Characterizing the Fate, Transport, and Remediation of Contaminants in Fractured Rock Aquifers

Allen M. Shapiro, USGS

USEPA-USGS Fractured Rock Workshop

EPA Region 10

September 11-12, 2019

Fate, Transport, and Remediation of Contaminants in Fractured Rock

Note: *This is a “DNAPL” and “chlorinated solvent” focused discussion. . .*

- Concepts and discussion can be extended to other Dense Non-Aqueous Phase Liquids (DNAPLs). . .

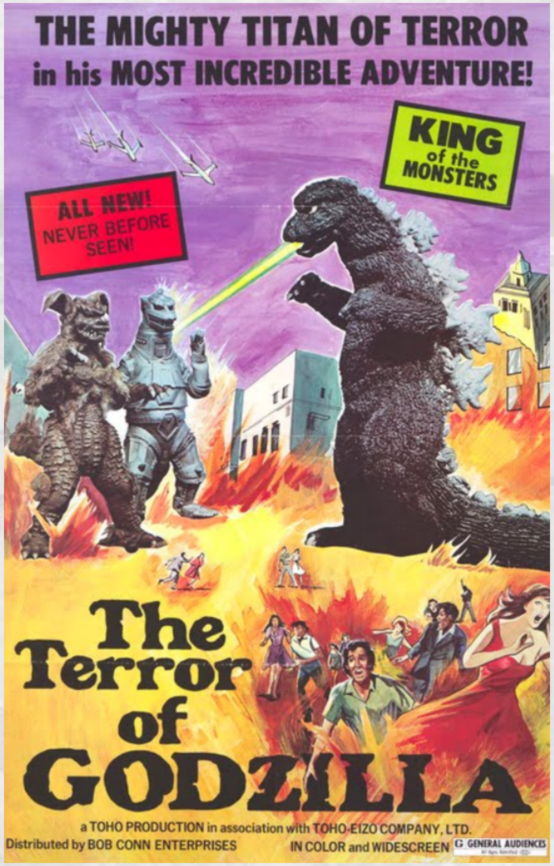
DNAPL	Density (kg/m^3)	Viscosity (cP)
Creosote compounds (e.g., naphthalene)	1,010 – 1,130	20 – 50
Coal tars	1,010 – 1,100	20-100
Polychlorinated Biphenyls (PCBs)	1,100 – 1,500	10 – 50
Chlorinated solvents (e.g., PCE, TCE, carbon tetrachloride)	1,100 – 1,600	0.57 – 1.0

- Aqueous-phase organic contaminants demonstrate “chemical processes” similar to other contaminants of interest. . . e.g., diffusion, sorption, abiotic and biotic degradation pathways

DNAPLs are scary. . . .

- DNAPL – Dense Non-Aqueous Phase Liquid
- Immiscible liquid, density > water, poorly soluble in water
- Common DNAPLs – Creosote, coal tar, PCB oils, chlorinated solvents, mercury
- Fluid properties (density, viscosity, interfacial tension, etc.) vary among DNAPLs. . .resulting in different characteristic behaviors in the subsurface. . .
- Density – mass per unit volume (e.g., units of gm/cm^3 or kg/m^3). . .density of water at 4^{o}C is 1,000 kg/m^3. . .DNAPL density varies from 1030 kg/m^3 to 1,700 kg/m^3
- Viscosity (dynamic) – measure of resistance to fluid flow. . . viscosity of water is 1.5 centipoise (cP) (5^{o}C) and 1.0 cP (20^{o}C). . some DNAPLs have viscosity > water, others have viscosity < water. . .leading to different time frames for DNAPL stabilization. . .viscosity of chlorinated solvents 0.57 – 1.0 cP

Why is this important? – *Identifying the basic properties of NAPL mixtures is critical in (1) hypothesizing the spatial extent of contaminant distribution in the subsurface, and (2) designing remediation technologies that rely on altering NAPL properties for mobilization and collection.*



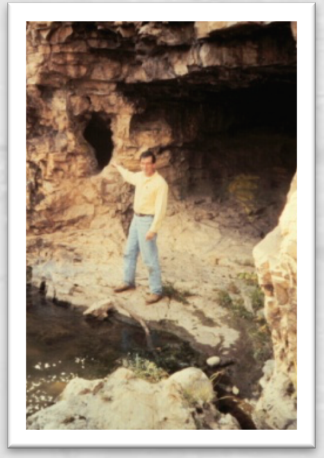
The Terror of Godzilla (1975)

. . .coupled with fractured rock. . .could lead to the "ultimate" in hydrogeologic disaster. . .

Granite and schist, Mirror Lake, NH

Sykesville Gneiss, Washington, DC

Silurian Dolomite, Argonne, IL

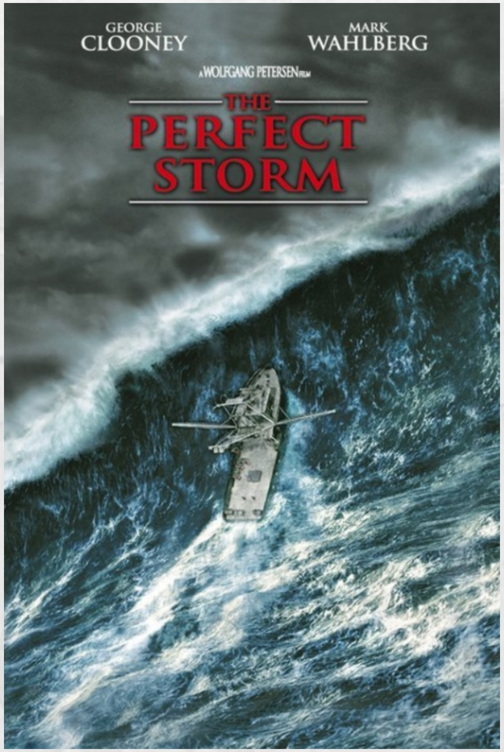


Madison Limestone, Rapid City, SD

Biscayne Limestone, Ft. Lauderdale, FL

Tonalite, Washington, DC

The Perfect Storm (2000)



<u>Chlorinated solvents</u> ($\rho_{TCE} > \rho_{water}$; $\nu_{TCE} < \nu_{water}$) in fractured rock – the "perfect storm" for spatially complex source areas, convoluted flow paths associated with aqueous phase plumes, exacerbated by high costs and challenges in monitoring. . .

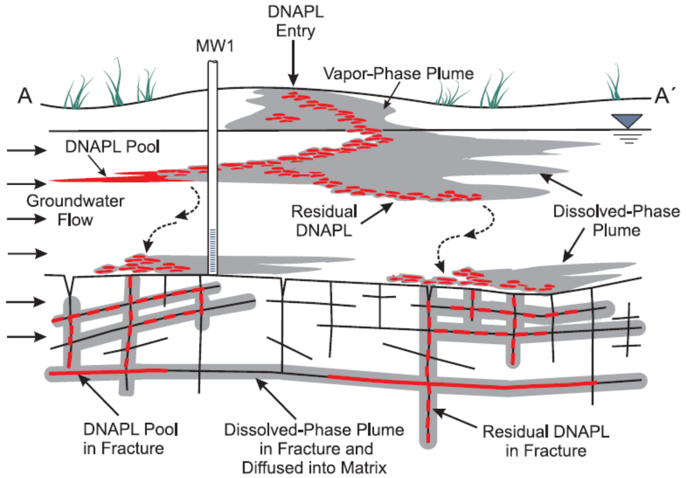
Diversity of Fractured Rock Aquifers

- ❑ Fractured rock aquifers are highly diverse (even within similar geologic environments). . .
- ❑ . . .however. . .all fractured rock aquifers share similar physical attributes. . .
- ❑ Similar attributes provide for. . .
  - Generic discussion of physical and chemical transport processes
  - Standardized approaches to characterization and monitoring
  - Design and application of diagnostic and modeling tools
  - Foundation for developing a *Conceptual Site Model* (CSM)
- ❑ Site-specific complexities are the details that flesh out the CSM. . .

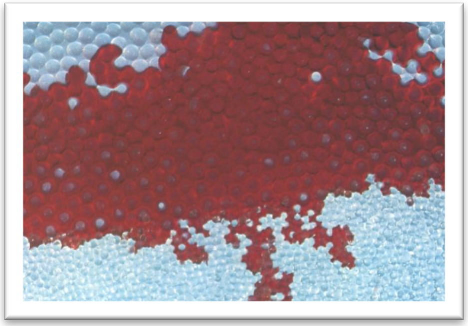
Expectations of DNAPLs in fractured rock:

Complex spatial distribution of contaminants

DNAPLs in geologic media



- Capillary forces define the distribution of DNAPLs
- Complex spatial distribution of DNAPLs (both vertically and laterally) from minor variations in pore space geometry
- DNAPLs at great depths - density > groundwater
- DNAPL "pool" heights force DNAPL into small pore throats; hydraulic conditions may not be capable of removing DNAPL from small pore throats
- Pumping and drilling may re-mobilize "pools" of DNAPL
- DNAPLs dissolve into groundwater
- Dissolved-phase DNAPLs diffuse into lower-permeability geologic materials
- VOCs sorb to geologic materials with organic carbon content



DNAPL pooling at a boundary between larger beads [0.85 – 1.23 mm] (upper region) and smaller beads [0.49 – 0.70 mm] (lower region)

Schwille 1988

Complex DNAPL migration in unsaturated sands. DNAPL shown in red (Sudan IV dye). Bedding dips 30° below horizontal

