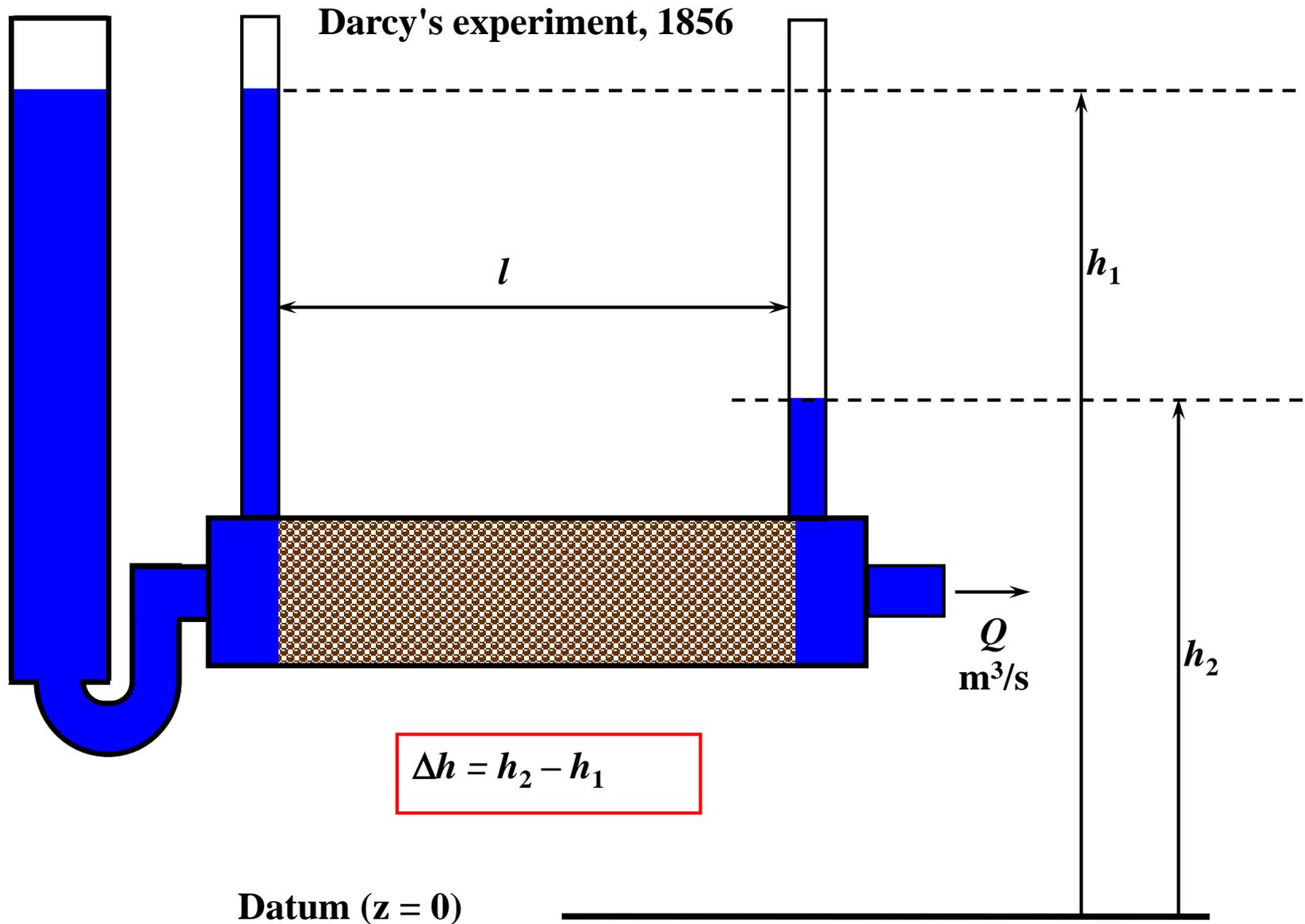


CENG 6405: Pollutant Fate and Transport

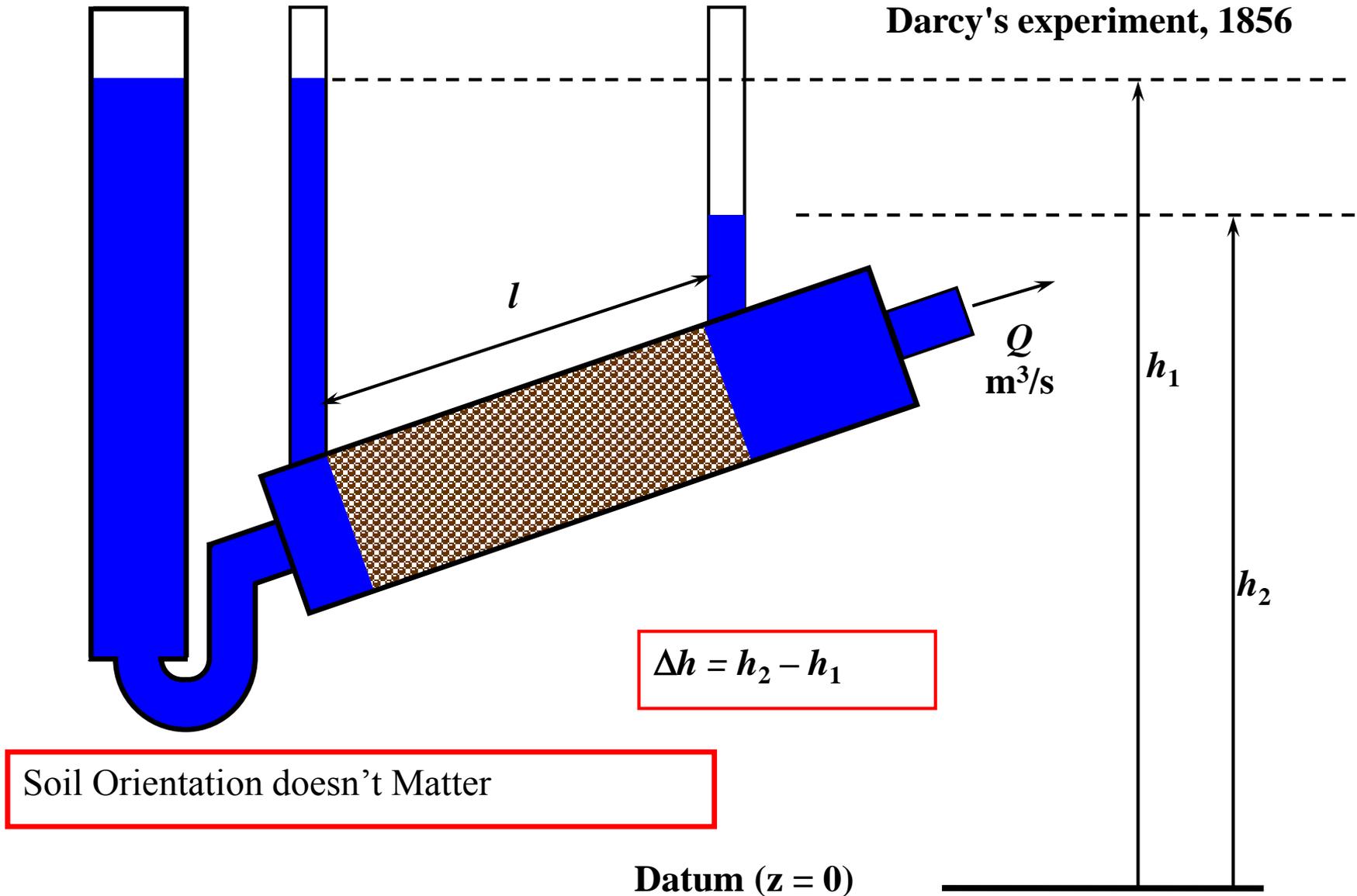
Chapter 3 Fate and Transport in Subsurface Water

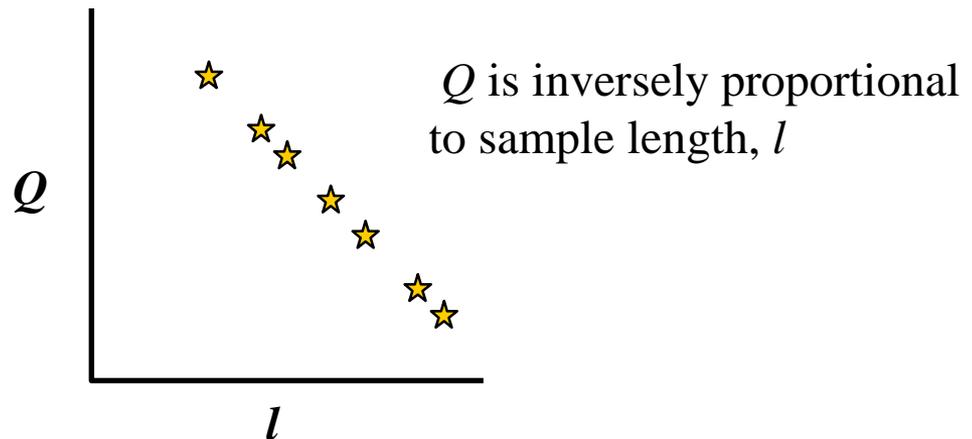
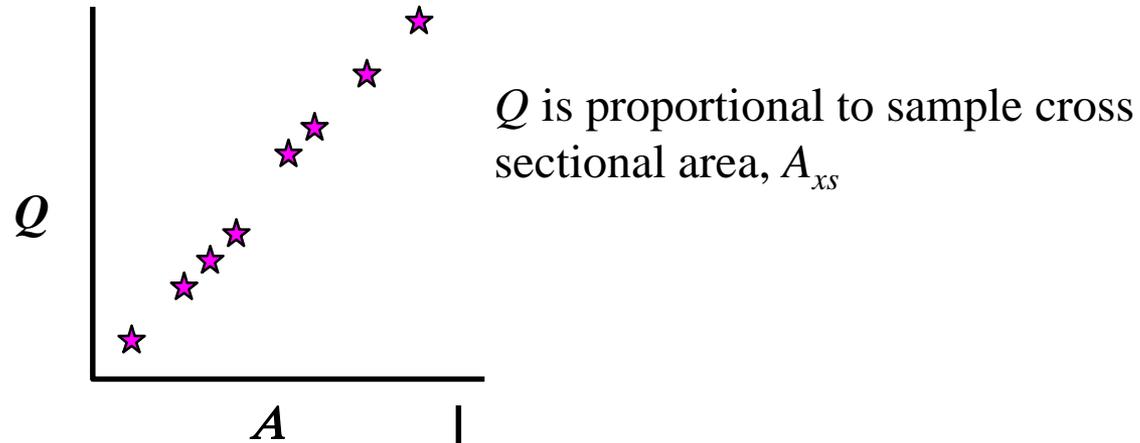
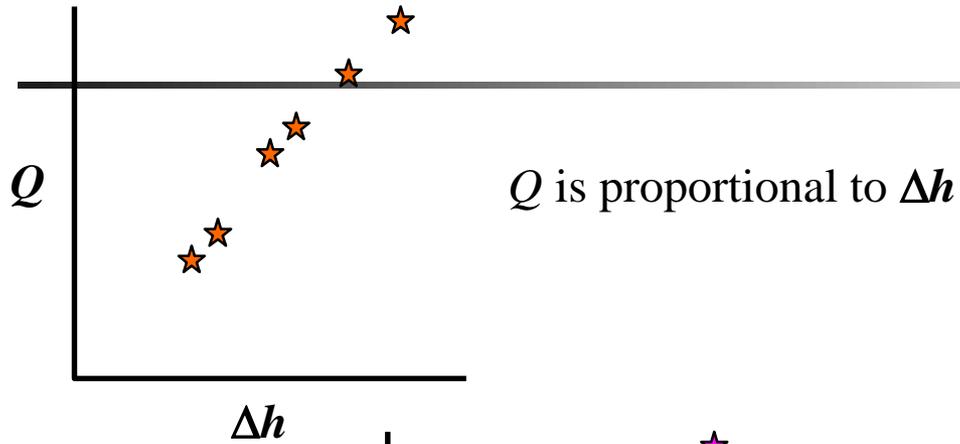
1. Basics of groundwater flow
2. Physical transport mechanisms in groundwater
3. Dispersion and retardation in groundwater
4. Movement of DNAPL's and LNAPL's

