

Module 2 – Hydrogeology and the Impacts of Subsurface Heterogeneity



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Module Overview

◆ Hydrogeology primer

- » Porosity
- » Hydraulic conductivity
- » Hydraulic gradient

◆ Contaminant fate and transport primer

- » Advection-Dispersion-Dissolution-Sorption-Degradation-Density-Viscosity-Mobility-Capillary Pressure-Back Diffusion
- » Unconsolidated systems
- » Fractured rock systems
- » DNAPL



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Hydrogeology Primer

- Porosity and Permeability
- Hydraulic Conductivity
- Hydraulic Gradient and Groundwater Velocity

2-3

Subsurface Environments:

No Place for Low Resolution

- ◆ **This cross section shows high variability in the type of material present in the subsurface**



2-4

- Main Idea** • *Measurements must be made at scales that are commensurate with the spatial scales of the environment.*



Notes



- ◆ Where exposed to visual observation the heterogeneity and spatial scales of variability of subsurface geologic environments are obvious. In environments where porosity, hydraulic conductivity, capillary pressures, and geochemistry change at the centimeter to meter scale, it is not sufficient to sample at the scale of meters and tens of meters (or larger).

Porosity and Permeability

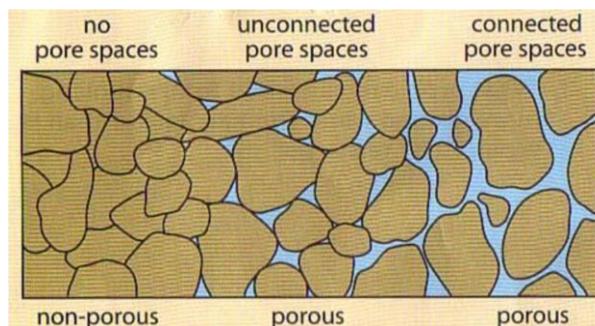
2-5

Porosity

- ◆ Ratio of volume of void space to total volume of medium
- ◆ Dimensionless (no units)
- ◆ Where the fluids reside

$$\Phi = \frac{V_{(\text{void})}}{V_{(\text{total})}}$$

Where: Φ = porosity
V = volume



2-6

Main Idea • Porosity represents void space.



Notes



- ◆ The pore spaces are where groundwater and contaminants exist. It is important to keep in mind that porosity and permeability are **not** the same thing. Porosity is required for a material to be permeable, but high porosity does not equal high permeability. Clays have significantly greater porosity than sand because they have layers of immobile water in their crystal structure but are orders of magnitude less permeable than sands.

Range of Values of Porosity from Freeze and Cherry 1979

Medium	n(%)
Unconsolidated deposits	
Gravel	25-40
Sand	25-50
Silt	35-50
Clay	40-70
Rocks	
Fractured basalt	5-50
Karst limestone	5-50
Sandstone	5-30
Limestone, dolomite	0-20
Fractured crystalline rock	0-10
Dense crystalline rock	0-5

Porosity

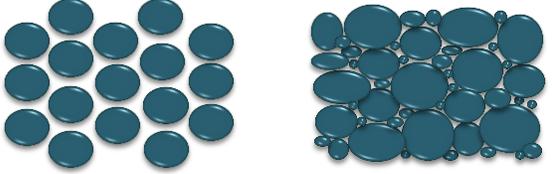
◆ **Grain size does NOT affect porosity**



These samples have the same porosity

◆ **Particle size distribution (sorting) affects porosity**

- » Well sorted (poorly graded) grains result in high porosity
- » Poorly sorted (well graded) grains result in low porosity



Well sorted, high porosity Poorly sorted, low porosity



2-7

- Main Idea** • *While grain size deceptively looks like it affects porosity, porosity actually depends on size distribution.*



Notes



- ◆ Fluids are stored in, and flow through the pore spaces in unconsolidated materials and sedimentary rock. Storage (i.e. porosity) is maximized if all the grains are the same size and are loosely packed, but it doesn't matter if the grains are large or small. Other factors that influence porosity are the shape of the grain (round grains pack tighter than oblong grains) and angularity (smooth grains pack tighter than grains with sharp edges). Finer grained materials tend to be better sorted and have higher porosity. Loosely packed spherical grains can have porosity as high as 48%. Generally, porosity in unconsolidated materials ranges from a few percent to 40 percent. Soils with organic matter and roots can have porosities up to 50 percent.
- ◆ Particle size distribution and sorting affect porosity because smaller grains can fill the void spaces between larger grains and use up the available pore space.
- ◆ Porosity can be measured in a lab from either intact cores or loose samples. Intact cores provide the most accurate measurement because the sorting is undisturbed.

Permeability

- ◆ The ability of the media to transmit fluids
- ◆ NOT the same as porosity
- ◆ Property of the soil (clay, silt, sand, or gravel)
- ◆ Grain size DOES affect permeability

The diagram illustrates three soil types based on pore space connectivity and permeability. The first soil has no pore spaces and is non-porous and non-permeable. The second soil has unconnected pore spaces, making it porous but non-permeable. The third soil has connected pore spaces, making it both porous and permeable.

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Main Idea • *In general, connected pore spaces have higher permeability than unconnected pore spaces. A site-specific relationship can be developed between porosity and permeability for some soils.*



Notes ◆ Permeability is the ability of the media to transmit water or other fluids. It is a property of the medium (clay, silt, sand, or gravel) and independent of the permeating fluid. Fluids must take a tortuous flow path along irregular pores between the particles. The more irregular the path, the lower the permeability. A mix of different grain sizes makes the path irregular, and small grains make pore areas smaller and more tortuous, which result in lower permeability.



- ◆ Permeability is a property of the soil (clay, silt, sand, or gravel)
- ◆ Permeability is NOT the same as porosity. Where grain size does not affect porosity, grain size DOES affect permeability.

Darcy's equation and definition of permeability

$$\vec{k} = -\mu \frac{\vec{U}}{\nabla P}$$

Permeability
Flux

Fluid viscosity
Pressure head

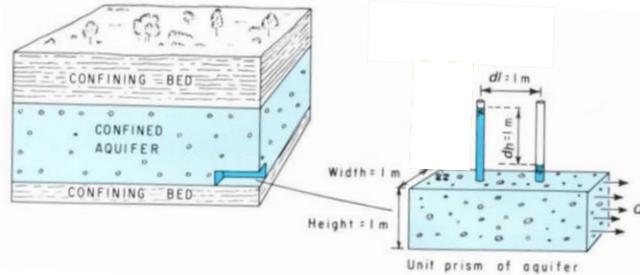
Main Idea

Equation and Definition of Permeability

- ◆ The standard unit is the Darcy (d) with units of m^2
- ◆ Darcy's Law defines permeability
 - » Flow rate is proportional to hydraulic gradient (i) and area (A)
 - » The constant of proportionality is k , permeability

$$Q = kiA$$

$$K = \frac{Q}{A} \left[\frac{-1}{dh/dl} \right]$$



USGS Water Supply Paper 2220

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Notes



- ◆ Permeability (k) is defined as the constant or proportionality between flow rate (Q) and hydraulic gradient (i) times flow area (A) or $Q = kiA$. This relationship is known as Darcy's Law, the fundamental principle of groundwater flow. That is why the standard permeability unit is the Darcy (d), with units of m^2 .
- ◆ In the context of groundwater flow we assume the permeating fluid is water, however the term permeability is often applied to other fluids used in environmental engineering, including air permeability (for SVE systems), oil permeability (for LNAPL sites), and sometimes injectant permeability (molasses, Fenton's reagent, surfactants).

Test Your Knowledge

◆ **Question 1: Which is a type of high porosity media?**

- A. Sand
- B. Fill
- C. Clay
- D. All of the above
- E. None of the above

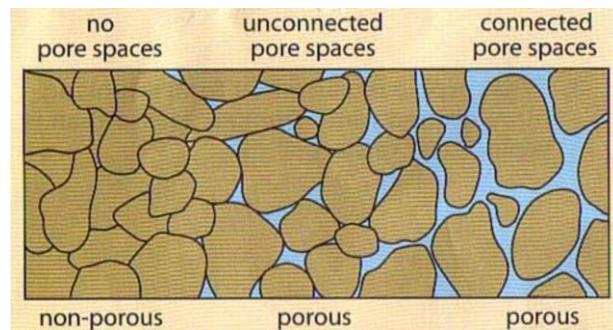


2-10

Test Your Knowledge

◆ **Question 2: Which part of the figure has the highest permeability?**

- A. Left-hand side
- B. Middle
- C. Right-hand side



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Hydraulic Conductivity

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Hydraulic Conductivity

◆ Measure of the “ease” with which a medium transmits water

◆ Hydraulic Conductivity (K)

- » Property of the medium and the fluid (water)
- » Important fluid properties are density and viscosity
- » Multiple fluids often coexist in the same system, such as water and DNAPL
- » Each fluid has a different conductivity within the same permeability regime
- » Can be roughly estimated by grain size

$$K = k \frac{\rho g}{\mu}$$

Where K = Hydraulic Conductivity (cm/s)

k = permeability (cm²)

ρ = density (fluid) (g/cm³)

g = gravity (cm/s²)

μ = viscosity (fluid) (g/s-cm)



2-13

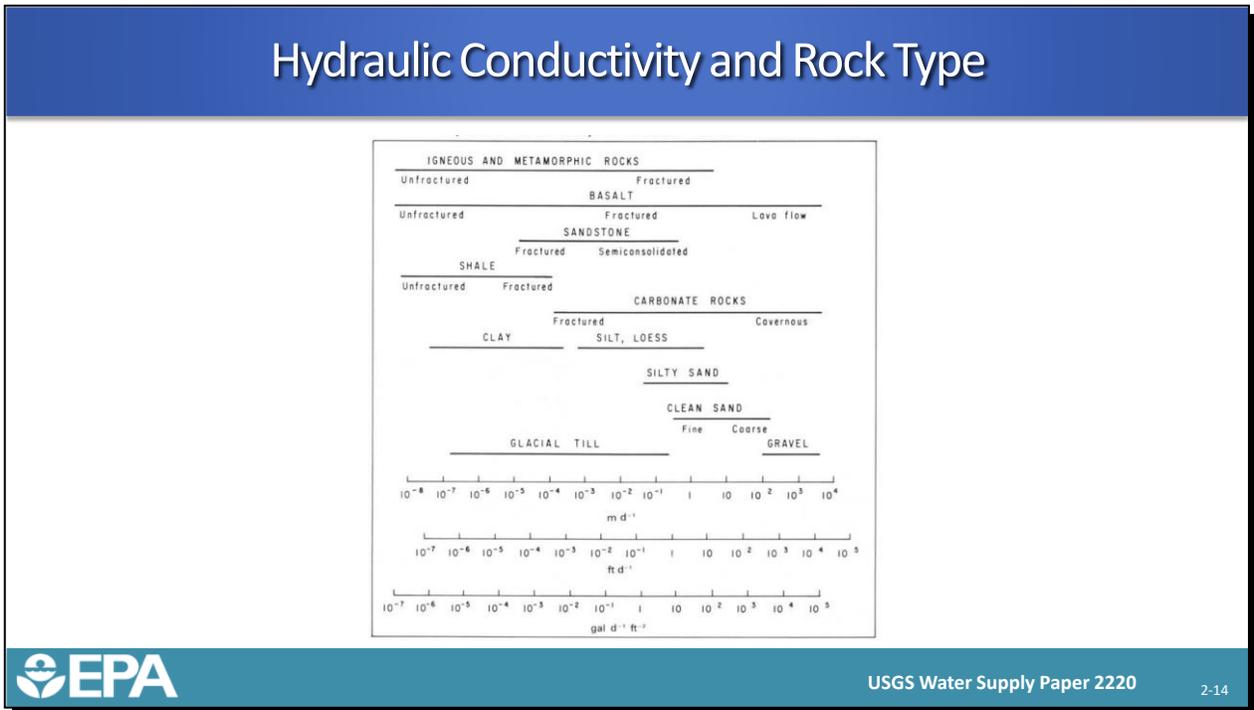
- Main Idea** • *Hydraulic conductivity is one of the most fundamental hydrogeological properties because it quantifies groundwater flow.*



Notes



- ◆ Hydraulic conductivity reflects the relative ease with which water can flow through a medium such as a clay, silt, sand or gravel. It is analogous to electrical conductivity in that sense. The terms permeability and hydraulic conductivity are often used interchangeably, but permeability is a property of the medium only while hydraulic conductivity is a function of the permeability AND the properties of the fluid flow through the medium, specifically the density and viscosity of the fluid. The distinction becomes important for systems in which several fluids may coexist, for example air, water and DNAPL would represent a three-phase flow system in which each fluid has a different conductivity within the same permeability regime.
- ◆ Hydraulic conductivity is calculated from aquifer tests or from core tests performed in the lab. It can also be estimated from empirical correlations that relate grain size distributions to hydraulic conductivity. Some real time direct sensing tools provide estimates of hydraulic conductivity and will be discussed in Module 4.
- ◆ Note that hydraulic conductivity is normally designated by an upper-case letter (K), and permeability is designated by a lower case or italicized letter (k or *k*)
- ◆ Hydraulic conductivity is usually reported in meters per day (m/d), centimeters per second (cm/sec) or feet per day (f/d) and can vary over 10 orders of magnitude. Sands typically have hydraulic conductivity of 1 to 10⁴ f/d and clays have permeabilities of less than 10⁻³ f/d.



Notes



- ◆ Hydraulic conductivity varies widely among rock types – with a range of 13 orders of magnitude. Because of this wide range, variation within an order of magnitude is usually not significant,
- ◆ Coarse rock has more K than fine rock, and fractured rock has more K than unfractured rock.
- ◆ Gravel is a rock type that typically has a comparatively high K, while shale and clay typically have a low K

Homogeneity and Isotropy of Hydraulic Conductivity (K)

◆ Homogeneous

» Variable K has same value regardless of position in space

◆ Heterogeneous

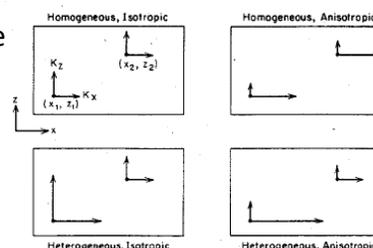
» Variable K has a different value depending on its position in space

◆ Isotropic

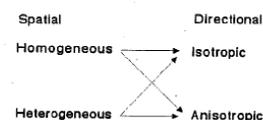
» Variable K has same value regardless of the direction in which it is measured

◆ Anisotropic

» Variable K has a different value depending on the direction in which it is measured



(from Freeze and Cherry, 1979)



Homogeneous, isotropic aquifers do not occur in nature



2-15

- Main Idea** • *Homogeneity and isotropy are terms that can apply to any number of variables but in this context the terms usually reference hydraulic conductivity.*



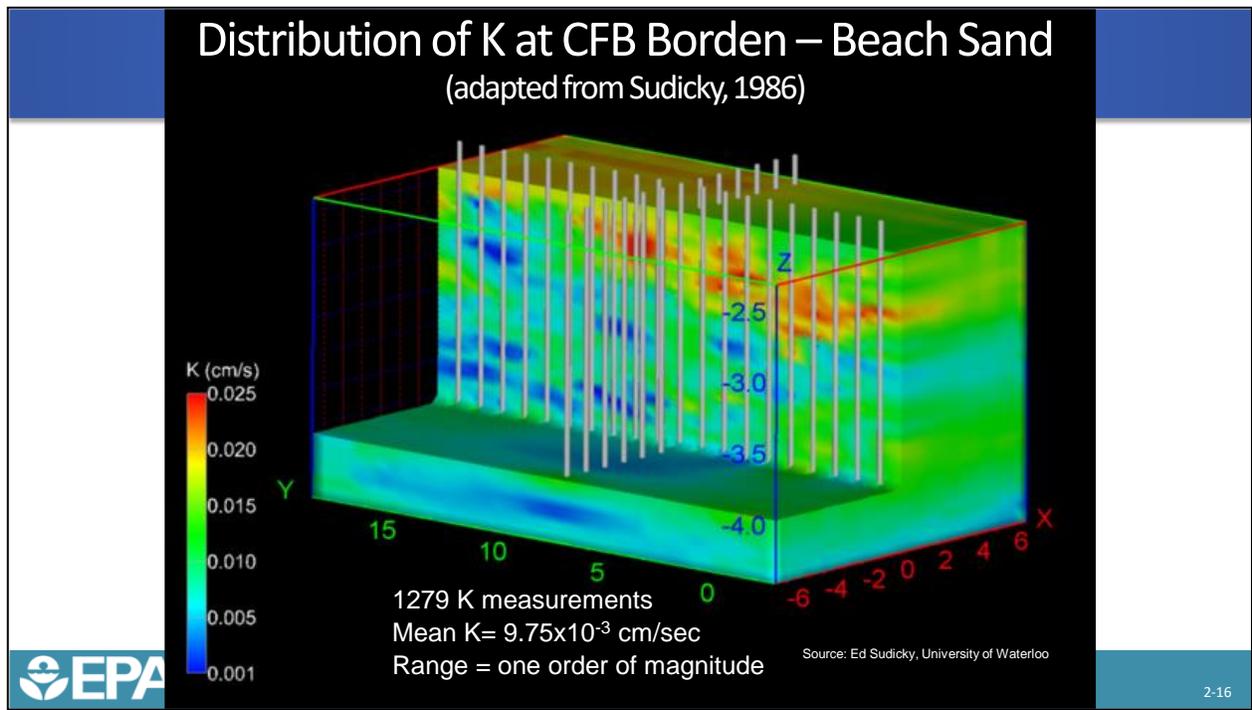
Notes



- ◆ Homogeneity refers to a variable that has the same value regardless of where it is measured in the system. A homogeneous aquifer would have consistent hydraulic conductivity throughout the aquifer, top to bottom and across the extent of the aquifer. Isotropy means that a variable has the same value regardless of the direction in which it is measured. An anisotropic aquifer would have different values for hydraulic conductivity depending on the direction in which it was measured (e.g. vertically and horizontally). Typically, analytical solutions to flow equations assume that aquifers are homogeneous and isotropic. These simplifying assumptions make the math work, unfortunately such aquifers do not exist in nature.