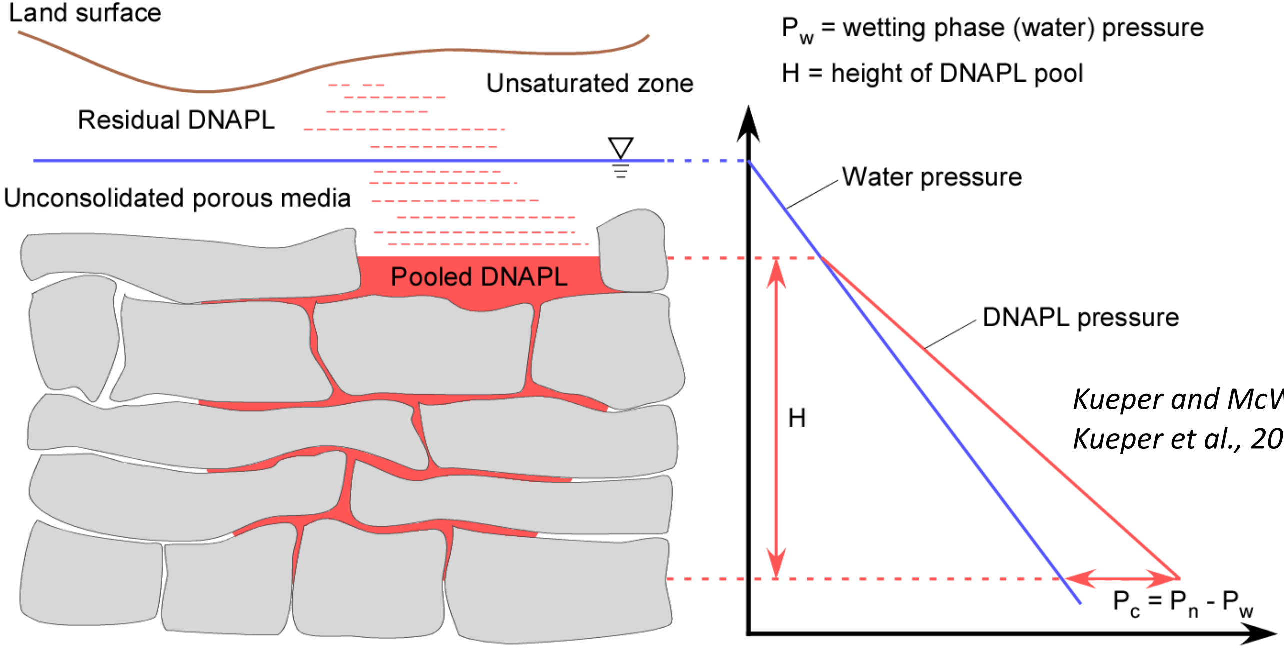
Poulsen and Kueper, 1992

Expectations of DNAPLs in fractured rock:

Complex spatial distribution of contaminants

Complex topology of fractures affects contaminant distribution. . .

P_c = capillary pressure
P_n = non-wetting phase (DNAPL) pressure
P_w = wetting phase (water) pressure
H = height of DNAPL pool



Kueper and McWhorter, 1992; Kueper et al., 2003

Entry of DNAPLs into fractures depends on physical properties of fractures and the DNAPL, and capillary forces. . .

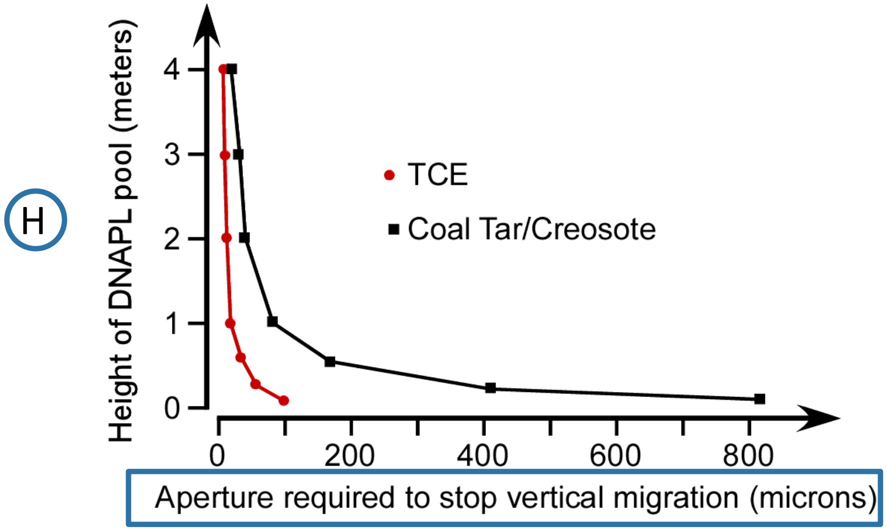
Expectations of DNAPLs in fractured rock:

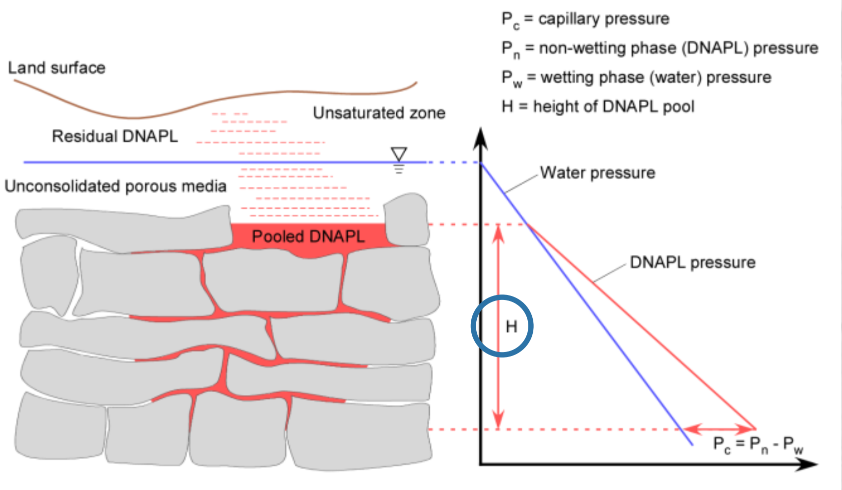
Complex spatial distribution of contaminants

Fracture aperture affects contaminant distribution. . .H is the height of DNAPL that will result in entry into an aperture of width b

$$H = \frac{2\,\sigma\cos\theta}{(P_n - P_w)gb}$$

b = fracture aperture
g = gravitational constant
θ = DNAPL - water contact angle
σ = DNAPL - water interfacial tension





Kueper and McWhorter, 1992;
Kueper et al., 2003

- •For a given “pool height” of DNAPL, fractures with apertures to the right of these curves would allow entry of DNAPL
- •9 micron (9 x 10^{-6} meters) fracture aperture needed to stop 1 meter “pool” height of TCE
- •Diameter of human hair ~50 microns
- •Pool heights of DNAPL can also force NAPL-phase into the pore throats in the rock matrix

Expectations: One can only conjecture about the volumetric extent of the DNAPL source zone and residual DNAPL in fractured rock. . .

What’s important ?

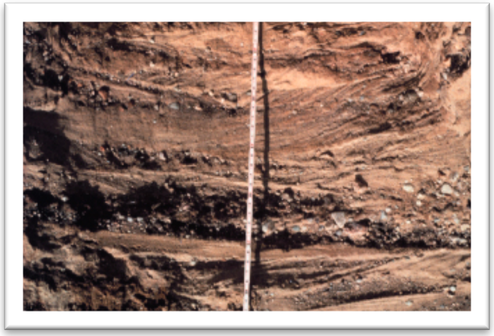
How do we approach this complexity for site investigations?

- Identify lithologic and structural controls on DNAPL source migration
- Site infrastructure affects source areas
- Design and installation of monitoring to avoid further contaminant spreading
- Use “multiple lines of evidence” to infer source areas

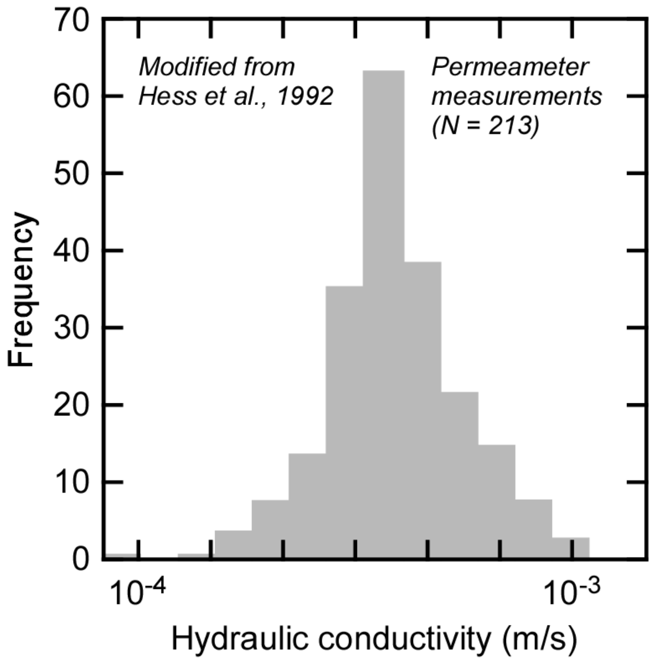
Why ?

