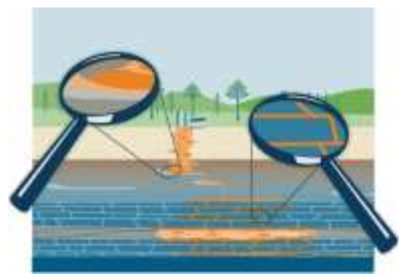
Back-to-Basics Part 1: Developing the CSM & Site Characterization

Understanding Subsurface Fate & Transport



Understanding Subsurface Fate & Transport

Purpose:

To provide an introduction to the basics of what is necessary to understand contaminant subsurface fate and transport

So you know where contaminant is so you can design a remedy that may actually work

Understanding Subsurface Fate & Transport: Agenda

- Geology
- Hydrogeology
  - Darcy's law
  - Heterogeneity
  - Diffusion/Dispersion
  - Mass Flux & Mass Discharge
- Contaminant Fate and Transport
  - Contaminant interaction with subsurface, including effects of:
    - pH, DO, and organic carbon content, mineral, and others
    - Role of Anthropogenic activities
- Lessons Learned

Geology

The movement of a substance (both groundwater and contamination) through the subsurface is in great part governed by the physical nature of the subsurface and how the substance interacts with the subsurface.

Therefore, in order to understand contaminant fate and transport, the site manager needs to also understand the site geology.

An important goal of any site investigation should be to at least identify the basic geology of a site and determine its effect on contaminant fate and transport.

Geology

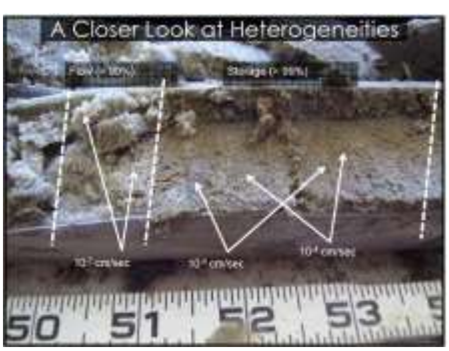
Examples of how the geology affects contaminant fate and transport include

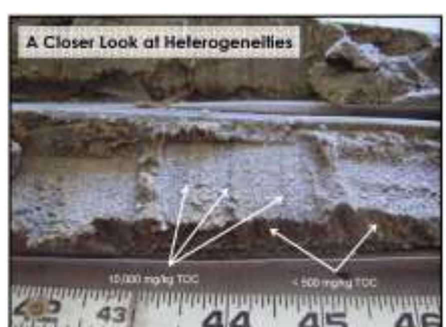
- Coarse grained materials more readily allow transport of contamination
- Finer grained materials may slow contaminant transport and may create contaminant "reservoirs" when contaminants diffuse from coarse grained materials into the fine grained materials.
  - These "reservoirs" are very hard to remediate
  - May act as long term sources of groundwater contamination in flow zones as the contamination migrates from the fine grained materials into the coarser grained materials.
- Very fine grained materials may serve as barriers to contaminant advective migration.

Geology

Examples of how the geology affects contaminant fate and transport include

- Heterogeneities in the subsurface cause contaminants to migrate faster or slower and in different directions than you normally expect, and can create different interactions between the aquifer matrix and contaminants





Geology!

If you get nothing else from this short course, you must understand that:

Geology controls groundwater flow!

Geology!

While of course geology controls groundwater flow, past land use can also create significant flow paths and other issues.

Geology: 30,000 ft view

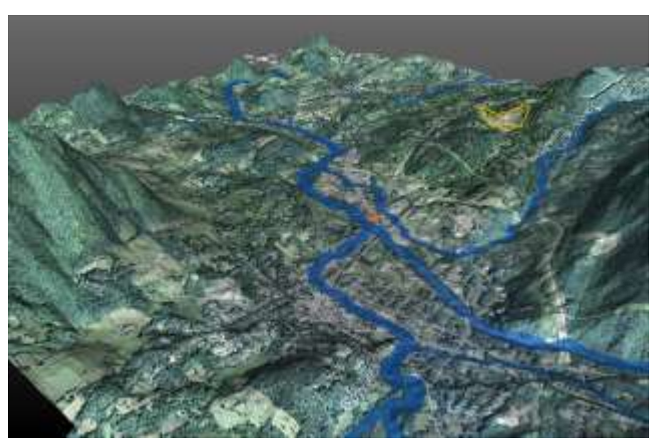
Typical landscape in New England has been to a very large extent controlled by the glaciers that covered New England in last ice age:

- Mountains were “smoothed” or sculpted (NH) by glaciers
- Glaciers transported and deposited unconsolidated materials
- Unconsolidated materials have often been reworked by water and anthropogenic activities.

Unconsolidated Geology

Typical New England Unconsolidated Geology

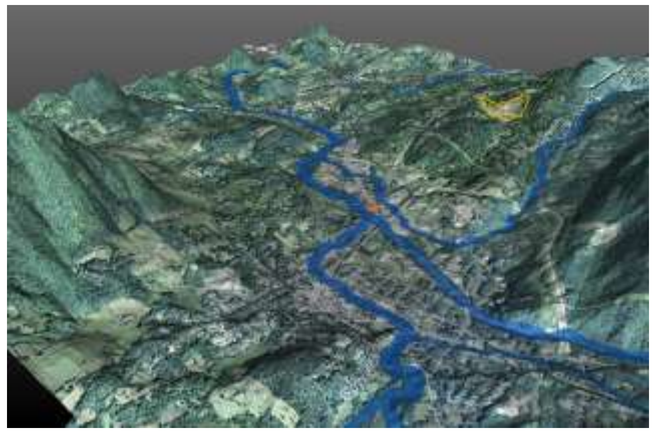
- Till
- Kame terraces/moraines
- End moraines
- Eskers
- Glacial lake and marine deposits
- Reworked by water



Unconsolidated Geology

Till

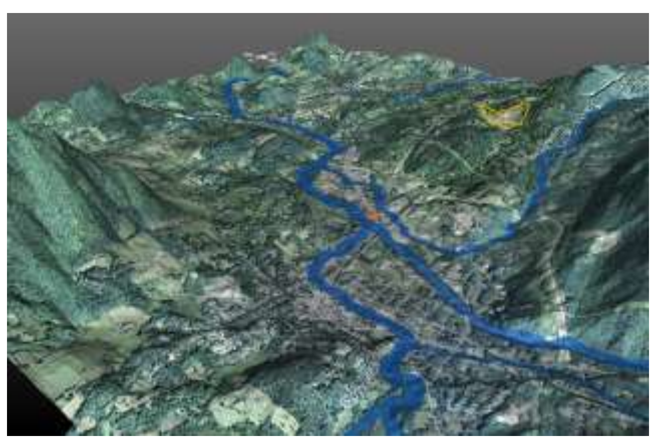
- Can be very thick
- Very heterogeneous
  - Grain Size
  - Materials
- Can be dry but fractured
- Compacted
- Difficult to drill
- Difficult to remediate



