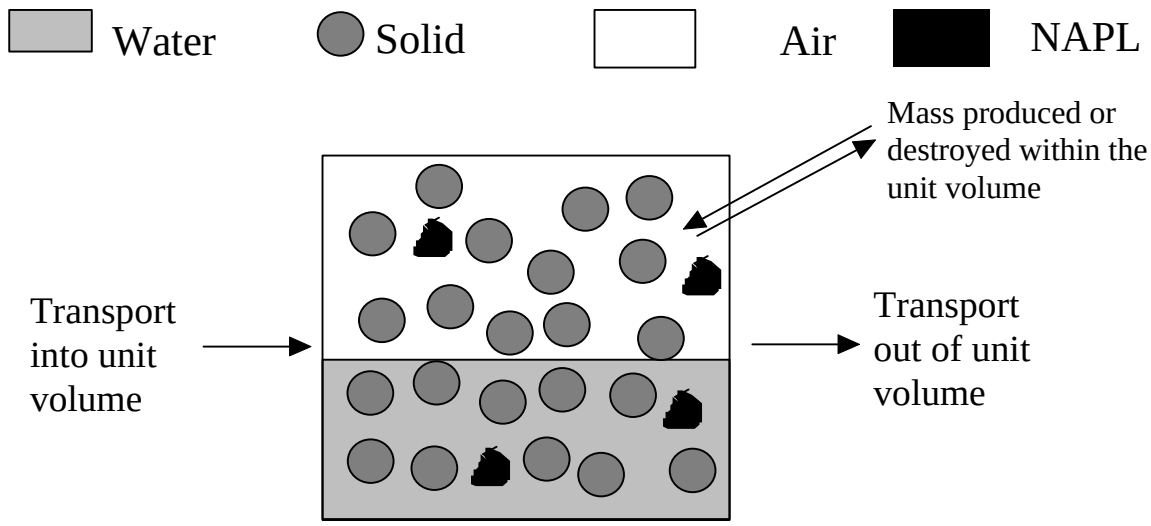
GOVERNING EQUATIONS for solute transport in porous media: General rules

- Governing equation based on MASS BALANCE:

Change in Mass Stored = Mass in - Mass out



Unit Volume

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

Change in mass stored per unit volume of porous medium.

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

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

UNITS: A = mass of contaminant/volume of medium
J = mass of contaminant/(area of medium x time)
ϕ = mass of contaminant/(volume of medium x time)

Transport Flux, *J*:

- Transport Mechanisms
  - Diffusion
  - Advection/Dispersion
- Transport Flux in Porous Media

TWO TRANSPORT MECHANISMS:

- Momentum/Fluid Velocity: Advection and Dispersion
- Molecular Interactions/Concentration Gradient: Diffusion

DIFFUSION: Mass transport due to concentration gradient.

Ficks First Law:

$$J_i^{dif} = -D_{i,j} \frac{\partial C}{\partial x_j} \qquad \text{(1-D)}$$

Diffusion flux is proportional to concentration gradient and in opposite direction.

Units Problem: D, C expressed in terms of fluid.
Space dimensions expressed in terms of media.

Need to adjust diffusion flux equation so that units agree.

$$\dot{M} = J\ A \qquad \boxed{\textit{Mass flow rate} = \textit{Flux} \times \textit{Area}}$$

<u>*Reference gradient to fluid*</u> <u>*Reference gradient to media*</u>

$$\dot{M} = -D_f A_f \frac{\partial C_f}{\partial x_f} \qquad \dot{M} = -D_m A_m \frac{\partial C_m}{\partial x_m}$$

Note: $A_f \neq A_m$; $C_f \neq C_m$; etc.