3.1 Basics of groundwater



Basics of groundwater





Darcy's Law

- Combine and insert a constant of proportionality

$$Q = -KA_{xc} [\Delta h/l]$$

- A_{xc} = sample cross-sectional area [m²]
 - *Perpendicular* to flow direction
- K = hydraulic conductivity [m/s]
- $\Delta h/l$ = hydraulic gradient [-]
- Sometimes written as $Q/A_{xc} = q = -K[\Delta h/l]$
 - Where q = specific discharge a.k.a. “Darcy velocity”
- Hydraulic gradient often written as a differential, dh/dl

Effect of Geologic Material and Fluid property

$$Q = -KA_{xc} [dh/dl]$$

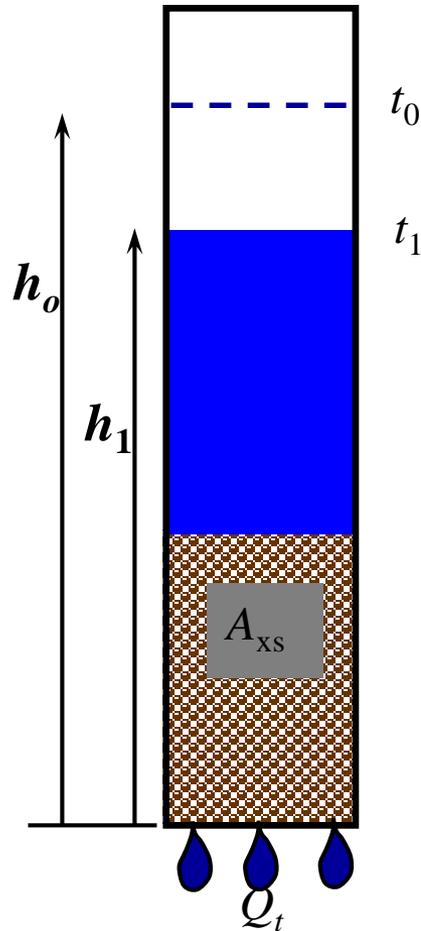
- Re-run experiments with different **geologic materials**
 - e.g., grain size
- General relationship still holds – but –
 - Need a new constant of proportionality (K)

K is a property of the porous material = Permeability

- Re-run experiments with a different **fluid**
 - e.g., petroleum, trichloroethylene, ethanol
- General relationship still holds – but –
 - Need a new constant of proportionality (K)

K is a property of the fluid = $\rho g/\mu$

How Fast is Groundwater Moving?



- Consider Darcy's experiment with a vertical sample

$$Q_t = -KA_{xs} (h_t/L) \quad \text{Divide through by } A_{xs}:$$

$$Q_t/A_{xs} = -K (h_t/L) = q \quad [\text{m/s}]$$

- q = Specific Discharge (Darcy velocity)

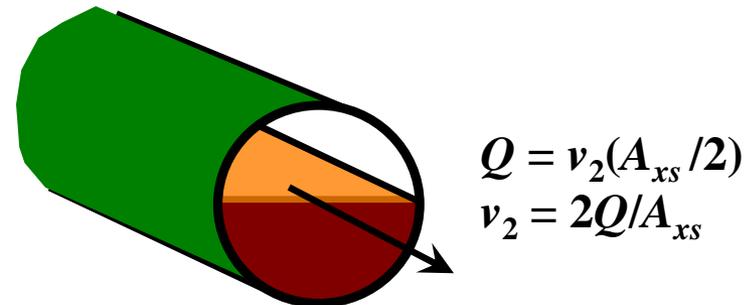
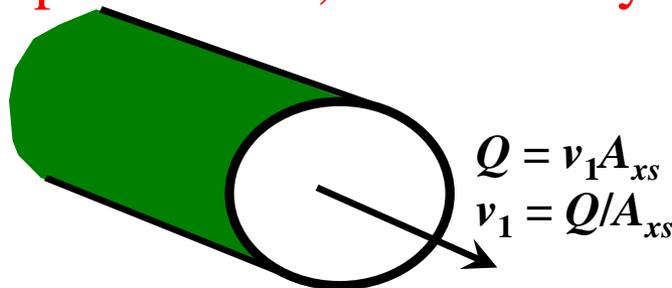
$$Q/A_{xs} = A_{xs} (h_o - h_1)/(t_1 - t_0) / A_{xs}$$

$$q = Q/A_{xs} = (h_o - h_1)/(t_1 - t_0)$$

- This is the velocity of water in the standpipe above the sample, not in the sample

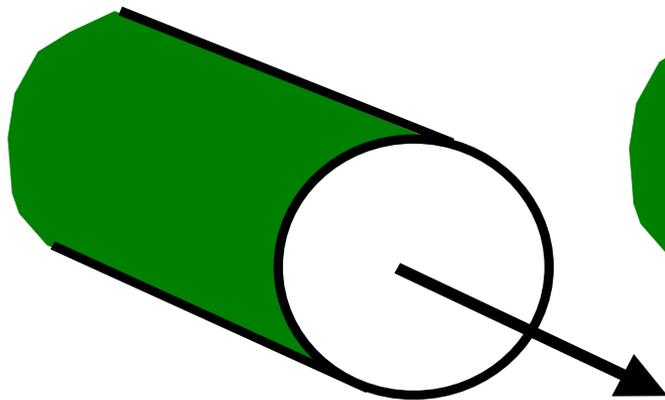
Specific Discharge – Darcy Velocity

- Specific discharge is an *apparent* velocity. Also called an *approach* velocity
 - Does not occur *in* porous media
- It is the velocity of the water, if the aquifer had been an open conduit
 - “Empty bed” velocity
- How is groundwater velocity in the porous medium related to specific discharge?
- Consider a pipe carrying water under pressure
- If a pipe became half clogged, but the flow through the pipe was kept constant, the velocity would double.

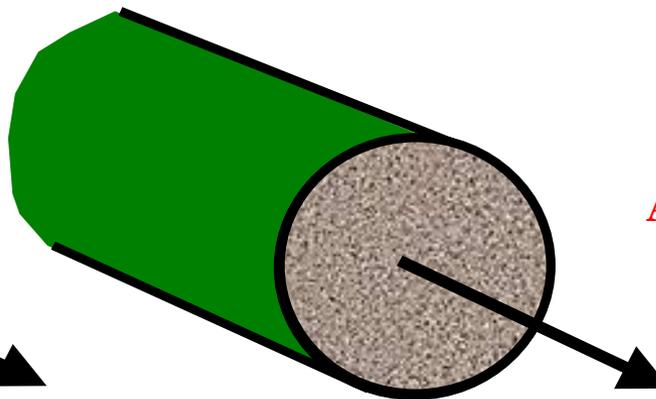


Effect of Porosity on Velocity

- Similarly, if the pipe was filled with sand having a porosity of 50%, only half the area is available for flow
 - If the flow through the pipe was kept constant, the velocity would double
- The area available for flow is therefore $n_e A_{xs}$
- Groundwater velocity $v = Q/A_{flow} = Q/n_e A_{xs} = q/n_e$



$$Q = v_1 A_{xs}$$
$$v_1 = Q/A_{xs}$$



$$Q = v_2 (A_{xs} / 2)$$
$$v_2 = 2Q/A_{xs}$$

Average linear velocity

Seepage velocity

$$v = Q/(n_e A_{xs})$$

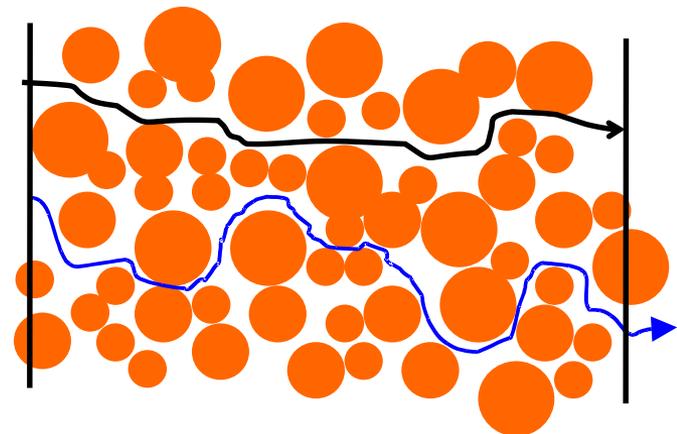
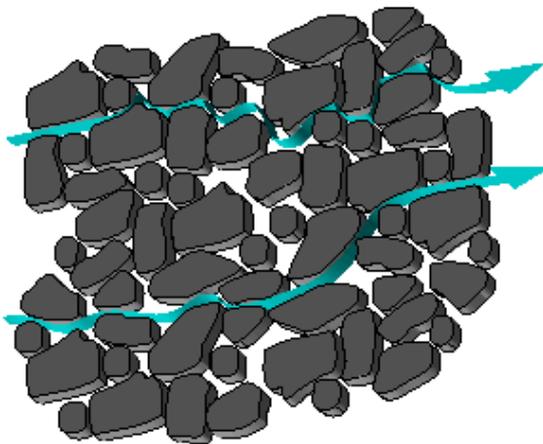
$$v = -K (dh/L) / n_e$$

Average Linear Velocity Vs Microscopic Scale

Average linear velocity

$$v = q/n_e = -K (dh/L)/n_e$$

- Pores have different sizes – velocity will differ in different size pores
- Water flowing near the pore walls will be slowed by viscosity, flow near the center of the pore throat will move fastest
- Flow paths are of different lengths, and some must split and branch around grains
- **Actual v will vary about the mean**



Groundwater Flow Equation

- The cube in Figure 1 is called the representative elementary volume (REV). Its volume is equal to $\Delta_x \Delta_y \Delta_z$. The flow of water through the REV is expressed in terms of the discharge rate (q), whose magnitude in the three coordinates will be q_x , q_y , and q_z .

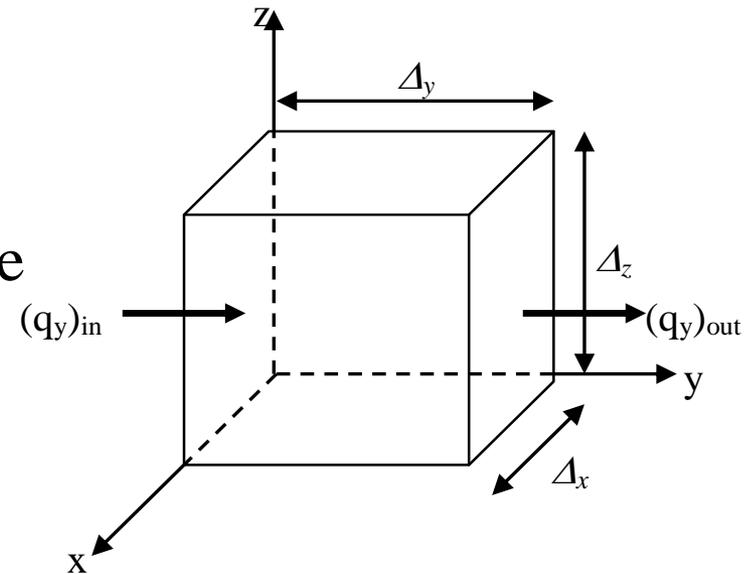


Figure 1 Representative elementary volume used in the derivation

- $$\frac{\partial}{\partial x} \left(K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial h}{\partial z} \right) = S_S \frac{\partial h}{\partial t} - R^*$$

- Where

- K_x , K_y , and K_z are components of the hydraulic conductivity.

- S_S specific storage ($[L^{-1}]$)

- R^* source/sink per unit volume of aquifer

- h is the Hydraulic head

Initial and boundary conditions

- For a well posed boundary value problem: (i) A solution must exist, (ii) The solution must be unique and (iii) The solution must be stable, in the sense that sufficiently small variations in the given data should lead to arbitrary small changes in the solution
- Initial and boundary conditions are needed for a unique solution of the groundwater flow equations for a specific flow domain of interest
- **Initial conditions:** specification of the distribution of the state variable (hydraulic head for the groundwater flow equation) at some initial time, usually at $t = 0$.

