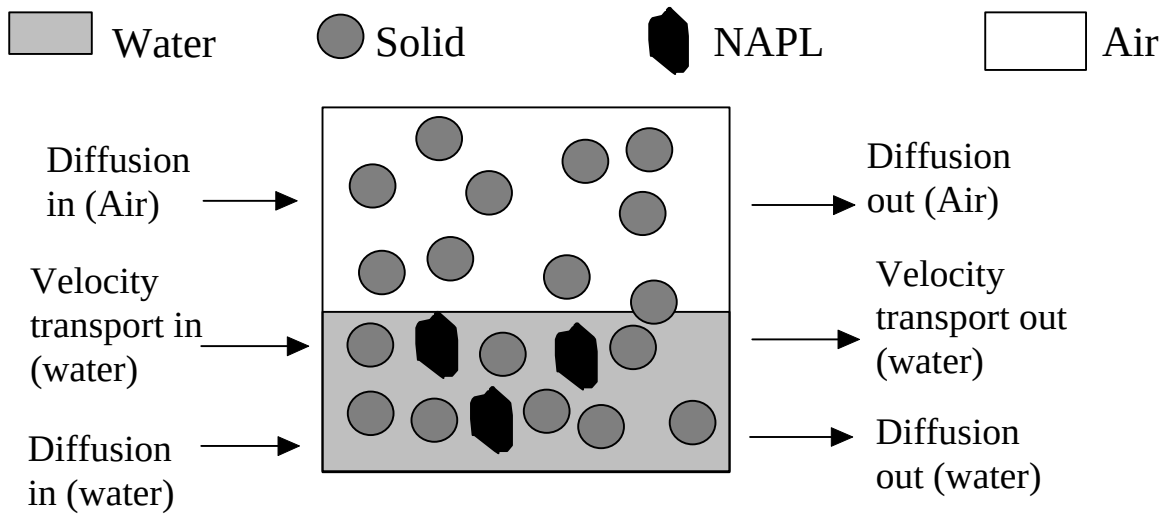
SUMMARY FROM LAST LECTURE:



Unit Volume

$$\frac{\partial A}{\partial t} = -\vec{\nabla} \bullet \vec{J} \quad \pm \quad \phi$$

<u>Sinks and sources</u> involve processes where solute mass is destroyed or created within the unit volume (e.g., biodegradation).

<u>Transport</u> in and out of the unit volume with fluid velocity and/or by diffusion in continuous fluid phases (water and air).

<u>Change in Storage</u> of solute in unit volume with time; involves all phases and interchange of solute between the phases.

Last Lecture: $\vec{J} = \vec{q}_w C_w - \theta_w \vec{D}_w \bullet \vec{\nabla} C_w - \theta_a \vec{D}_a \bullet \vec{\nabla} C_a$

This Lecture: A = ?; combining and simplifying $\frac{\partial A}{\partial t} = -\vec{\nabla} \bullet \vec{J}$

<u>Mass Storage</u>: mass of contaminant per unit volume of media in all phases.

$A = \Sigma A_i$

where: A = mass contaminant per unit volume of media
i = phase in media (water, solid, air, NAPL)

$$A = \theta_w C_w + \theta_a C_a + \theta_N C_N + \rho_B S$$

Total mass of contaminant per unit volume of media

Mass of contaminant in water

Mass of contaminant in air

Mass of contaminant in NAPL

Mass of contaminant in/on solid

Units: θ = volume of phase *i*/volume of media
C = mass of contaminant in *i*/volume of phase *i*
ρ_B = mass of solids/volume of media
S = mass of contaminant in/on solids/mass of solids

<u>Note</u>:

θ_w, θ_a (and θ_N) are obtained from the flow equation(s)

$n = \theta_w + \theta_a + \theta_N$

$\rho_B = \rho_s(1 - n)$ ρ_s = solids density ≈ 2.65 for silica minerals
ρ_B = solid bulk density ≈ 1.5 - 1.8 g/cm^3

$$\Delta \text{Storage} = \frac{\partial A}{\partial t} = \sum \frac{\partial A_i}{\partial t}$$
$$= \frac{\partial(\theta_w C_w)}{\partial t} + \frac{\partial(\theta_a C_a)}{\partial t} + \frac{\partial(\theta_N C_N)}{\partial t} + \frac{\partial(\rho_B S)}{\partial t}$$

To simplify:

1. Make assumptions about flow field.
2. Make assumptions about porous medium.
3. Make assumptions about the NAPL.
4. Find relationships between concentrations in different phases.