- Designing “source zone” mass reduction to reduce contaminant longevity and limit plume migration

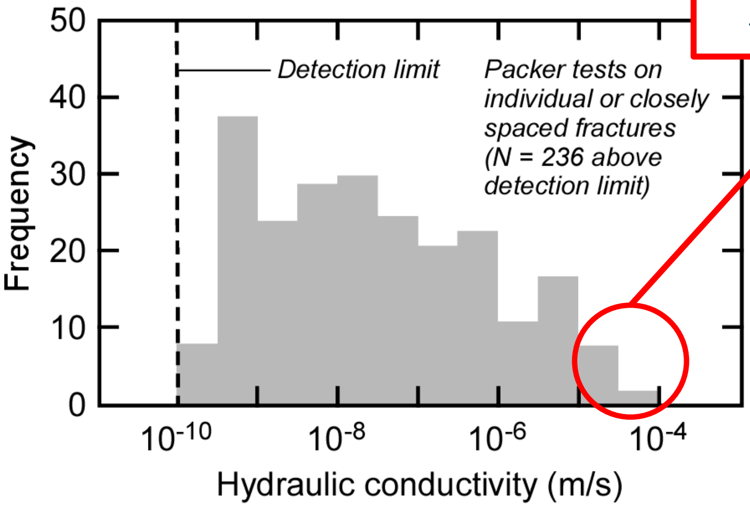
Expectations of fractured rock: ***Large variability in capacity of fractures to transmit groundwater***



Sand and Gravel Glacial Outwash
Cape Cod, MA



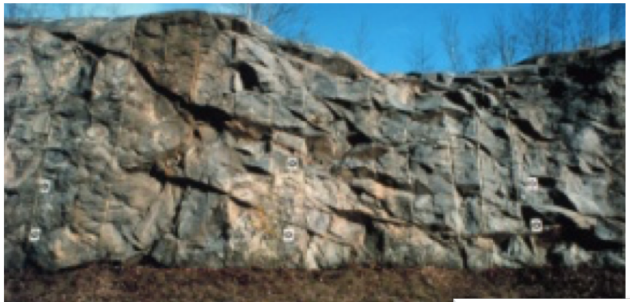
Fractured Granite and Schist
Mirror Lake Watershed, NH



- These few fractures are 100's to 1000's of times more permeable than other fractures . . .
- Few fractures control the majority of groundwater flow. . .
- Characterizing connectivity of the most permeable fractures is critical. .

Expectations of fractured rock: *Abrupt spatial changes in hydraulic properties*

Expect both vertical and horizontal variability. . .

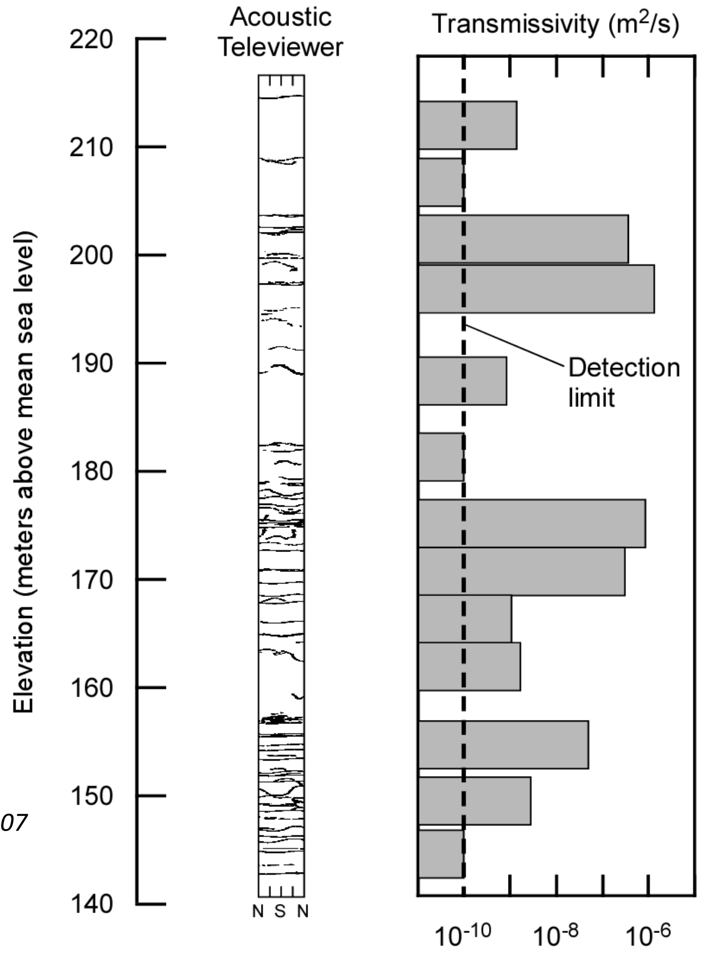


Granite and Schist

Packer apparatus used for testing individual or closely spaced fractures

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

Borehole H1
Mirror Lake Watershed, NH



K of the intrinsic rock (matrix) porosity is orders of magnitude less than that of fractures

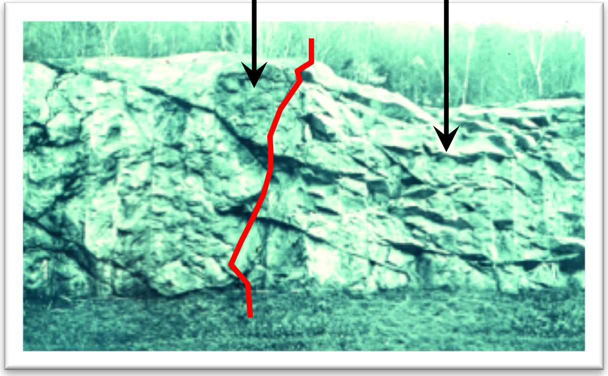
Expectations of fractured rock: *Complex fracture connectivity*

Local and regional stress distribution, lithology, and weathering lead to complex connectivity of fractures and their hydraulic properties. . .

Schist: fewer fractures; longer, undulating fracture surfaces

Granite: higher fracture density; shorter, more planar fractures

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



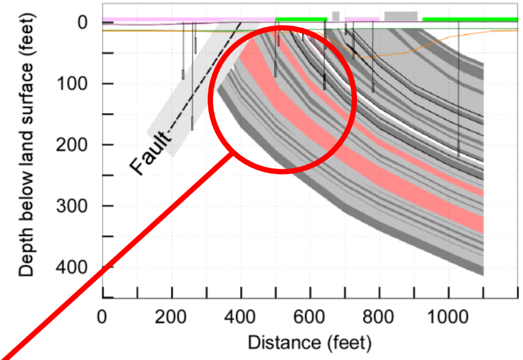
Lockatong Mudstone, Newark Basin
West Trenton, New Jersey

Weathering alters fractures

Bedding plane parting along black, carbon-rich section of mudstone

Joints perpendicular to bedding (parallel and perpendicular to rock face)

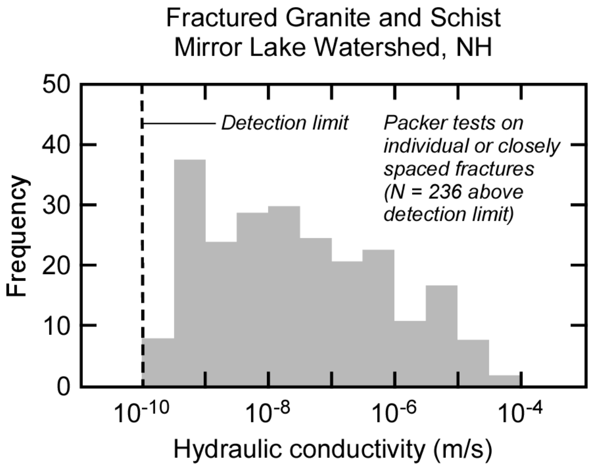
Joints perpendicular to bedding are (frequently) bound by strata (but, sometimes are extend through multiple strata)



Fracture density perpendicular to bedding varies with proximity to fault

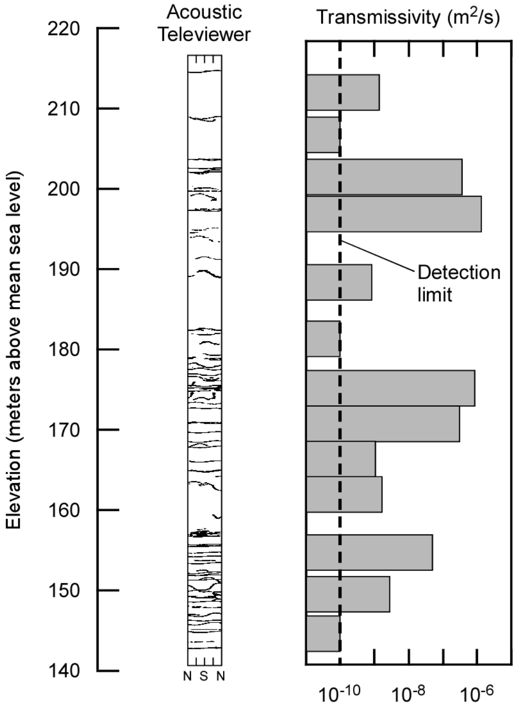
Expectations of fractured rock: ***Convoluted groundwater flow paths over dimensions of meters to kilometers***