It is often expected that porous media such as sandy aquifers are anisotropic such that the vertical hydraulic conductivity is substantially lower than the horizontal hydraulic conductivity. However, horizontal anisotropy also occurs. One important effect of anisotropy is that actual flow does not occur in the direction of the hydraulic gradient, but rather at some angle from it. This makes prediction of the contaminant transport significantly more difficult.

Source: Freeze, R. Alan and John Cherry. Groundwater. Prentice-Hall, 1979.



Main Idea



- *The spatial structure of hydraulic conductivity is closely related to the nature and degree of hydrodynamic dispersion in aquifers.*

Notes



- ◆ The simplifying assumption of homogeneity implicit in much of the classical hydrogeological applications leads to descriptions of the hydraulic conductivity of an aquifer. However, aquifers have many different zones of many different hydraulic conductivity values. It is the spatial distribution of these values that determines the paths that groundwater actually follows and the routes by which contaminants are transported.
- ◆ This image shows the results of work done by Ed Sudicky at the University of Waterloo at the time of the Stanford-Waterloo Natural Gradient Tracer Test at Canadian Forces Base Borden in Ontario, Canada. The interpolation and visualization in this image was done by Seth Pitkin using Ed Sudicky's data. Ed Sudicky collected a series of 2 meter long cores spaced 1 meter apart horizontally in a cross pattern. He then divided the cores into 5 cm thick segments and ran permeameter tests on each segment, resulting in 1,279 measurements of hydraulic conductivity. The Borden aquifer is commonly referred to as relatively homogeneous in appearance and is a sand deposited in a beach environment. This image shows the distribution of the K values in 3 dimensions. Note that there is a substantial vertical exaggeration in the image. The spatial structure of hydraulic conductivity is such that there are thin zones of high K material adjacent to thin zones of lower K material.

Reference



Source: Ed Sudicky, University of Waterloo

Research originally published in: Sudicky, E.A., 1986. A natural Gradient Experiment on Solute Transport in a Sand Aquifer: Spatial Variability of Hydraulic Conductivity and Its Role in the Dispersion Process. *Water Resources Research* Vol 22, No. 13 pages 2069-2082, December.

Hydraulic Conductivity Correlation Lengths

Location	Setting	Horizontal K Correlation Length (m)	Vertical K Correlation Length (m)	Investigator
Chalk River, Ontario	Aeolian/fluviol medium to fine sand	1.5	0.47	Indelman et al. (1999)
Borden CFB, Ontario	Beach sand	2.8	0.12	Sudicky (1986)
Otis ANG Base Cape Cod Massachusetts	Glacial sand and gravel	2.9 - 8	0.18 - 0.38	Hess et al. (1992)
Columbus AFB, Mississippi	Fluvial gravel	12.7	1.6	Rehfeldt et al. (1992)
Aeffligen Hydrothermal Site Switzerland	Glacial gravel	15 - 20	0.05 – 0.06	Hufschmied (1986)



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- Main Idea** • *Hydraulic conductivity is consistent over different scales vertically and horizontally. Vertical heterogeneity is much higher than horizontal heterogeneity.*



- Notes** ♦ Other investigators have since performed similar studies and have found similar results. With the exception of Columbus AFB, all of the investigators have found vertical correlation lengths in the centimeter scale with horizontal correlation lengths in the meter to a few tens of meters.



- Reference** References:



Hess, Kathryn M., Steven H. Wolf and Michael Celia, 1992. Large-Scale Natural Gradient Tracer Test in Sand and Gravel, Cape Cod, Massachusetts. *Water Resources Research*, Vol. 28, No. 8, pages 2011-2027, August.

Indelman, P., 1999. Averaging of Unsteady Flows in Heterogeneous Media of Stationary Conductivity. *Adv, Water Resources*. 22(7) pages 729-740.

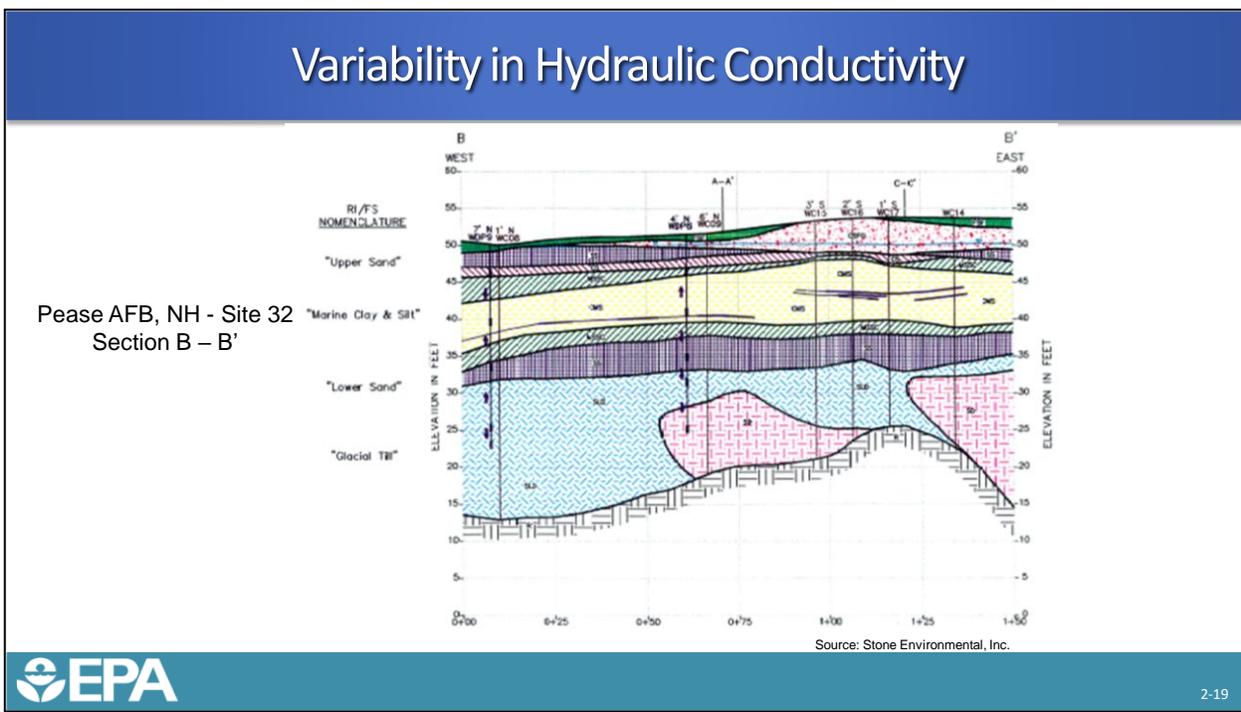
Rehfeldt, K.R., J.M. Boggs and L.W. Gelhar, 1992. Field study of dispersion in a heterogeneous aquifer. 3: Geostatistical analysis of hydraulic conductivity. *Water Resources Research* 28, no. 12: 3309-3324.

Sudicky, E.A., 1986. A natural Gradient Experiment on Solute Transport in a Sand Aquifer: Spatial Variability of Hydraulic Conductivity and Its Role in the Dispersion Process. *Water Resources Research* Vol 22, No. 13 pages 2069-2082, December.

Test Your Knowledge

- ◆ Which has a greater correlation distance, and therefore less heterogeneity in the subsurface?
 - A. Vertical direction
 - B. Horizontal direction
 - C. Both are the same





- Main Idea** • *The next three slides show heterogeneity in hydraulic conductivity over different scales at a contaminated site. This is the typical cross section you would see in a report.*

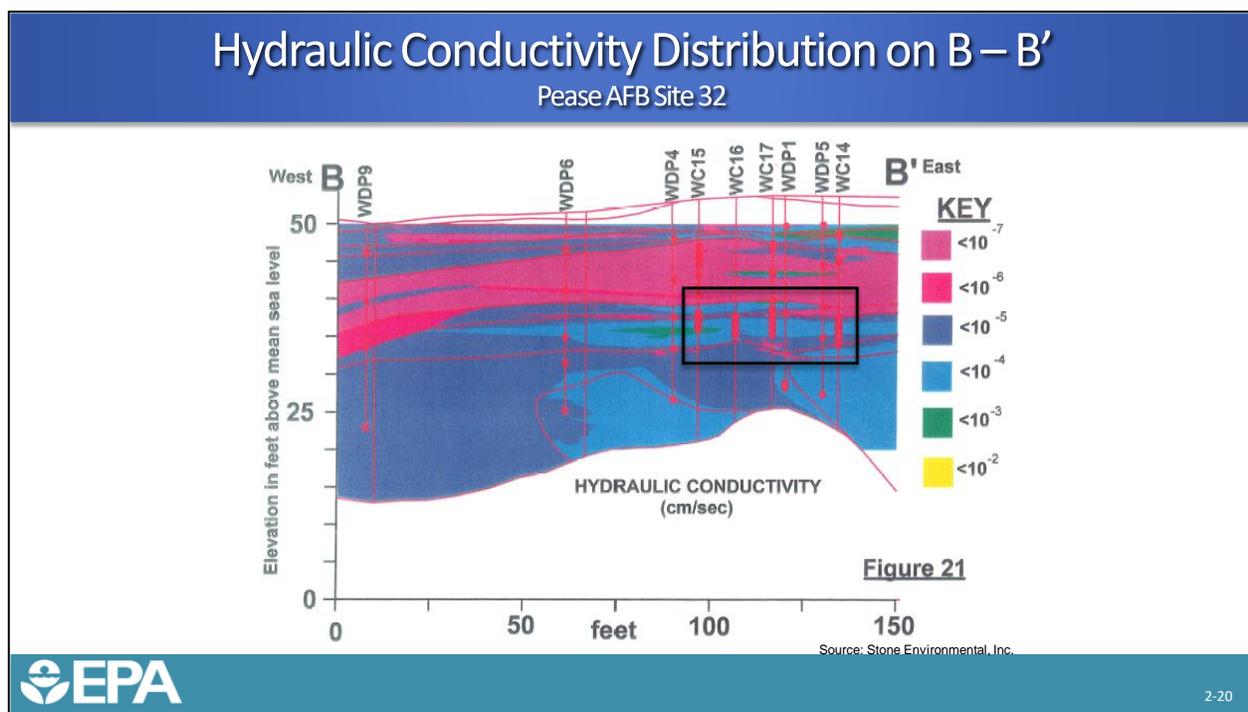


- Notes** ◆ While most of the research in the preceding table was done at sites that were largely described as sand or sand and gravel aquifers, many sites facing practitioners are much more complicated geologically. The cross section above is at Site 32 at Pease AFB in Portsmouth, NH.



This section is only 150 feet long and about 40 feet thick but has a large range of material types from “fill” at the top to a poorly sorted “upper sand” unit, a marine clayey silt unit, a lower sand unit and a till. Sand stringers exist within the marine clayey silt. This type of environment is far from the homogeneous and isotropic ideal.

Source: Seth Pitkin, The Johnson Company, Inc. and the University of Waterloo. 1996. 2-14.



Main Idea



The small red dots are where hydraulic conductivity measurements were made in borings. The K data was contoured to show ranges of K that generally match the geologic cross section.

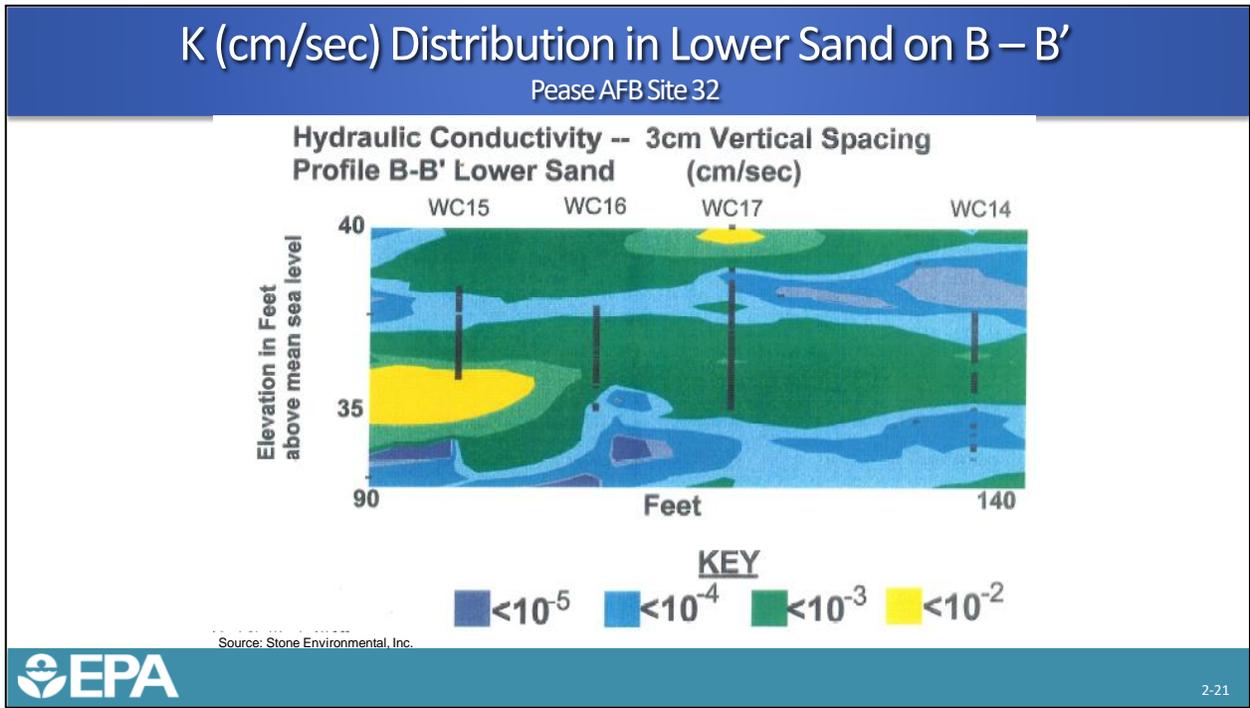
Notes



- ◆ This image is the same cross section that we looked at previously, but we are now looking at the distribution of the hydraulic conductivity (measured horizontally). K distributions generally reflect the geologic descriptions in the previous image with the Marine Clayey Silt having the lowest hydraulic conductivity values and the lower sand having the highest K s. We see K values ranging across at least 5 orders of magnitude over a small vertical slice.

In the next image, we will zoom in on the lower sand between about 90 and 140 feet horizontally and about 30 to 40 feet elevation to see the detail of the K distribution in that small portion of the flow system.

Source: Seth Pitkin, The Johnson Company, Inc. and the University of Waterloo. 1996.



Main Idea • When looking at a finer scale we see heterogeneity in the K values.



Notes



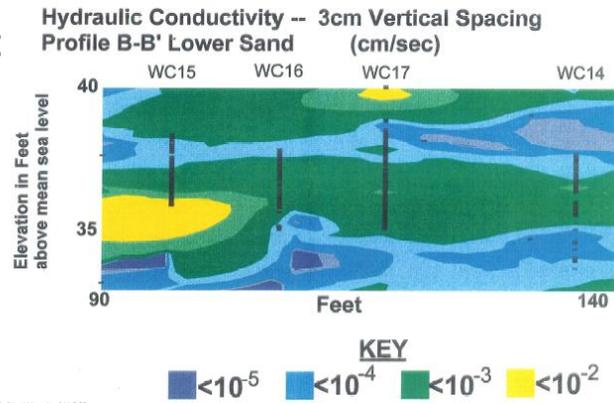
- ◆ In this blown up detail of the lower sand it can be seen that even this small unit, with the highest conductivities in the flow system, is actually made up of a complex spatial K distribution ranging across 3 to 4 orders of magnitude.
- ◆ This type of variability in K has a profound effect on groundwater flow and transport pathways. In addition, contrasts in K of 2 or more orders of magnitude may be sufficient to cause flow to bypass the lower K zones and to result in those zones becoming “immobile porosity” zones in which diffusive flux dominates and which function as storage volumes for solutes.

Source: Seth Pitkin, The Johnson Company, Inc. and the University of Waterloo. 1996.

Test Your Knowledge

◆ Which color in this figure corresponds to the highest hydraulic conductivity (K)?

- A. Dark Blue
- B. Light Blue
- C. Green
- D. Yellow



Source: Stone Environmental, Inc.



2-22

Hydraulic Gradient and Groundwater Velocity

2-23

Hydraulic Gradient

- ◆ Driving force for flow
- ◆ Water flows downhill
- ◆ Vertical and horizontal gradients

(from Freeze and Cherry, 1979)

2-24

Main Idea • Hydraulic gradient, also known as head, is the driving force for groundwater flow.