- For example

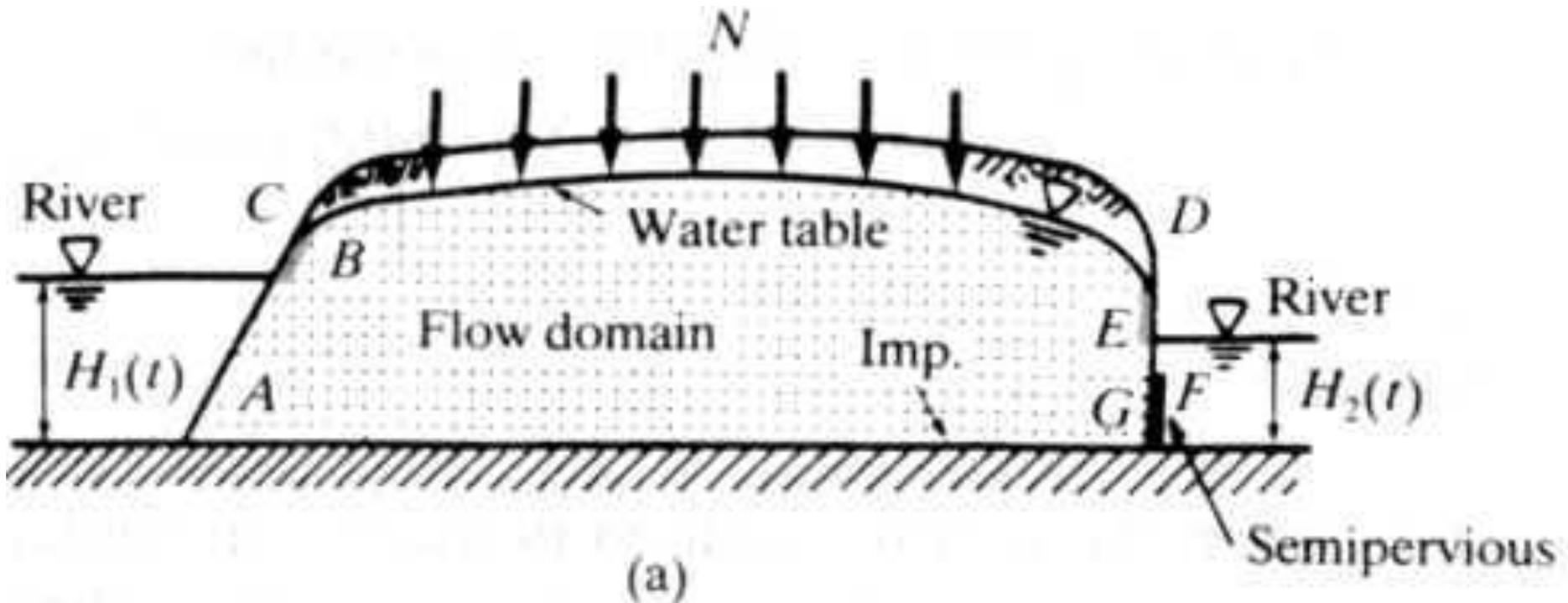
$$h = h(x, y, z, 0) = f(x, y, z) \quad \text{in } D$$

- In which $f(x, y, z)$ is a known function, D is the flow domain.

-
- **Boundary conditions:** specification of the interaction between the flow domain and its surrounding environment, which is a mathematical representation of the physical reality
 - Known water fluxes
 - Known values of state variables, such as hydraulic head, that the external domain imposes on the flow regime
 - Different initial and boundary conditions result in different solutions
 - Three mathematical boundary conditions:
 1. Dirichlet : where the solution h is known
 2. Neumann: where the gradient of the solution h is known
 3. Cauchy: where by the solution depends on the character of the medium at the boundary location.

■ **Example:**

- Dirichlet: AB and EF boundaries
- Neumann: BC, CD, DE and GA boundaries
- Cauchy: FG boundary

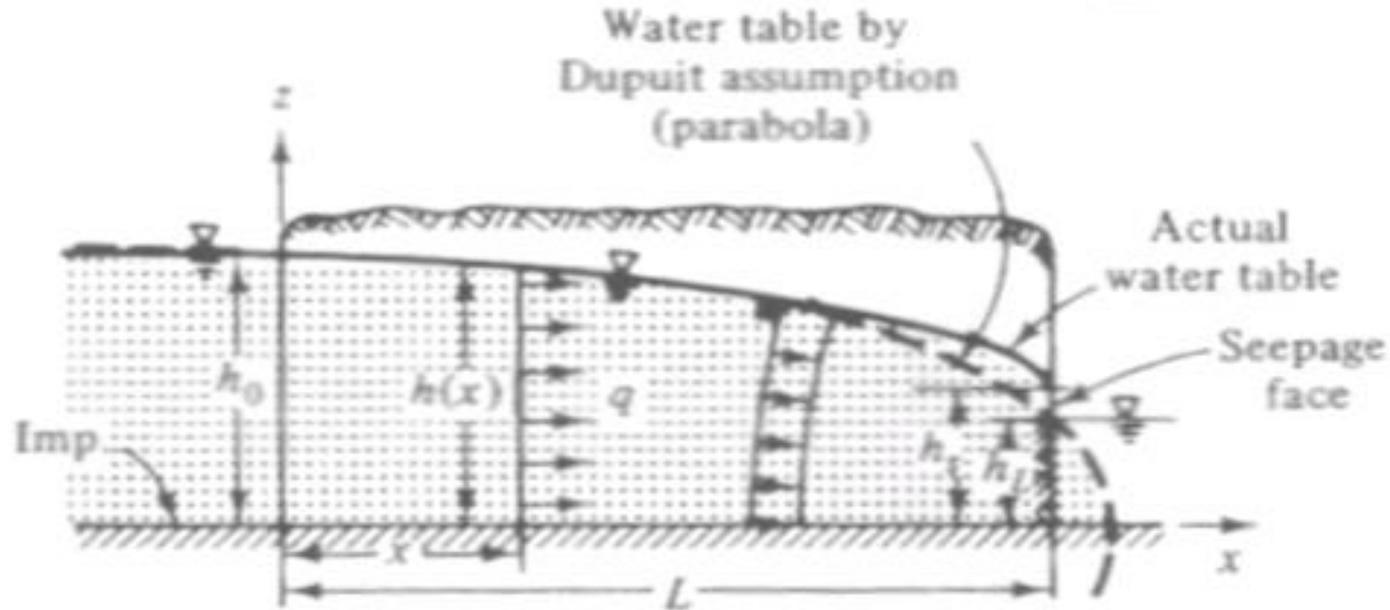


Dupuit assumption

- The boundary of an unconfined aquifer (z) is indeed the solution (h) that needs to be determined.
- **Dupuit assumptions:** First developed by Dupuit (1863) and then advanced by Forchheimer (1930), or called Dupuit-Forchheimer theory
 - From observations, the slope of phreatic surface (water table) is very small (commonly 1/1000)
 - Two assumptions
 - The hydraulic gradient is equal to the slope of the free surface and is invariant with depth
 - The equipotential lines are vertical, i.e., the flow lines are horizontal, i.e., $\frac{\partial p}{\partial z} = -\rho g$

Dupuit assumption

- Example : two-dimensional steady-state flow without accretion



(After Bear and Verruijt, 1987)

Fig. 2.7. Steady unconfined flow between two reservoirs (Bear, 1979).

- $Q_x = -Kh \frac{dh}{dx} = \text{constant} \gg Q_x dx = -Kh dh \gg Q_x \int_0^L dx = -K \int_{h_0}^{h_L} h dh$
- $\gg Q_x(L - 0) = -K \left(\frac{h_L^2 - h_0^2}{2} \right) \gg Q_x = \frac{K}{2L} (h_0^2 - h_L^2)$ **(Dupuit equation)**

Dupuit assumption

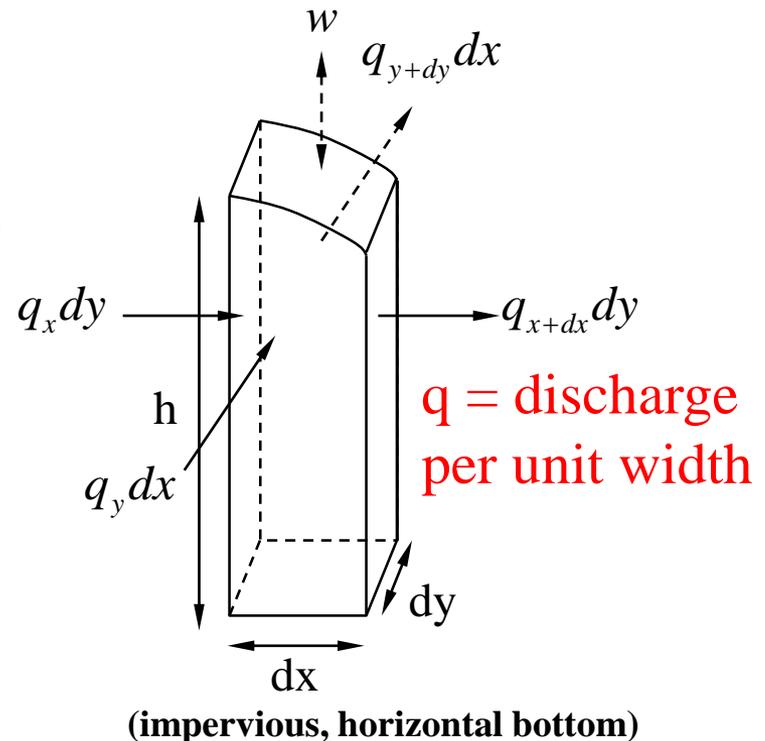
Example : three-dimensional **steady-state** flow with accretion

Mass in – mass out = $\Delta M = 0$ (steady state)

Under Dupuit assumptions: $h(x, y, z) \rightarrow h(x, y)$

- $K \left(\frac{\partial^2 h^2}{\partial x^2} + \frac{\partial^2 h^2}{\partial y^2} \right) = -2w$
- w [L/T] : rate of water into or out of the unconfined aquifer per unit area of the unconfined aquifer i.e., $w > 0$ for infiltration, $w < 0$ for evaporation

(Adapted from Fetter, 1994)



Dupuit assumption

Furthermore, for one-dimensional flow,

Eq(2) reduces to: $\frac{d^2}{dx^2} (h^2) = -\frac{2w}{K}$

$$h(x=0) = h_1$$

BC's : $h(x=L) = h_2$

General solution : $h^2(x) = -\frac{w}{K}x^2 + c_1x + c_2$

$$h(x=0) = h_1 \Rightarrow c_2 = h_1^2$$

$$h(x=L) = h_2 \Rightarrow c_1 = \left(\frac{h_2^2 - h_1^2}{L} \right) + \frac{wL}{K}$$

$$h^2(x) = h_1^2 - \frac{(h_1^2 - h_2^2)x}{L} + \frac{w}{K}(L-x)x$$

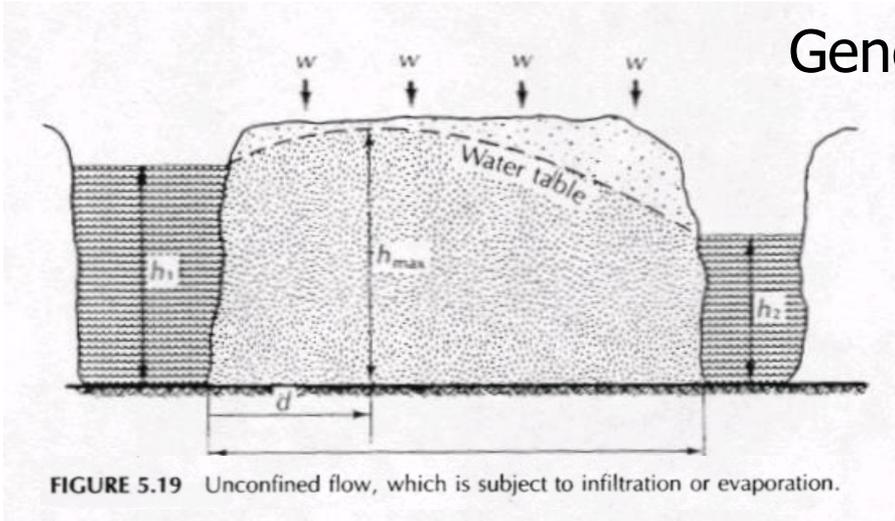


FIGURE 5.19 Unconfined flow, which is subject to infiltration or evaporation.

