CALIFORNIA STATE UNIVERSITY
LONG BEACH

Fate and Transport of Contaminants in Fractured Bedrock

Matthew W. Becker, Ph.D.

Professor and Conrey Chair in Hydrogeology,
Department of Geological Sciences, California State University Long Beach

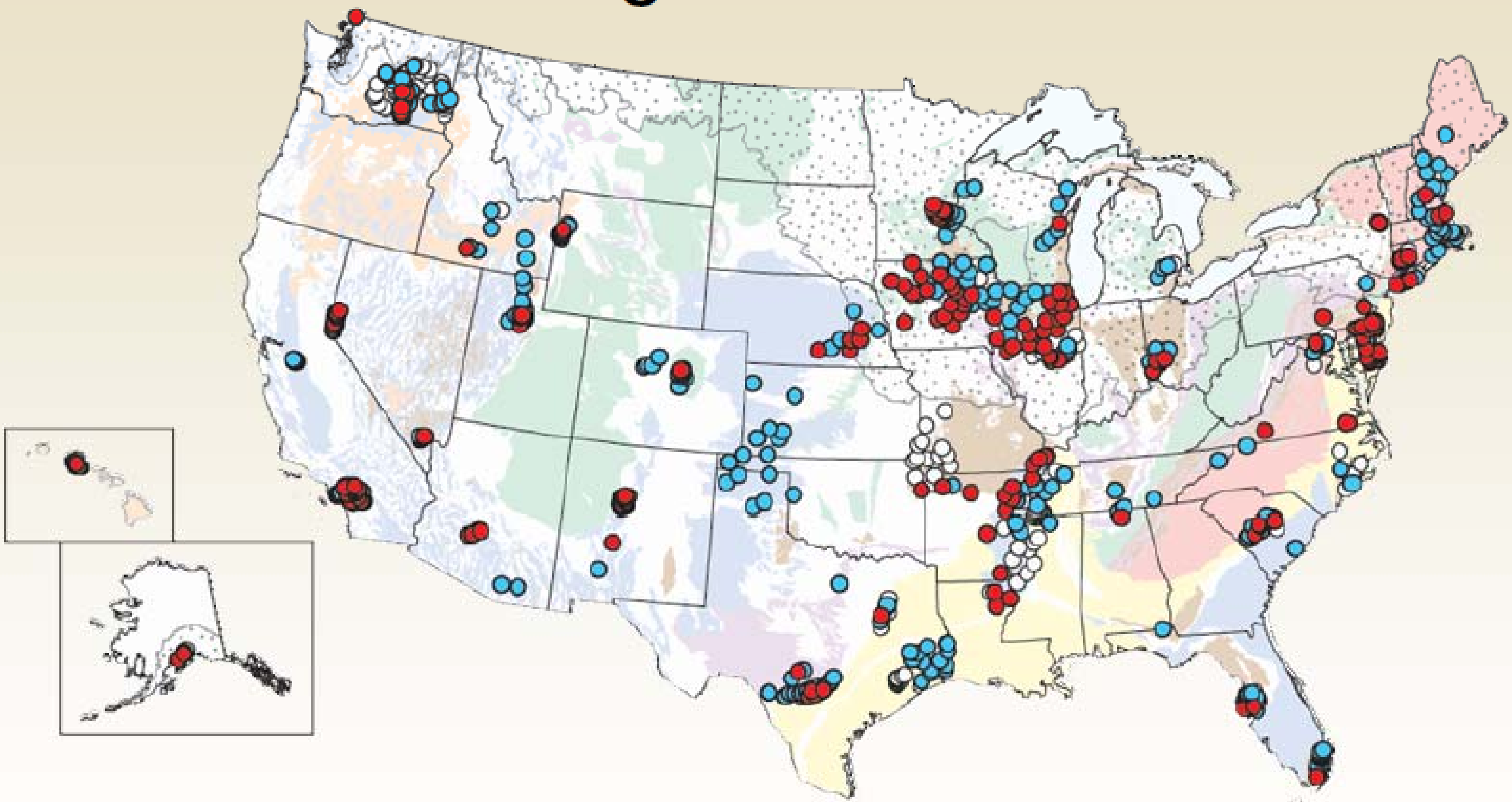
Outline

1. Ubiquity of Contamination
2. Transport Processes
3. Transport in Fractured Bedrock
4. Reactions

Is my groundwater clean?