However, we can relate these variables:

$x_m = \alpha x_f$; $\alpha \leq 1$ (tortuosity)

$C_m = \theta C_f$; $\theta < 1$

$A_m = \dfrac{A_f}{\alpha\theta}$; because: $\theta = \dfrac{A_f x_f}{A_m x_m}$

Now, rewrite mass flow equation with *D*, *C* in terms of fluid, and *x*, *A* in terms of media:

$$\dot{M} = -D_f A_m \alpha\theta \frac{\partial C_f}{\frac{1}{\alpha}\partial x_m} = -D_f A_m \alpha^2 \theta \frac{\partial C_f}{\partial x_m}$$

Dividing by A_m to get the flux:

$$J^{dif} = -D_f \alpha^2 \theta \frac{\partial C_f}{\partial x_m}$$

Combine these terms

$$D_{f(eff)} = D_f \alpha^2 = D_o \tau(\theta)$$

Effective diffusion coefficient for solute in fluid in porous media

Diffusion coefficient in bulk fluid

Tortuosity factor = function of fluid saturation in porous media.

$\tau(\theta = n) \approx 0.5$ *to* 0.8
$\tau(\theta << n) \rightarrow 0$

So the diffusion flux (3-D) for water and air are:

$$\vec{J}_w^{dif} = -\theta_w \vec{D}_w \bullet \vec{\nabla} C_w$$

$$\vec{J}_a^{dif} = -\theta_a \vec{D}_a \bullet \vec{\nabla} C_a$$

Units:

$$\frac{\cancel{L^3 \text{fluid}}}{\cancel{L^3} \text{medium}} \times \frac{\cancel{L^2 \text{meduim}}}{\text{time}} \times \frac{\text{mass solute}}{\cancel{L^3 \text{fluid}} \times L \text{ medium}}$$

- The fluid content (θ) term converts concentration units to a media basis.
- The tortuosity factor (τ) incorporated in the diffusion coefficient converts bulk fluid diffusion to porous media diffusion.

Solved unit conversion problem. However, solute transport is controlled primarily by velocity mechanisms.

VELOCITY or MOMENTUM MECHANISMS:

ADVECTION: Transport with AVERAGE fluid flow

$$\vec{J}_w^{adv} = \vec{q}_w C_w$$

Units: $\dfrac{\cancel{\text{Vol. water}}}{\text{Area media x time}} \times \dfrac{\text{Mass solute}}{\cancel{\text{Vol. water}}}$

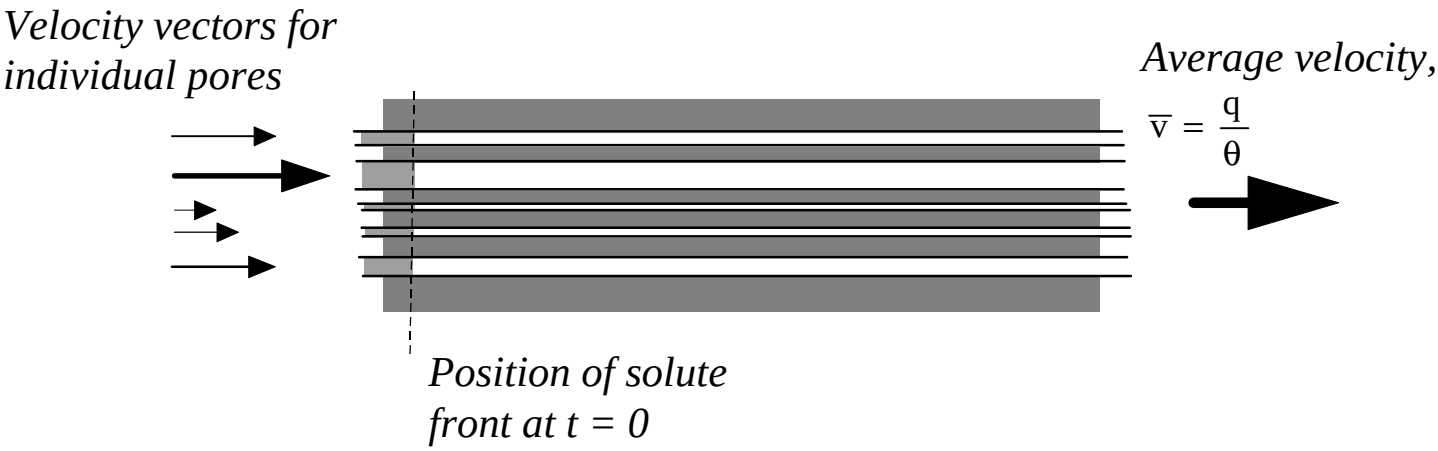
HYDRODYNAMIC DISPERSION: Transport due to nonuniform fluid flow