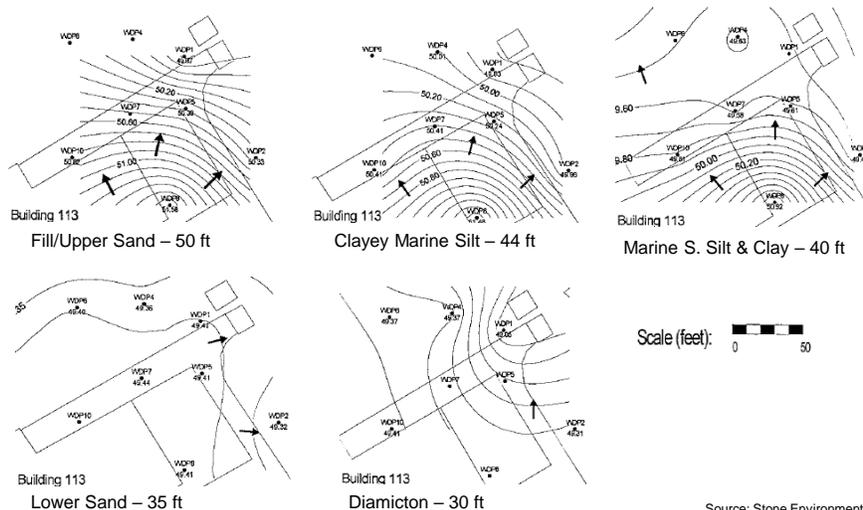
Notes



- ◆ The hydraulic gradient is a vector quantity, meaning it has both a direction and a magnitude. While we most often look at and think about the hydraulic gradient in two-dimensional, plan view terms (for example, the slope of the water table), it is critical to remember that it is 3-dimensional. The 3-dimensional gradient is represented by piezometric maps shown on the next slide.
- ◆ Hydraulic gradient is calculated from water level data. The most important quality control aspects of water level measurements are an accurate well elevation (and knowing the measuring point of the well) and taking the water level readings at the same time, within a few hours, if possible. A round of water levels (called a *synoptic* round) should include as many wells as possible, even if they are not used for sampling.

Source: Freeze, R. Alan and John Cherry. Groundwater. Prentice-Hall, 1979.

Hydraulic Gradient Variability with Depth at Pease AFB Site 32



2-25

Notes



- ◆ This series of diagrams shows the distribution of hydraulic head on planes at 5 different elevations at Pease AFB site 32. The data come from ten clusters of 5 piezometers over an area of less than half an acre. It is clear that both the direction and magnitude of the hydraulic gradient vary substantially with depth at the site. This is not uncommon, but it is a mistake to think that the gradient at the water table is representative of the hydraulic gradient throughout the vertical profile of the flow system.

Source: Seth Pitkin, The Johnson Company, Inc. and the University of Waterloo. 1996.

Groundwater Velocity

◆ Also called seepage velocity

$$\text{velocity} = \frac{Ki}{\Phi}$$

Where K = hydraulic conductivity

i = hydraulic gradient

Φ = porosity



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- Main Idea** • *The rate of groundwater flow can be calculated using K, gradient and an estimate of porosity.*



Notes



- ◆ The rate at which groundwater flows is dependent on the groundwater gradient, hydraulic conductivity and the porosity. Gradient can be calculated from the water level readings in two wells where the distance between the wells is known, and estimates of hydraulic conductivity and porosity. Because gradient and porosity are unitless seepage velocity will have the same units as hydraulic conductivity.
- ◆ Higher gradients and higher porosity will result in faster groundwater flow rates.

Test Your Knowledge

◆ **What is the difference between permeability and hydraulic conductivity?**

- » A. Permeability is a property of the medium, while hydraulic conductivity is a property of the fluid AND medium
- » B. Hydraulic conductivity is a property of the medium, while permeability is a property of the fluid AND medium
- » C. Hydraulic conductivity is measured only horizontally.
- » D. None of the above



2-27

Questions on Hydrogeology Primer?



2-28

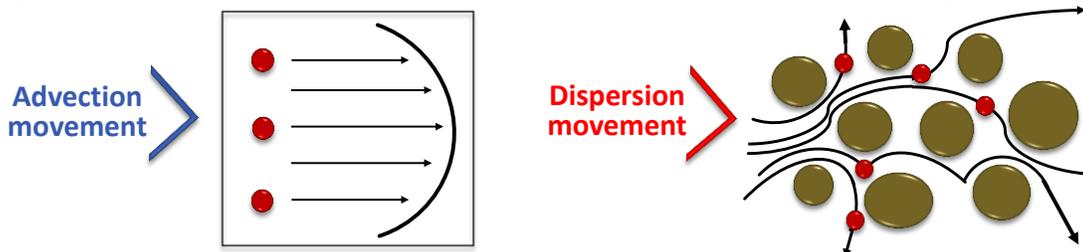
Contaminant Fate and Transport Primer

- Advection and Dispersion
- Contaminant Phases
- Hydrodynamic Dispersion

2-29

Advection and Dispersion

- ◆ **Advection** - Movement of groundwater and dissolved contaminants at the average linear groundwater seepage velocity in the direction of the hydraulic gradient
- ◆ **Dispersion** – Spreading and mixing of solutes in groundwater in the direction of a concentration gradient



2-30

- Main Idea** • *Advection is the movement of groundwater itself, but dispersion is the mixing of solutes WITHIN groundwater, driven by equilibrium.*



Notes

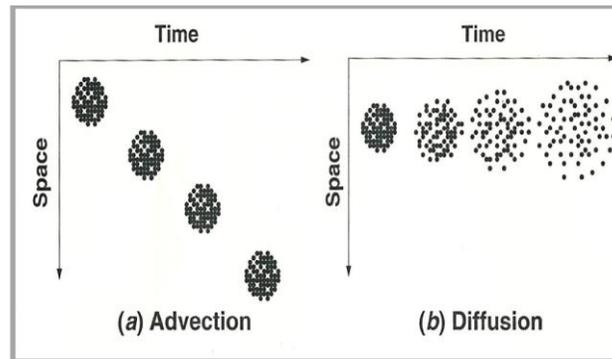


- ◆ **Advection:** Advection is the bulk flow of groundwater. It is described by the average linear velocity or the so called “seepage velocity.” This average linear velocity is calculated as the hydraulic conductivity times the hydraulic gradient all divided by the porosity of the medium. All of these variables (K, gradient and porosity) vary greatly over short distances. This in turn means that the average linear velocity of groundwater varies considerably over short spatial intervals.
- ◆ **Dispersion:** Dispersion accounts for spreading and mixing of solutes in groundwater as the groundwater flows through a porous medium. Hydrodynamic dispersion is made up of a mechanical dispersion term (due to the different travel paths that “particles” of water take during their journey) plus effective molecular diffusion. Diffusion is driven by the movement of molecules from high concentration to low concentration as they try to reach concentration equilibrium.

Diffusion

◆ Diffusion – Movement of dissolved contaminants from areas of higher concentration to areas of lower concentration

» Occurs on a molecular level



Chapra, 1997

2-31

Main Idea • *Diffusion is a slow process that occurs on a molecular level. It occurs because solutions of different concentrations try to reach equilibrium.*



Notes



◆ **Diffusion** is the movement of dissolved contaminants from areas of higher concentration to areas of lower concentration. The figure illustrates the difference in contaminant movement between advection and diffusion. Advection is time and space dependent and diffusion is primarily time dependent.

» Diffusion occurs on a molecular level.

Dual Porosity Systems

- ◆ Systems in which there are (relatively) high and low permeability units
- ◆ Nearly all advective flow takes place through the pores in the high permeability materials (mobile porosity)
- ◆ Water in the saturated pore spaces in the low permeability materials (immobile porosity) is dominated by diffusive, rather than advective flux
- ◆ Pore water in the low permeability materials essentially serves as storage for solutes



2-32

Main Idea



- *Historically, hydrogeologists have been interested in the relatively high permeability portions of flow systems and have viewed low permeability units as objects which confine or separate the permeable units.*

Notes



- ◆ A dual porosity system is one in which there are units with significant porosity but low permeability (for example, silts and clays or very poorly sorted materials like tills) and other units with significant porosity and high permeability.

Flow (or advection) takes place in the high permeability zones, typically called the mobile porosity. Flow typically bypasses the lower permeability zones (typically called the immobile porosity). However, diffusive flux into the immobile porosity results in significant storage of solutes in the immobile porosity. This stored solute mass can later diffuse back out of the immobile porosity and act as a long term secondary source of contamination.

Dual Porosity in Unconsolidated Media

Immobile Porosity
Relatively low permeability bypassed by advective flow and dominated by diffusive flux

Mobile Porosity
Relatively high permeability and dominated by advective flow

The diagram illustrates a cross-section of the ground. At the top, there are blue barrels representing a source. Below the surface, there are layers of CLAY and SAND. A red layer labeled DNAPL (Dense Non-Aqueous Phase Liquid) is shown between the sand layers. Below the sand layers is another layer of CLAY, and at the bottom is FRACTURED SEDIMENTARY ROCK. On the right side, vertical arrows indicate the UNSATURATED ZONE above the water table and the SATURATED ZONE below it. Arrows from the text on the left point to the clay and sand layers respectively.

Source: Chuck Newell and Tom Sale

2-33

- Main Idea** • *The low permeability layers have higher capillary pressures than the sands and act as barriers to DNAPL flow.*



- Notes** ◆ This diagram was prepared by Chuck Newell and Tom Sale to illustrate their 14-compartment model which will be discussed later. The diagram shows low permeability (immobile porosity) layers interspersed with higher permeability sands (mobile porosity) in a flow system into which a DNAPL has been released. Transport in the mobile porosity is dominated by advection (or active flow) while transport in the immobile porosity is dominated by diffusion.



Diagram taken from Sale, Tom and Charles Newell, 2011. [A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents](#). ESTCP Project ER-200530.

Hydrodynamic Dispersion

◆ Natural Gradient Tracer Tests

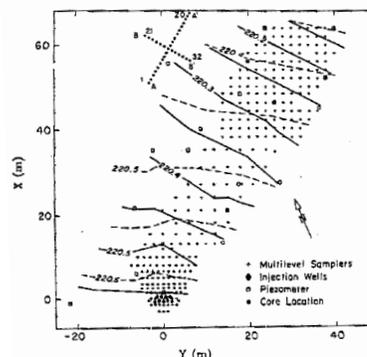
- » Sudicky 1979
- » Stanford/Waterloo – 1982
- » USGS Cape Cod – 1986
- » Rivett et al. 1991

◆ Dispersion is scale (time/distance) dependent

◆ Transverse horizontal dispersion is weak

◆ Transverse vertical dispersion is even weaker

◆ Longitudinal dispersion is significant



Stanford-Waterloo Natural Gradient Tracer Test Layout, Water Resources Research, 1982



2-34

- Main Idea** • *This large scale, rigorous and robust study indicated that transverse (at right angles to the principal direction of flow) dispersion was a weak process.*



Notes



- ◆ In the 1970's and early 1980's, it was thought that hydrodynamic dispersion was a relatively strong process and that it resulted in fan-shaped plumes with fairly low concentration gradients and significant dilution.

However, work beginning with Ed Sudicky's Ph.D. thesis at the University of Waterloo in 1979 raised doubt about this view of dispersion. The Stanford Waterloo natural gradient tracer test was a seminal event in contaminant hydrogeology published in *Water Resources Research* in 1982. Vertical transverse dispersion was found to be very weak, essentially on the order of molecular diffusion. Similar work by other researchers followed, including a large-scale test conducted by the USGS at the Massachusetts Military Reservation on Cape Cod verified the results of the Stanford Waterloo experiment. These tracer tests used conservative tracers such as chloride to assess transport. Later experiments such as those by Mike Rivett and others used reactive contaminants such as chlorinated solvents to assess transport and further confirmed the results of the conservative tracer tests.

Note the location of the "Sudicky Star" on the plan view diagram of the Stanford Waterloo Tracer test at CFB Borden. The Sudicky Star is the location of the study of hydraulic conductivity distributions that was shown earlier.

Test Your Knowledge

Question 1: True or False

Dispersion is most likely responsible for thick vertical zones of contamination.



2-35

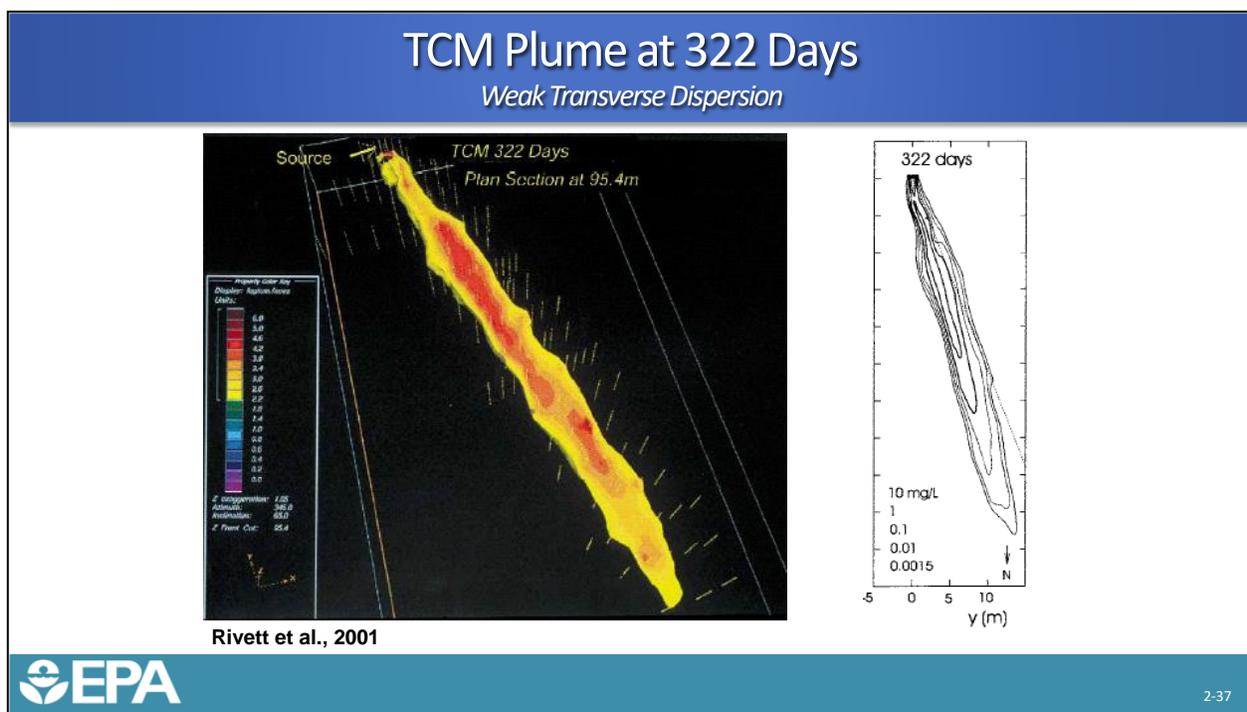
Test Your Knowledge

Question 2: Short Answer

What is responsible for vertical dispersion (or lack thereof)?



2-36



Main Idea • *Plumes tend to be long and narrow with very steep concentration gradients.*



Notes



- ◆ This is a view of the trichloromethane plume emanating from the “emplaced source” at CFB Borden. The results of this experiment, carried out by Rivett et. al. illustrate the effects of weak transverse hydrodynamic dispersion. This means that, not only do hydraulic conductivity measurements, porosity measurements and hydraulic gradient measurements vary significantly over short distances, contaminant concentrations are expected to vary by orders of magnitude over short distances transverse to the direction of transport. Plumes, particularly plume cores, are expected to have widths similar to the width of the source.

Source: Rivett, M. O., S. Feenstra and J. A. Cherry. "A Controlled Field Experiment on Groundwater Contamination by a Multicomponent DNAPL: Creation of the Emplaced-source and Overview of Dissolved Plume Development." *Journal of Contaminant Hydrology* 49.1-2 (2001): 111-49.

Contaminant Phases And Their Processes

- Gas phase (volatilization)
- Dissolved phase (solute)
- Non Aqueous Phase Liquid (NAPL)

2-38

Main Idea • *The physical state of the contaminant affects its movement in the subsurface.*



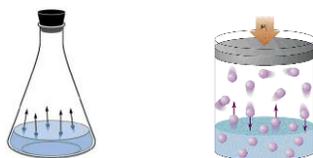
Notes



- ◆ Contaminants exist in groundwater in three phases: non-aqueous phase liquid as a gas or dissolved in water. Contaminants can also sorb to solid matter such as organic matter on the soil particles or directly to mineral surfaces.

Gas Phase

- ◆ **Volatilization creates soil gas plumes (vapor), indoor air contamination and depletes mass in groundwater**
- ◆ **From NAPL in unsaturated zone, governed by vapor pressure**
 - » For a compound in a multi-component NAPL the vapor pressure is a function of Raoult's law
- ◆ **From solute in groundwater, governed by Henry's Law**
 - » Warning: many forms of Henry's constants with different units!



2-39

Main Idea • *The contaminated gaseous phase occurs because of volatilization.*



Notes



- ◆ If there is a NAPL source in the ground, the volatilization is governed by the vapor pressure of the compounds comprising the NAPL. If it is a multicomponent NAPL then Raoult's Law applies to calculating the concentration in the gas phase. If the gas phase is derived from solutes in the groundwater, then it is governed by Henry's Law.
- ◆ **Raoult's Law** defines the relationship between the concentration in air and the concentration in the NAPL mixture: It states that the mole fraction of each substance in a mixture is equal to the mole fraction of the vapor pressure of that substance.

$$C_G = X_t(P^0/RT)$$

- Where X_t = mole fraction of compound in NAPL [-]
- P^0 = Pure compound vapor pressure [atm]
- R = Universal gas constant [$m^3 \cdot atm / mole / ^\circ K$]
- T = Temperature [$^\circ K$]

- ◆ The concentration of a volatile substance in groundwater may be converted to the concentration in air by applying **Henry's Law** which states that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid.

$$H' = C_G/G_w$$

- Where C_G = The concentration in air and
 - C_w = The concentration in water.
- ◆ H' is called Henry's law constant and is different for every chemical. Compounds with low Henry's Law constants will have generate lower concentrations in air than compounds with a high Henry's Law constant.

Reference



Henry's Law constants are available from EPA are available at:

<https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/esthenry.html>.

The EPA recommends use of its Vapor Intrusion Screening Levels (VISL)

Calculator and associated user's guide (<http://www2.epa.gov/vaporintrusion>).