<u>Flow Field Assumptions</u>:

- Steady State $\frac{\partial(\theta_w C_w)}{\partial t} = \theta_w \frac{\partial C_w}{\partial t}$; $\frac{\partial(\theta_a C_a)}{\partial t} = \theta_a \frac{\partial C_a}{\partial t}$

<u>Porous Medium Assumptions</u>:

- Nondeformable medium $\frac{\partial(\rho_b S)}{\partial t} = \rho_b \frac{\partial S}{\partial t}$

<u>NAPL Assumptions</u>:

- Single-component NAPLs (e.g., TCE) do not experience concentration changes with time ($C_N = \rho_N$).

$$\frac{\partial(\theta_N C_N)}{\partial t} = \rho_N \frac{\partial \theta_N}{\partial t}$$

- Some multiple component NAPLs (e.g., fuels) contain only a small fraction of soluble components. Most of the NAPL is insoluble and the fluid content of the NAPL remains virtually constant.

$$\frac{\partial(\theta_N C_N)}{\partial t} = \theta_N \frac{\partial C_N}{\partial t}$$

Relationships between Concentrations in Different Phases:

- Water is the wetting phase, usually in contact with all other phases, so find $C_i = f(C_w)$ [e.g., partitioning equilibria]
- We are interested in both equilibrium relationships AND rate of change of mass storage [interphase mass transfer rates].

More on this in Lec 12.

BUILD AND SIMPLIFY A GOVERNING EQUATION:

Start with the mass balance equation:

$$\frac{\partial A}{\partial t} = -\vec{\nabla} \bullet \vec{J} \quad \pm \quad \phi$$

Change in mass stored per unit volume of porous media.

Change in mass flux across the unit volume of porous media.

Mass created or destroyed within the unit volume of porous media.

Ignore sources and sinks for now, and expand the equation:

$$\frac{\partial(\theta_w C_w)}{\partial t} + \frac{\partial(\theta_a C_a)}{\partial t} + \frac{\partial(\theta_N C_N)}{\partial t} + \frac{\partial(\rho_B S)}{\partial t} = -\vec{\nabla}\bullet(\vec{q}_w C) + \vec{\nabla}\bullet(\theta_w \vec{D}_w \bullet \vec{\nabla} C_w) + \vec{\nabla}\bullet(\theta_a \vec{D}_a \bullet \vec{\nabla} C_a)$$

Change in storage in water phase

Change in storage in air phase

Change in storage in NAPL

Change in storage in sorbed phase

Transport in water phase due to advection

Transport in water phase due to dispersion and diffusion

Transport in air phase due to diffusion

What are the assumptions? How can we simplify the MBE?

<u>Assumptions in the MBE</u>:

- Porous media is a continuum (REV concept).
- Truncated Taylor expansion of flux terms.
- Transport limited to advection/dispersion in water phase and diffusion in air phase.
- No sources or sinks.
- Also: any assumptions used to solve the water flow equations (not shown).

Other common assumptions:

- Water is incompressible (ρ_w = constant).
- Porous medium is nondeformable (n = constant).

Richards Equation (ρ_w = constant):

$$\frac{\partial(\theta_w C_w)}{\partial t} = -\vec{\nabla} \bullet (\vec{q}_w C_w)$$ *isolate water storage and advection*

$$C_w \frac{\partial \theta_w}{\partial t} + \theta_w \frac{\partial C_w}{\partial t} = -C_w \vec{\nabla} \bullet \vec{q}_w - \vec{q}_w \bullet \vec{\nabla} C_w$$ *expand terms*

$$\frac{\partial \theta_w}{\partial t} = -\vec{\nabla} \bullet \vec{q}_w$$ *note Richards eqn identity and cancel.*

$$\frac{\partial C_w}{\partial t} = -\frac{\vec{q}_w}{\theta_w} \bullet \vec{\nabla} C_w = -\vec{v}_w \bullet \vec{\nabla} C_w$$

Removing the Richards Eqn identity and dividing by q_w, note dependence of concentration on the velocity vector!