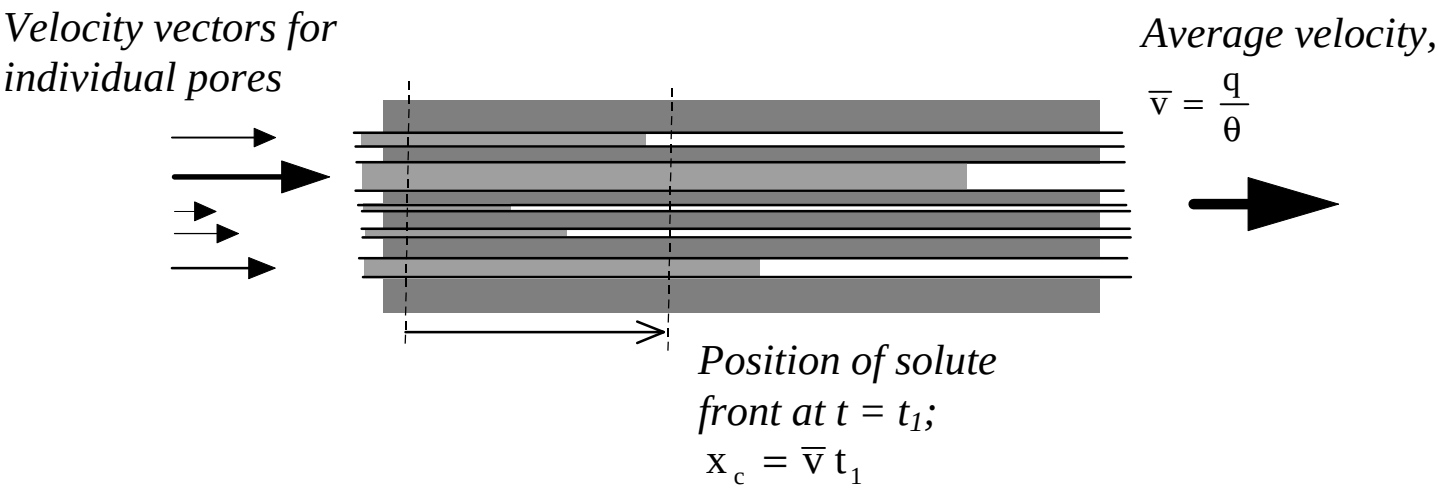
Advection describes transport by AVERAGE water velocity

Actually groundwater moves over many different velocities due to:

- Different pore diameters
- Branching pores
- Velocity profile within a pore

Consider soil as a bundle of capillary tubes of different diameters.

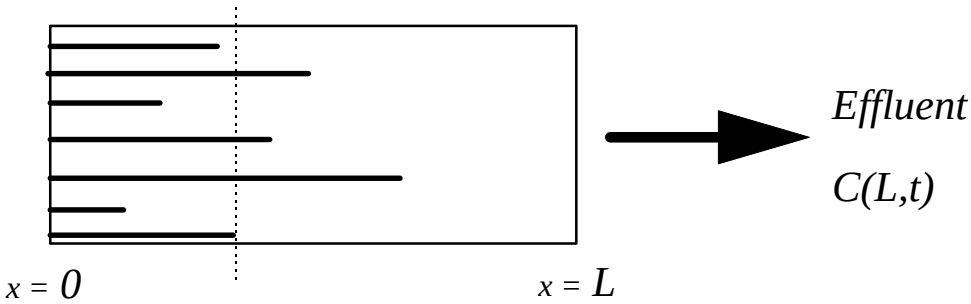




Advection predicts transport by AVERAGE velocity.

- Solute moves FASTER than average in larger pores.
- Solute moves SLOWER than average in smaller pores.