(After Fetter, 1994)

Hence

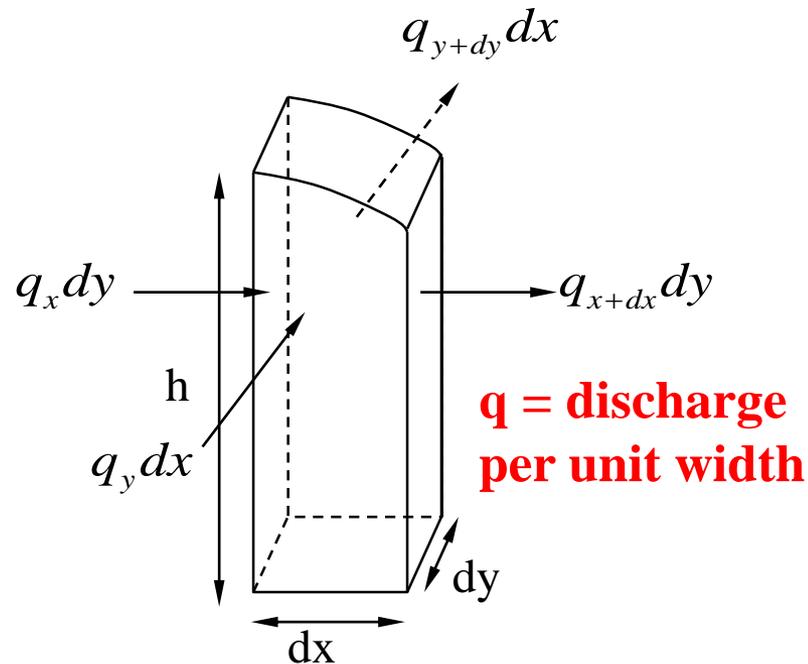
$$h(x) = \sqrt{h_1^2 - \frac{(h_1^2 - h_2^2)x}{L} + \frac{w}{K}(L-x)x} \quad (3)$$

$$d = \frac{L}{2} - \frac{K}{2Lw} (h_1^2 - h_2^2)$$

$$h_{\max} = \sqrt{h_1^2 - \frac{(h_1^2 - h_2^2)d}{L} + \frac{w}{K}(L-d)d}$$

Transient 2D unconfined flow

For incompressible fluids and homogeneous and isotropic aquifers



(impervious, horizontal bottom)

Mass in – mass out = ΔM

Under Dupuit assumptions:

$$h(x, y, z) \rightarrow h(x, y)$$

$$\frac{\partial}{\partial x} \left(h \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(h \frac{\partial h}{\partial y} \right) = \frac{S_y}{K} \frac{\partial h}{\partial t}$$

(Boussinesq Equation)

$$S_y = \text{specific yield} \equiv \frac{\Delta V_w}{A \Delta h}$$

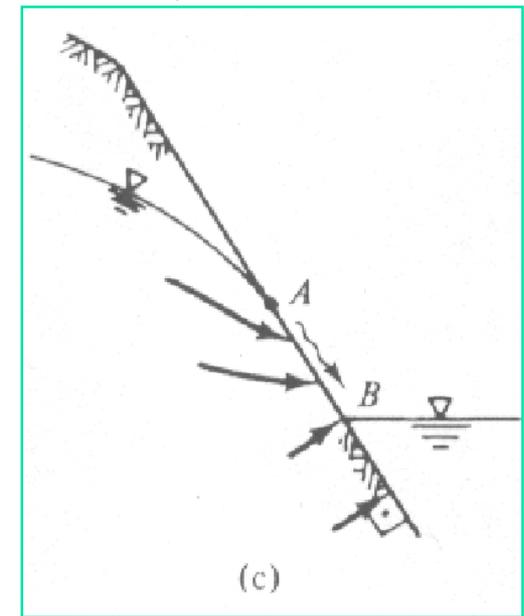
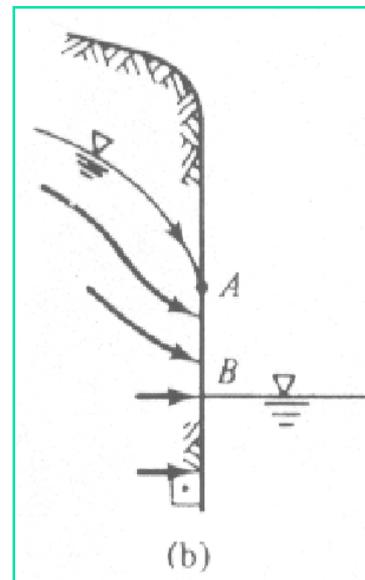
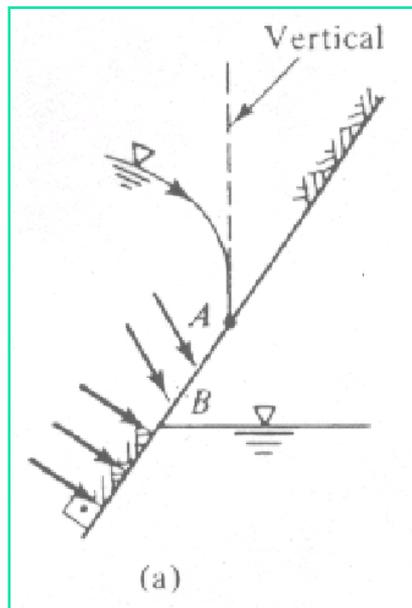
- Boussinesq equation is a non-linear PDE, which can not be solved analytically except under some idealized conditions
- **Approximations:** Drawdown in the aquifer is small, i.e., $h \approx b$ (averaged thickness assumed to be constant over the aquifer)
- From the Boussinesq equation

$$\blacksquare \frac{\partial}{\partial x} \left(h \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(h \frac{\partial h}{\partial y} \right) \cong \frac{\partial}{\partial x} \left(b \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(b \frac{\partial h}{\partial y} \right) = \frac{S_y}{K} \frac{\partial h}{\partial t}$$

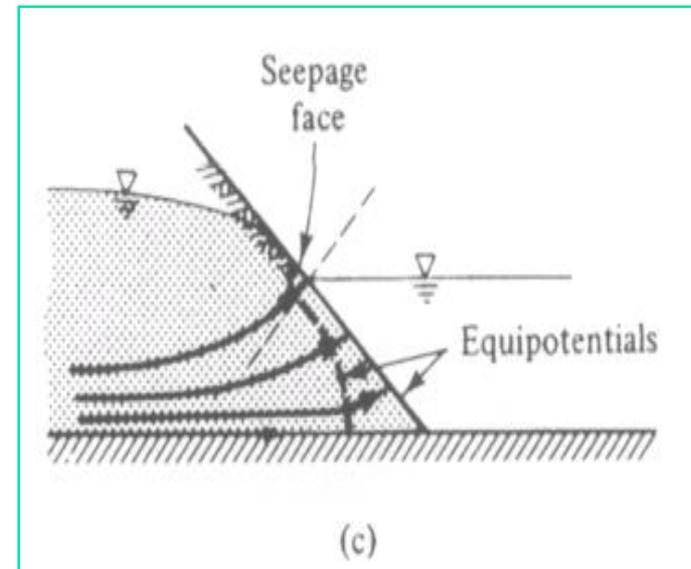
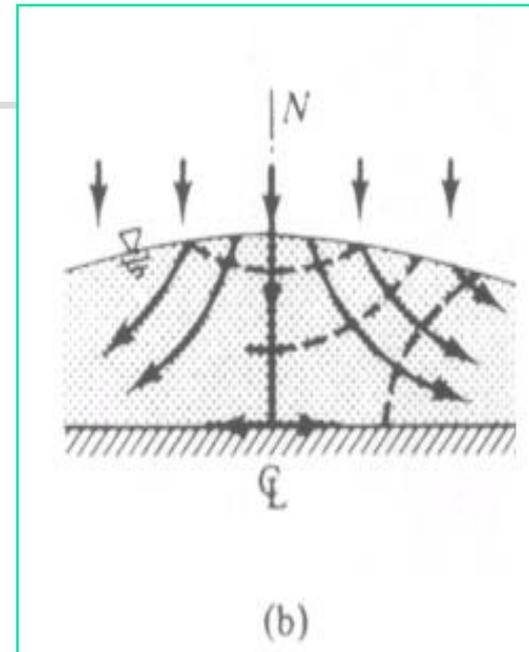
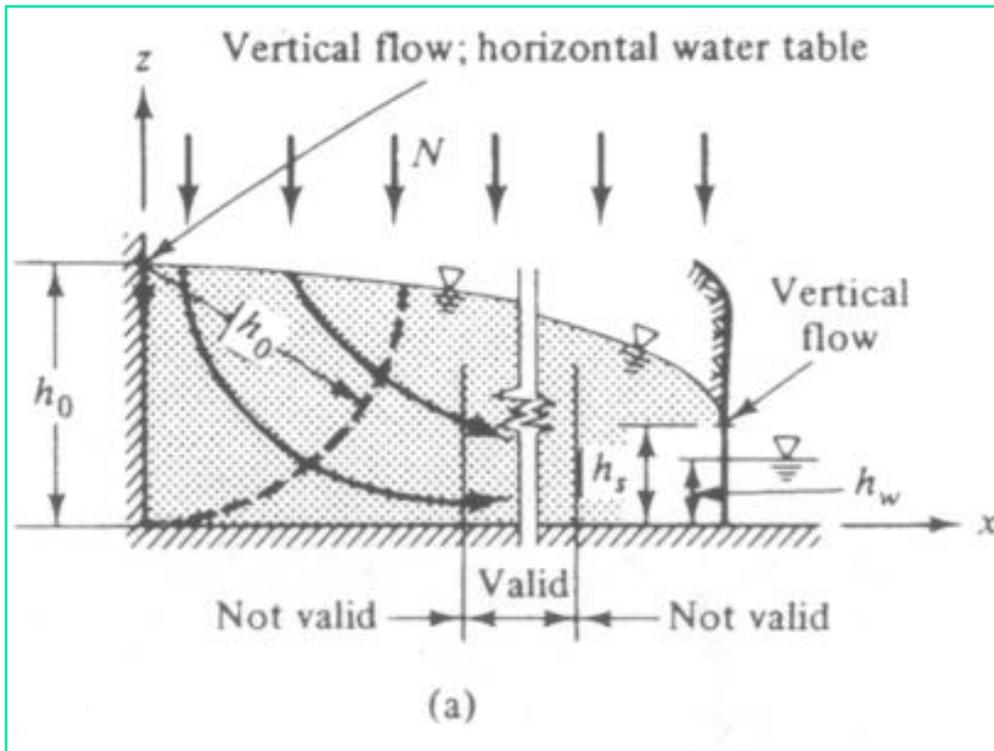
$$\blacksquare \gg \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} = \frac{S_y}{Kb} \frac{\partial h}{\partial t}$$

(Note that (the last equation) is similar to the 2-D flow in a confined aquifer, except that S , Storativity of a confined aquifer, is used instead of $\frac{S_y}{b}$)

- Conditions when Dupuit assumption does not work
 - Vertical flow is not negligible (Vertical impervious boundary; Crest of water table (or water divide); Seepage face)
- **Rule of thumb (Bear and Verruijt, 1987): Dupuit assumption is valid at distances from the downstream end larger than twice the average height of the flow domain.** However, discharge calculated from Dupuit assumption is a satisfactory estimation for most cases