- In 2010 the USGS surveyed 955 public supply wells across the country.
- They looked for 337 chemicals/properties (not pharmaceuticals)
- They compared these to:
  - EPA Maximum Contaminant Levels (MCL) for regulated contaminants
  - USGS Health-Based Screening Levels (HBSL) for unregulated contaminants (non-enforceable guidelines developed by the USGS in collaboration with the EPA and other water partners)

1 in 5 source-water samples had concentrations greater than benchmarks

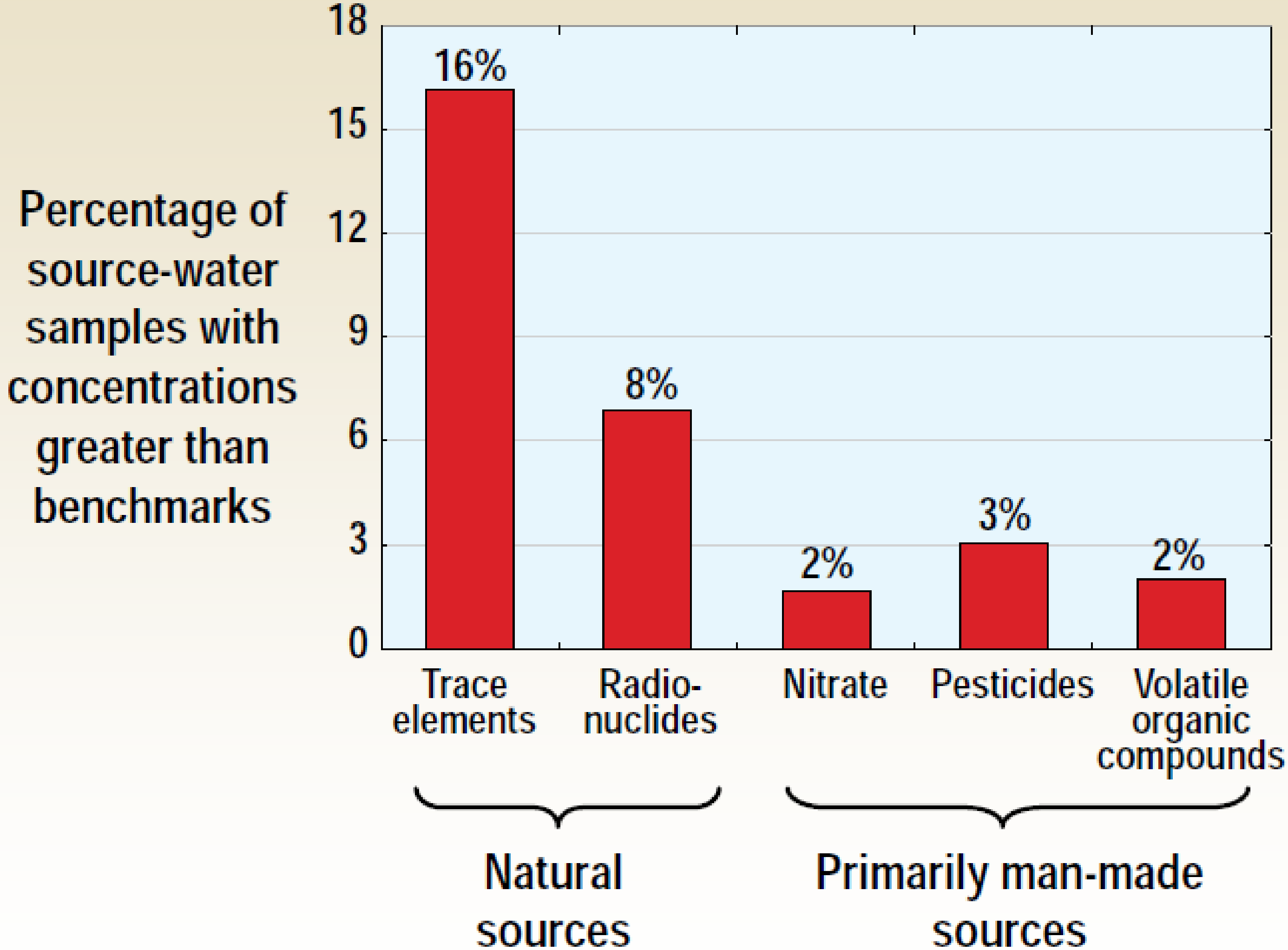


● Greater than MCL or HBSL (22%)

● Greater than one-tenth of MCL or HBSL (58%)