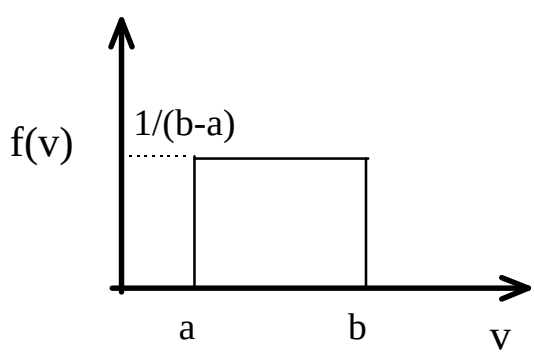
Consider the soil as a bundle of capillaries of finite length, L
Calculate concentration of solute in effluent at x = L



Average Effluent Concentration = <*C(L,t)*>

$$\langle C(L,t)\rangle = \frac{\int_{v_{min}}^{v_{max}} v\, C\, f(v)\, dv}{\int_{v_{min}}^{v_{max}} v\; f(v)\, dv}$$

To solve, we need a function for f(v):

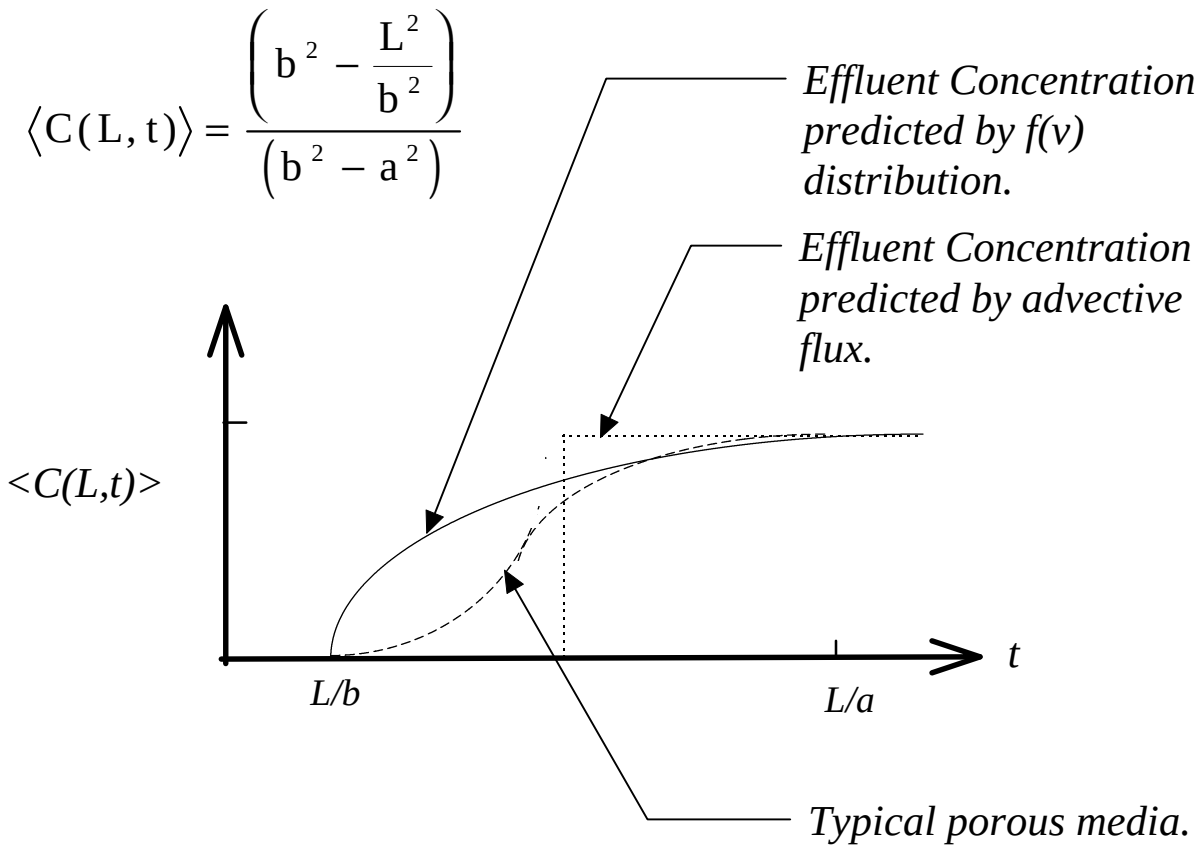


f(v) = 0; v<a and v>b

$$f(v) = \frac{1}{b-a};\ a \le v \le b$$

Solving for the average effluent concentration:

$$\langle C(L,t)\rangle = \frac{\left(b^2 - \frac{L^2}{b^2}\right)}{\left(b^2 - a^2\right)}$$



- First solute arrives at $t = L/b$ (b = velocity in largest tube).
- All solute arrives by $t = L/a$ (a = velocity in smallest tube).
- In actual porous media, cross-connections smoothes the curve.