Examples of seepage face



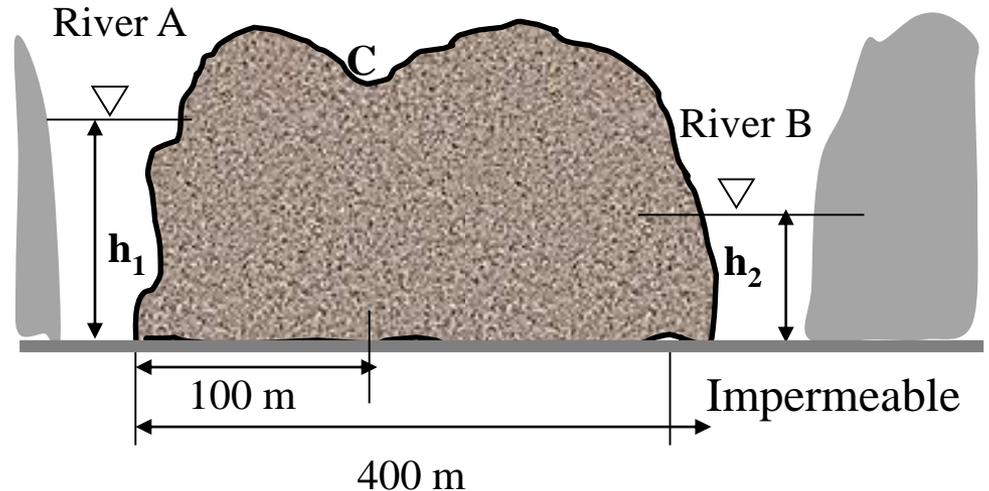
- Examples where Dupuit assumption is not valid

Example

- An unconfined aquifer of clean sand and gravel is located between two fully penetrating rivers (see the figure below) and has a hydraulic conductivity of 0.01 cm/s . At point C (100 m away from River A and at 1592 m elevation) a marsh land was observed during study time. A pollutant is disposed over the marsh land. If The water surface elevations in rivers A and B are 1590 m and 1585 m, respectively with the rivers bed level is at 1580 m elevation. Estimate:
 - The maximum elevation of the water table and the location of the stagnation point.
 - The travel time for the pollutant to River A (Take effective porosity of 0.35)

Solution

- $K = 0.01 \text{ cm/s} = 8.64 \text{ m/day}$
- $h_1 = 1590 - 1580 = 10 \text{ m}$
- $h_2 = 1585 - 1580 = 5 \text{ m}$
- $h_c = 1592 - 1580 = 12 \text{ m}$



- h_c being greater than the two rivers elevation implies the presence of positive accretion w (recharge) thus a 2D Dupuit equation with accretion will be used.

$$h^2(x) = h_1^2 - \frac{(h_1^2 - h_2^2)x}{L} + \frac{w}{K}(L - x)x$$

- $w = ??$, Substituting the value of h_c at $x = 100\text{m}$ will define the w .

$$12^2 = 10^2 - \frac{(10^2 - 5^2) \times 100}{400} + \frac{w}{8.64} (400 - 100) \times 100$$

$$\Rightarrow w = 0.018072 \text{ m/day} = 2.09 \times 10^{-7} \text{ m/s}$$

Solution

- The maximum water table elevation occurs at the location of groundwater divide computed as:

- $d = \frac{L}{2} - \frac{(h_1^2 - h_2^2)K}{2Lw} = \frac{400}{2} - \frac{(10^2 - 5^2) \times 8.64}{2 \times 400 \times 0.018072} = 200 - 44.8 = 155.2m$ from river A

- The maximum head at the divide is computed as:

- $$h_{\max} = \sqrt{h_1^2 - \frac{(h_1^2 - h_2^2)d}{L} + \frac{w}{K}(L - d)d} =$$
$$\sqrt{10^2 - \frac{(10^2 - 5^2) \times 155.2}{400} + \frac{0.018072}{8.64}(400 - 155.2) \times 155.2} = 12.26m$$

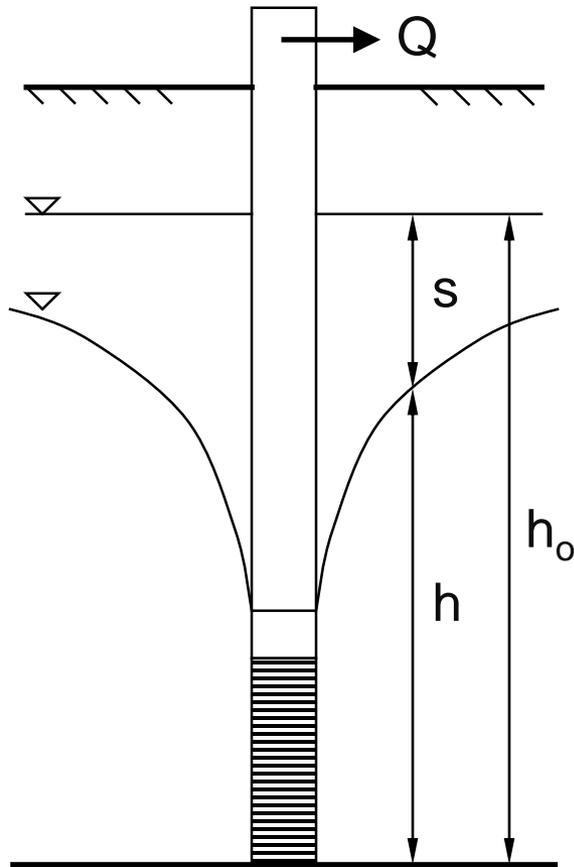
- The average pore water velocity is computed using Darcy's law:

- $v_A = \frac{K}{n_e} \left(\frac{\Delta h}{\Delta x} \right) = \frac{8.64}{0.35} \left(\frac{12 - 10}{100} \right) = 0.494m/day$

- The travel time to river A: $t = \frac{L_A}{v_A} = \frac{100}{0.494} = 202.55days$

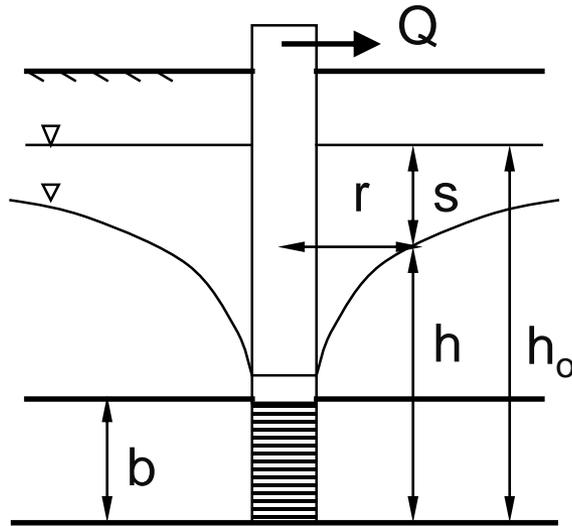
Practice Exercise: Is the contamination a threat to River B?

Flow to a pumping well



- **Static Water Level [SWL] (h_0)** is the equilibrium water level before pumping commences
- **Pumping Water Level [PWL] (h)** is the water level during pumping
- **Drawdown ($s = h_0 - h$)** is the difference between SWL and PWL
- **Well Yield (Q)** is the volume of water pumped per unit time
- **Specific Capacity (Q/s)** is the yield per unit drawdown
- **Radius of influence:** the radius of the region beyond which no drawdown is observed due to the well.