USGS

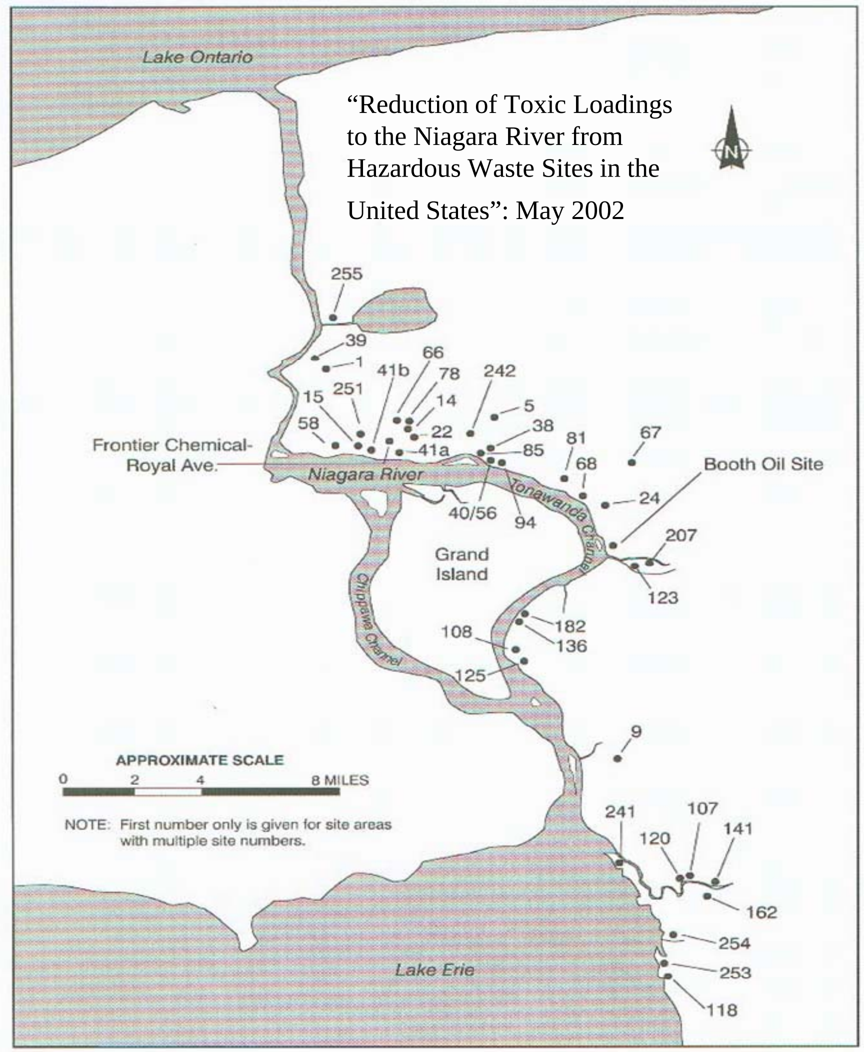
Contaminants from natural sources accounted for most concentrations greater than benchmarks



USGS

Industrial Areas

- In places with a history of industry, pollution is greater
- In Niagara Falls area there are over 200 hazardous waste sites that discharge contamination to the Niagara River.

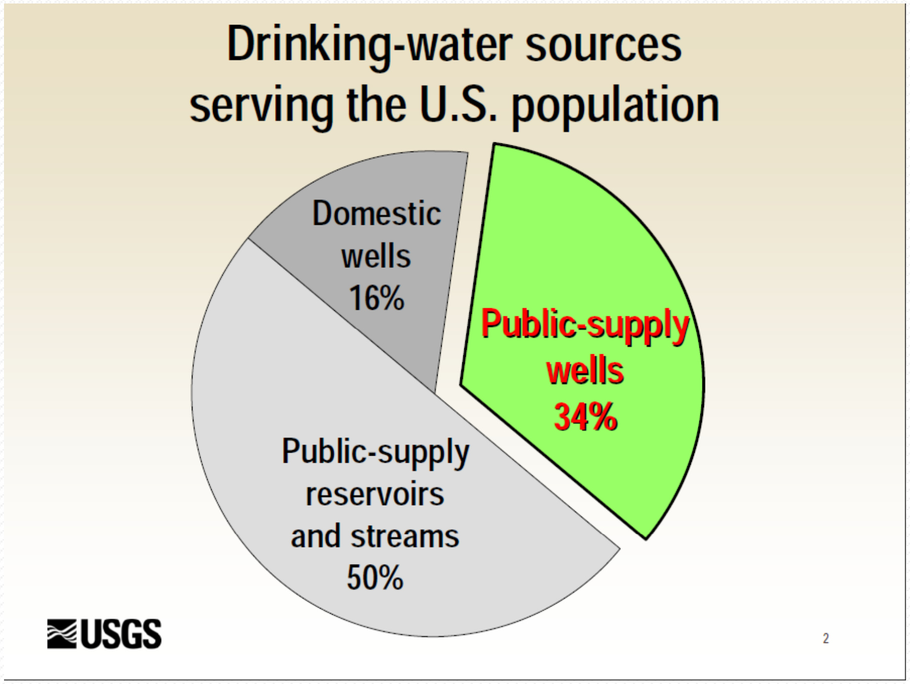


Groundwater Quality

vs.