☐ **Large variability in capacity of fractures to transmit groundwater**



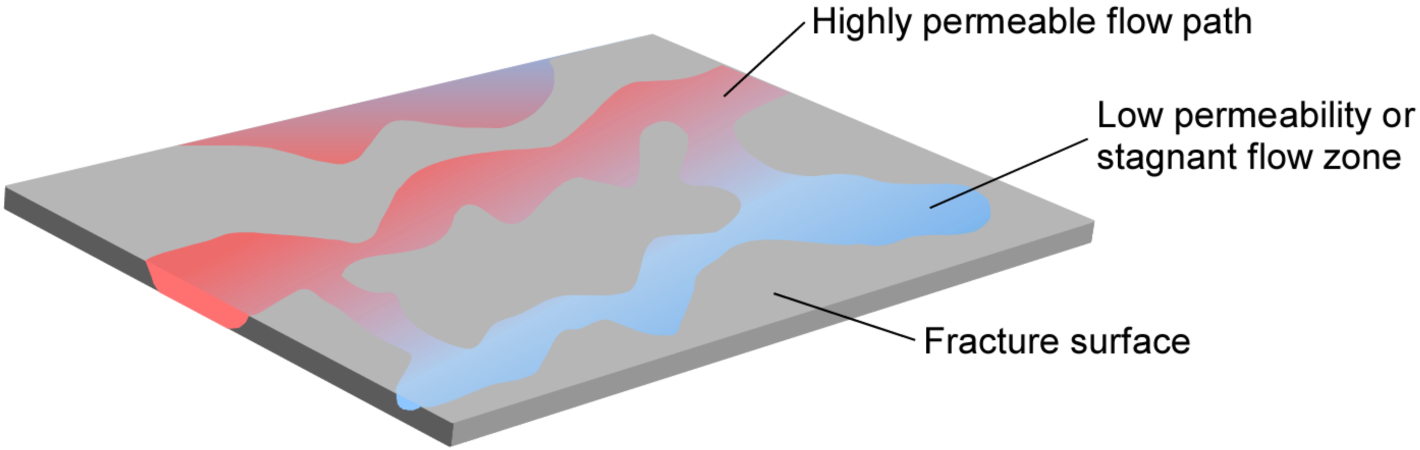
☐ **Complex fracture connectivity**

☐ **Abrupt spatial changes in hydraulic properties**



Expectations of fractured rock: *. . .even within individual fractures there is a complex flow regime*

Fracture surfaces have complex topology. . .fracture aperture varies due to points of contact and asperities between fracture walls



. . .similar to the large variability in hydraulic properties that is anticipated from one fracture to the next, there is large variability in hydraulic properties within an individual fracture. . .

Neretnieks et al., 1982; Tsang and Neretnieks 1998

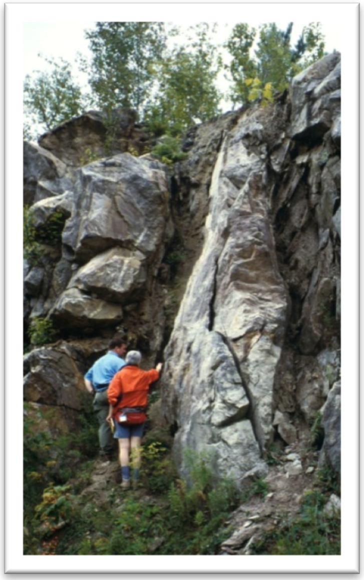
Convoluted groundwater flow paths within individual fractures

Expectations of fractured rock: ***. . .there is more to fractured rock than just "fractures" . . .hierarchy of void space***

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

Iron-hydroxide precipitate staining the rock matrix (***primary/intrinsic rock porosity***)

Fractures exposed on a road cut (***fracture porosity***)

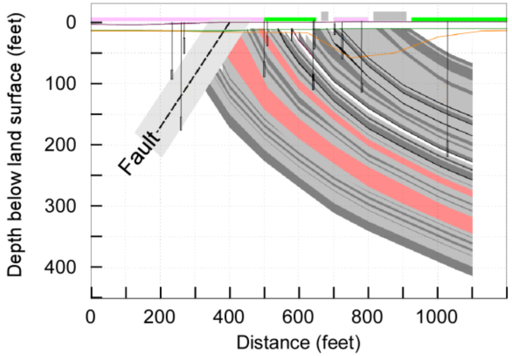


Fault zone exposed on a road cut

Lockatong Mudstone,
West Trenton, New Jersey

Residual wetting of rock core (***primary/intrinsic rock porosity***)

Fractures parallel and perpendicular to bedding (***fracture porosity***)



Schematic cross section perpendicular to bedding showing ***fault zone*** location

Expectations of fractured rock: ***Hierarchy of void space***

Representative "*time*", "*length*", & "*void volume*" will differ for each type of void space. . .controls on groundwater flow and chemical transport. . .

Intrinsic porosity (rock matrix) & low-K fractures. . .

Length: **centimeters ➡ decimeters ➡ meters**

Time: **years ➡ decades ➡ centuries ➡ millennia**

Most permeable fractures. . .

Length: **meters ➡ kilometers**

Time: **hours ➡ days ➡ years**

Large scale geologic features (e.g., fault & shear zones. . .hydraulic conduits or hydraulic barriers

Length: **centimeters ➡ meters ➡ kilometers**

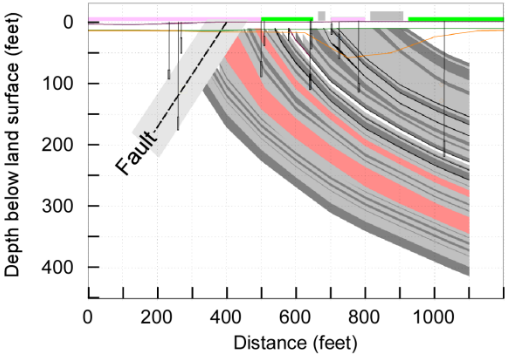
Time: **hours ➡ years ➡ decades ➡ centuries ➡ millennia**

***Void Volume*. . .how much contaminant mass resides in each type of void space ?**

Lockatong Mudstone, Newark Basin
West Trenton, New Jersey

Residual wetting of rock core (***primary/intrinsic rock porosity***)

Fractures parallel and perpendicular to bedding (***fracture porosity***)



Schematic cross section perpendicular to bedding showing ***fault zone*** location

Expectations: Convoluted groundwater flow paths and hierarchy of void space. . .

What's important ?

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

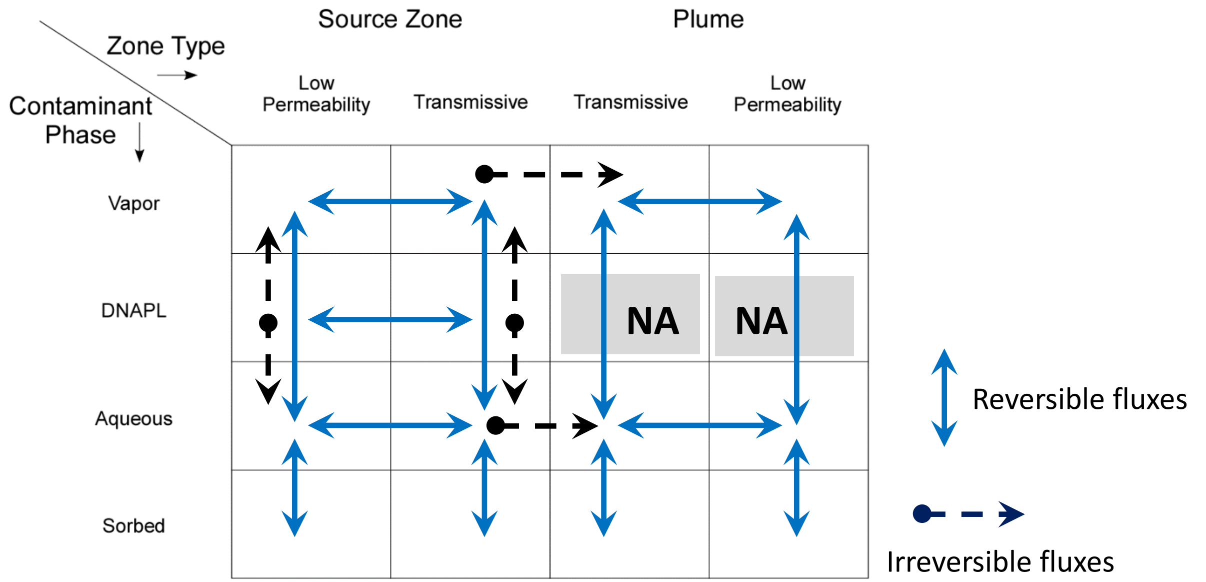
- Identify lithologic and geomechanical controls on fracturing
- Identify most permeable features and barriers to groundwater flow over relevant dimensions
- Spatial connectivity of permeable features
- Mapping and characterization of *every fracture is* *<u>not</u>* warranted
- Physical and chemical characteristics of rock matrix

Why ?

- Identify the spatial extent of aqueous-phase contaminant movement. . .
- Design groundwater containment to prevent further contaminant migration. . .
- Design and evaluate potential success of "source area" remediation. . .