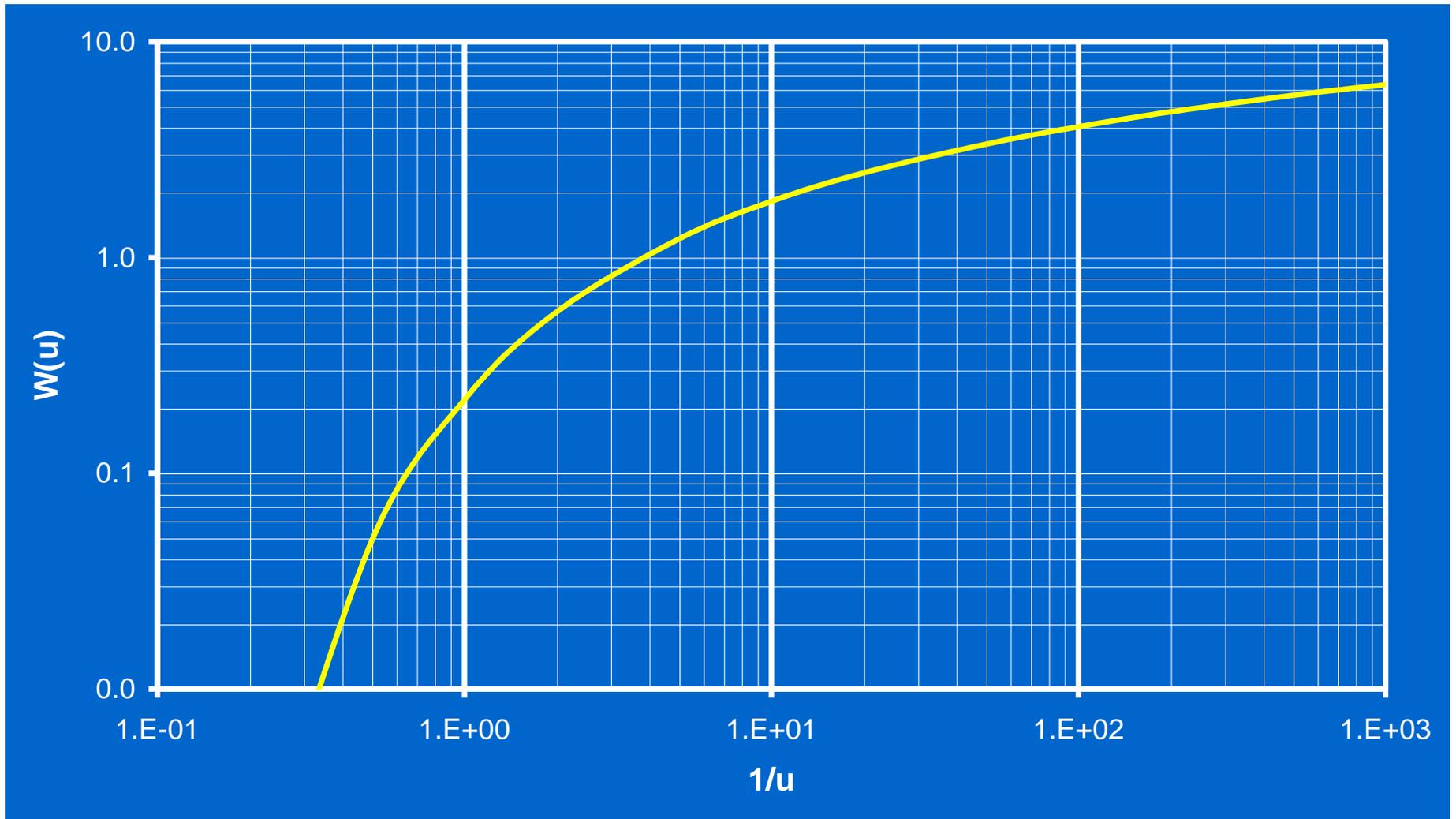
Unsteady radial confined flow



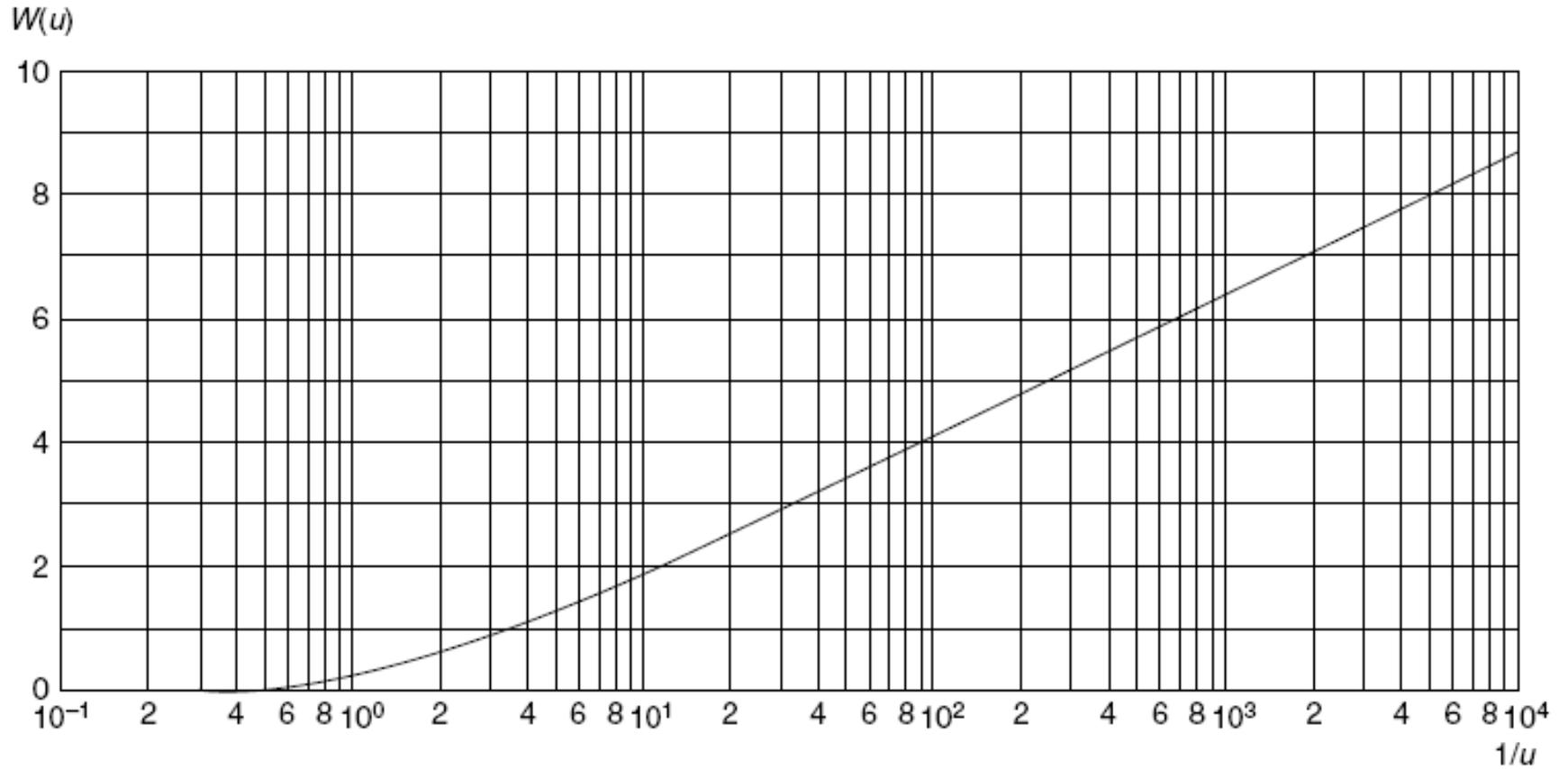
- **Assumptions**
Isotropic, homogeneous, infinite aquifer, 2-D radial flow
- **Initial Conditions**
 $h(r,0) = h_0$ for all r
- **Boundary Conditions**
 $h(\infty,t) = h_0$ for all t
- PDE: $\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right) = \frac{S}{T} \frac{\partial h}{\partial t}$

- Change the dependent variable by letting: $u = \frac{r^2 S}{4Tt}$
- The ultimate solution is: $h_0 - h = \frac{Q}{4\pi T} \int_u^\infty \left(\frac{e^{-u}}{u} \right) du$
- Where the integral is called the exponential integral written as the well function $W(u)$. **This is the Theis Equation**

Theis Plot : $1/u$ vs $W(u)$



Cooper Jacob



Cooper Jacob

- In the above figure, the Theis well function $W(u)$ is plotted vs. $1/u$ on semi-log paper.
- This figure shows that, for large values of $1/u$, the Theis well function exhibits a straight-line segment.
- The Jacob method is based on this phenomenon. Cooper and Jacob (1946) showed that, for the straight-line segment, s can be approximated by

$$s = \frac{Q}{4\pi T} W(u) = \frac{Q}{4\pi T} \ln \left(\frac{2.25Tt}{r^2 S} \right) = \frac{2.3Q}{4\pi T} \log \left(\frac{2.25Tt}{r^2 S} \right)$$

- with an error less than 1%, 2%, 5%, and 10% for $1/u$ larger than 30, 20, 10, and 7, respectively.
- The Cooper-Jacob simplification expresses drawdown (s) as a linear function of $\ln(t)$ or $\log(t)$.

Example

- A well (10'' in diameter) is constructed 1000m from a waste disposal site. The well taps a confined aquifer of 25m thick, having $T = 0.01 \text{ m}^2/\text{s}$ and S of 0.0001.
 - If the well yield is fixed to be $100 \text{ m}^3/\text{day}$, and operates a quarter of a day, is the well safe from contamination?
- **Solution**
 - Daily requirement 100 m^3 , to be supplied within a quarter of a day, the well yield shall be $100 / (6\text{hr} \times 60\text{min} \times 60 \text{ sec}) = 0.00463 \text{ m}^3/\text{s}$
 - $10'' = 25.4 \text{ cm}$, Radius of the well = 0.127m

Solution

- From Cooper Jacob equation the well radius of influence (1000 m) would be reached at

$$s = \frac{2.3Q}{4\pi T} \log \left(\frac{2.25Tt}{r^2 S} \right) \Rightarrow 0 = \frac{2.3Q}{4\pi T} \log \left(\frac{2.25Tt}{r^2 S} \right) \Rightarrow \frac{2.25Tt}{r^2 S} = 1$$

$$t = \frac{r^2 S}{2.25T} = \frac{1000^2 \times 0.0001}{2.25 \times 0.01} = 4444.44 \text{ sec} = 1.2346 \text{ hrs}$$

- At this time the drawdown at the well location will be

$$s_w = \frac{2.3Q}{4\pi T} \log \left(\frac{2.25Tt}{r_w^2 S} \right)$$
$$\Rightarrow s_w = \frac{2.3 \times 0.00463}{4\pi \times 0.01} \log \left(\frac{2.25 \times 0.01 \times 4444.44}{0.127^2 \times 0.0001} \right)$$
$$= 0.66 \text{ m}$$

Solution

- The average velocity of the groundwater particle would be

$$\blacksquare v = \frac{K}{n_e} \left(\frac{\Delta h}{\Delta x} \right) = \frac{T}{bn_e} \left(\frac{\Delta h}{\Delta x} \right) = \frac{0.01}{25 \times 0.35} \left(\frac{0.66 - 0}{1000} \right) = 7.55 \times 10^{-7} m/s$$

- Travel time to the well

$$\blacksquare t = \frac{L}{v} = \frac{1000}{7.55 \times 10^{-7} s} = 1.33 \times 10^9 s = 42.02 years$$

- The radius of influence at the end of each pumping operation time i.e. 6hr (21600 sec) time would be

$$\blacksquare s = \frac{2.3Q}{4\pi T} \log \left(\frac{2.25Tt}{r^2 S} \right) \Rightarrow 0 = \frac{2.3Q}{4\pi T} \log \left(\frac{2.25Tt}{R^2 S} \right) \Rightarrow \frac{2.25Tt}{R^2 S} = 1$$

$$\Rightarrow \frac{2.25 \times 0.01 \times 21600}{R^2 \times 0.0001} = 1 \Rightarrow R = 2204.541 m$$

Solution

- The drawdown in the well at 21600sec time would be

$$\blacksquare s_w = \frac{2.3 \times 0.00463}{4\pi \times 0.01} \log \left(\frac{2.25 \times 0.01 \times 21600}{0.127^2 \times 0.0001} \right) = 0.72m$$

- The drawdown at the waste location

$$\blacksquare s_w = \frac{2.3 \times 0.00463}{4\pi \times 0.01} \log \left(\frac{2.25 \times 0.01 \times 21600}{1000^2 \times 0.0001} \right) = 0.06m$$

- The average velocity of the particle at the waste location

$$\blacksquare v = \frac{K}{n_e} \left(\frac{\Delta h}{\Delta x} \right) = \frac{T}{bn_e} \left(\frac{\Delta h}{\Delta x} \right) = \frac{0.01}{25 \times 0.35} \left(\frac{0.72 - 0.06}{1000} \right) = 7.55 \times 10^{-7} m/s$$

$$\blacksquare \text{The travel time would be } t = \frac{L}{v} = \frac{1000}{7.55 \times 10^{-7} s} = 1.33 \times 10^9 s = 42.02 \text{ years}$$

- Since the time it take to reach the well (in both cases) is very long the water is safe to use.

3.2. Physical transport mechanisms in soil

- ***Advective Transport (J_c)***: is the passive transport of dissolved constituents with the flowing water. In this case, water and the solutes move at the same average rate:

$$\blacksquare J_c = J_w C = -C \left[K(h) \frac{dh}{dx} \right]$$

- Where C is the volume-averaged solute concentration, J_c is the solute flux, and J_w is the water flux (Darcy velocity, represents the flow velocity averaged over an entire cross sectional area).
- To estimate solute travel or arrival times, the mean pore water velocity (u) is used: $u = \frac{J_w}{\theta}$
 - θ is the water content
- Thus solute flux may also be characterized as: $J_c = u\theta C$

Diffusive Transport (J_d)

- In bulk water at rest is given by *Fick's Law*: $J_d = -D_o \frac{dC}{dx}$
 - where D_o is the diffusion coefficient in bulk water.
- The diffusion coefficient in porous media is **less than D_o** . Because air and solid particles form barriers to liquid diffusion, the apparent soil-liquid diffusivity (D_s [L^2/t]) is a function of the available path for diffusion determined by the tortuosity $T(\theta)$.
- Tortuosity $T(\theta)$, results from the geometry of the medium (i.e., texture and structure) and the volumetric water content. (E.g. Jury et al, 1991):

- $D_s = D_o \theta T(\theta) = D_o \frac{\theta^{(10/3)}}{n^2}$ Where n is porosity.

- The flux of diffusing solutes in an unsaturated porous medium is thus: $J_d = -D_s \frac{\partial C}{\partial x}$

Dispersive Transport (J_h)

- Differences in flow velocities at the pore scale (due to different pore sizes and shapes) cause the solute to be transported at different rates and thus lead to mixing (or dispersion) of an incoming solution within an antecedent solution.
- The process is macroscopically similar to mixing by diffusion (thermal motion); however, it is passive (i.e., not driven by concentration gradients) and is entirely dependent on water flow. The solute flux due to mechanical (or hydrodynamic) dispersion (J_h) is described by an equation similar to Fick's Law for diffusion:

$$\blacksquare J_h = -D_h \frac{\partial C}{\partial x}$$

- where D_h is the hydrodynamic dispersion coefficient (L^2/T)

-
- D_h is dependent on the interstitial pore water flow velocity (u [L/T]), and on the dispersivity (λ [L]) of the soil (a function of pore sizes and shapes) accordingly:

$$\blacksquare D_h = \lambda \left(\frac{J_w}{\theta} \right)^N = \lambda u^N$$

- where N is an empirical factor usually assumed to equal **1** (i.e., a linear dependency of D_h on u). The value of λ may range from 1 cm in small columns to a few meters in field experiments. In most cases the relative effect of hydrodynamic dispersion can exceed that of diffusion.
- Because of the macroscopic similarity between diffusion and hydrodynamic dispersion, it is common to combine their coefficients (assuming that they are additive) in to a *diffusion-dispersion coefficient* (D_e): $D_e(\theta, u) = D_s + D_h$

The Advection-dispersion equation

- ***The ADE for conservative Solutes:*** The total flux of dissolved solutes in soil (J_s) is the result of combined transport by the three mechanisms discussed above, and may be described by the *convection dispersion model*:

$$\blacksquare J_s = -D_e \frac{\partial C}{\partial x} + J_w C$$

- Where J_s is the total mass of solute transported across a unit cross-sectional area of soil per unit time, J_w is the water flux (Darcian flux), D_e is the combined diffusion-dispersion coefficient, and $\partial c/\partial x$ is the spatial solute gradient.
- D_e is dominated by the dispersion process under most flow conditions.

- Combining the above equation with the continuity equation (conservation of mass) yields:

$$\frac{\partial(\theta C)}{\partial t} = -\frac{\partial J_s}{\partial x} = \frac{\partial}{\partial x} \left(D_e \frac{\partial C}{\partial x} - J_w C \right)$$

- Assuming steady state water flow in a homogeneous soil profile (J_w and θ are constant in time and space), reduces the above equation to the familiar form of the *advection-dispersion equation* for conservative (**inert and non-adsorbing**) solutes:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} \quad \text{Equation A}$$

- where $D = D_e/\theta$, $u = J_w/\theta$, and R is known as the *retardation factor* which in this case is simply $R=1$.

$$C(x, t) = \frac{M}{A} \frac{1}{\sqrt{4\pi \frac{D}{R} t}} \exp \left(-\frac{\left(x - \frac{u}{R}t\right)^2}{4 \frac{D}{R} t} \right)$$

Flux and Resident Concentrations

- In solving transport problems there are two chemical concentrations of interest:
 - (i) the *total resident concentration*, denoted as c^r , which is the mass of solute per volume of soil; and
 - (ii) the *flux concentration*, c^f , which is the ratio of the solute mass flux (J_s) to the water flux (J_w), i.e., $c^f = J_s / J_w$.
- The difference between these two concentrations may be illustrated by the outcome of a hypothetical measurement of the effluent leaving a soil column *vs.* the solution concentration at a given soil volume within the column. This is somewhat analogous to the relationship between changes in volumetric water content and the water flux leaving a soil volume.