Unconsolidated Geology

Kame terraces/moraines

- Deposited by physical action of the glacier
- Often on the sides of valleys
- Less heterogeneous than till
- Kame terraces may be unsaturated



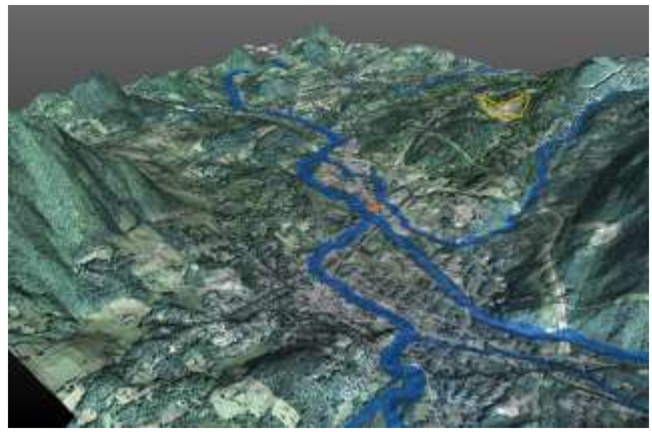
Unconsolidated Geology

Eskers

- Deposited by steams flowing under glaciers
- Can be great aquifers

Outwash plains

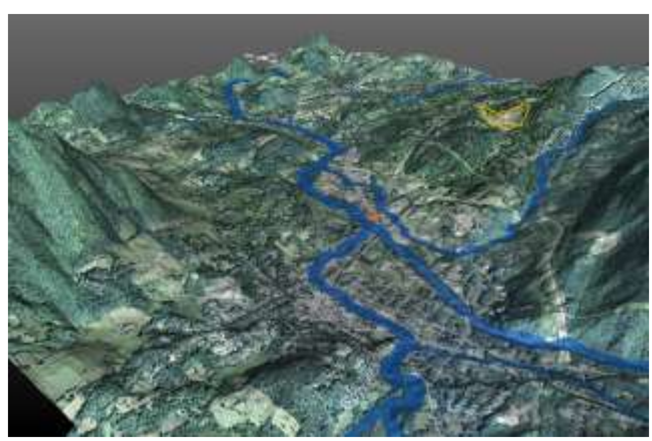
End moraines



Unconsolidated Geology

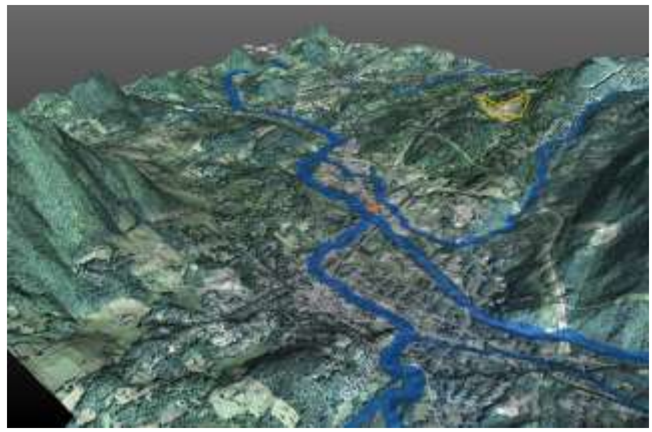
Glacial lacustrine and marine deposits

- Deposited in water so may be less heterogeneous
- Lacustrine and marine clays
- Deltaic deposits



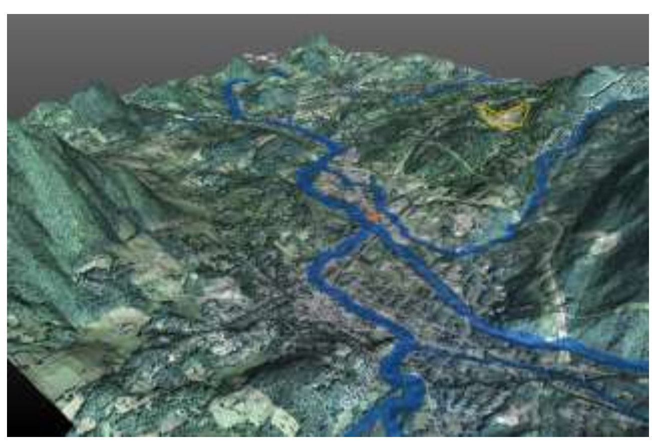
Unconsolidated Geology

Unconsolidated materials, especially in valleys, will be reworked by recent alluvial activity (including deposition).



Unconsolidated Geology

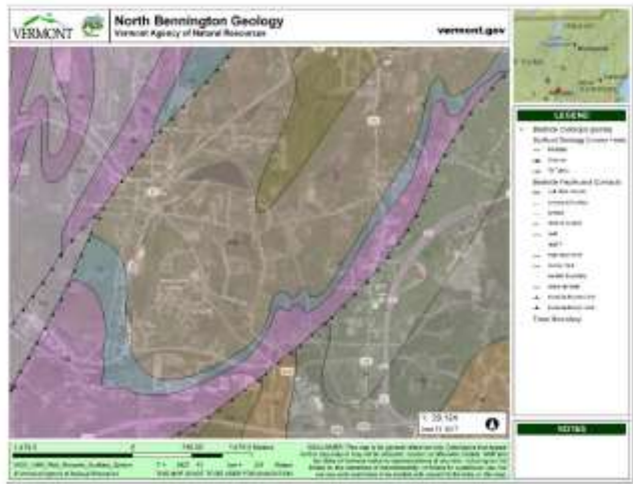
In New England, much of the early industrial development, and many of our cities was/are in valleys where materials are often thicker, than in the highlands.



Bedrock Geology

Typical New England Bedrock Geology

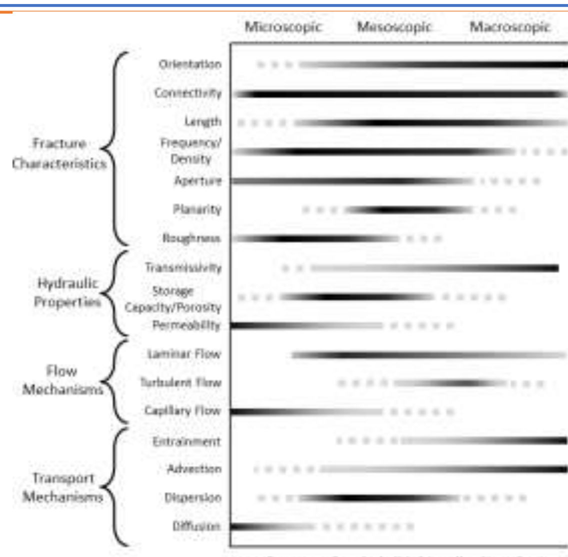
- Very Diverse
  - Igneous
  - Metamorphic
  - Sedimentary
- **Primary and Secondary porosity**
- Structural Considerations
  - Folding/Faulting/Bedding Planes