Similar expectations and attributes in different fractured rock settings are the basis for establishing a framework for Conceptual Site Models

Organic Contaminants:
14 - Compartment Model and Contaminant Fluxes between Compartments

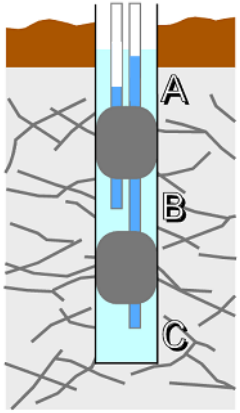


(modified from Sale et al., 2008; Sale and Newell, 2011; ITRC 2011)

- Conceptualize processes that affect contaminant “storage” and contaminant fluxes
- Define site characterization, monitoring, and modeling to quantify contaminant “reservoirs” and contaminant fluxes
- Identify contaminant “reservoirs” and fluxes that dominate process outcomes
- Identify spatial and temporal scales that dominate processes outcomes

Consequences of complex groundwater flow paths:

Monitoring hydraulic conditions



Characterizing fluid advection and the migration of aqueous phase contaminants . . . monitoring hydraulic head in discrete intervals of boreholes

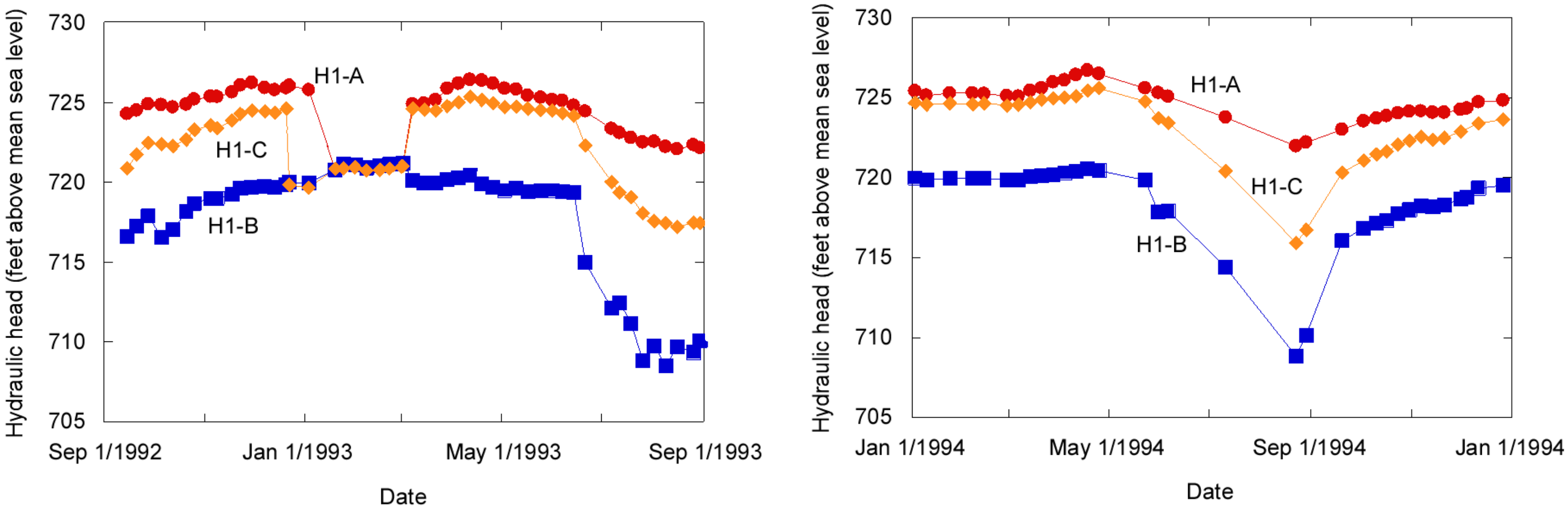
Elevation of monitoring
intervals in borehole H1

H1-A: 633.9 - 732.0 ft above msl

H1-B: 522.6 - 630.9 ft above msl

H1-A: 459.0 - 519.6 ft above msl

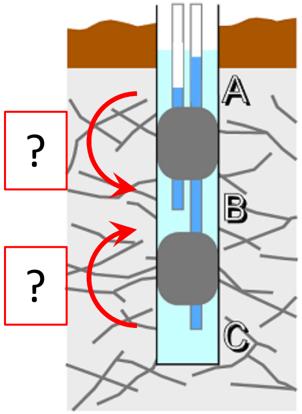
Maintaining the integrity of multilevel monitoring equipment. . . proper monitoring of hydraulic head is critical to inferring directions of groundwater flow.

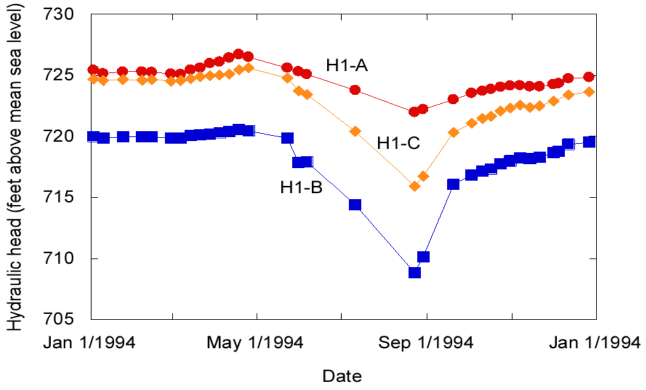


Hydraulic head in intervals of Borehole H1, Mirror Lake Watershed, Grafton County, NH

Consequences of complex groundwater flow paths:

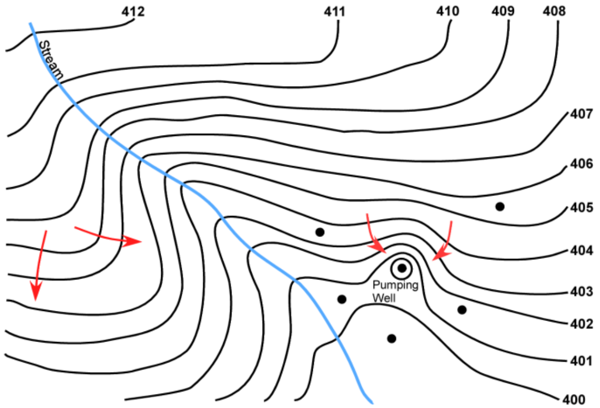
Characterizing groundwater flow





Hydraulic head in intervals of Borehole H1, Mirror Lake Watershed, Grafton County, NH

Is it reasonable to assume groundwater flow is perpendicular to lines of equipotentional?



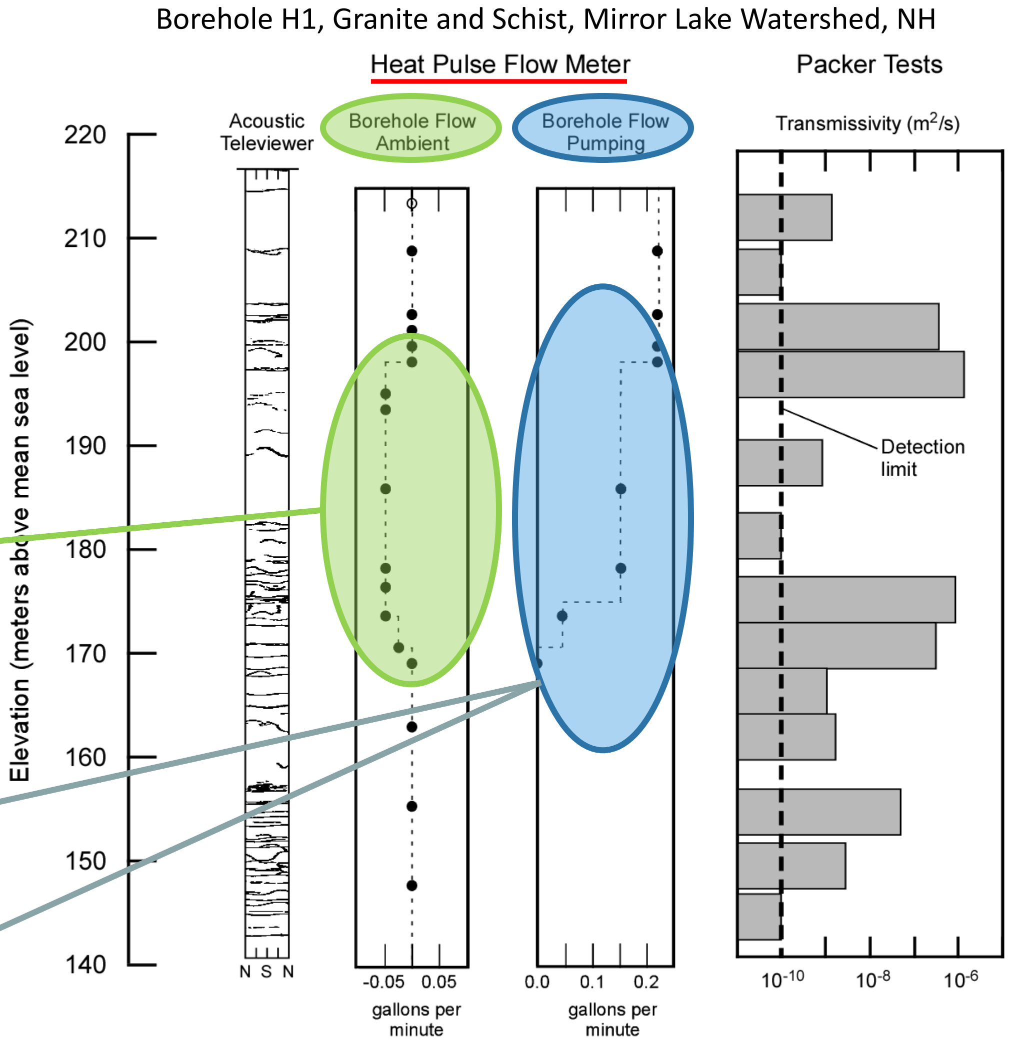
Hypothesized distribution of hydraulic head and groundwater flow lines based on surface topography, stream elevations, and bedrock monitoring wells

Characterizing hydraulic head is a 3-D concept. The direction of groundwater flow must be inferred in concert with the characterization of permeable features and flow barriers.