This tool provides screening level concentrations for groundwater, soil vapor and indoor air to assist Agency staff with making a VI determination based on limited, initial data.

Gas Phase Plumes

- ◆ Gas phase plumes can transport contaminant mass via concentration, density, pressure or even temperature gradients
- ◆ Gas phase transport is relatively rapid
- ◆ Soil gas plumes can create “interface zone” groundwater plumes
- ◆ Groundwater solute plumes can create soil gas contamination but only if the plume is within the upper meter of the aquifer
- ◆ Soil gas plumes infiltrate buildings and degrade indoor air quality
- ◆ Potential for human exposure



2-40

- Main Idea** • *Gas phase plumes are of concern because they can result in exposures through contamination of indoor air in residences and businesses.*



- Notes** ◆ Soil gas plumes can move rapidly and in directions separately from the direction of groundwater transport. Soil gas plumes move in response to concentration gradients, pressure gradients, density gradients and temperature gradients. Soil gas plumes can create thin but high concentration interface zone groundwater plumes at the water table. Also groundwater contamination at or near the water table (within about a meter of the water table) can cause soil gas plumes.



For more information on vapor intrusion, visit <http://www2.epa.gov/vaporintrusion>.

Reference



OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air, June 2015, OSWER No. 9200.2-154.

Dissolved Phase (Solute)

- ◆ **Governed by solubility**
 - » Polarity
 - » Molecular size
- ◆ **For a compound in a multi-component NAPL the effective solubility is a function of the amount of that component in the mixture**
- ◆ **Effective solubilities of individual compounds change over time as more soluble compounds become depleted**



2-41

- Main Idea** • *NAPL will dissolve in groundwater at different rates depending on the chemical properties of the contaminant.*



Notes



- ◆ Solute plumes in groundwater can result from the dissolution of compounds from a NAPL. Each compound has an aqueous solubility which is influenced by the polarity of the compound and the size of the molecule. If the NAPL is a multicomponent mixture, the solubility for any given component is the effective solubility which is determined in accordance with Raoult's law (see previous slide's notes).
- ◆ As the more soluble compounds dissolve out of the NAPL their mole fraction decreases and the mole fraction of the other compounds increases, causing the effective solubilities of the compounds to change. This results in changes in the ratios of compounds dissolved in water over time.
- ◆ Solubilities of common contaminants vary widely. Examples of a few common contaminants:
 - Trichloroethene – 1,100 mg/l
 - Tetrachloroethene – 200 mg/l
 - Carbon Tetrachloride – 790 mg/l
 - Aroclor 1260 (PCB) – 2.7 ug/l (six orders of magnitude lower than TCE)

Reference



Source: *An illustrated handbook of DNAPL transport and fate in the subsurface*

https://clu-in.org/download/contaminantfocus/dnapl/Chemistry_and_Behavior/uk_dnapl_manual.pdf

Dissolution: Rate of Mass Transfer

- ◆ **Mass transfer is greater in zones of residual than in pools and is greater in high flow zones than low flow zones**
- ◆ **Disconnect between mass flux and concentration**
 - » Sample from a high flux zone may have a relatively low concentration
 - » Sample from a low flux zone may have a high concentration



2-42

- Main Idea** • *The rate of mass transfer is dependent of the surface area of the NAPL in contact with water. Thus, mass transfer rates are higher in zones of residual NAPL as opposed to pools.*

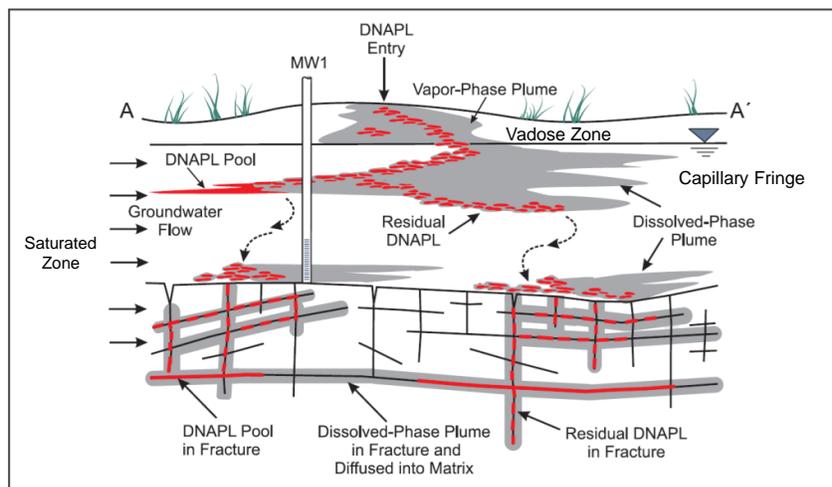


- Notes** ◆ In assessing the likely persistence of a plume resulting from a NAPL source, one would need to estimate the volume of NAPL (never an easy or accurate undertaking), but would also need to assess the rates of mass transfer from the NAPL to the dissolved phase. There is more mass per unit volume in a “pool” of NAPL but since the contact area is lower the mass transfer rate is lower. NAPL saturations are highly variable spatially causing the mass transfer rates to vary tremendously over short distances.



Mass transfer rates are also affected by the concentration gradient. This is dependent on the velocity of groundwater flow where faster flow results in higher gradients and increased mass transfer. In low velocity areas, the gradient is much lower resulting in a low mass transfer rate. This results in a disconnect between mass flux and concentration where low velocity (low permeability) zones may have high concentrations but very low mass flux.

NAPL Density: LNAPL and DNAPL



Kueper and Davies, EPA Groundwater Issue, 2009

2-43

- Main Idea** • *NAPLs are much more difficult to deal with because of the complex interactions with soil, groundwater, and air.*

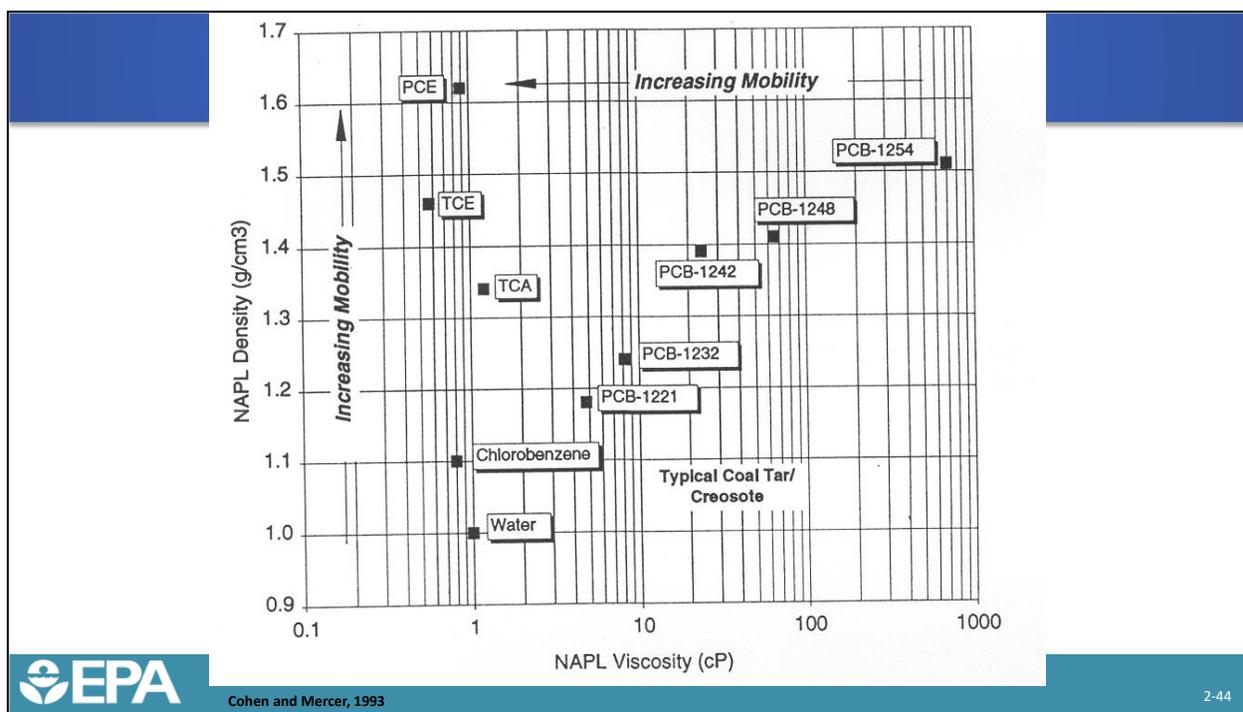


Notes



- ◆ One of the most fundamental properties of NAPLs is the density (or specific gravity) of the NAPL. If the specific gravity is less than 1 the NAPL is termed a light non-aqueous phase liquid (LNAPL) that is buoyant and floats on water. If the specific gravity is greater than 1 the NAPL is termed a dense non-aqueous phase liquid (DNAPL) and sinks in water. The NAPL serves as a source of ongoing solute, gas phase and sorbed contamination.
- ◆ Schematic illustration of contamination associated with a DNAPL release. Note that DNAPL migrates in three dimensions, and that residual DNAPL accumulated above bedrock is the result of the release at the ground surface. Figure is not to scale.

Source: Pankow, James F. and John A. Cherry. Dense Chlorinated Solvents and Other DNAPLs in Groundwater: History, Behavior and Remediation. Portland, OR: Waterloo, 1996



Main Idea • The density, coupled with the viscosity of the NAPL, determines the mobility of the DNAPL.



Notes



- ◆ This diagram from Mercer and Cohen shows the relative mobilities of various liquids as function of their density and viscosity. Those liquids in the upper left of the diagram are the most mobile while those in the lower left are the least mobile.
- ◆ As was discussed earlier, the permeability is a property intrinsic to a porous medium while hydraulic conductivity is the permeability specific to water. One can calculate a conductivity to a fluid given the permeability, the density and the viscosity of the NAPL.
- ◆ NAPL with high densities and low viscosities are more mobile than those with low densities and high viscosities.

Source: Cohen, R.M. and J.W. Mercer. 1993. DNAPL Site Characterization. Boca Raton, Florida: Smoley.

Effects of Capillary Pressure Variability on NAPL Distribution

Tan = Coarser sand
Lower capillary pressure

Red = DNAPL

Blue = Finer sand
Higher capillary pressure

EPA

Bernie Kueper 2-45

- Main Idea** • *The distribution of capillary pressure controls the movement of DNAPL in the soil. Capillary pressure is a function of grain size so change in grain size (heterogeneity) is an important factor in the movement of DNAPL.*



Notes



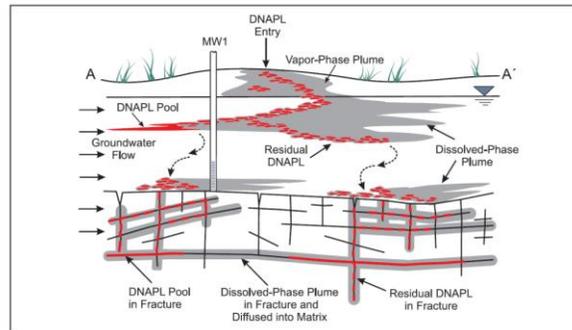
- ◆ Changes in soil texture result in changes of the capillary pressure distribution in the soil. In this experiment conducted by Bernie Kueper, formerly at the University of Waterloo and now at Queens University, several grades of silica sand were placed in a sand tank and a constant head of DNAPL (showed dyed red in the photo) was put on the top of the system. The DNAPL cannot penetrate the finer sands due to the higher capillary pressures in those units. The distribution of grain sizes (and hence capillary pressures) controls the distribution of the DNAPL.

Source: Photo of a sand tank experiment undertaken by Bernie Kueper (Queen University, formerly University of Waterloo) provided to Seth Pitkin by John Cherry (University of Guelph, formerly University of Waterloo).

Test Your Knowledge

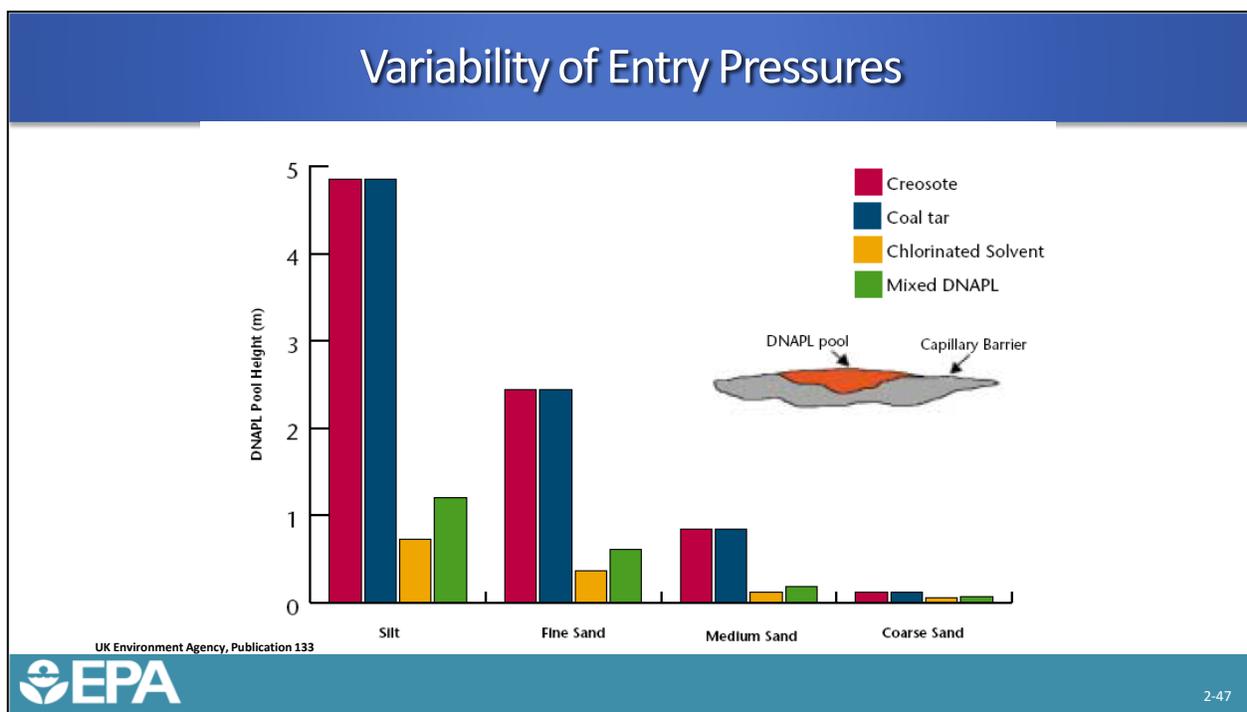
◆ In which medium do you think DNAPL will have the largest pool height?

- A. Silt
- B. Fine sand
- C. Medium sand
- D. Coarse sand



Kueper and Davies, EPA Groundwater Issue, 2009

2-46



- Main Idea** • Grain size and physical properties of the DNAPL control capillary pressure and the movement of DNAPL in the soil.



- Notes** ◆ This diagram from the UK DNAPL Manual shows how combinations of grain sizes and NAPL densities and viscosities affects the height of the column of NAPL required to enter a particular soil texture.

In general, mobile NAPLs like PCE overcome capillary barriers much more readily than viscous near-neutral density NAPLs like coal tar or creosote. Required pool heights range from a few centimeters for a chlorinated solvent to enter a gravel to nearly 5 meters for a coal tar to enter a silt.

Source: UK Environment Agency, Publication 133,
<http://publications.environment-agency.gov.uk/PDF/SCHO0604BHIT-E-E.pdf>.

Residual NAPL

- ◆ Even after pumping has removed all the available mobile NAPL, a large mass of NAPL contamination will remain as residual NAPL in the Aquifer
- ◆ The residual serves as an on-going source for dissolved plumes and soil gas contamination
- ◆ Residual can be remobilized by changing conditions (for example, hydraulic gradient)



2-48

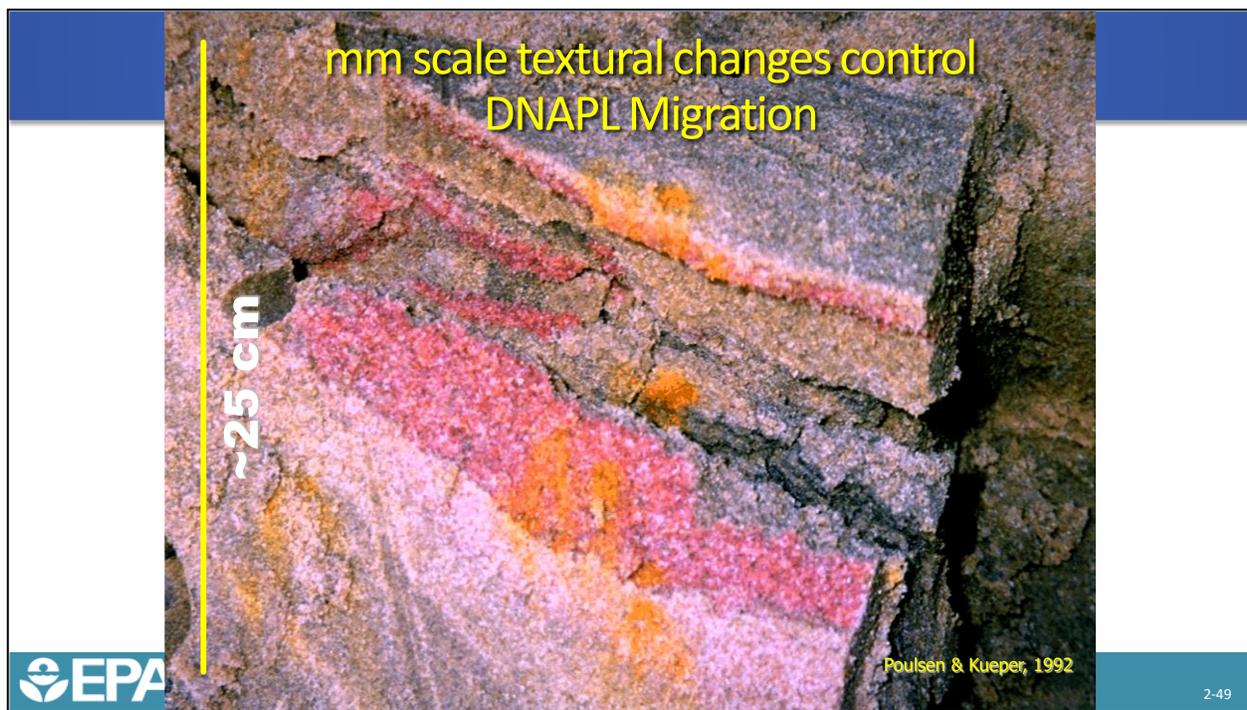
- Main Idea** • *This residual NAPL can serve as a long-term source of solute (and soil gas) contamination.*



Notes



- ◆ When referring to contamination the term “residual” should be reserved for NAPL saturations that are at the level where no further NAPL drainage will occur. If NAPL is pumped or recovered from wells, there will be a point at which no further NAPL is recovered by the well. Even after this occurs NAPL still exists in the formation at residual saturations.
- ◆ Non NAPL contamination that is sorbed or held in the immobile porosity is not properly called residual contamination; rather, it is sorbed or immobile dissolved contamination.