Bedrock Geology

Intersection of Scale and Fracture Flow Properties

- Macroscopic
- Mesoscopic
- Microscopic



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Bedrock Geology

Macroscopic Flow: The Big Picture

- Occurs and Regional or Site-wide Scale
- Regional factors influence flow
  - Faults
  - Rivers
  - Changes in lithology
- Remote Sensing and Terrane Analysis to evaluate interaction of multiple structures
  - Orientation, length, connectivity
  - Karst is considered as a whole
  - Overall flow behaving as continuous Darcian flow system
- Knowing how structures interact helps direct investigation at smaller scales

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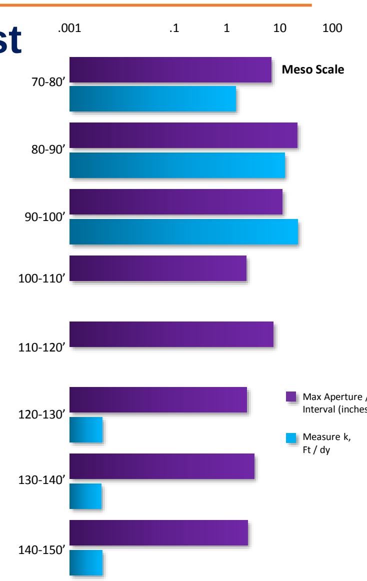
Bedrock Geology

Mesoscopic Flow: Where we Learn the Most

- Plume delineation, flow between multiple wells/boreholes
  - Orientation, aperture, density, length, and connectivity
  - Influence of matrix characteristics
- Boreholes and Outcrops
  - Fracture analysis
  - Hydraulic testing
- Flow in fracture sets
  - Impact of turbulent flow may become evident
  - Advection, entrainment, dispersion
- Primary scale of investigation
  - Majority of investigation and characterization techniques



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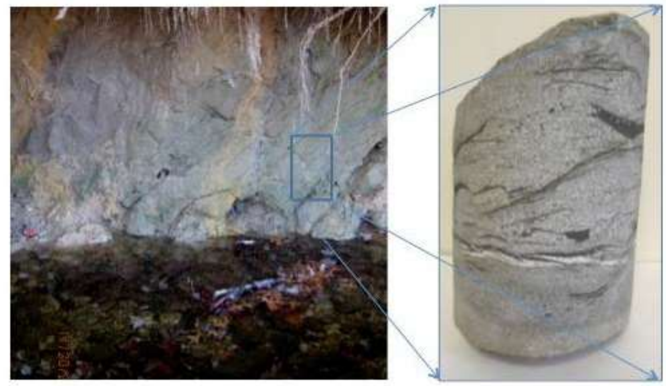
Bedrock Geology

Microscopic Flow: Tools for Fine-Tuning your Site Understanding

- Individual fractures to matrix interaction
- Microscopic and individual fracture analysis
  - Individual fracture characteristics
  - Core samples
- Flow between fractures & matrix
  - Changes the morphology of the fracture (Roughness & planarity)
  - Aperture increases or decreases by infilling and dissolution
  - Diffusion and capillary flow
- Interface between fracture and matrix and matrix storage effects F&T



We may not get down to this scale very often

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Site Specific Geology

When you first become involved with a site, initial site specific information on geology may be obtained from:

- Published literature:
  - State geological survey
  - Universities
- Previous site investigation reports
  - For your site
  - For nearby sites
- Aerial Photographs and Maps (geologic and other)

Site Specific Geology

Conduct Site Visit

- Is the site in a valley where unconsolidated materials may be thick, or in the mountains where depth to bedrock is shallow?
- While not specifically geology, what are the present and past land uses

Develop Initial Conceptual Site Model (CSM)