Consequences of complex groundwater flow paths:

Monitoring geochemical conditions

Monitoring geochemical conditions in fractured rock. . .boreholes open to multiple fractures. . .



Ambient conditions. . .water enters the borehole at fracture locations and exits at other fracture locations. . .potential to spread contaminants. . .

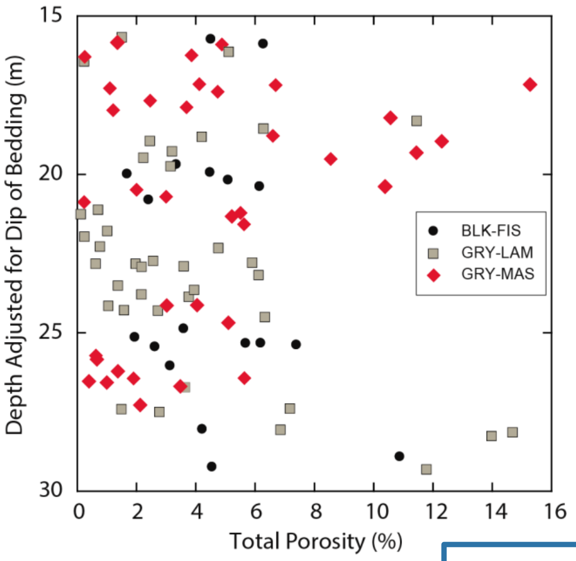
Pumping. . .mixing contributions from multiple fractures . . .

Pumping. . .groundwater drawn preferentially from most transmissive fractures. . .

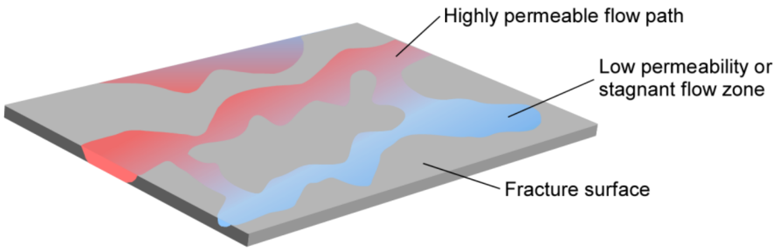
Expectations of fractured rock: *(Hierarchy of void space)*

“Flow limited” regions of the formation are a reservoir for chemical storage

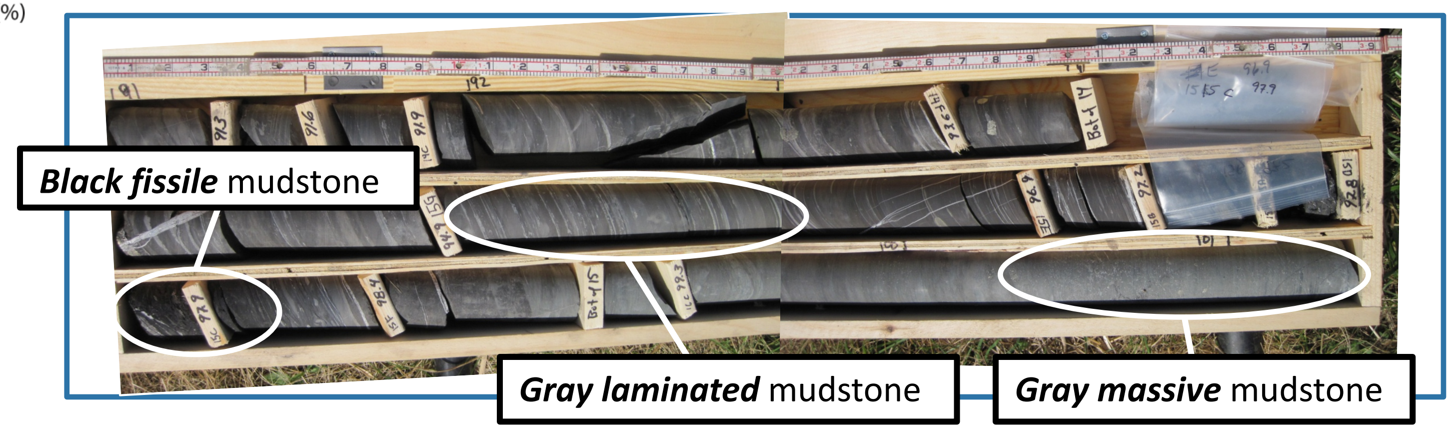
The primary/intrinsic porosity of the rock (rock matrix) and “tight” fractures offer a fluid-filled void space available through chemical diffusion . . .



Intrinsic porosity of Lockatong mudstone, West Trenton, NJ



Fracture surfaces have complex topology. . .creating preferential flow paths and ***stagnant flow zones***. . .



Black fissile mudstone

Gray laminated mudstone

Gray massive mudstone

The effect of “flow limited” aquifer regions on chemical migration. . .

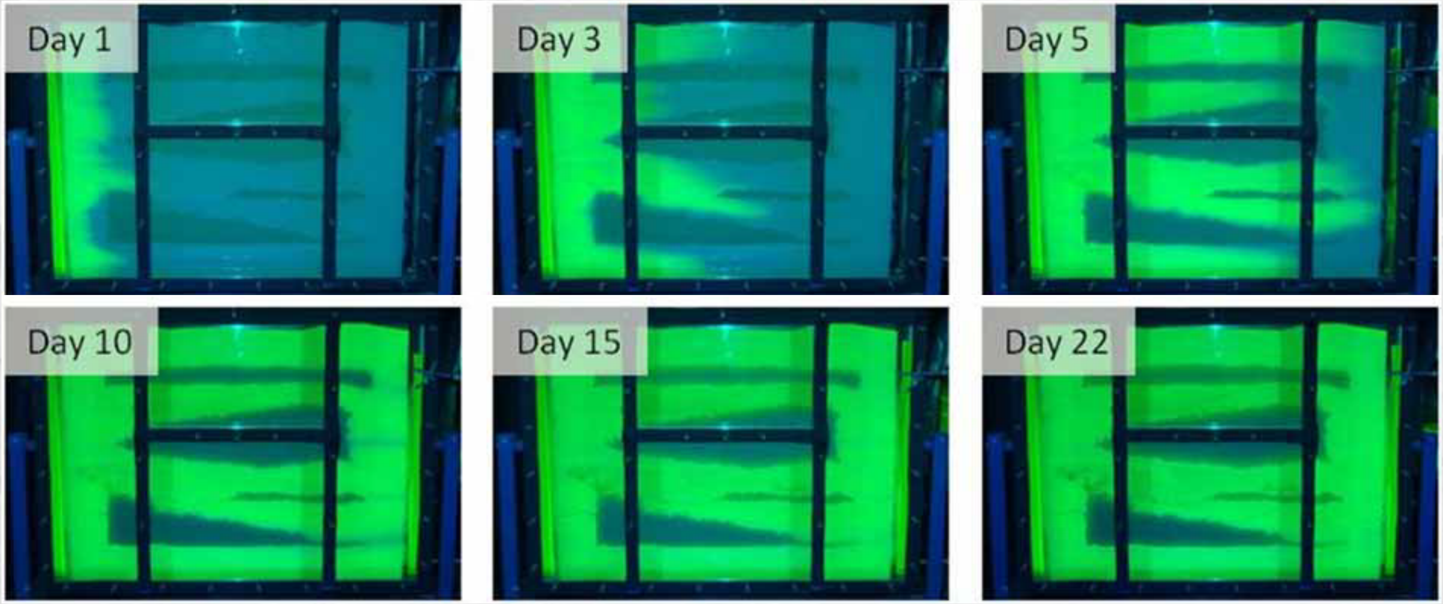
Low-permeability material embedded in a permeable sand. . .

from Doner and Sale, Colorado State University

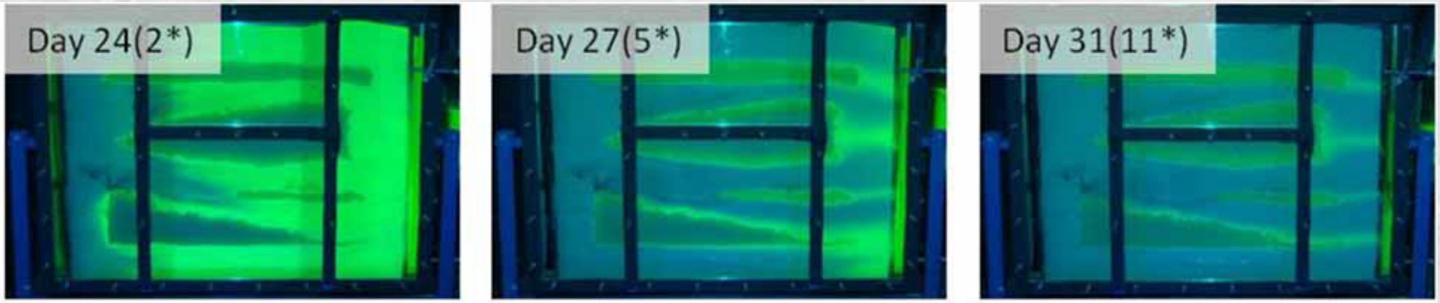
- *Low permeability material may not be significant with respect to volumetric groundwater flow. . .*
- *During contaminant “loading”, dye diffuses from permeable pathways to low-permeability materials due to concentration gradient*
- *During “flushing”, dye diffuses from low-permeability materials to permeable pathways due to concentration gradient*

Retention and slow release of contaminants in “flow limited” regions of the aquifer. . .a significant impediment to achieving remedial objectives in a reasonable time frame. . .

