(x,t)$

Distance, $x$
1-D SOLUTIONS

Transport of a Conservative Substance from Pulse and Continuous Sources

### Dimensions

<table>
<thead>
<tr>
<th>1-D</th>
<th>1-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{M}$, $\dot{\mathcal{M}}$ are instantaneous or continuous plane sources</td>
<td></td>
</tr>
<tr>
<td>$\mathcal{M}$ [M/L^2]</td>
<td>$\dot{\mathcal{M}}$ [M/L^2T]</td>
</tr>
</tbody>
</table>

### Pulse Input of Mass $\mathcal{M}$

$$ C = \frac{\mathcal{M}}{2n\pi^{1/2}t^{1/2}} \exp\left(-\frac{(x-vt)^2}{4D_t^2}\right) $$

- $x = 0 \rightarrow v$
- $t = 0$ to $t = t_i$

### Continuous Input of Mass Per Unit Time $\dot{\mathcal{M}}$ Starting at Time $t = 0$

$$ C = \frac{\dot{\mathcal{M}}}{2nv} \text{erfc}\left(\frac{x-vt}{2\sqrt{D_t}t}\right) $$

- $x = 0 \rightarrow v$
- Mass input here
- Front at time $t$

### Continuous Input of Mass Per Unit Time $\dot{\mathcal{M}}$ in Steady State

$$ C = \frac{\dot{\mathcal{M}}}{nv} \text{ (for } x > 0) $$

- $x = 0 \rightarrow v$
- Mass input here

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# 2-D SOLUTIONS

Transport of a Conservative Substance from Pulse and Continuous Sources

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Pulse Input of Mass $\dot{M}$</th>
<th>Continuous Input of Mass Per Unit Time $\dot{M}$ Starting at Time $t = 0$</th>
<th>Continuous Input of Mass Per Unit Time $\dot{M}$ in Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{M}$  $\dot{M}$ are instantaneous or continuous line sources $\dot{M} \left[ \frac{M}{L} \right]$</td>
<td>$C = \frac{M}{4n\pi t \sqrt{D_x D_y}} \exp \left[ \frac{(x-vt)^2}{4D_x t} + \frac{y^2}{4D_y t} \right]$</td>
<td>$C = \frac{\dot{M}}{4n\pi^{1/2} (vt)^{1/2} \sqrt{D_y}} \exp \left[ \frac{(x-vt)^2}{2D_x} \right] \operatorname{erfc} \left( \frac{r-vt}{2\sqrt{D_x t}} \right)$</td>
<td>$C = \frac{\dot{M}}{2n\pi^{1/2} (vt)^{1/2} \sqrt{D_y}} \exp \left[ \frac{(x-vt)^2}{2D_x} \right]$</td>
</tr>
<tr>
<td>$\dot{M}$</td>
<td><img src="image1.png" alt="Pulse Input of Mass $\dot{M}$" /></td>
<td><img src="image2.png" alt="Continuous Input of Mass Per Unit Time $\dot{M}$ Starting at Time $t = 0$" /></td>
<td><img src="image3.png" alt="Continuous Input of Mass Per Unit Time $\dot{M}$ in Steady State" /></td>
</tr>
</tbody>
</table>

### 3-D SOLUTIONS

**Transport of a Conservative Substance from Pulse and Continuous Sources**

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Pulse Input of Mass $M$</th>
<th>Continuous Input of Mass Per Unit Time $\dot{M}$ Starting at Time $t = 0$</th>
<th>Continuous Input of Mass Per Unit Time $\dot{M}$ in Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M, \dot{M}$ are instantaneous or continuous point sources</td>
<td>$C = \frac{M}{8n\pi^{3/2}t^{3/2} \sqrt{D_x D_y D_z}} \exp \left[ \frac{(x-vt)^2}{4D_x t} + \frac{y^2}{4D_y t} + \frac{z^2}{4D_z t} \right]$</td>
<td>$C = \frac{\dot{M}}{8n\pi r \sqrt{D_y D_z}} \exp \left[ \frac{(x-r)v}{2D_x} \right] \text{erfc} \left( \frac{r-vt}{2\sqrt{D_x t}} \right)$</td>
<td>$C = \frac{\dot{M}}{4n\pi r \sqrt{D_y D_z}} \exp \left[ \frac{(x-r)v}{2D_x} \right]$</td>
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