- Main Idea** • The distribution of the DNAPL is controlled by subtle soil textural changes at the millimeter scale.



Notes



- ◆ This photograph was taken in a test pit at an experimental release site at Canadian Forces Base Borden. In this experiment by Mette Paulson (now Mette Broholm) and Bernie Kueper, two releases of the same volume of PCE were staged at adjacent locations. The PCE (dyed red with Sudan IV) was released at the surface. In the first case the DNAPL was released all at once. In the second release a Mariotte bottle was used to simulate a drip release over time. Once both releases had occurred and sufficient time had passed for the DNAPL to come to rest, the sites were excavated and the distribution of the PCE was mapped. In this photo, which shows approximately a 25 cm vertical section of the test pit wall, the red DNAPL can be plainly seen. It does not take a clay contact to direct DNAPL flow, variability in sand grain size distribution can do it.

Source: Poulsen, M.M. and B.H.Keuper, 1992. A Field Experiment to Study the Behavior of Tetrachloroethylene in Unsaturated Porous Media. Environmental Science and Technology. Volume 26, No. 5 pages 889-895.

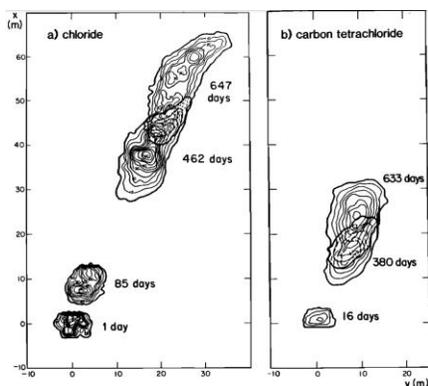
In this photograph the DNAPL appears to be a continuous layer, however over time the layers break up and only small, separated droplets of DNAPL remain. These are called *ganglia* or *blebs* and can be difficult to detect because they are so small, generally between 1 and 10 grain diameters.

Mass Flux

- Sorption
- Degradation
- Plume Stages
- Mass Flux Distribution
- Back Diffusion

2-50

Sorption



Sorption of Carbon Tetrachloride is greater than sorption of Chloride

- ◆ Sorption of solutes to organic matter on the solid particles results in retardation of the plume
- ◆ Sorption of metals to minerals and clay results in retardation of the plume
- ◆ Sorption is reversible, mass is not destroyed or permanently sequestered
- ◆ Results in “chromatographic separation” of different contaminants in the plume



MacKay et al., 1986

2-51

- Main Idea** • Sorption is reversible, so the mass is not destroyed or permanently sequestered, it is simply delayed.



Notes



- ◆ Sorption is the attachment of contaminant molecules to stationary organic matter (in the case of organic contaminants – metals will sorb directly to mineral surfaces). The molecules may come out of aqueous solution or from the gas phase. In the case of groundwater solute plumes, sorption retards (or delays) the advance of the plume front. The retardation factor (R) is dependent on the porosity, bulk density and organic carbon content of the aquifer. All of these vary spatially (though organic carbon content is far more variable than porosity and bulk density) so retardation factors vary significantly over short distances.

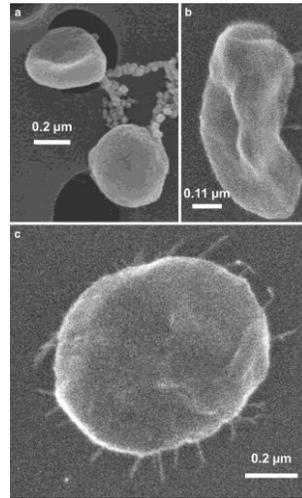
Do not confuse sorption with the common English word “absorption” – absorption incorporates a substance in one state into another of a different state (like ammonia gas absorbing into water). **Sorption** is the **attachment** of molecules, so nothing is destroyed or permanently sequestered – making it **reversible**.

Sorption also results in a chromatographic effect in multi-component plumes in which compounds with different solubilities and affinities for organic matter travel at different speeds through the aquifer.

MacKay, D.M., D. L. Freyberg, P. V. Roberts and J.A. Cherry, 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: 1. Approach and Overview of Plume Movement. Water Resources Research, Vol. 22, No. 13, Pages 2017-2029, December 1986.

Degradation

- ◆ Degradation eliminates contaminant mass
- ◆ Biotic and abiotic
- ◆ Degradation rates dependent on
 - » Presence, health of relevant organisms
 - » Redox conditions (electron acceptors)
 - » Nutrient availability
 - » Nature of contaminant
 - » Combinations of contaminants (cometabolism, enzyme induction, toxicity effects)
- ◆ Progeny may be more toxic, mobile, and recalcitrant than parent compound
- ◆ All conditions vary spatially in 3-D



Dehalococcoides sp.



Löffler et al., 2012

2-52

- Main Idea** • *Degradation destroys the mass but can result in breakdown products that are more toxic and mobile.*

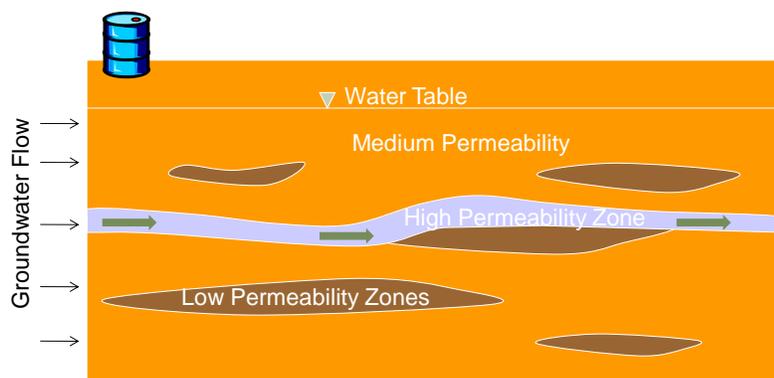


- Notes** ◆ Degradation, either biotic or abiotic is the only process that actually eliminates mass. Degradation rates are dependent on many things, all of which are highly spatially variable.



Source-Plume Evolution: Pre-Release

Remember, groundwater flux is dominant in high-permeability (k) zones
Groundwater velocity in high-k zones \gg average value



Thin sand bed with DNAPL

Highly simplified illustration of heterogeneous geology



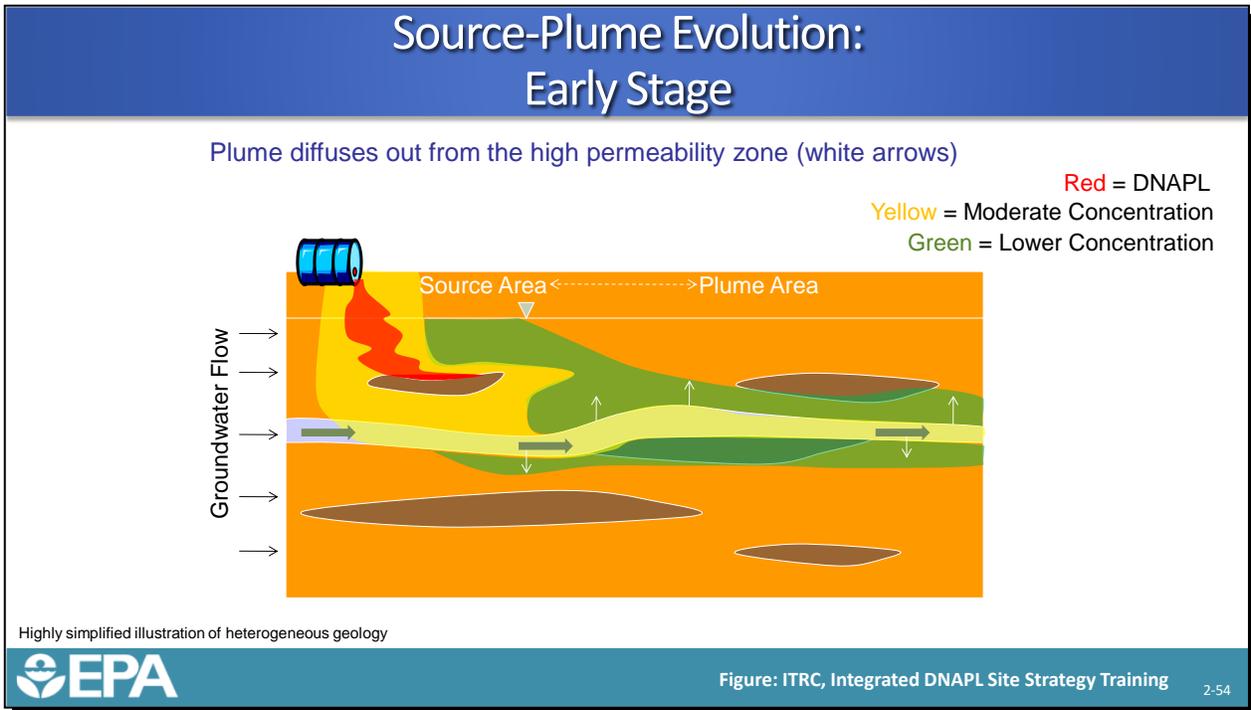
Figure: ITRC, Integrated DNAPL Site Strategy Training
Photos: Courtesy of Beth Parker

2-53

Notes

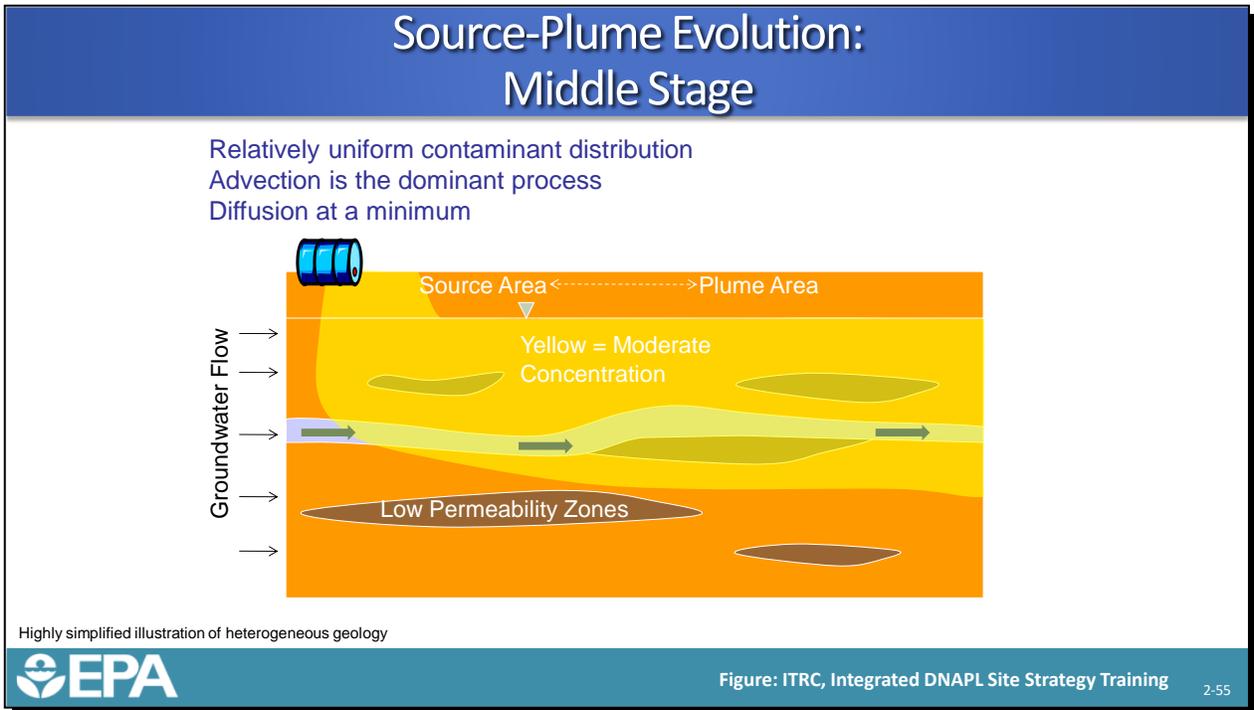


- ◆ This slide shows a simplified illustration of heterogeneous geology in an unconsolidated environment. In this example, the lavender zone is highly permeable compared to the orange zone and the brown zones. The groundwater velocity in the highly permeability zone is much greater than the average value for the system as a whole.
- ◆ The high conductivity zone can be very small and still transport large mass of contaminants. The two photos in the upper right show a core with a very thin zone of sand just a few millimeters thick that is transporting DNAPL (dyed red). In this example from a controlled release test at CFB Borden, the DNAPL escaped from the confined test cell via vertical fractures in the confining clay and very thin sand beds that allowed horizontal transport.



Notes

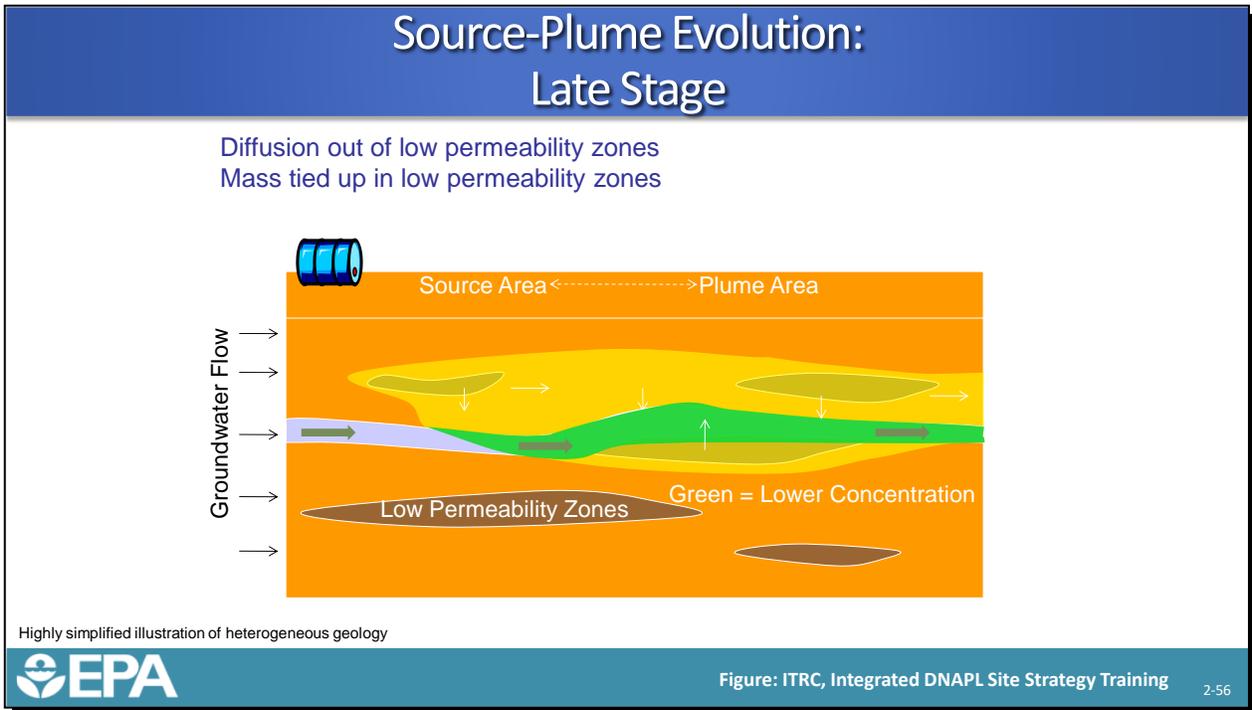
- ◆ This slide depicts a DNAPL release in the early stage. In most circumstances, sites have progressed beyond the early stage by the time an environmental investigation is initiated. However, early stage is important to understand as the starting point. The dominant process in the early stage is diffusion of contaminants from high to low concentration out of the high permeability zone.



Notes



- ◆ In the middle stage, the dominant process has relatively uniform contaminant distribution with diffusion at a minimum.



Notes



- ◆ The dominant process in the late stage is characterized by diffusion of contaminants out of the low permeability zones, with contaminant mass tied up in the low permeability zones.