Conduct Site Investigation and refine CSM

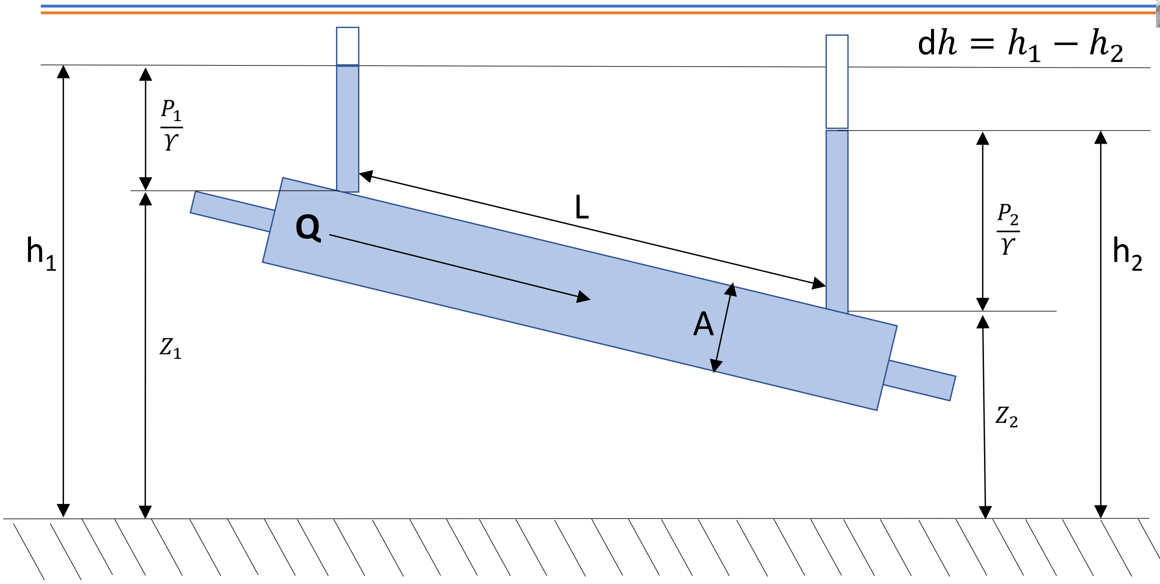
Geology

CSM and Site Investigation: Discussed this afternoon

ITRC Integrated DNAPL Site Characterization and Tools Selection

https://www.itrcweb.org/DNAPL-ISC_tools-selection/Default.htm

Hydrogeology Darcy's Law



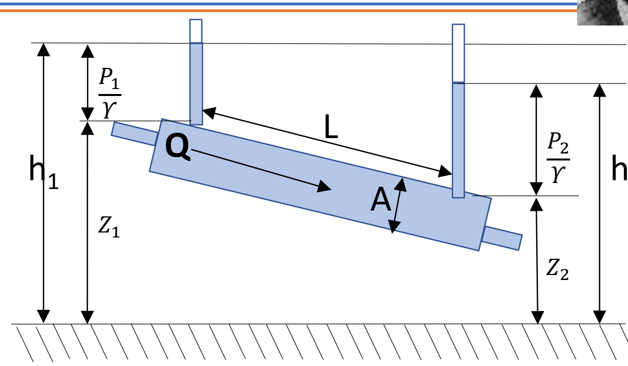
Hydrogeology Darcy's Law

Hydraulic Head

$h_1 = Z_1 + \frac{P_1}{\gamma}$

$h_2 = Z_2 + \frac{P_2}{\gamma}$

$$Z_1 + \frac{P_1}{\gamma} = Z_2 + \frac{P_2}{\gamma} + dh$$



Difference in head, $dh = h_1 - h_2$

Z = elevation head

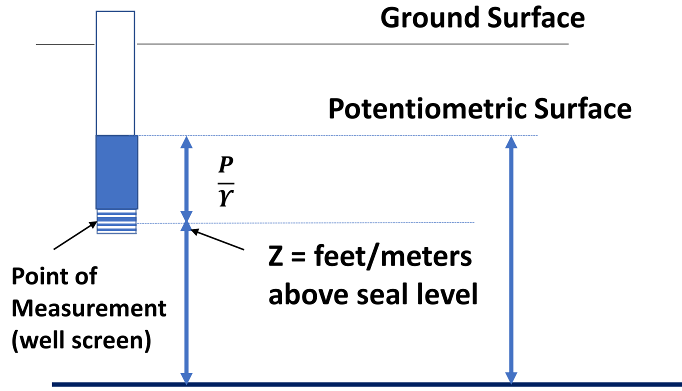
$\frac{P}{\gamma}$ = pressure head

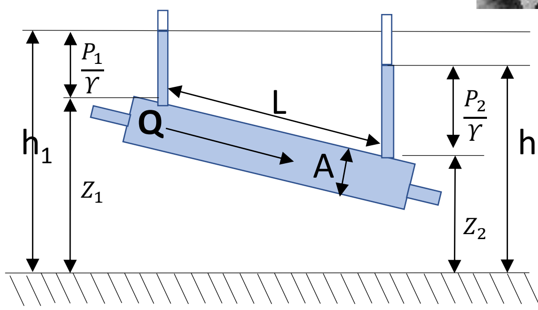
$\gamma = \rho g$ = specific weight of water

ρ = fluid density, g = gravity

Hydrogeology Darcy's Law

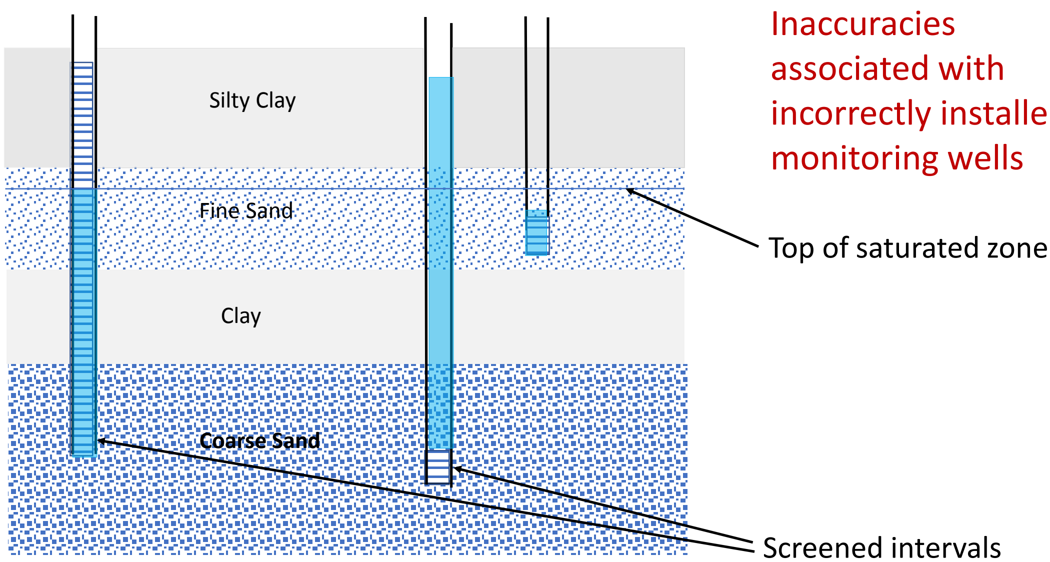
Components of head in a monitoring well:





Hydrogeology Darcy's Law

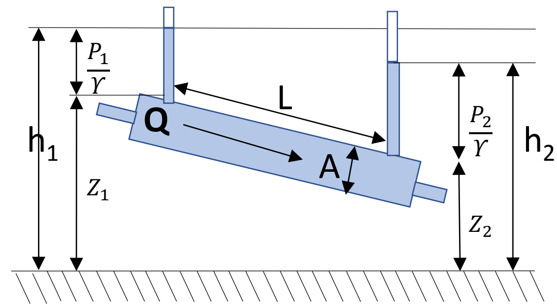
Inaccuracies associated with incorrectly installed monitoring wells



Hydrogeology Darcy's Law

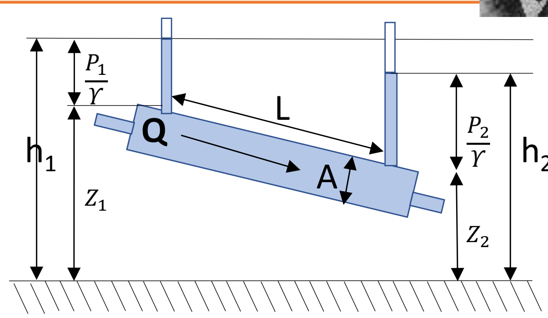
Darcy determined there was a relationship between flow (Q), area (A), and head (h).

The rate of water flow through a tube is proportional to the difference in the height of the water between the two ends of the tube, and inversely proportional to the length of the tube.



Hydrogeology Darcy's Law

From this relationship, is possible to derive a number of equations that help describe groundwater flow



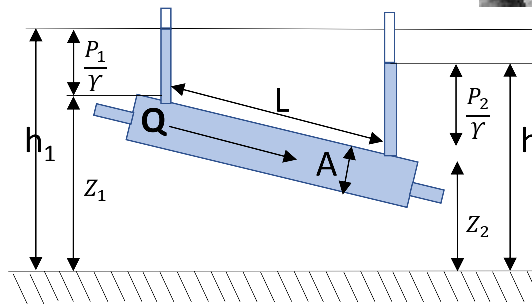
$$v = \frac{Q}{A} = q = -K\left(\frac{h_1 - h_2}{L}\right) = -Ki \qquad \frac{Q}{A} = -Ki \qquad Q = -KiA$$

q = Darcy flux (L/T) K = Hydraulic Conductivity (L/T) i = $\left(\frac{h_1 - h_2}{L}\right)$ (L/L unitless)

Hydrogeology Darcy's Law

In regards to velocity :

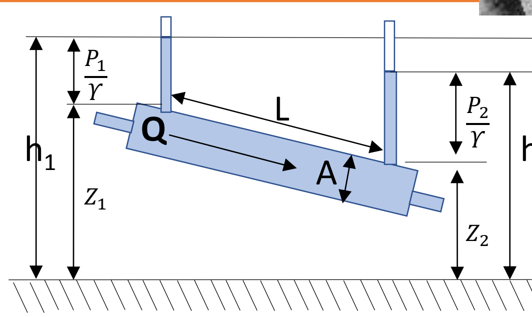
The Darcy equation describes the flow rate per specific unit surface area. It does not consider **that flow in the subsurface actually occurs in the effective porosity that is located between the pore grains of the formation. Therefore, the equation has to be changed where n_e is effective porosity:**



$$v = \frac{Q}{A} \quad \text{becomes} \quad v = \frac{Q}{An_e}$$

Hydrogeology Darcy's Law

The flow is also proportional to a coefficient, K. In hydrogeology, this needs to be adjusted to account for the formation:



Q = KiA

k = Cd^2 Intrinsic or Darcy permeability (L^2)

$$K = -\frac{Cd^2\,g}{\mu}$$ K = Hydraulic Conductivity (L/T

C = a dimensionless shape
d = average diameter of matrix grains

ρg = specific weight of fluid
μ = viscosity of fluid

Hydrogeology

Issues with Darcy's Law

Actual Groundwater flow:

1. Saturated and Unsaturated flow
2. Steady-state and transient flow
3. Flow in aquifers and aquitards
4. Flow in homogeneous and heterogeneous systems
5. Flow in isotropic and anisotropic media
6. Flow in granular media and fractured rocks

Darcy's Law **Assumes**:

1. Saturated flow
2. Steady-state flow
3. Flow in aquifers and aquitards
4. Flow in homogeneous systems
5. Flow in isotropic me dia
6. Flowin granular media

However, Darcy's law is useful and we can modify it to reflect the real world

Courtesy Fred Payne, Arcadis

Hydrogeology

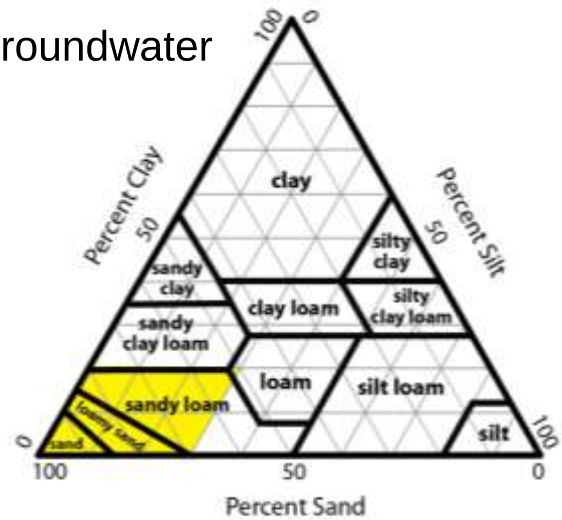
Courtesy Fred Payne, Arcadis

High-Energy Deposition

Hydrogeology

Where the highest amount of groundwater flow occurs.

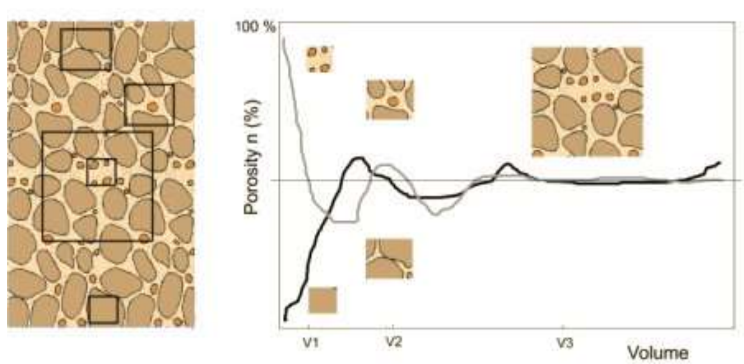
- Many soil types are not very conductive
- The conductive soils are laid down in high-energy environments
- High-energy environments are typically heterogeneous and anisotropic



Courtesy Fred Payne, Arcadis

Representative Elementary Volume (REV)

- Volumetric dimensions of the scale on which the continuum approach can be used
- Domain of porous media



ITRC ISC-1 Figure 2-3.

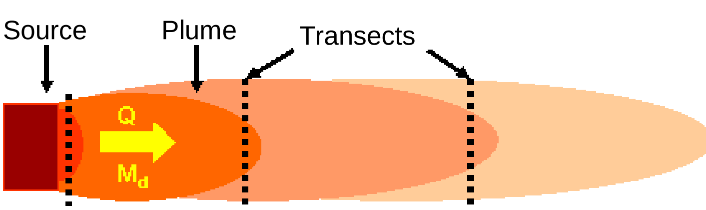
Hydrogeology

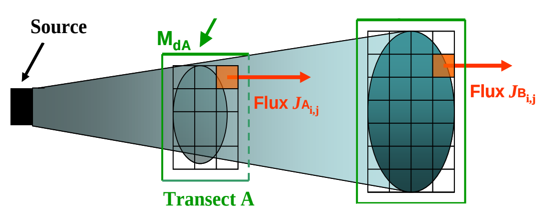
- Theis (1967): “I consider it certain that we need a new conceptual model, containing the known heterogeneities of natural aquifers, to explain the phenomenon of transport in groundwater.”

Photo: USGS

Contaminant Fate and Transport

Dissolved Phase Contaminant Transport





ITRC MASSFLUX-1, 2010

Contaminant Fate and Transport

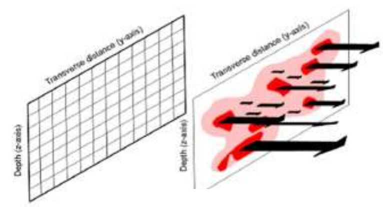
Advective Transport:

$$v_x = \frac{K_i}{n_e} \quad or \quad \frac{K}{n_e}\frac{dh}{dl}$$

In most aquifers, advection is the dominant transport mechanism for dissolved contaminants. The simplest equation used to describe how fast contamination is carried is the equation for the average linear velocity of groundwater:

Where:

- v_x = the average linear velocity (L/T)
- K = hydraulic conductivity (L/T)
- n_e = effective porosity (%)
- i = gradient $\frac{dh}{dl}$ (L/L: dimensionless)



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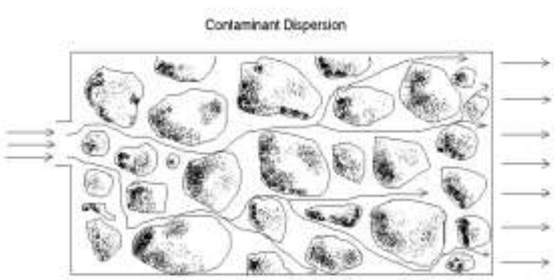
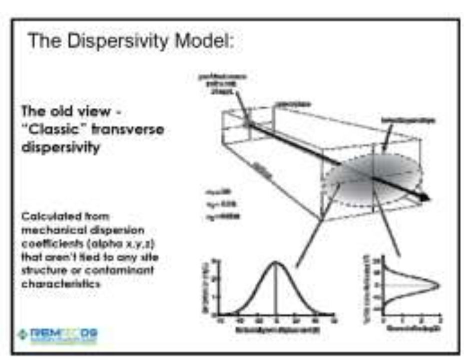
Contaminant Fate and Transport

Hydrodynamic Dispersion (Dispersivity)





ITRC MASSFLUX-1, 2010

However: With an understanding of the role heterogeneity in groundwater flow, diffusion replaces dispersivity as dominant spreading mechanism