- Spread of concentration due to VELOCITY distribution is more important than diffusion.
- We don't know the velocity distribution; we use average velocity (advection) and correct for velocity distribution using a dispersion coefficient (spreading)
- The "***D***" term in the solute transport equation is used for DISPERSION instead of diffusion as originally intended.

DISPERSION COEFFICIENT:

The "***D***" term in the solute transport equation accounts for two processes:

- Diffusion
- Hydrodynamic Dispersion (mixing)

Dispersion occurs both:

- Along the direction of flow (Longitudinal, caused by: variation in velocity due to different pore sizes; uneven flow paths)
- Across the direction of flow (Transverse, caused by: branching pore channels)

Dispersion Coefficient is related to the velocity by DISPERSIVITY, α

$$D_h = \alpha v^n$$

Usually we assume a linear relationship (n=1) and define dispersivity in both longitudinal and transverse directions:

$$D_{i,i} = \alpha_L v_i \qquad D_{i,j} = \alpha_T v_i \quad i \neq j \qquad \alpha_L > \alpha_T$$

First estimate: $\alpha_L \approx L/10$ $\alpha_T \approx L/100$ *units: length*
where: L = scale of problem

Dispersivity is a scale-dependent parameter [value incr. with incr. scale].

- Very small scale: velocity profiles in uniform pores.
- Darcy scale: velocity distribution in different sized pores in homogeneous media.
- Field scale: velocity distributions due to heterogeneities.

The "***D***" term in the solute transport equation becomes [flow in the *x* direction only ($v_y = v_z = 0$]:

$$D_{x,x} = D_o \tau(\theta) + \alpha_L v_x \approx \alpha_L v_x$$
$$D_{y,x} = D_{z,x} = D_o \tau(\theta) + \alpha_T v_x \approx \alpha_T v_x$$

<u>What Transport Mechanisms are important?</u>

Transport can occur in fluid phases (water, air, NAPL)
- solid phase is immobile

For this class, lets assume:

Fluid	**Velocity Mechanisms**	**Diffusion**
Water	yes	yes
Air	no	yes
NAPL	no	yes*

Assume water is the only mobile fluid; air and NAPL are immobile
⇒ How good is this assumption?

<u>AIR</u>: what causes air to move in porous media?
- Infiltrating water displaces air.
- Changes in atmospheric pressure.
- Soil venting systems.

<u>NAPL</u>: when are NAPLs mobile in porous media?
- When NAPL originally enters the porous media.
- Free-product recovery efforts.

⇒ When these processes are significant, we must incorporate multi-phase flow for both fluid flow and solute transport.
⇒ Generally, unless we are specifically attempting to make air or NAPL move (soil venting or free product recovery) we structure the problem so that these phases can be considered immobile.

Diffusion in NAPLs:

Diffusion in NAPL phase is generally not a significant transport mechanism because:

- There are no concentration gradients in single-component NAPLs.
- For transport in a phase to be significant, that phase must be continuous over a significant volume of the porous medium.
    - NAPLs often exist as discontinuous, entrapped ganglia.
    - Pooled NAPL is continuous, but the extent of the pool is often much smaller than the volume of the porous medium modeled.

Expand the mass flux component of the mass balance equation:

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$$J = J_w^{velocity} + J_w^{diffusion} + J_a^{vel} + J_a^{dif} + J_N^{vel} + J_N^{dif}$$

Total contaminant mass flux in all phases

Mass fluxes in water phase

Mass fluxes in air phase

Mass fluxes in NAPL phase

The simplified total flux becomes:

$$J = J_w^{vel} + J_w^{dif} + J_a^{dif} = J_w^{adv} + J_w^{disp+dif} + J_a^{dif}$$

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