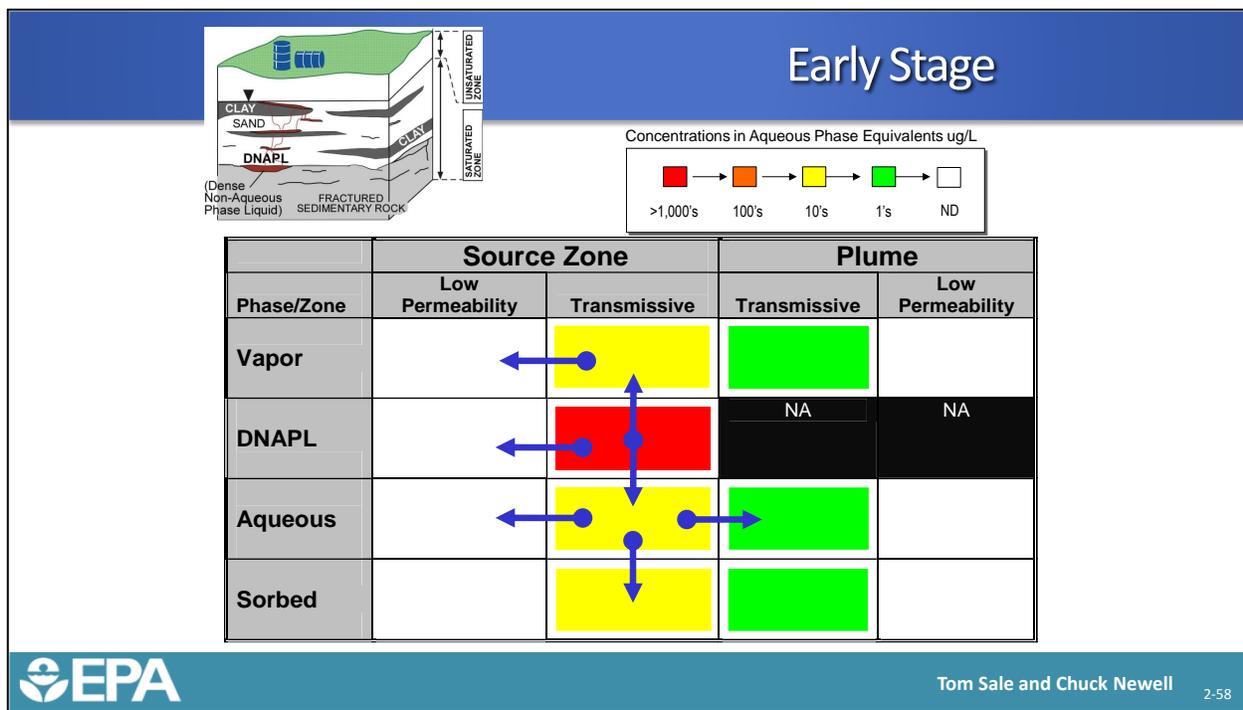
Participant Poll

◆ **Most of the groundwater sites I have been involved with have:**

- A. An early stage plume
- B. A middle stage plume
- C. A late stage plume



2-57



Main Idea • The next few slides present a model of contaminant movement from the source to downgradient areas for each phase and porosity type.



Notes ♦ This series of slides focuses on mass distribution of contamination over time. This conceptual modeling tool was developed by Chuck Newell at GSI and Tom Sale at Colorado State University. The scheme is known as the 14-compartment model and it illustrates 17 different fluxes that may be relevant at a particular site.



This scheme divides the site up into 1) a source zone and 2) a dissolved plume.

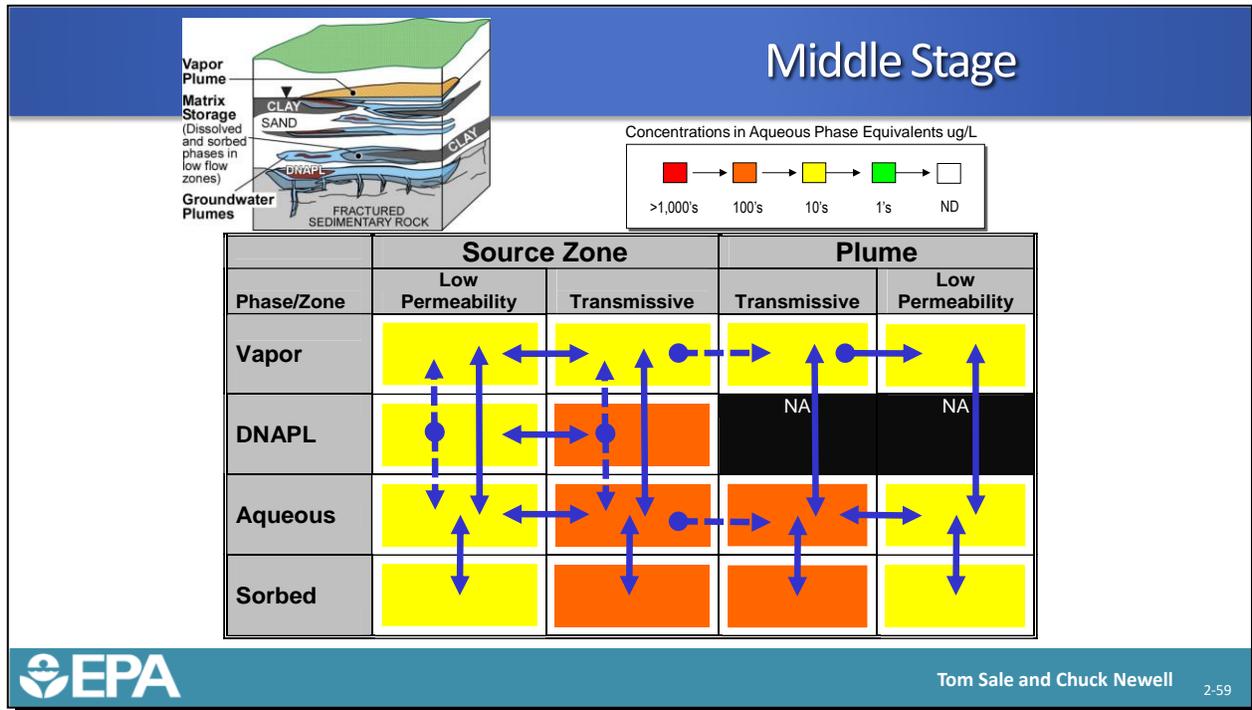
Each of these zones is divided into portions characterized by high permeability and low permeability zones. On the vertical axis the contaminants are shown as existing in either vapor, DNAPL, aqueous phases or sorbed.

Because by definition there cannot be DNAPL outside of the source area, there are 14 compartments rather than 16.

In this early stage diagram, DNAPL has entered the permeable portions of the source area and has dissolved at high concentrations into groundwater in the permeable portions of the source area and is diffusing into the low permeability zones in the source area. Similarly volatilization from the NAPL has resulted in high concentrations in the high permeability portions of the vadose zone and diffusion into the low permeability zones. At this point the dissolved plume only exists in the permeable zone.

It is rare these days to see a site in the early stages of DNAPL release.

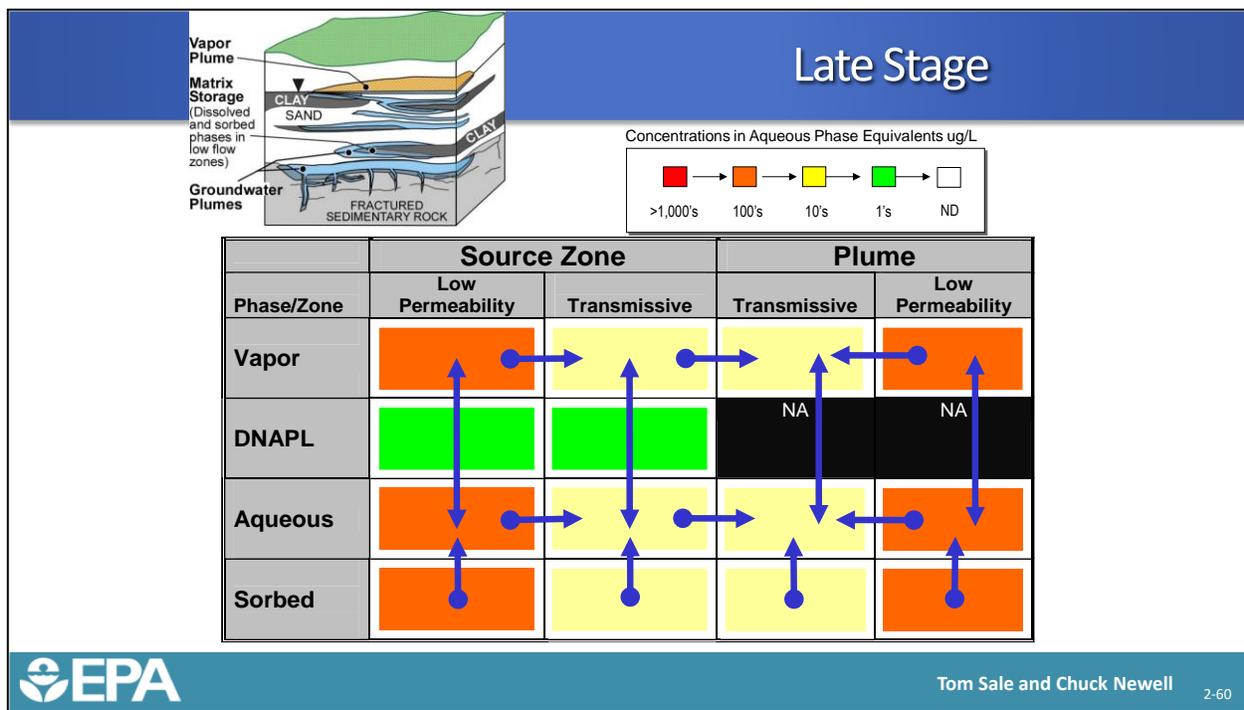
Source: Sale, Tom and Charles Newell, 2011. *A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents*. ESTCP Project ER-200530.



Notes

- ◆ By the middle stage, DNAPL has entered the low permeability portions of the source zone. Mass flux is occurring back and forth between high and low permeability zones by diffusion as vapor and solutes. DNAPL continues to provide mass in both aqueous and vapor phases. In the plume zone there are high concentrations of vapor, solutes and sorbed contaminants in the transmissive parts of the plume. Relatively little mass in any phase is present in the low permeability zones in the plume area.
- ◆ Dashed lines indicate irreversible fluxes.

Source: Sale, Tom and Charles Newell, 2011. [A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents](#). ESTCP Project ER-200530.



Notes



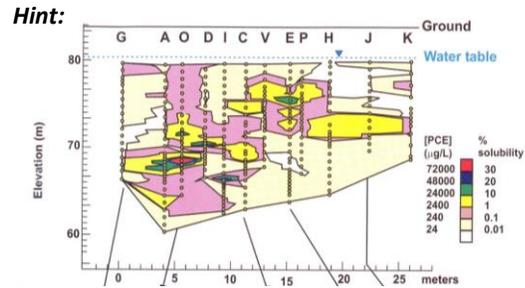
- ◆ By the late stage, the DNAPL is gone from the source zone, having dissolved and volatilized away. Concentrations of all phases of contaminants in the transmissive portions of the source zone have declined. High concentrations and significant mass remain in the low permeability portions of the source zone. Concentrations in the plume region have declined but remain above cleanup levels (Safe Drinking Water Act maximum contaminant levels).

Source: Sale, Tom and Charles Newell, 2011. A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents. ESTCP Project ER-200530.

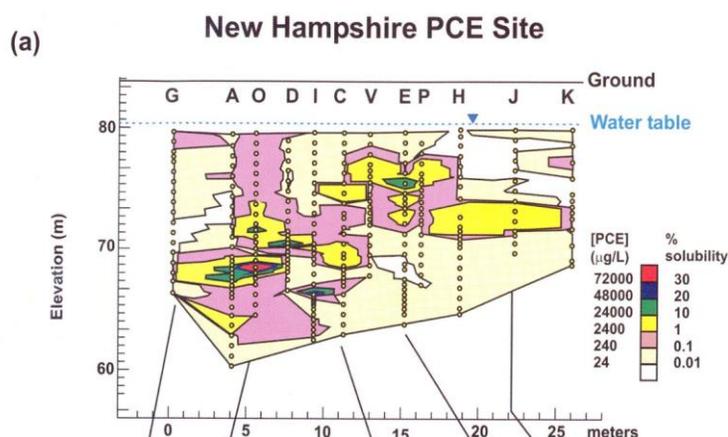
Test Your Knowledge

◆ **Most of the contaminant mass discharges through...**

- » 1% - 5% of the plume cross sectional area
- » 5% - 10% of the plume cross sectional area
- » 20% - 50% of the plume cross sectional area
- » 50% - 75% of the plume cross sectional area
- » None of the above



Mass Flux Distribution



75% of mass discharge occurs through 5% to 10% of the plume cross sectional area

Optimal Spacing is ~0.5 m



Guilbeault et al., 2005

2-62

- Main Idea** • *This is one of the most important concepts in this course! Most mass discharge occurs in a small percentage of the area of the plume, with profound implications on site strategy.*



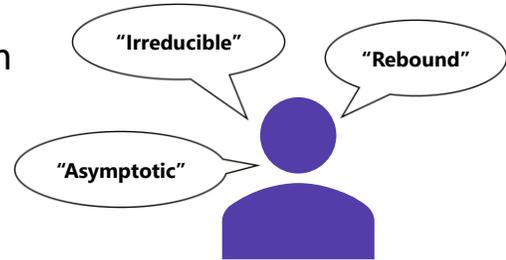
Notes



- ◆ Martin Guilbeault, Beth Parker and John Cherry were the first to report (at least in a peer reviewed format) the finding that the vast majority of contaminant mass discharge occurs through a very small percentage of the overall cross sectional area of the plume. This is a logical consequence of the weak nature of transverse hydrodynamic dispersion and the discrete and complex distribution of many source materials (particularly DNAPLs).
- ◆ Guilbeault et al. (2005) used very closely (15 cm) spaced groundwater samples to define the solute distributions at three sites around North America. The finding that 75% of the mass discharge occurs through only 5 to 10% of the plume cross sectional area has profound implications for how sites need to be investigated and how remedies need to be focused.
- ◆ The authors also found that the optimal vertical sample spacing based on their work at the three sites was approximately 45 cm. This is a very close spacing and the cost of investigating sites by collecting and analyzing samples at such a close spacing would be prohibitive. This issue can be overcome through the use of collaborative data (e.g., screening with a MIP or LIF) followed by targeted sampling at the required spacing only in key portions of the profile (and plume). The use of onsite labs can also reduce the amount of sampling required by providing near real-time feedback on the spatial structure of contaminant distributions (in particular, when you are sampling outside of the 5% to 10% of the cross sectional area through which the vast majority of the flux occurs.)

What is Back Diffusion?

- ◆ **Slow release of contaminants stored in lower K zones (dissolved and sorbed phase) back to higher K zones**
- ◆ **Occurs when concentrations at interfaces between high-low K zones decline**
 - » natural source depletion
 - » Source and plume zone remediation
- ◆ **Can be primary cause of long-term plume persistence IF source is isolated or remediated**



2-63

- Main Idea** • *This process serves as a long-term secondary source of contamination.*



Notes



- ◆ The term “back diffusion” refers to the movement of contaminant mass out of low permeability units into higher permeability units by diffusion. Referring back to the concept of dual porosity systems that was discussed earlier, and the 14-compartment model time series that was presented, the immobile porosity of the low permeability zones serves as a sink or storage area for contaminant mass during early stages of the plume life. Large amounts of contaminant mass diffuse into this immobile porosity when concentrations are high in the permeable zones. It is the diffusion of this mass stored in the immobile porosity back out into the mobile porosity that is referred to as back diffusion. Unfortunately, these secondary sources of contamination are not limited to the original source area but are found throughout the entire footprint of the plume.

Source: Steve Chapman – G360 Centre for Applied Groundwater Research, University of Guelph.

Advection, Diffusion, and Back Diffusion Video

<https://www.youtube.com/watch?v=6GI3IFJGzL0&feature=youtu.be>



2-64

Questions on Contaminant Fate and Transport?



2-65

Fractured Rock

- Definitions
- Diversity of fractured rock aquifers
- Contaminant flux in fractured rock

2-66

Participant Poll

◆ **I have worked on a fractured rock site:**

- » Yes
- » No



2-67

What is Fractured Rock?

◆ In bedrock, groundwater can flow through:

- » The original pore space (primary porosity)
- » Fractures (secondary porosity)



Limestone Outcrop with water in fractures - Short, 2011



2-68

- Main Idea** • *Groundwater flow and the fate and transport of contaminants in fractured rock are influenced by the characteristics of the rock and thus differ from unconsolidated deposits.*



Notes



- ◆ Due to the differences, approaches to characterizing and remediating unconsolidated deposits may prove unsuccessful in a fractured rock environment.
- ◆ Groundwater can flow through both primary porosity (also called "matrix porosity") and secondary porosity.
 - » Primary porosity, the air-filled voids present when a rock forms (e.g., pore spaces between sand grains in a poorly cemented sandstone), is a function of the rock's texture.
 - » Secondary porosity develops after the rock has formed, either by fracturing or dissolution, such as the solution channels and cavities found in karst limestone.

Types of Fractures

- ◆ **Fractures include faults, joints, bedding planes**
- ◆ **Chemical and/or physical processes can change the size of fractures**
 - » Karst – dissolution widens fractures and bedding planes
 - » Fractures can be filled with secondary minerals (calcite, quartz)



Fractured sandstone - Bentkowski



2-69

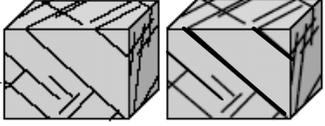
Notes



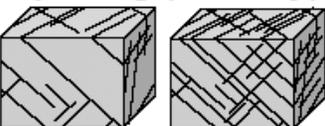
- ◆ There are several types of fractures:
 - » Faults: A planar fracture because of rock-mass movement
 - » Joints: A planar fracture without shear displacement
 - » Bedding planes: A planar surface that visibly separates layers of rock. It often marks a change in the circumstances of deposition, though they can form in layered metamorphic rocks like schist.
- ◆ Chemical and/or physical processes can change the size of fractures.
 - » Chemical: An example is dissolution widening fractures and bedding planes in karst
 - » Physical: An example is when fractures are filled with secondary minerals like calcite or quartz.