Contaminant Fate and Transport

- Simplifying the subsurface as homogeneous & isotropic has not worked well for remediation-scale plume geometry
- **Anisotropy replaces isotropy**
- Non-ideal behavior is as pronounced in the vertical

Borden Tracer Simulation – Combined Heterogeneity and Diffusivity Effects

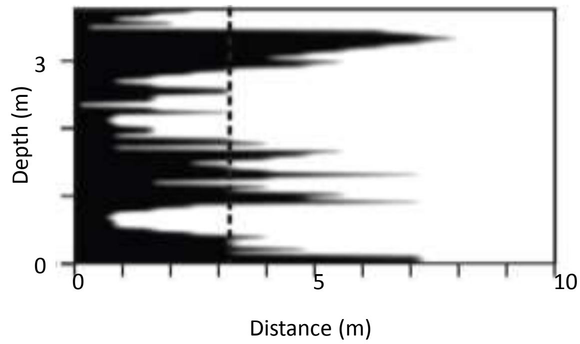
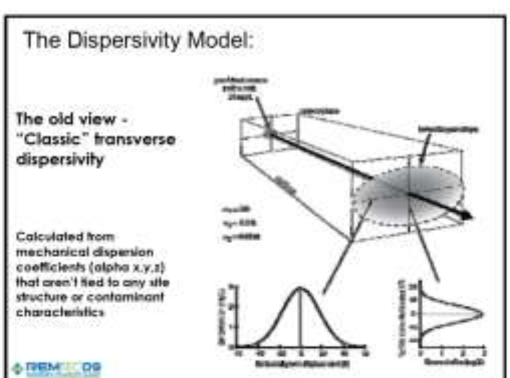
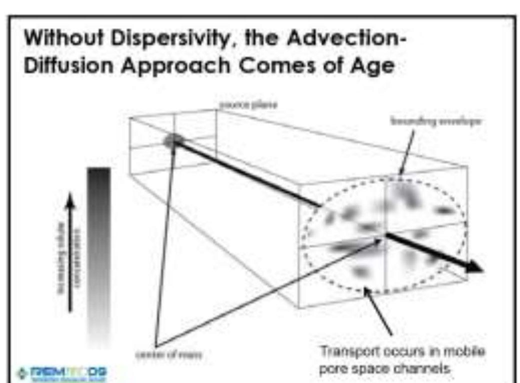


Figure courtesy of Fred Payne, Arcadis

Contaminant Fate and Transport

- As the length scale of interest decreases Diffusion replaces Dispersion in plume behavior
- Geologic heterogeneity and anisotropy also lead to numerous small plumes within each groundwater plume





Figures courtesy of Fred Payne, Arcadis

Contaminant Fate and Transport

Molecular Diffusion

I don't plan on discussion the molecular diffusion equations but if you would like:

Fick's first law is used to describe molecular diffusion:

$$J = -D_d\,(dC/dx)$$

Where:

- J = mass flux of solute per unit area per unit time
- D_d = diffusion coefficient (L^2/T)
- C = solute concentration (M/L^3)
- dC/dx = concentration gradient ($M/L^3/L$) (change in C/change in x)

Fick's second law is used to describe molecular diffusion when concentrations are changing over time:

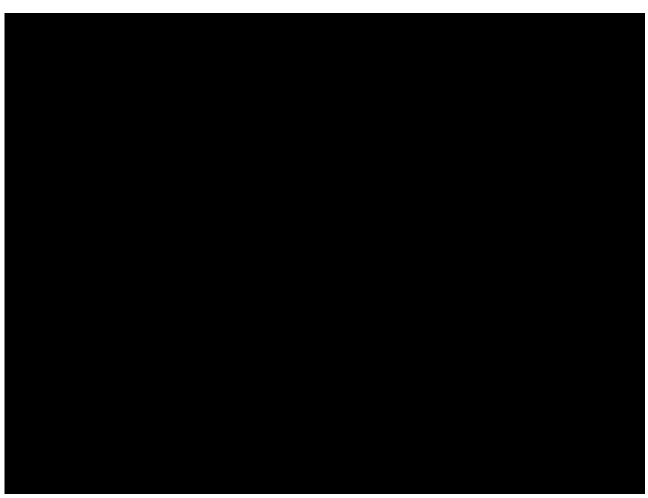
$$\partial C/\partial t = D_d(\partial^2 C/\partial x^2)$$

Where

$\partial C/\partial t$ equals the change in concentration with time ($M/L^3/T$)

Contaminant Fate and Transport

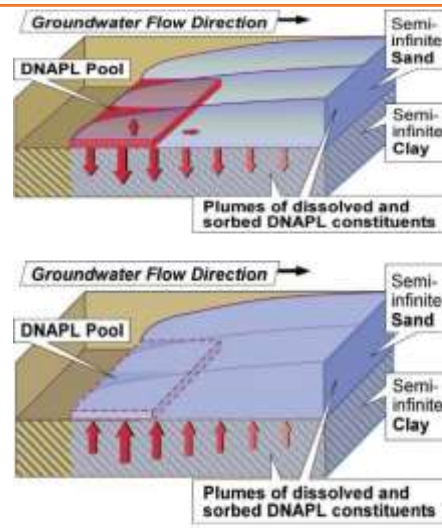
Back Diffusion



Courtesy Tom Sale, Colorado State University

Contaminant Fate and Transport

- Early time
  - Molecular Diffusion into low permeability zones in the aquifer matrix: "Matrix Diffusion"
- Late time
  - "Back Diffusion" out of low permeability zones into higher permeability zones



ITRC IDSS-1, Figure 2-5 & 2-6

Contaminant Fate and Transport

Mass Flux (*J*) is the flux of a contaminant is being **carried per unit area of the aquifer**.

The one dimensional mass flux equation is:

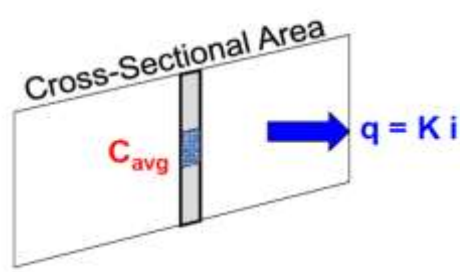
$$J = q_x C = \frac{Ki}{n_e} C$$

Where

J = contaminant flux per unit area, units of $M/L^2/T$ (mass/area/time)

C = Contaminant Concentration in units of M/L^3 (mass/volume)

q = specific discharge ($L^3/L^2/T$)