Dye injection. . .



Flushing. . .

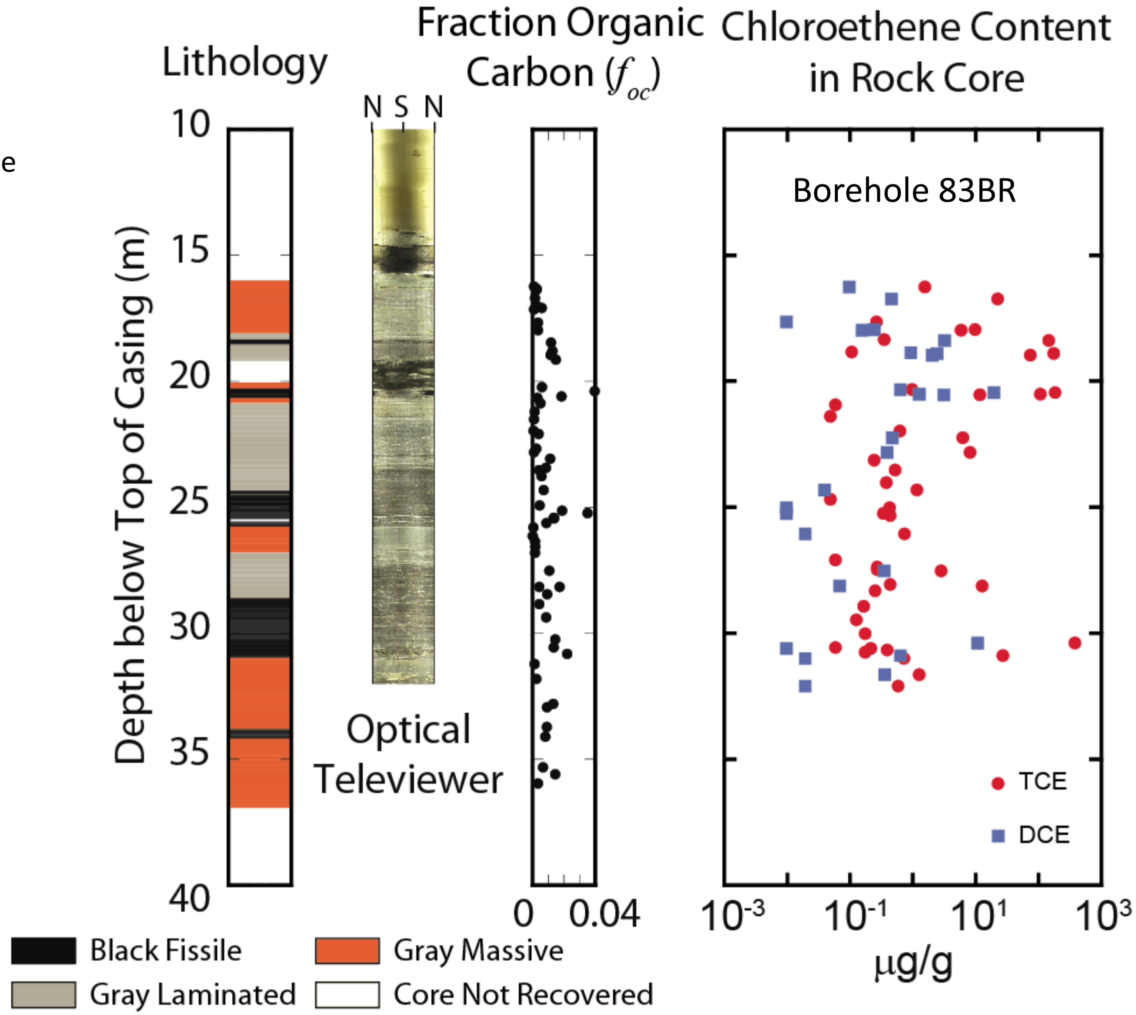


Expectations of fractured rock:

“Flow limited” regions of the formation are a reservoir for chemical storage

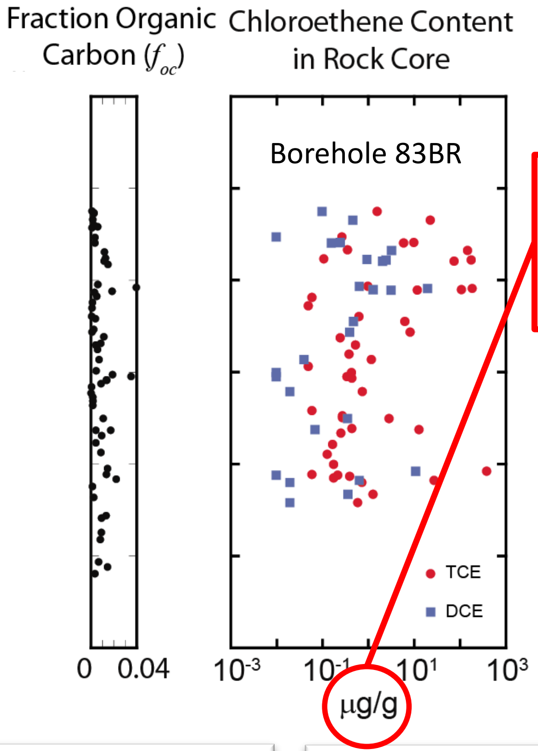
Analyzing samples of rock core collected from a TCE-contaminated mudstone aquifer demonstrate significant TCE-mass in the rock matrix. . .

Lockatong Mudstone
Naval Air Warfare Center, West Trenton, NJ



Expectations of fractured rock:

"Flow limited" regions of the formation are a reservoir for chemical storage. . .in the aqueous and sorbed phases



What is the distribution of TCE between the aqueous and sorbed phase in the rock matrix? A simple calculation. . . .

- µg/g –> micrograms of TCE per gram of rock
- includes TCE in aqueous phase and sorbed phase

Assume:

- Aqueous TCE concentration in rock matrix – C_{aq} - 10,000 µg/L (~ 1% of aqueous solubility of TCE)
- Rock matrix porosity – n - 5%
- Rock matrix bulk density – ρ_b – 2.6 g/mL
- Fraction organic carbon – f_{oc} – 0.02
- Partitioning coefficient for TCE – K_{oc} – 126 mL/g

TCE mass in aqueous phase:

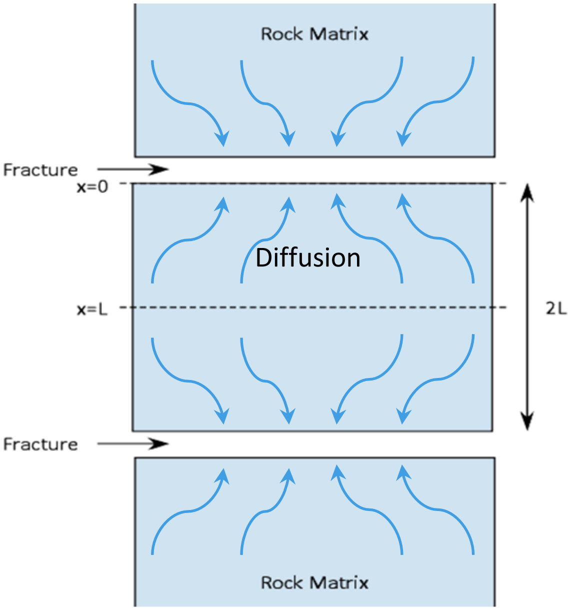
$$\frac{C_{aq} n}{\rho_b} = 0.19\ \mu\text{g/g}$$

TCE mass sorbed to rock matrix:

$$K_d C_{aq} = (K_{oc} f_{oc}) C_{aq} = 25.2\ \mu\text{g/g}$$

Expectations of fractured rock:

“Flow limited” regions of the formation are a reservoir for chemical storage . . . for how long?



$$R\frac{\partial C}{\partial t} - D_d\frac{\partial^2 C}{\partial x^2} = 0$$

$$R = 1 + \frac{\rho_b K_d}{n}$$

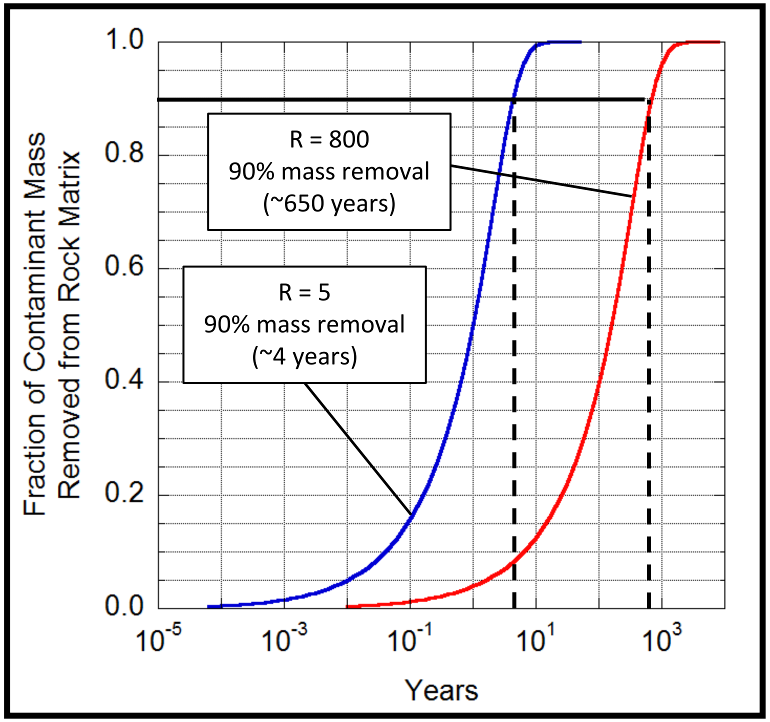
$$K_d = K_{oc} f_{oc}$$

R – retardation factor

n – porosity

ρ_b – bulk density

f_{oc} – fraction organic carbon



R = 800
90% mass removal
(~650 years)