Flux and Resident Concentrations

- These concentrations are related through the solute continuity equation (for an inert solute assuming vertical flow along z):

$$\blacksquare \frac{\partial c^r}{\partial t} = - \frac{\partial J_s}{\partial z}, \quad J_s = c^f J_w$$

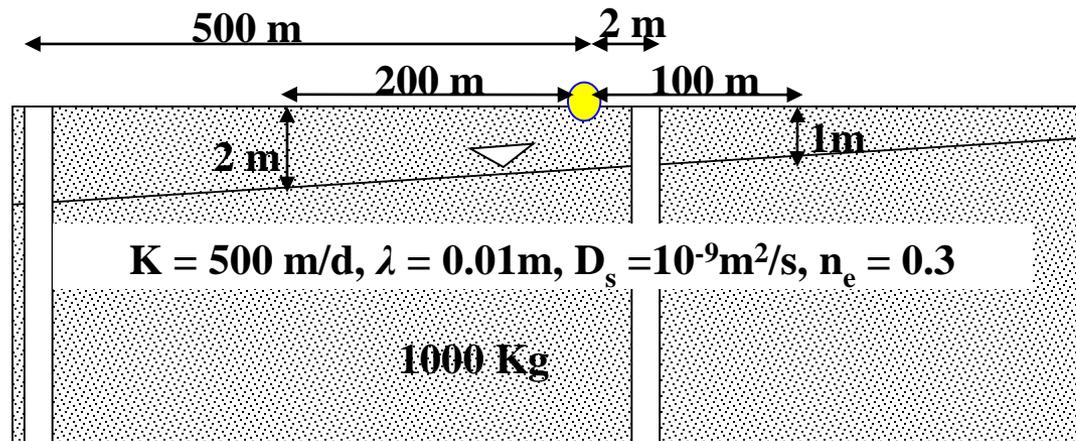
- and under steady state flow conditions:

$$\blacksquare \frac{\partial c^r}{\partial t} + J_w \frac{\partial c^f}{\partial z} = 0$$

- An alternative representation was given by van Genuchten and Wierenga (1986): $c^f = c^r - \frac{D}{u} \frac{\partial c^r}{\partial z}$
- It useful to note, however, that the difference between c^r and c^f can be ignored for $D/(uL) < 1$ and at depths $z > ut$ where t is the time of observation (Parker and van Genuchten, 1984).

Example

- A 1000kg spill of a contaminant into an aquifer has occurred. The spill was short and over a small area having hydraulic conductivity of 500m/d, effective porosity of 0.3, diffusivity of $10^{-9} \text{ m}^2/\text{s}$ and dispersivity (λ) of 0.01 m. You have a depth to water measurement at 100m east of the spill 1m and at 200 m west of the spill it is 2m. The surface elevation is flat. There are two drinking wells, one 2 m east of the spill and another is 500 m west of the spill. Calculate the concentrations that will arrive at these wells.



Solution:

- Given: $M = 1000 \text{ Kg}$; $K = 500 \text{ m/d}$; $n_e = 0.3$
- Depth at -100 m 1m and at 200 m 2.0 m (taking the waste disposal site as the origin and positive direction towards the west).

- **The equation to solve is**
$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}$$

- **Calculate Darcy velocity:**

$$q = -K \frac{\Delta h}{\Delta l} = -500 \text{ m/d} \times \frac{1 - 2}{300} = 1.667 \text{ m/d}$$

- The average linear velocity would be $u = q/n_e = 1.667/0.3 = 5.5556 \text{ m/day}$
- **Hydrodynamic dispersion coefficient (D):** = Diffusivity (D_s) + Dispersive coefficient (λu) = $10^{-9} \text{ m}^2/\text{s} + 0.01 \text{ m} \times 5.5556 \text{ m}/(86400 \text{ s}) = 10^{-9} + 6.43 \times 10^{-7} = 6.431 \times 10^{-7} \text{ m}^2/\text{s} = 5.5556 \times 10^{-2} \text{ m/d}$ (note D_s is basically negligible)

Solution

- **Retardation (nothing is given) take it to be $R = 1$**
- The solution to the above equation for instantaneous injection of waste (1000kg) is given by

$$\blacksquare C(x, t) = \frac{M}{A} \frac{1}{\sqrt{4\pi \frac{D}{R} t}} \exp\left(-\frac{\left(x - \frac{u}{R}t\right)^2}{4\frac{D}{R}t}\right) = \frac{1000}{A} \frac{1}{\sqrt{4\pi \times \frac{0.0556}{1} t}} \exp\left(-\frac{\left(x - \frac{5.556}{1}t\right)^2}{4 \times \frac{0.0556}{1} t}\right)$$

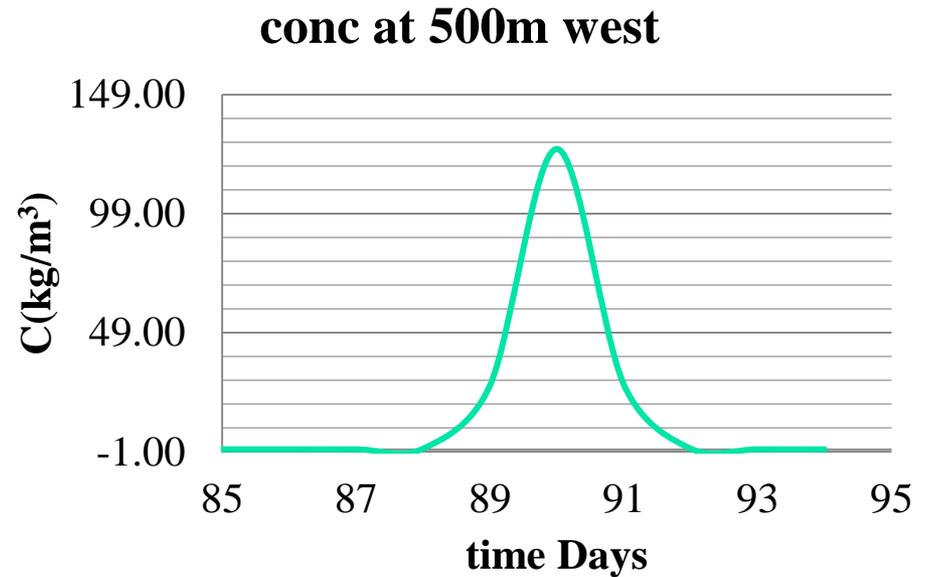
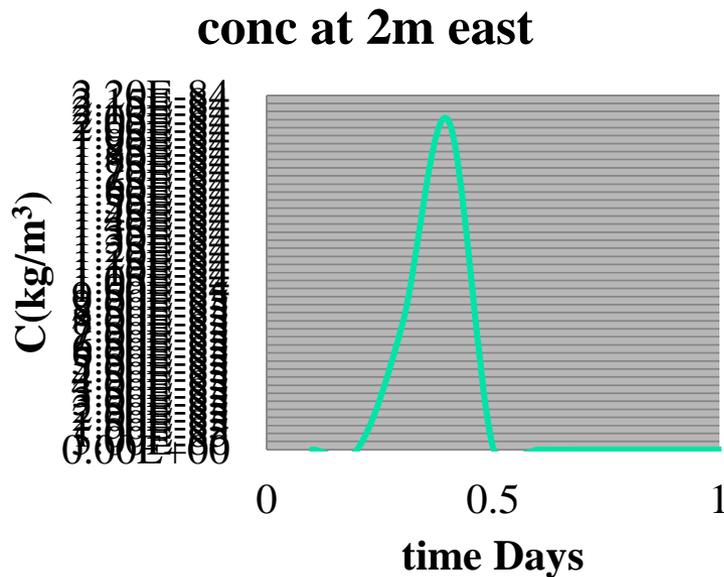
- The concentration per unit area of the aquifer would be

$$\blacksquare C(x, t) = \frac{1000}{\sqrt{4\pi \times 0.0556 t}} \exp\left(-\frac{(x - 5.556t)^2}{4 \times 0.0556 t}\right)$$

- **Case 1 at 2m east of the waste $x = -2$ m will be substituted**
- **Case 2 at 500m west of the waste $x = 500$ m will be substituted**

Solution

- The concentration profiles with time is as shown in the following figures



3. Dispersion and Retardation in soil

- In some cases we may consider changes in the mass of solute adsorbed onto the solid soil matrix. The adsorbed mass is given by $\rho_b s$, where ρ_b is the soil's bulk density and s is the adsorbed concentration (mass of solute per mass of soil). The modified continuity equation (including the adsorbed solute) is given as:

$$\blacksquare \frac{\partial(\theta C + \rho_b s)}{\partial t} = \frac{\partial}{\partial x} \left(D_e \frac{\partial C}{\partial x} - J_w C \right)$$

- Often, the mass of the adsorbed solute can be related to its concentration in the solution by an *adsorption isotherm*. In its simplest form, s and C are assumed to be related by a linear (or linearized) equilibrium isotherm given by:

$$\blacksquare s = k_d C,$$

- Where k_d is known as the *distribution coefficient*.

Retardation factor

- Under steady state water flow conditions where J_w and θ are constant in time and space, and with a linear adsorption isotherm (eq. above), the resulting ADE is identical to **equation A**.

$$\blacksquare R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x}, \text{ where } D = D_e/\theta, u = J_w/\theta$$

- Except the *retardation factor*, R , is now defined as:

$$\blacksquare R = 1 + \frac{\rho_b k_d}{\theta}$$

- Note that, if there are no interactions between the soil and the solute, then $k_d = 0$ and $R = 1$.

The ADE with Chemical and Biological Degradation

- In some cases the transported solute undergoes chemical or biological degradation (e.g., radioactive decay or microbial transformation). It is useful to distinguish between processes taking place in the solution and on the solid phase. The liquid phase continuity equation is given by (van Genuchten and Wagenet, 1989):

$$\blacksquare \frac{\partial(\theta C)}{\partial t} = -\frac{\partial J_s}{\partial x} - J_a - \theta \mu_l C$$

- where C is volume averaged concentration (i.e., c^r), J_a is the transfer rate from the soil solution to the sorbed phase [$\text{ML}^{-3}\text{T}^{-1}$], J_s is the solute flux density [$\text{ML}^{-2}\text{T}^{-1}$], and μ_l is a first-order decay coefficient [T^{-1}] which satisfies: $dC/dt = -\mu_l C$.
- Combining: $\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x} \left(D_e \frac{\partial C}{\partial x} - J_w C \right) - J_a - \theta \mu_l C$

ADE with ...

- A similar mass balance for the sorbed phase yields:

$$\blacksquare \rho_b \frac{\partial s}{\partial t} = J_a - \rho_b \mu_s s$$

- Where s is the sorbed concentration, and μ_s is a first-order decay coefficient [T^{-1}] for the sorbed phase (i.e., $ds/dt = -\rho_s s$).
- Combining the above equations yields:

$$\blacksquare \frac{\partial(\theta C + \rho_b s)}{\partial t} = \frac{\partial}{\partial x} \left(D_e \frac{\partial C}{\partial x} - J_w C \right) - \theta \mu_l C - \rho_b \mu_s s$$

- The above equation may be reduced to a slightly modified ADE

$$\blacksquare R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \mu C$$

$$\blacksquare C(x, t) = \frac{M}{A} \frac{1}{\sqrt{4\pi \frac{D}{R} t}} \exp \left(- \frac{\left(x - \frac{u}{R} t \right)^2 + 4 \frac{D \mu}{R^2} t}{4 \frac{D}{R} t} \right)$$

ADE with ...