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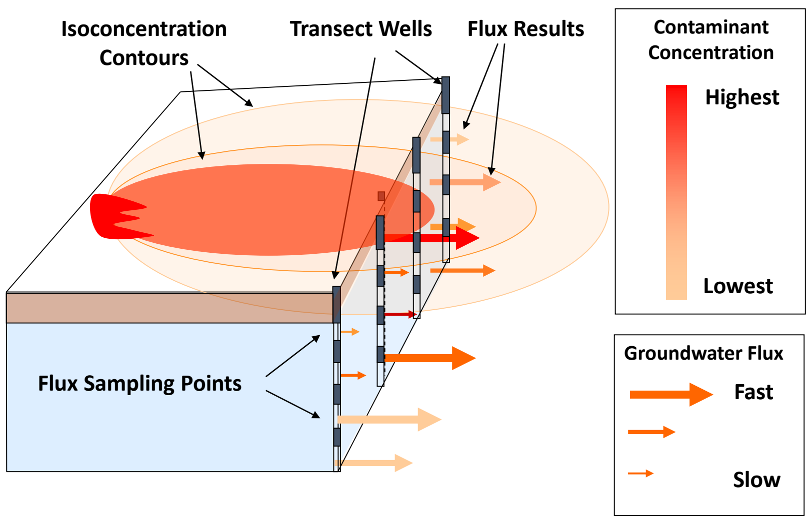
Contaminant Fate and Transport

Mass Flux Can Be Highly Variable



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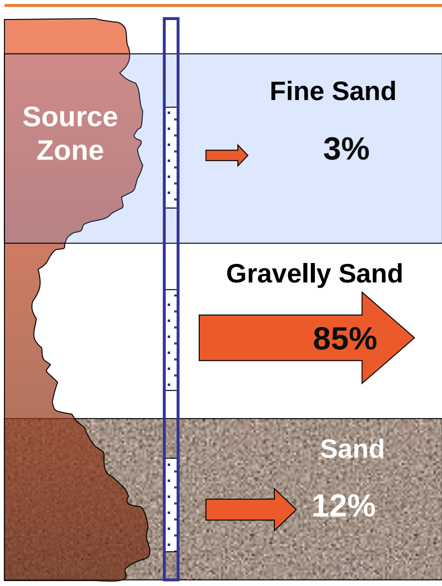
Contaminant Fate and Transport

Mass Flux (*J*) = KiC



K = 1.0 m/day
i = 0.003 m/m
C = 10,000 µg/L
Mass Flux = 0.03 g/day/m²

K = 33.3 m/day
i = 0.003 m/m
C = 10,000 µg/L
Mass Flux = 1 g/day/m²

K = 5.0 m/day
i = 0.003 m/m
C = 10,000 µg/L
Mass Flux = 0.15 g/day/m²

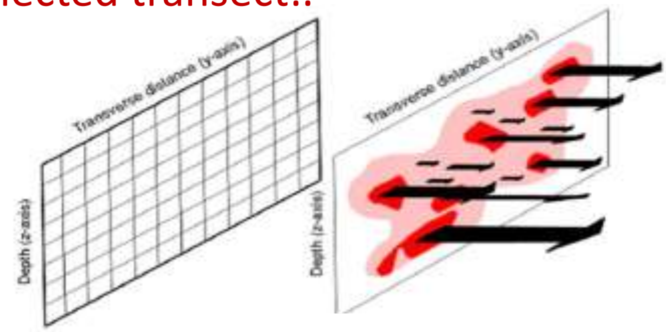
Mass Flux and Concentration

ITRC MASSFLUX-1, 2010

Contaminant Fate and Transport

Mass Discharge (M_d) is the integration of the contaminant mass fluxes across a selected transect:.

$$M_d = \int_A J dA$$



A = Area of the control plane in units of L^2
J – spatially variable contaminant mass fluxes

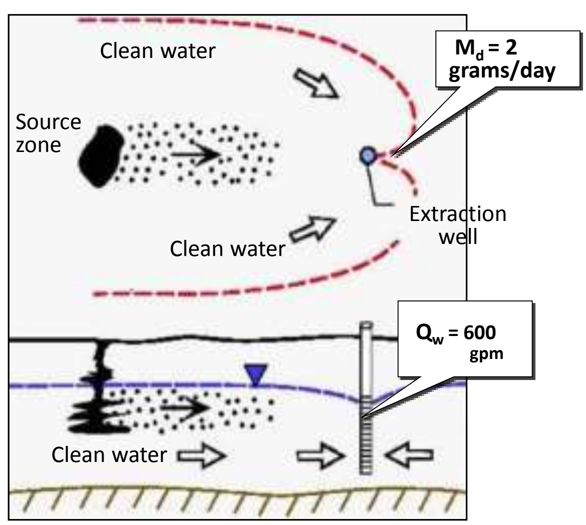
ITRC MASSFLUX-1, 2010

Contaminant Fate and Transport

Can use Mass Discharge of plume to predict constituent of concern concentration in downgradient water supply well

$$C_{well} = M_d \div Q_{Well}$$

C_{well} = Concentration in extraction well
Q_{well} = Pumping rate for extraction well



https://www.itrcweb.org/GuidanceDocuments/MASSFLUX1.pdf

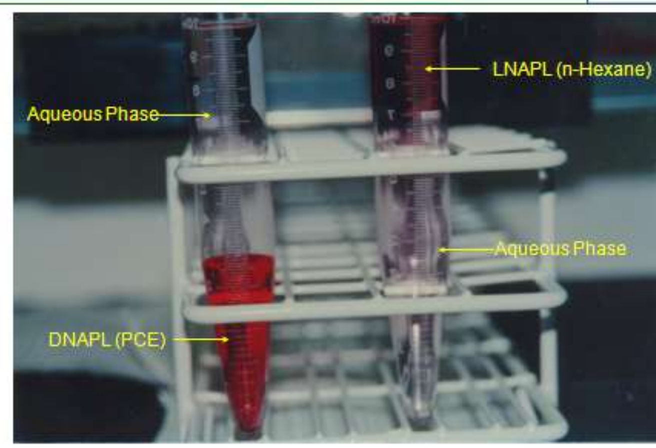
Contaminant Fate and Transport

Non-Aqueous Phase Contaminant Transport:

Dense Non Aqueous Phase Liquids (DNAPL)

Light Non Aqueous Phase Liquids (LNAPL)

DNAPL and LNAPL in water (with Oil-Red-O, an organic soluble dye)



Contaminant Fate and Transport

	Source Zone		Plume	
Phase/Zone	**Low Perm.**	**Transmissive**	**Transmissive**	**Low Perm.**
Vapor				
NAPL			NA	NA
Aqueous				
Sorbed				

Vapor Intrusion
Capillary Barrier
Matrix Diffusion
Matrix Diffusion
Sorption

ITRC IDSS-1, Table 2-2 from Sale and Newell 2011

KEY POINT: **The 14-Compartment Model helps Stakeholders align on the Life Cycle of the Site and Characterization Objectives**

Contaminant Fate and Transport

NAPL Chemical & Physical Properties

- Density
- Solubility
- Viscosity
- Volatility
- Composition

https://www.itrcweb.org/DNAPL-ISC_tools-selection/

NAPL Interactions with the Sub-Surface Media Affecting Mobility

- Interfacial Tension
- Wettability
- Capillary Pressure
- Saturation
- Residual Saturation

https://www.itrcweb.org/GuidanceDocuments/IntegratedDNAPLStrategy_IDSSDoc/IDSS-1.pdf

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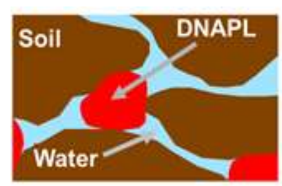
NAPL Saturation