Factors Governing Flow in Fractured Media

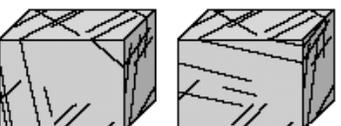
Aperture



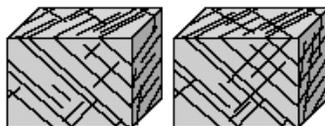
Spacing (Density)



Orientation



Connectivity



The Cubic Law relates fracture flow to fracture aperture: $q = cb^3$

Where: q = flowrate
 b = fracture aperture
 c = parameter incorporating hydraulic gradient


2-70

Main Idea



- Groundwater flow in fractures is dependent on the characteristics of the fractures, including their width, density, orientation and how well connected they are.

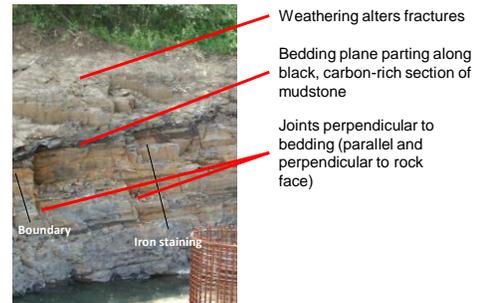
Notes



- ◆ Groundwater flow in fractured rock is different than the Darcy-type flow in porous media that we have discussed so far. The most important variables in fractured rock are (1) the aperture (or width of the opening of the fracture), (2) the spacing of the fractures, (3) the degree of connection of the fractures with one another, and (4) the orientation of the fractures. In fracture the hydraulic conductivity is a function of the aperture of the fracture and as with all hydraulic conductivity it is also a function of the density and viscosity of the fluid involved. The relationship of the hydraulic conductivity to the aperture is called the cubic law.

Challenges with Fractured Bedrock

- ◆ Diversity of fractured rock aquifers
- ◆ Abrupt changes in hydraulic properties
 - » Spatial
 - » Depth
- ◆ Complex fracture connectivity



Lockatong Mudstone, NJ



2-71

- Main Idea** • *There are a wide range of properties that affect flow in fractured rock aquifers and a high degree of heterogeneity.*

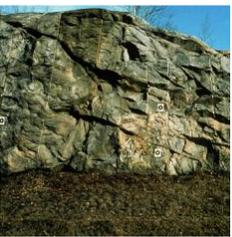


Notes



- ◆ In fractured rock hydraulic properties can change over very short horizontal or vertical distances.
 - Rock types change across short distances because of the way they were formed. In ancient river or coastal settings, sand lenses may be only a few feet thick or wide or may grade into silts and clays over just a few feet. In volcanic rocks layers or vertical zones of lava may cut through older rocks.
 - Fractures are not evenly distributed within the rocks and can occur as widely spaced individual fractures or concentrated groups of fractures. The unfractured rock will have lower hydraulic conductivity than the adjacent fractured areas
- ◆ The interconnection of fractures is very complex and is usually not able to be mapped on a fine scale, nor is it necessary in most cases.

Diversity of Fractured Rock Aquifers:

Primary Porosity	<p><i>Granite and schist, Mirror Lake Watershed Grafton County, NH</i></p>  <p>Iron-hydroxide precipitate staining the rock matrix (primary/intrinsic rock porosity)</p>	<p><i>Lockatong Mudstone, Newark Basin West Trenton, NJ</i></p>  <p>Residual wetting of rock core (primary/intrinsic rock porosity)</p>
Secondary Porosity	 <p>Fault zone exposed on a road cut</p>  <p>Fractures exposed on a road cut (fracture porosity)</p>	 <p>Fractures parallel and perpendicular to bedding (fracture porosity)</p>





2-72

- Main Idea** • *The diversity of rock aquifers -depending on geology and porosity - has a large effect on contaminant fate and transport.*

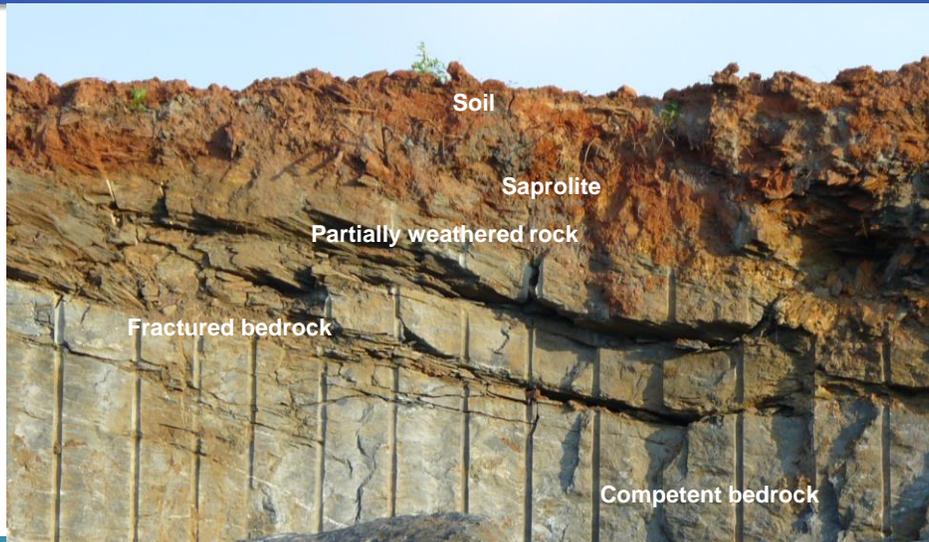


Notes



- ◆ Over the next several slides you should gain an appreciation of why the fractured rock environment should be viewed in high resolution. These slides were developed by Alan Shapiro with the USGS and utilize both an igneous/metamorphic rock environment and a sedimentary rock environment to illustrate the diversity of fractured rock.
- ◆ On the left are photos of the granite and schist at Mirror Lake, New Hampshire and on the right are photos from the sedimentary rock in the Newark Basin, New Jersey.
- ◆ Top photos show primary or intrinsic porosity which is the porosity of the rock that developed at the time of its deposition or formation.
- ◆ Secondary porosity develops after deposition/formation of the rock. It includes fracture and fault zone porosity as well as voids/spaces in carbonate rocks created by the chemical process of leaching, i.e. karst.

Vertical Diversity in Bedrock Sequences



2-73

Notes



- ◆ This picture shows the complexity of bedrock with several layers:
 - » Soil - plants, roots, soil horizons developed.
 - » Saprolite – nearly completely weathered rock that retains some of the texture of the parent rock.
 - » Partially weathered rock with interstitial space for water flow.
 - » Fractured Bedrock – with potential porous storage space for groundwater flow and contaminant transport
 - » And unweathered bedrock, with virtually no porosity other than a very occasional fracture, so nearly no groundwater can flow.
- ◆ Matter of scale: This photo shows this sequence in an outcrop of about 20' thickness, but it could just as well be 200' thick. Usually, each zone is a transition, different for each site. The depth of weathering often depends upon the mineral composition of the parent rock and the amount of groundwater moving through the system. The fractures can be a result of regional tectonics, but horizontal stress relief fractures which are a first phase of weathering the bedrock. Consult your local Hydro to understand the regional geologic framework.

Abrupt spatial changes in hydraulic properties

Expect both vertical and horizontal variability. . .

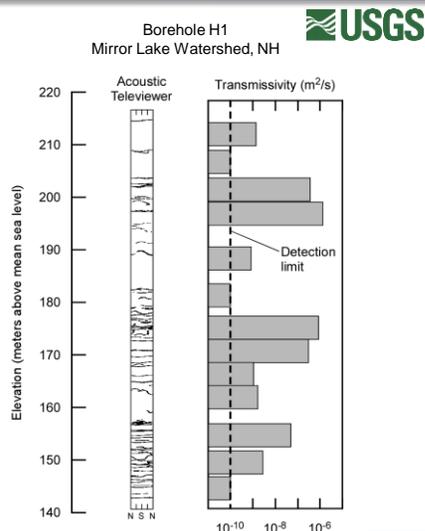
Schist: fewer fractures;
longer, undulating fracture
surfaces



Granite and schist, Mirror Lake Watershed
Grafton County, New Hampshire

Granite: higher
fracture density;
shorter, more
planar fractures

**K of the matrix is orders of magnitude
less than that of fractures**



Shapiro and Hsieh, 1998; Shapiro et al., 2007

2-74

- Main Idea** • *Low resolution investigation of fractured rock may miss the abrupt spatial changes in hydraulic properties of the rock.*



Notes



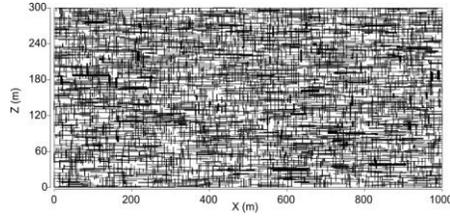
- ◆ Expect both vertical and horizontal variability.
- ◆ The hydraulic conductivity (K) of the rock matrix is order of magnitudes less than the fractures.
- ◆ As illustrated in the log on the right, the transmissivity of distinct intervals in the rock column changes abruptly.

Test Your Knowledge

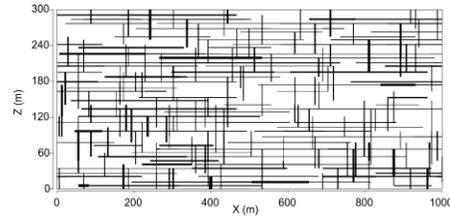
◆ In which network would you expect contaminants to travel the farthest?

- A. Dense network
- B. Sparse network

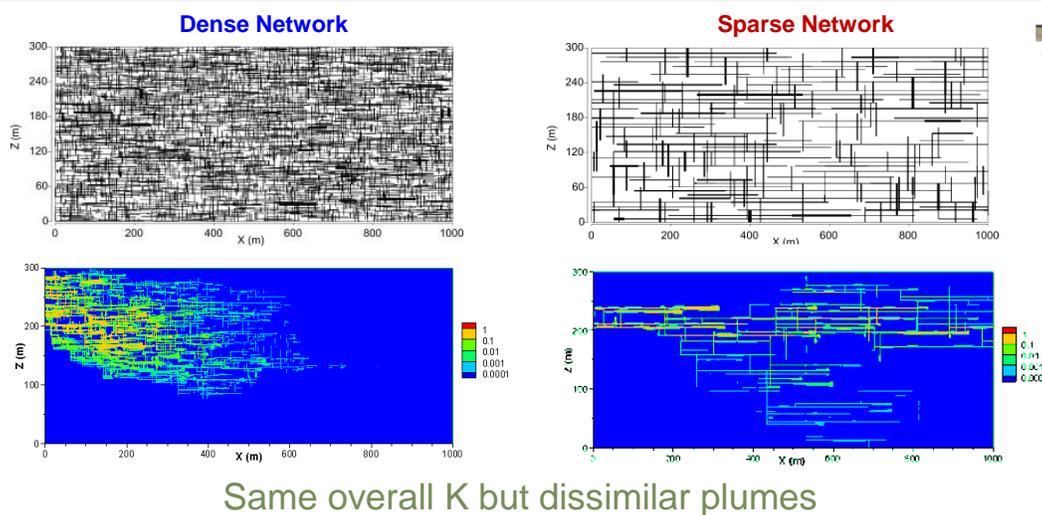
Dense:



Sparse:



Interplay Between Matrix & Fractures Controls Plume Behavior



2-76

- Main Idea** • *The connectivity of fractures determines how actively they are in transmitting water. Contamination travels farther in the sparse network and the contamination is not as densely packed.*

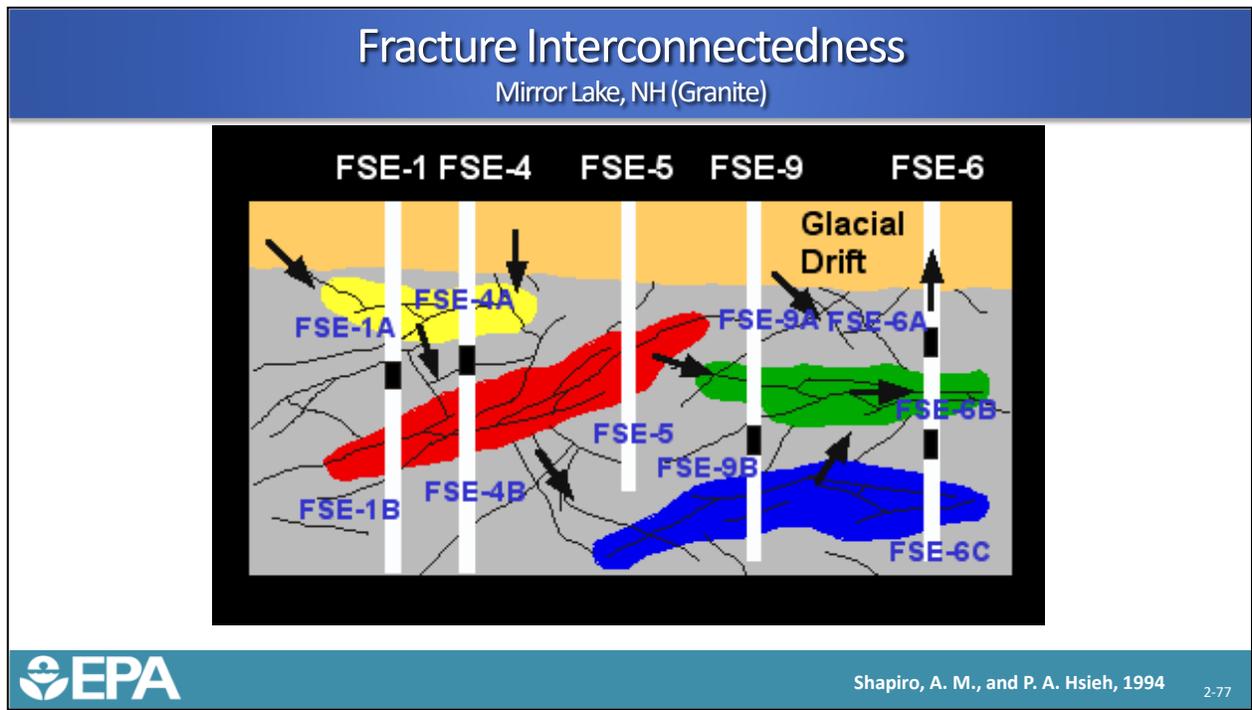


Notes



- ◆ The dense network of well-connected fractures results in the distribution of concentrations shown 50 years after a release.
 - » The plume has migrated approximately 600 meters from the source.
 - » The large number of fractures and narrow apertures result in low velocity and relatively high surface area for diffusion of solutes from the fractures into the matrix porosity.
 - » This diffusion into the matrix results in retardation of the plume advance.
- ◆ In the sparse network, the same source results in a plume that has migrated all the way through the 1000-meter domain in 50 years.
 - » Large aperture fractures result in high velocity and relatively low surface area for diffusion of solutes from the fractures into the matrix porosity.
 - » Low retardation.

Source: Parker, Beth L. Investigating Contaminated Sites on Fractured Rock using the DFN Approach. In: Proceedings of the 2007 U.S. EPA/NGWA Fractured Rock Conference: State of the Science and Measuring Success in Remediation, September 24-26. Portland, Maine.

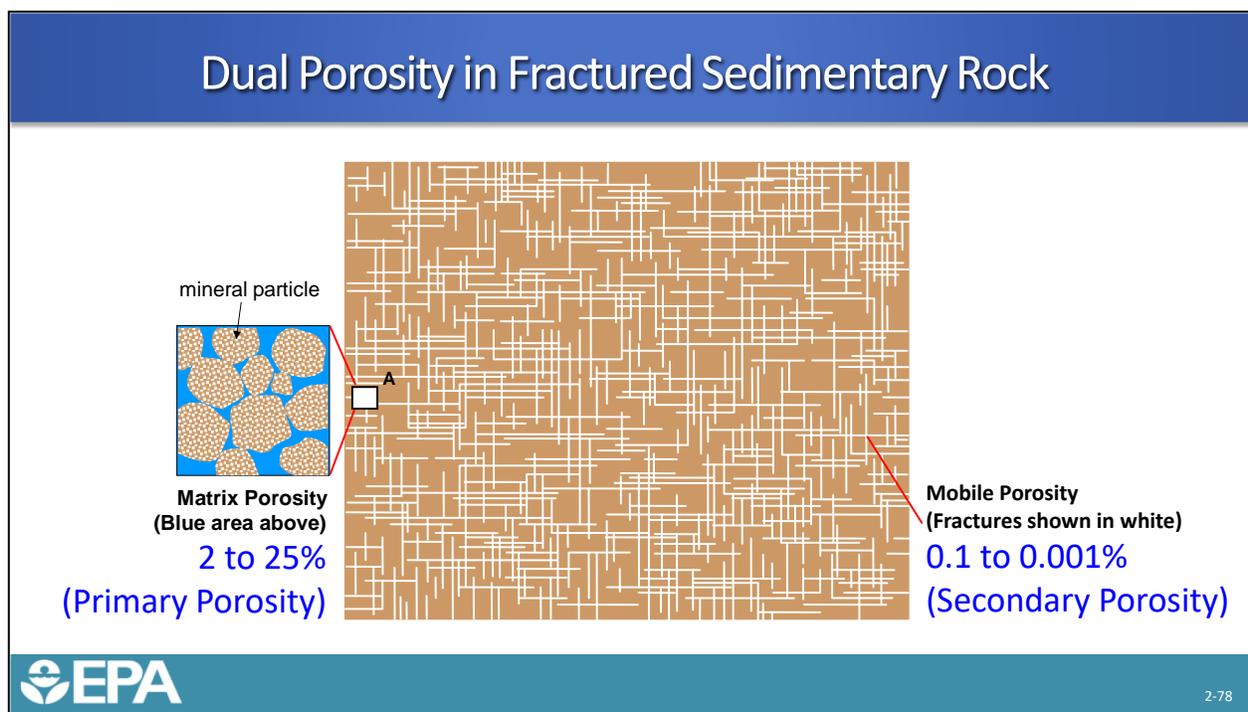


Notes



- ◆ An extensive study of fractured granite by the USGS at their experimental site in Mirror Lake, NH resulted in a finding that the flow system was dominated by several zones in which fractures were well interconnected, but that the connections between these zones were not so good. Overall flow was governed by the bottlenecks between the well-connected zones.