Constant water density allows simplification of the water storage and water advection terms.

Constant porosity results in constant solids bulk density.

MBE reduces to:

$$\theta_w \frac{\partial C_w}{\partial t} + \frac{\partial(\theta_a C_a)}{\partial t} + \frac{\partial(\theta_N C_N)}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -\vec{q}_w \bullet \vec{\nabla} C_w + \vec{\nabla} \bullet (\theta_w \vec{D}_w \bullet \vec{\nabla} C_w) + \vec{\nabla} \bullet (\theta_a \vec{D}_a \bullet \vec{\nabla} C_a)$$

MBE still too complex for analytical solution. Further simplify:

- Determine relationships between concentrations in each phase (usually in reference to the water phase).
- Simplify fluid (air and NAPL) content differentials with time.
- Simplify dispersion/diffusion coefficients and fluid content differentials with space (air and water).
- Align axes with direction of water flow.

To simplify the differential terms, we still have two powerful assumptions we may be able to use:

- Steady state fluid flow.
- Homogeneous medium and fluid conditions.

Steady state fluid flow: Fluid contents do not change with time! (Does NOT mean solute transport is at a steady state!)

- θ_a comes out of time differential.

Homogeneous conditions:

- Dispersion/diffusion coefficients and fluid contents come out of the space differentials.
- Implies a homogeneous medium and a constant fluid content everywhere in space. (When is this likely or unlikely?)

$$-\vec{\nabla} \bullet \vec{J}_w^{disp} = \vec{\nabla} \bullet \left(\theta_w \vec{D}_w \bullet \vec{\nabla} C_w\right)$$
$$= \left(\vec{\nabla}\theta_w\right) \bullet D_w \bullet \vec{\nabla} C_w + \theta_w \vec{\nabla} \bullet \vec{D}_w \bullet \vec{\nabla} C_w + \theta_w \vec{D}_w \bullet \vec{\nabla}^2 C_w$$

$$\frac{d\theta_w}{dx_i} = 0 \quad \text{and} \quad \frac{dD_w}{dx_i} = 0$$ *two of the terms equal zero.*

So: $$-\vec{\nabla} \bullet \vec{J}_w^{disp} = \theta_w \vec{D}_w \bullet \vec{\nabla}^2 C_w$$

Assume also that NAPL is complex and consists primarily of nonsoluble components:

$$\frac{\partial\left(\theta_N C_N\right)}{\partial t} = \theta_N \frac{\partial C_N}{\partial t}$$

Simplified MBE (*only concentration terms in differentials*):

$$\theta_w \frac{\partial C_w}{\partial t} + \theta_a \frac{\partial C_a}{\partial t} + \theta_N \frac{\partial C_N}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -\vec{q}_w \bullet \vec{\nabla} C_w + \theta_w \vec{D}_w \bullet \vec{\nabla}^2 C_w + \theta_a \vec{D}_a \bullet \vec{\nabla}^2 C_a$$

Simplifications/Assumptions:

1. All assumptions in creating basic water and solute MBE
2. Constant water density
3. Constant porosity
4. Steady state flow field
5. Homogeneous flow field
6. Constant NAPL saturation

Further simplifications:

1. Water flows in the x direction ($q_y = q_z = 0$)
2. No air or NAPL phases ($\theta_a = \theta_N = 0$)

$$\theta_w \frac{\partial C_w}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -q_w \frac{\partial C_w}{\partial x} + D_L \theta_w \frac{\partial^2 C_w}{\partial x^2} + D_T \theta_w \frac{\partial^2 C_w}{\partial y^2} + D_T \theta_w \frac{\partial^2 C_w}{\partial z^2}$$

Change in storage in the sorbed phase

Longitudinal dispersion transport

Transverse dispersion (z-direction)

Change in storage in water phase

Advective transport

Transverse dispersion (y-direction)

Still needed: Relationship between concentrations in different phases.