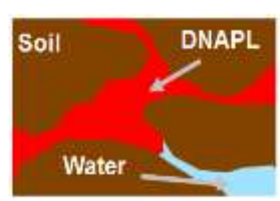
- Saturation (*S*)
  - S is the proportion (percentage) of the pore space occupied by a fluid (NAPL, air, or water)
  - Ranges from 0 to 1.0 (0 to 100%)
- Residual Saturation (S_r)
  - S_r is the saturation of NAPL remaining when **NAPL is no longer mobile**

- When $S < S_r$
  - NAPL will be immobile unless NAPL or solid phase properties change



- When $S > S_r$
  - NAPL may be mobile or
  - NAPL may be potentially mobile but not moving

(Pennell et al., 1996, ES&T)



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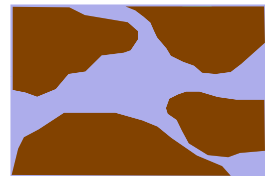
Contaminant Fate and Transport

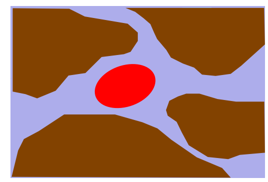
▶Relative permeability (k_r)

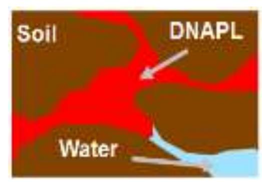
The value of k_r, ranges from 0 to 1.0 as a non-linear function of saturation (S)

- k_r for groundwater = 1.0 at NAPL S = 0
- k_r for DNAPL approaches 1 at as NAPL S approaches 1

(Parker and Lenhard 1987)







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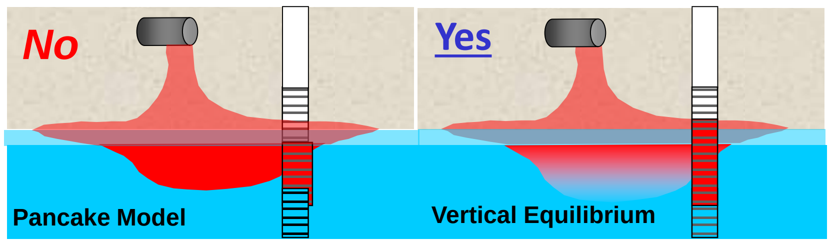
Contaminant Fate and Transport LNAPL Myths

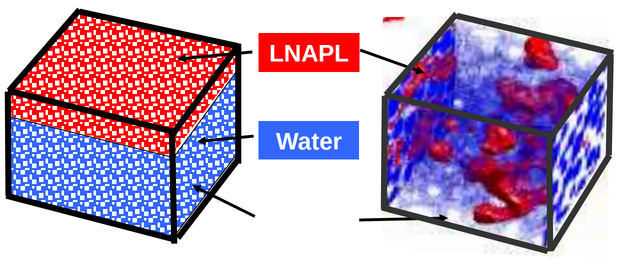
1. LNAPL enters soil pores just as easily as groundwater
2. You can hydraulically recover all of the LNAPL from the subsurface
3. All soil pores in an LNAPL plume are completely filled with LNAPL
4. LNAPL floats on the water table or capillary fringe like a pancake and doesn't penetrate below the water table
5. LNAPL thicknesses in monitor wells are exaggerated (compared to the formation) by factors of 2, 4, 10, etc.
6. LNAPL thicknesses in monitor wells are always equal to the LNAPL thicknesses in the formation
7. If you see LNAPL in a monitor well it is mobile and migrating
8. LNAPL plumes spread due to groundwater flow
9. LNAPL plumes continue to move long after the release is stopped

ITRC 2009 LNAPL 1 Internet Training Module

Contaminant Fate and Transport



- Assumes LNAPL floats on water table
- Uniform LNAPL saturation



- LNAPL penetrates below water table
- LNAPL and water coexist in pores

ITRC 2009 LNAPL 1 Internet Training Module

Attenuation and Retardation of Dissolved Contaminants During Transport

Focus of this talk is on Organic Contaminants

Sorption:

- **Adsorption: reversible, retards contaminant migration**
- chemisorption
- absorption
- ion exchange

Attenuation and Retardation of Dissolved Contaminants During Transport

Sorption:

$$C^* = K_d C$$

Where:

C = Concentration of solute in groundwater, mg/l (M/L^3)

C* =Mass of solute sorbed per unit dry weight of aquifer matrix, usually mg/kg (M/M)

K_d = adsorption distribution coefficient mL/g or L/kg (L^3/M)

$$K_d = K_{oc} f_{oc}$$

Where:

K_{oc} = organic carbon partition coefficient, (ml/g [L^3/M]) describes the compound's affinity to organic carbon. K_{oc} values are available in published literature

f_{oc} = fraction organic carbon (%), site/soil specific parameter determined from soil analysis. If it is not possible to analyze soils for f_{oc}, there are tables available provide estimates of general f_{oc} values for generic soil types.

Attenuation and Retardation of Dissolved Contaminants During Transport

Retardation Factor

$$R = 1 + \left(\frac{\rho_d \boldsymbol{K_d}}{n}\right)$$

ρ_b = Bulk Density of the porous media ((kg/m^3 or g/cm^3 [M/L^3])

Reversible: The amount sorbed to the organic carbon in soil is based on the concentration of the contaminant in water and its affinity for carbon

Maintains plume longevity

Contaminant Fate and Transport

Semi Volatile Organics (SVOC's)

Generally SVOC's will rapidly sorb to aquifer matrix.

- Most SVOC's have high K_{oc} values and will not readily be transported by advective flow
- May however sorb to colloidal particles in groundwater
- When sampling groundwater, in order to understand what mass of contaminants is actually being transported, and what concentraions might be in drinking water, the groundwater sample should not be filtered as filtering will preferentially remove some, but not all of the colloidal particles in groundwater.

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Inorganic Contaminants (Metals)

Generally, metals are relatively immobile in groundwater with typical groundwater chemistry as a result of adsorption, precipitation, chemisorption, or ion exchange reactions onto the aquifer matrix .

- However, changes in pH or REDOX can help mobilize metals
- Metals can also sorb to colloidal partials and be transported by these particles
- Metals can also be found dissolved in liquids discharged to the subsurface and transport with them.

Contaminant Fate and Transport

Inorganic Contaminants (Metals)

- Low flow sampling without filtering is also a must when analyzing groundwater for metals

Inorganic Contaminants (non-metals)

- These include compounds can include Chlorides and Nitrates
- We typically do not address when responding to a release of hazardous materials but they can have some uses.
- As chlorides do not readily sorb to the aquifer matrix, they can be used as tracers
- Nitrates can be an indication of ANFO in groundwater

Contaminant Fate and Transport

At some sites it may be necessary to assess whether a bioremediation remedy is an option:

- pH:
- TOC (total organic carbon)
- REDOX conditions: DO, methane and , mineral, and other content
- Bio, sulfate, iron, magnetite
- Oxidant demand

Understanding Fate and Transport

Questions?