Source: Shapiro, A. M. and P. A. Hsieh. 1994. Overview of research at the Mirror Lake site: use of hydrologic, geophysical and geochemical methods to characterize flow and transport in fractured rock. In U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Colorado Springs, Colorado, September 20-24, 1993, D.W. Morganwalp and D.A. eds. USGS Water Resources Investigation Report 94-4015, U.S. Geological Survey, Reston, VA.



- Main Idea** • *While most groundwater flows through fractures, the matrix porosity provides much more storage capacity.*

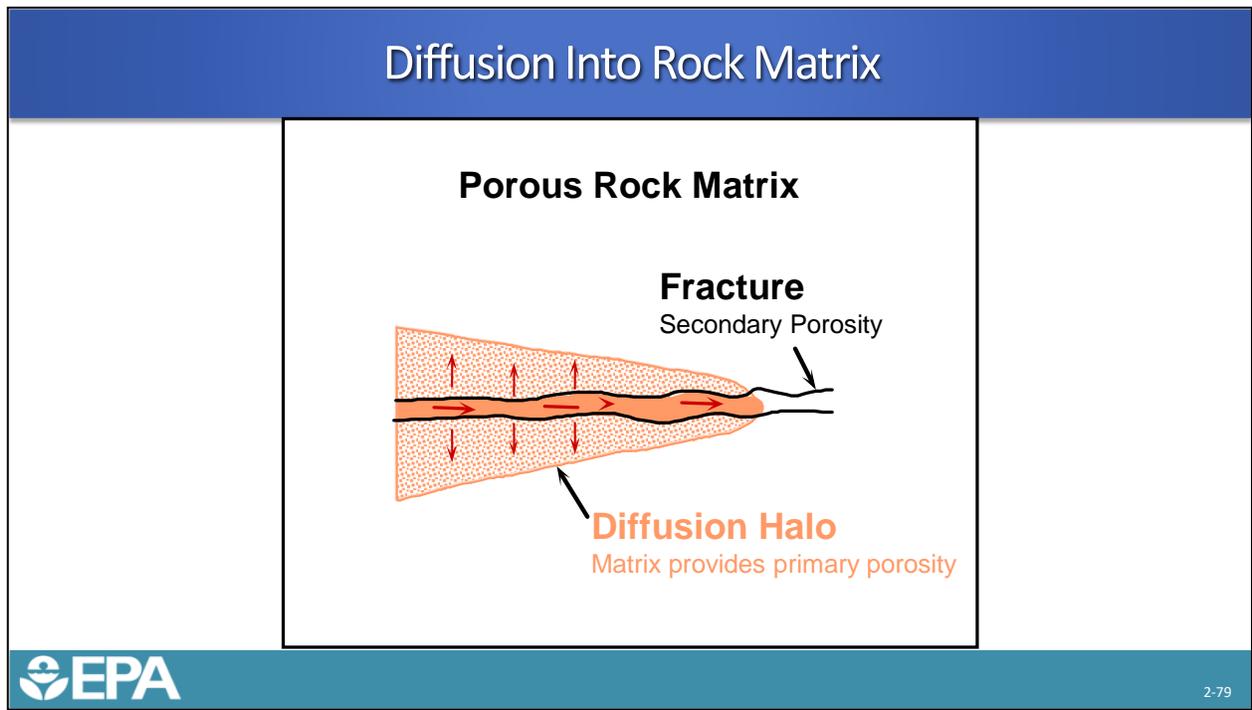


Notes



- ◆ In fractured porous media, such as sedimentary rocks, the fractures represent the mobile porosity and the rock itself, or the matrix (as it is often called) is the immobile porosity. The matrix porosity is called the primary porosity and the fractures are called the secondary porosity. In fractured sedimentary rock essentially all the flow occurs in the fractures, but the secondary porosity is very small in these systems, ranging from 0.1 to 0.001%. The matrix (primary) porosity is quite large in comparison ranging from perhaps 2% to 25%. This primary porosity represents a very large storage volume for solutes.

Diagrams from Professor Beth L. Parker, University of Guelph G360 - Centre for Applied Groundwater Research.



Main Idea • *Diffusion halos are caused by plume retardation.*

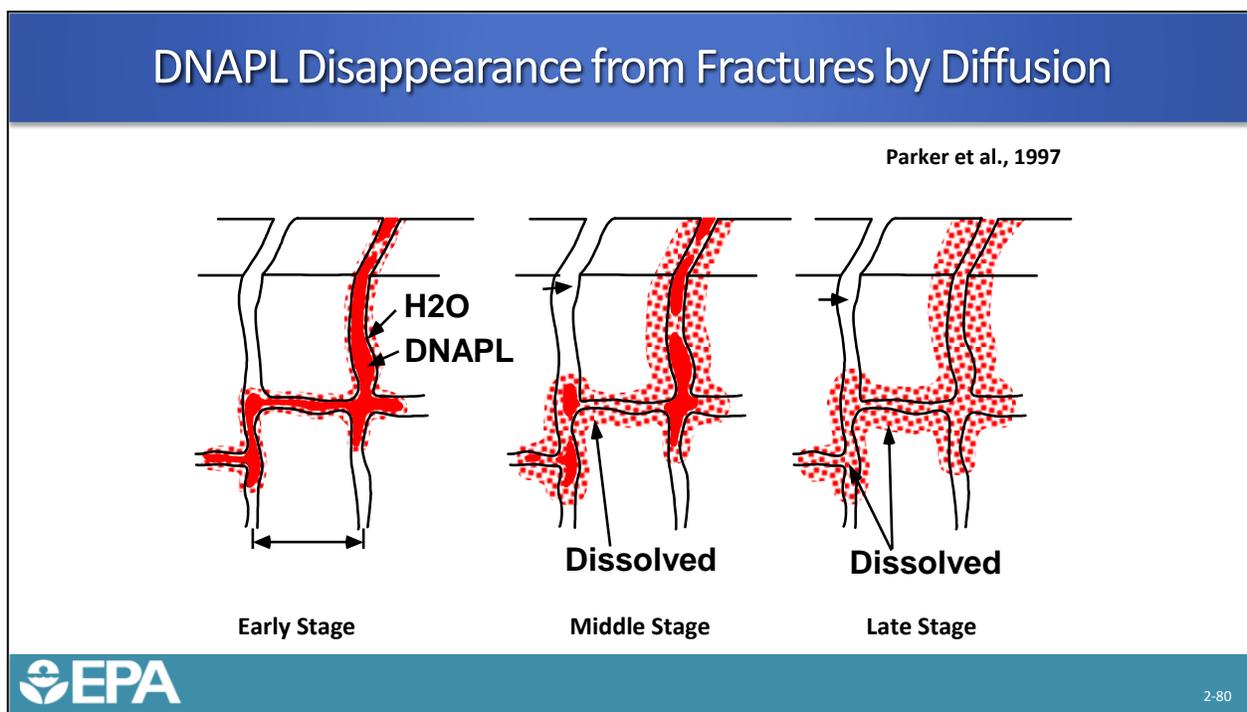


Notes



- ◆ As shown in this diagram by Beth Parker, in fracture sedimentary rock solutes migrating along a fracture set up a concentration gradient between the high concentrations in the fracture and the lower (initially zero) concentrations in the primary (immobile) porosity. Contaminant mass moves into the primary porosity by diffusion, removing mass from transport and causing retardation of the plume front. A halo of contaminant concentrations in the matrix around the fracture develops.

Source: Parker, Beth L. Robert W. Gillham and John A. Cherry 1994. Diffusive Disappearance of Immiscible Phase Organic Liquids in Fractured Geologic Media. Groundwater Volume 32, No. 5.



- Main Idea** • *The time it takes to remove NAPL is not consistent, but instead depends on many factors.*

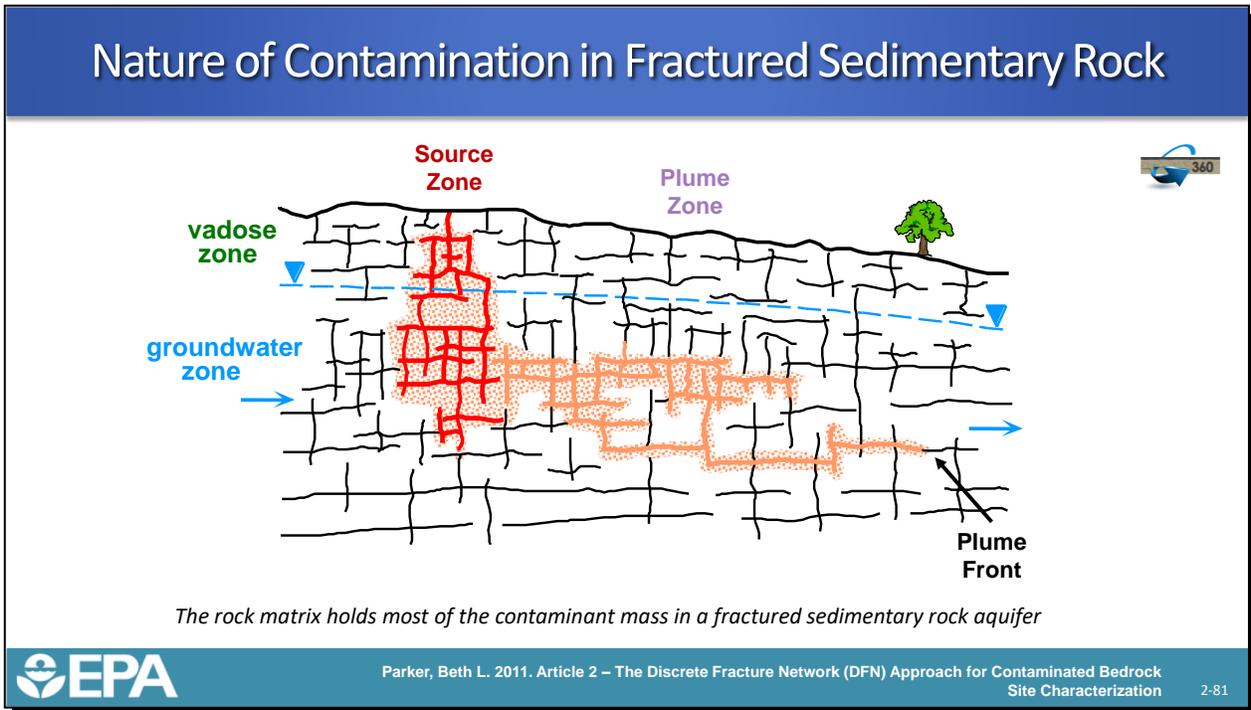


Notes



- ◆ The time for disappearance of stationary, single-component immiscible-phase liquid (NAPL) from planar fractures
 - » due to dissolution and subsequent diffusion
 - » is directly dependent on the ratio of mass storage capacity of dissolved and sorbed contaminant in the matrix to the initial storage capacity for immiscible-phase liquid in the fractures.
 - » A ratio greater than one indicates the number of times the fracture void volume can be completely replenished with the immiscible phase before disappearance ceases.
 - » However, each successive fracture replenishment requires longer time for disappearance due to consumption of part of the matrix storage capacity caused by previous fracture loadings.

Source: Parker, Beth L., David B. McWhorter and John A. Cherry. 1997. Diffusive Loss of Non-Aqueous Phase Organic Solvents from idealized Fracture Networks in Geologic Media. *Groundwater*. Volume 35, No. 6.



Notes



- ◆ The figure above shows that the rock matrix holds most of the contaminant mass in a fractured sedimentary rock aquifer.

Parker, Beth L. 2011. Article 2 – The Discrete Fracture Network (DFN) Approach for Contaminated Bedrock Site Characterization. Center for Applied Groundwater Research. April.

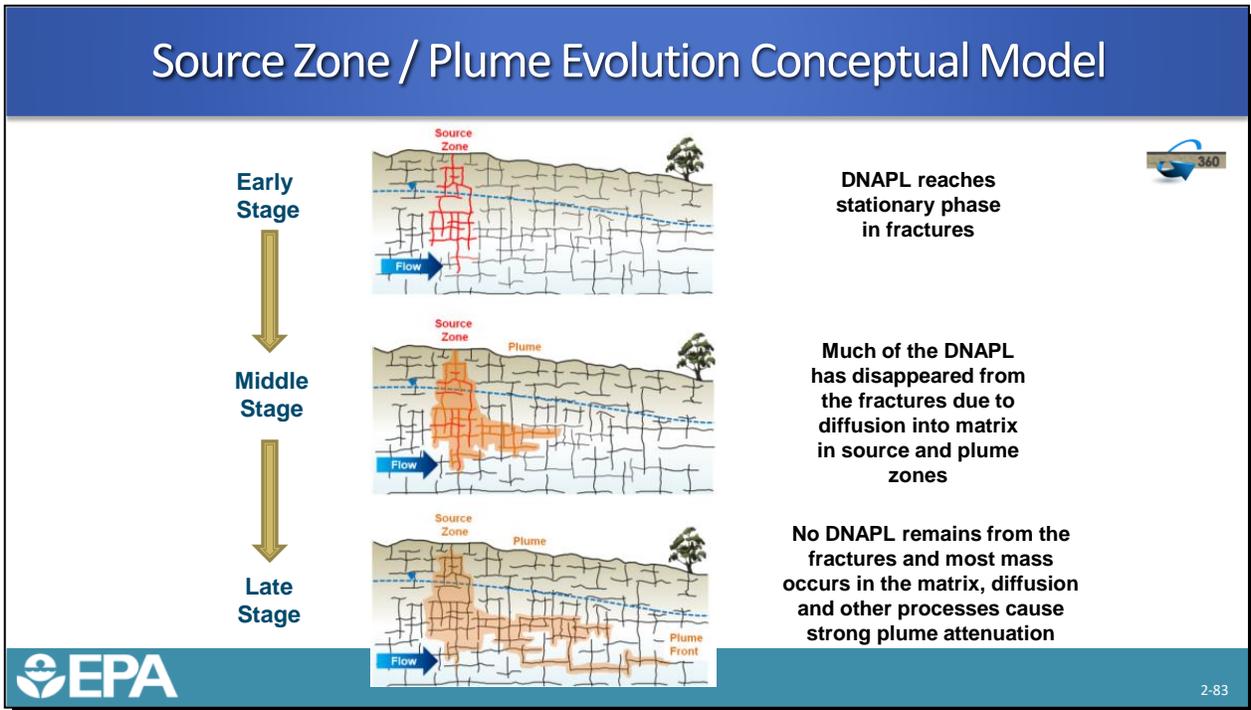
Test Your Knowledge

◆ **True or False: In the late stages of a plume, DNAPL can “disappear” in the matrix.**

- » True
- » False



2-82



Main Idea • *DNAPL moves downward via fractures first before diffusing laterally.*



Notes



- ◆ Early in plume evolution: DNAPL reaches stationary phase in fractures prior to lateral diffusion.
- ◆ Intermediate plume evolution: Much DNAPL disappeared from source zone as it diffuses into the matrix in the source and plume zones.
- ◆ Late in plume evolution: No DNAPL remains in the stationary phase and most mass occurs in the matrix, diffusion and other process cause strong plume attenuation
- ◆ Source: Beth Parker

Approaching Fractured Rock Aquifers



◆ How do we approach this level of complexity for site- and regional-scale investigations?

- » Identify lithologic and geomechanical controls on fracturing
- » Identify most permeable features and barriers to groundwater flow over relevant dimensions
- » Identify spatial connectivity of permeable features
- » Note: Mapping and characterization of every fracture is not warranted or required

◆ What are our goals?

- » Identify the extent of aqueous-phase contaminant movement
- » Design groundwater containment to prevent further contaminant migration
- » Design “source area” remediation



2-84

Main Idea • This slide presents an approach to data collection for fracture investigations.



Notes



- ◆ How do we approach this level of complexity for site – and regional – scale investigations?
 - » Identify lithologic and geomechanical controls on fracturing
 - » Identify most permeable features and barriers to groundwater flow over relevant dimensions
 - » Identify spatial connectivity of permeable features
 - » Note: Mapping and characterization of every fracture is not warranted/required
- ◆ What are the goals of fractured rock characterization?
 - » Identify the extents of aqueous-phase contaminant movement...
 - » Design groundwater containment to prevent further contaminant migration...
 - » Design “source area” remediation...
 - » Modules 4 and 5 will explore some tools and techniques for characterizing and analyzing contamination in fractured rock aquifers.

Questions on Fractured Rock?



In Review

- ◆ **Subsurface factors that affect groundwater flow vary widely over short vertical and horizontal distances**
- ◆ **Contaminant fate and transport is sensitive to hydrogeological variations**
- ◆ **DNAPL presents a particularly difficult challenge**
- ◆ **Both unconsolidated and fractured rock aquifers are very heterogeneous and vary greatly over small scales**

Questions on Module 2?