- Assuming a linear sorption process (i.e., $s = k_d C$) yields a *retardation factor*, R ,

- $R = 1 + \frac{\rho_b k_d}{\theta}$

- And introducing an *effective degradation constant*, μ , as:

- $\mu = \mu_l + \frac{\rho_b \mu_s k_d}{\theta}$

- In cases where $\mu_l = \mu_s$, μ in the above equation reduces to:

- $\mu = \mu_l R$.

Mobile-Immobile Model and Effects of Soil Structure

- Preferential flow of solute often yields highly asymmetrical break through curves (BTC's). The reasons behind this phenomenon are the large differences in transport pathways in the media.
- In aggregated soils, there are large pores associated with intra-aggregate porosity and a small inter-aggregate pore system. The result is an incomplete mixing between these pore systems, which causes “tailing” (slow arrival of solutes transported through the inter-aggregate pore system).
- Pore water velocity may also influence “tailing”. Tailing becomes more pronounced as pore water velocity decreases.
- A theoretical approach to quantify “tailing”, assumes the existence of exchange between rapidly flowing regions and stagnant zones.

- The model can be describe with two fractions of soil water - a mobile phase, θ_m , and an immobile (stagnant) phase, $\theta_{im} = \theta - \theta_m$. The total solute mass is a weighted sum: $C^T = C_m \theta_m + C_{im} \theta_{im}$.
- The governing equation for mobile-immobile (MIM) solute transport is (van Genuchten and Wierenga, 1976):

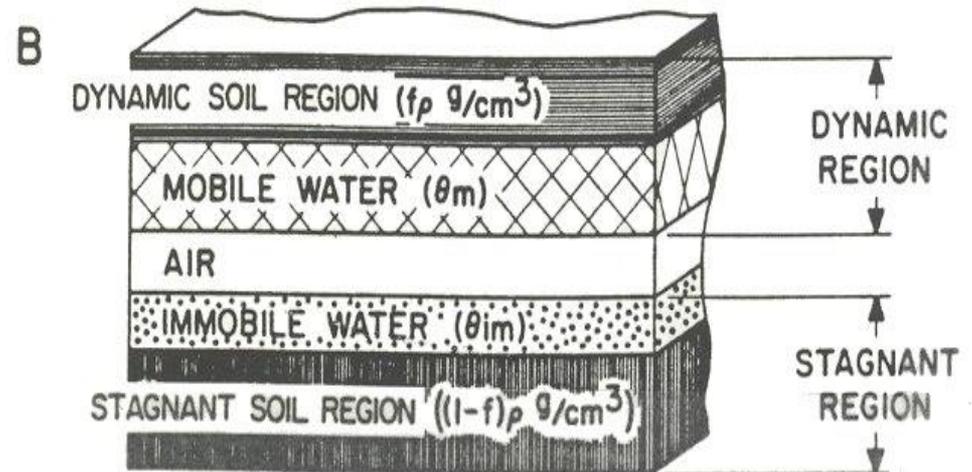
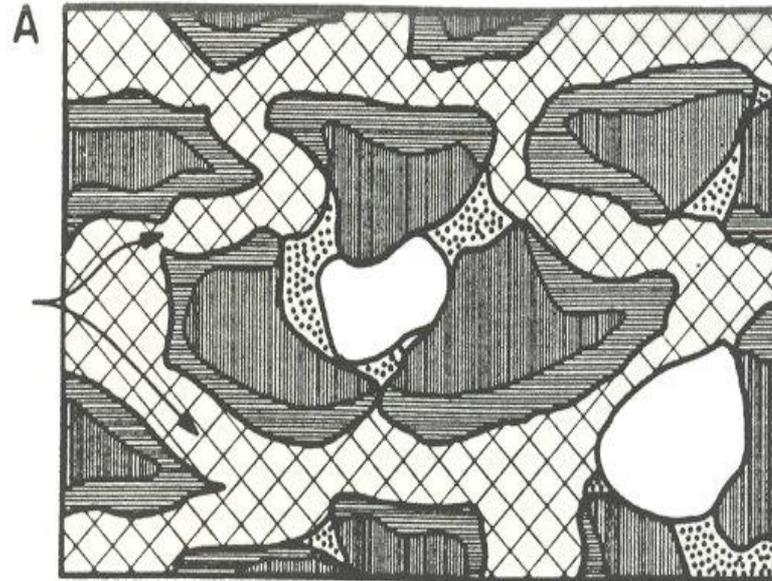
$$\blacksquare \theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - u_m \theta_m \frac{\partial C_m}{\partial x}$$

- and the rate-limited transfer between the mobile and immobile phases is given by:

$$\blacksquare \theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im})$$

- where α is a mass transfer coefficient [T^{-1}].

- A scheme of unsaturated aggregated media (a) actual distribution, and (b) a simplified representation (van Genuchten and Wierenga, 1976).

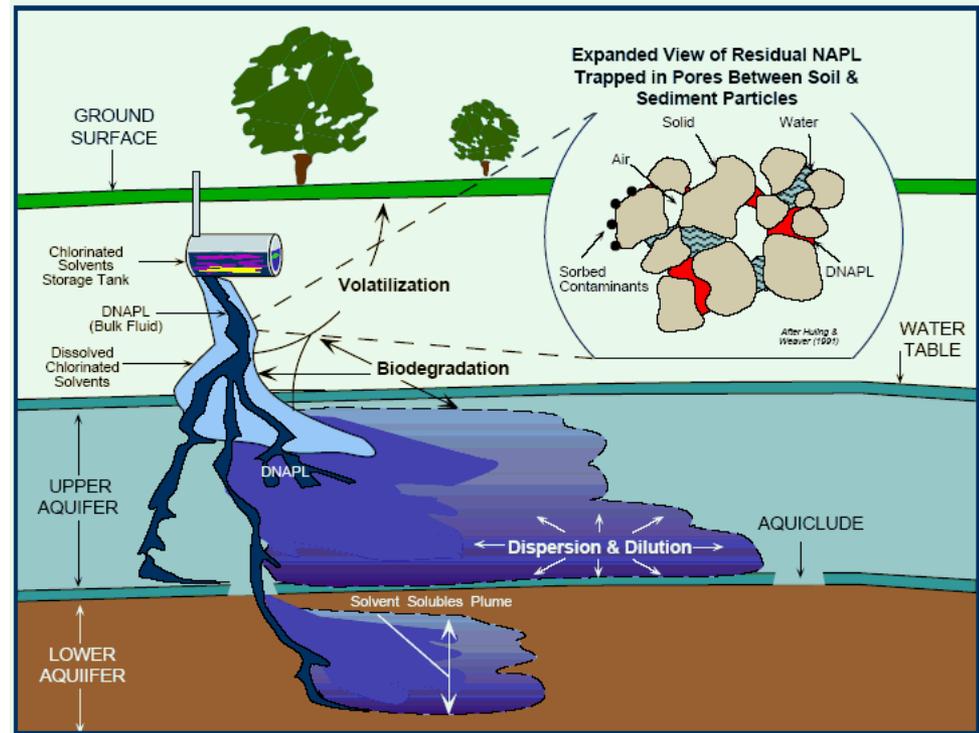


4. Movement of DNAPL's and LNAPL's

- Multi-phase transport involves the gas phase and one or more liquid phases.
- The movement of a chemical which occurred in two immiscible fluids, viz., water and the gas phase is the common multi-phase transport phenomenon in the subsurface.
- Flow and transport processes become even more complicated when we deal with the simultaneous movement of two immiscible liquids, with or without the presence of a gas phase, as it occurs during spills of nonaqueous phase liquids (NAPLs).
- NAPLs which are denser than water are known as dense NAPLs (DNAPLs) and NAPLs which are lighter than water are known as light NAPLs (LNAPLs).

Dense Non-Aqueous Phase Liquids

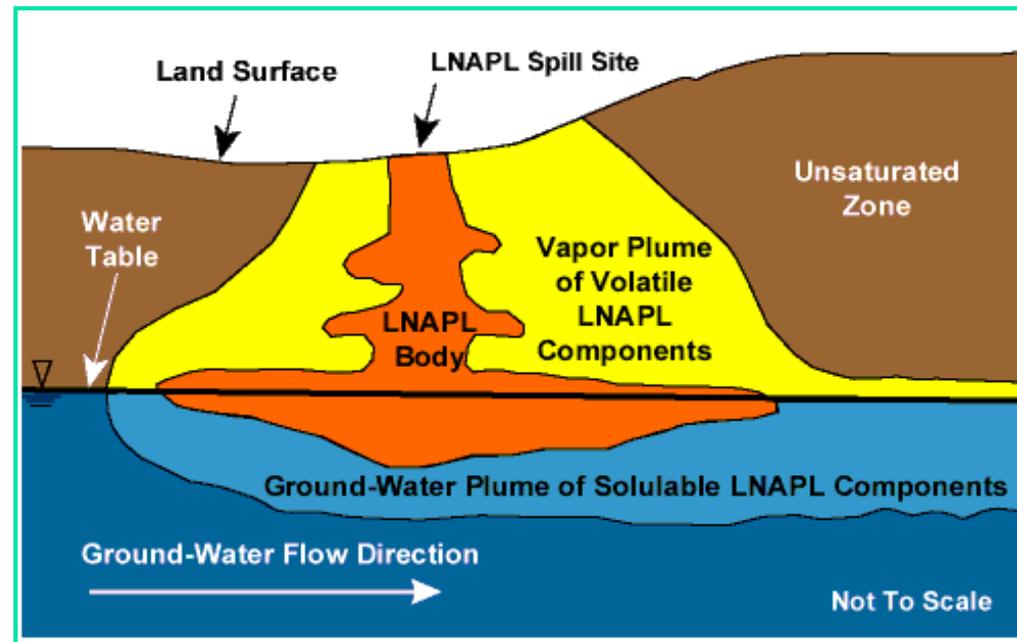
- NAPLs –
 - Insoluble in water and
 - Separate phase
- Dense NAPLs –
 - More dense than water
 - Chlorinated hydrocarbons
 - Trichloroethylene-TCE
 - Tetrachloroethylene-PCE
 - Density increases with increasing halogenation



Density difference of 0.1% causes sinking

Light Non-Aqueous Phase Liquids

- Light NAPLs
 - Lighter than water
 - Petroleum hydrocarbons
 - Oil
 - Gasoline
- Density difference between water and NAPL of 1% can influence flow
- Low viscosity NAPLs migrate more rapidly than high viscosity NAPLs



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- The main reason for distinguishing between LNAPLs and DNAPLs is that a LNAPL plume tends to "float" in the vicinity of the groundwater table whereas a DNAPL plume tends to "sink" into the aquifer bottom
 - While LNAPLs and DNAPLs behave quite differently near the capillary fringe and below the groundwater table, their general behavior in the unsaturated zone is quite similar.
 - Both types of NAPLs generally migrate downward in the unsaturated zone under the actions of gravity and capillarity (surface tension effects), and may even spread out over lenses of low-hydraulic-conductivity materials.

-
- As the spill progresses downward through the unsaturated zone, some residual NAPL is retained around the soil grains and trapped in the pore spaces due to surface tension effects.
 - If a sufficiently large quantity of NAPL enters the subsurface, it will eventually reach the capillary fringe.
 - LNAPL will accumulate at the water table, while DNAPL will penetrate the water table,
 - If DNAPL's pressure exceeds the required displacement pressure, it accumulates over less permeable lenses or layers or at the bottom of the aquifer.
 - In either case, a certain amount of NAPL will be immobilized in the unsaturated and saturated zones as residual NAPL.

-
- The residual NAPL will then act as a source of subsurface contamination due to the dissolution of the residual NAPL into the flowing groundwater or into the recharge water infiltrating at the surface.
 - The mobile (free-phase) NAPL, which accumulates on the water table or over layers or lenses of low permeability material, will also act as a source of groundwater contamination due to dissolution of the NAPL, Which may act as a source of contamination for many years
 - While the mobile (free-phase) NAPLs may be pumped out of an aquifer by means of wells, the immobile residual NAPLs can only be removed by special means such as steam injection or surfactant-aided mobilization.

-
- The spatial distribution of a LNAPL plume will be greatly affected by the fluctuations of the water table.
 - The distribution of the LNAPL in turn affects its rate of dissolution and the behavior of the resulting dissolved contaminant plume.
 - The spatial variations of the aquifer material properties also play an important role in the behavior of both LNAPL and DNAPL plumes.