R = 5
90% mass removal
(~4 years)

A simple model to calculate TCE longevity in the rock matrix

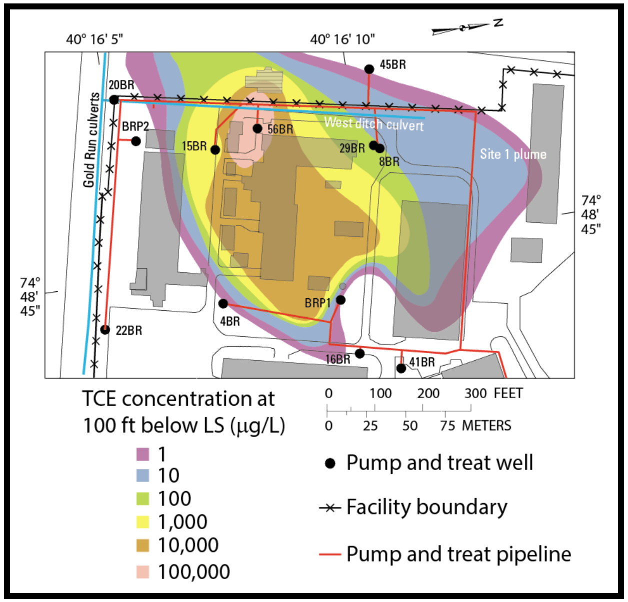
1. 1-D diffusion & linear equilibrium sorption
2. TCE initially uniformly distributed in rock matrix
3. Fractures flushed with TCE-free water

Centimeter scale processes will influence decisions on applying remediation technologies

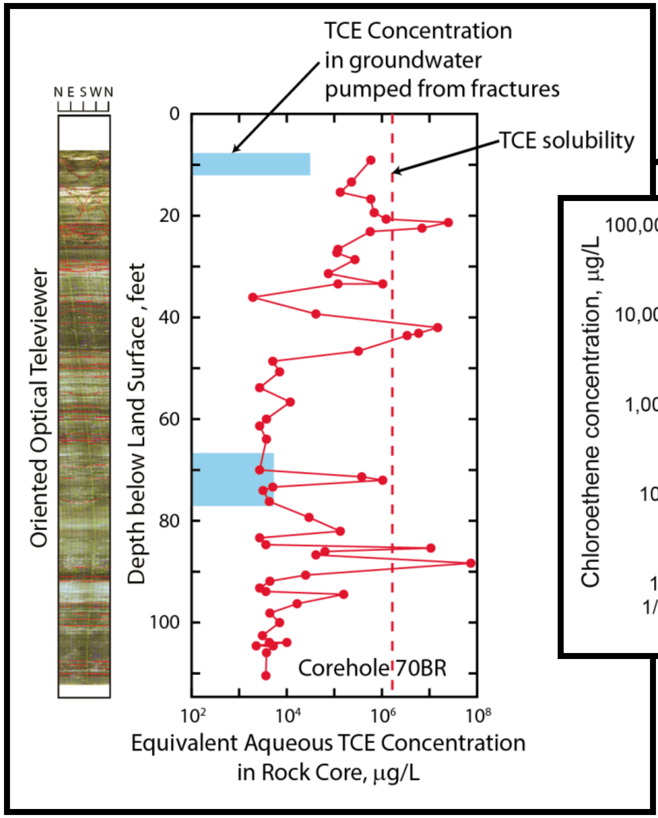
Consequences of contaminant retention in “flow limited” regions of the aquifer :

Quantifying the mass of contaminants in the subsurface

Interpolated distribution of TCE determined from water samples collected from monitoring intervals. . .aqueous concentration from permeable fractures

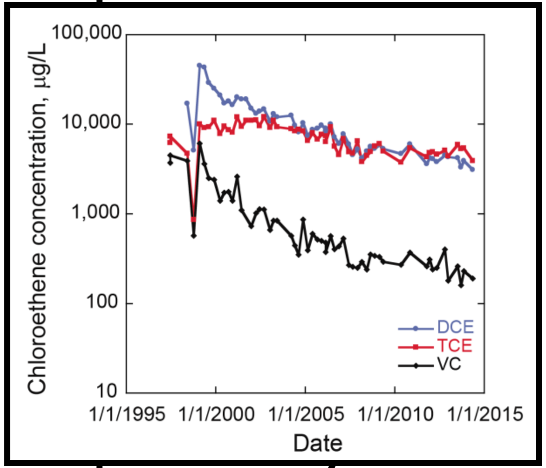


Lockatong mudstone, West Trenton, NJ



TCE content in rock core

~95% TCE mass in rock matrix



Continuous Pumping Borehole 15BR

Expectations: Contaminant mass in “flow limited” regions of the aquifer constitute a spatially pervasive, long-term contaminant source . . .

What’s important ?

How do we approach this complexity for site investigations?

- Identify processes controlling the retention and release of contaminants in “flow limited” regions of aquifer (diffusion, sorption/desorption). . .
- Identify processes that may act to attenuate contaminant mass (biotic and abiotic conditions). . .in “flow limited” regions and “permeable” flow paths. . .
- Identify appropriate “models” and “parameters” and estimate contaminant longevity. . .

Why ?

- *Remediation technologies* (flushing and amendment addition) may be *ineffective* for “flow limited” regions. . .
- Decisions on applying remediation must recognize potential longevity of contaminant mass in “flow limited” regions. . .
- Decisions on long-term site management must recognize contaminant longevity. . .

Summarizing Thoughts

- Fractured rock aquifers have similar physical "attributes and expectations". . . the starting point for the development of Conceptual Site Models. . . site-specific complexities provide details of Conceptual Site Models. . .

- Hierarchy of void space (matrix, fractures, regional geologic features) implies the need to characterize processes at multiple scales to make informed decisions on characterization and remediation. . .

- Convoluted groundwater flow paths control source zone and plume contaminant movement. . .

- "Centimeter"-scale processes can control retention and release of contaminants from "flow limited" regions of the aquifer. . .

Selected References

(Note: This is not an exhaustive list. Please contact ashapiro@usgs.gov for a more extensive list of references.)

Day-Lewis, F. D., Slater, L. D., Robinson, J., Johnson, C. D., Terry, N. and Werkema, D. 2017. An overview of geophysical technologies appropriate for characterization and monitoring at fractured-rock sites. **Journal of Environmental Management** 204: 709-720. https://doi.org/10.1016/j.jenvman.2017.04.033.

Interstate Technology and Regulatory Council (ITRC). 2015. Integrated DNAPL site characterization and tools selection. Interstate Technology & Regulatory Council, DNAPL Site Characterization Team. Washington, DC. Retrieved July 17, 2016, from http://www.itrcweb.org/DNAPL-ISC_tools-selection/.

Paillet, F. L. 1993. Using borehole geophysics and cross-borehole flow testing to define hydraulic connections between fracture zones in bedrock aquifers. **Journal of Applied Geophyisics** 30(3): 261-279.

Sale, T., Newell, C., Stroo, H., Hinchee, R. and Johnson, P. 2008. Frequently asked questions regarding management of chlorinated solvents in soils and groundwater. Department of Defense, Environmental Security Technology Certification Program (ESTCP). 34p. https://www.serdp-estcp.org/Tools-and-Training/Environmental-Restoration/DNAPL-Source-Zones.

Sale, T., Parker, B. L., Newell, C. J. and Devlin, J. F. 2013. Management of contaminants stored in low permeability zones. State-of-the-Science Review, SERDP Project ER-1740. Strategic Environmental Research and Development Porgram. 348p. https://www.serdp-estcp.org/content/download/23838/240653/file/ER-1740%20State%20of%20the%20Science%20Review%20Report.pdf.

Shapiro, A. M. 2002. Cautions and Suggestions for Geochemical Sampling in Fractured Rock. **Groundwater Monitoring & Remediation** 22(3): 151-164. 10.1111/j.1745-6592.2002.tb00764.x.

Shapiro, A. M., Hsieh, P. A., Burton, W. C. and Walsh, G. J. 2007. Integrated Multi-Scale Characterization of Ground-Water Flow and Chemical Transport in Fractured Crystalline Rock a the Mirror Lake Site, New Hampshire, *in* **Subsuface Hydrology: Data Integration for Properties and Processes**. eds., D. W. Hyndman, F. D. Day-Lewis and K. Singha. American Geophysical Union, Washington, DC. p. 201-226.

Shapiro, A. M., Evans, C. E. and Hayes, E. C. 2017. Porosity and pore size distribution in a sedimentary rock: Implications for the distribution of chlorinated solvents. **Journal of Contaminant Hydrology** 203: 70-84. https://doi.org/10.1016/j.jconhyd.2017.06.006.