Groundwater Supply

- In a modern world, there is no longer a meaningful difference between groundwater supply and groundwater quality.



Fate and Transport

- Sometimes chemicals get into groundwater …this is their story…
- Migration, transformation, reaction with subsurface materials all fall under "fate and transport"

Disclaimer

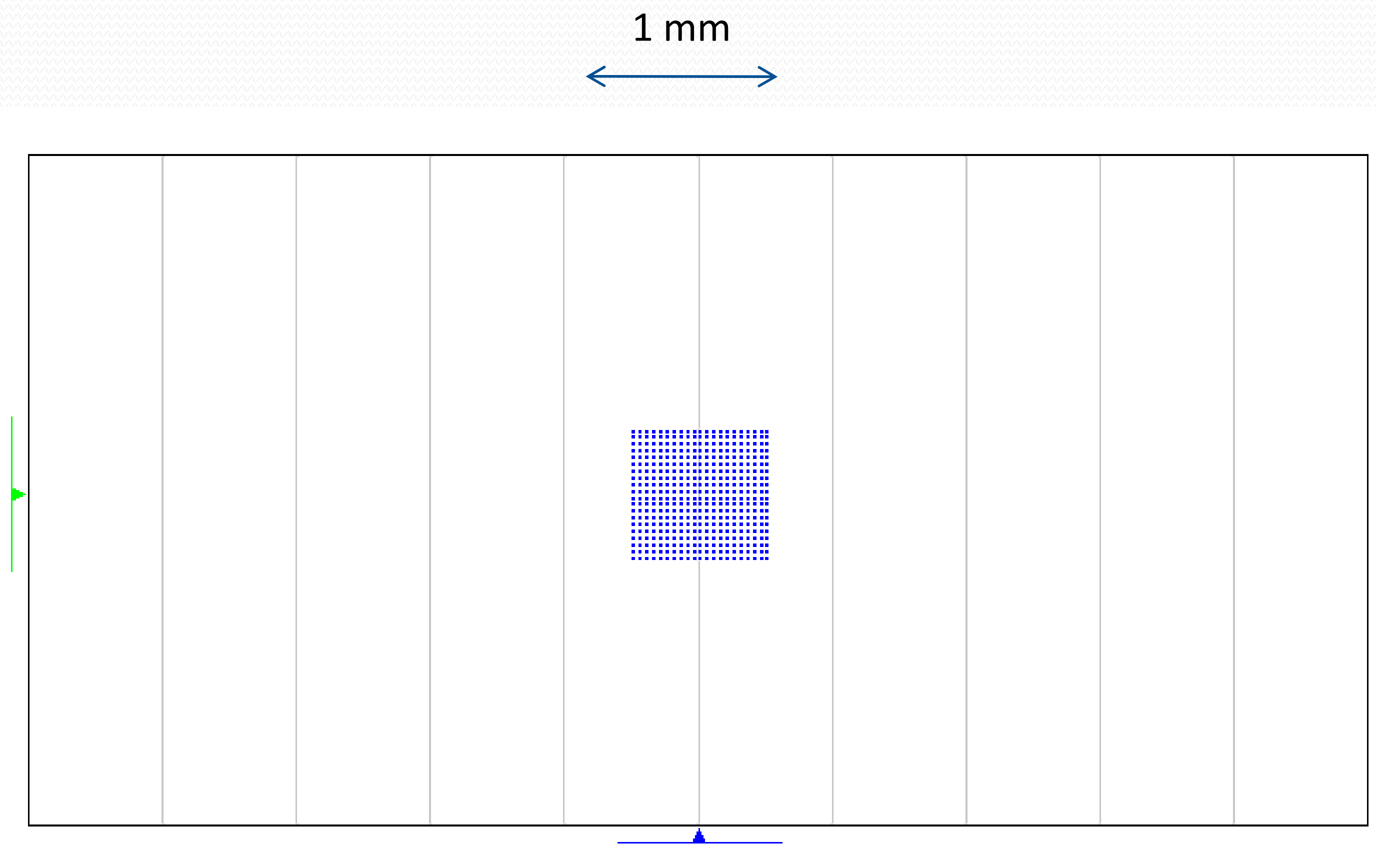
- Fate and transport generally subject for hydrogeologists (me)
- Environmental geochemistry generally subject for geochemists (not me)

The Basic Transport Process

- Diffusion: random movement of molecules
- Advection: movement with water flow
- Dispersion: spreading due to mixing

Transport Processes

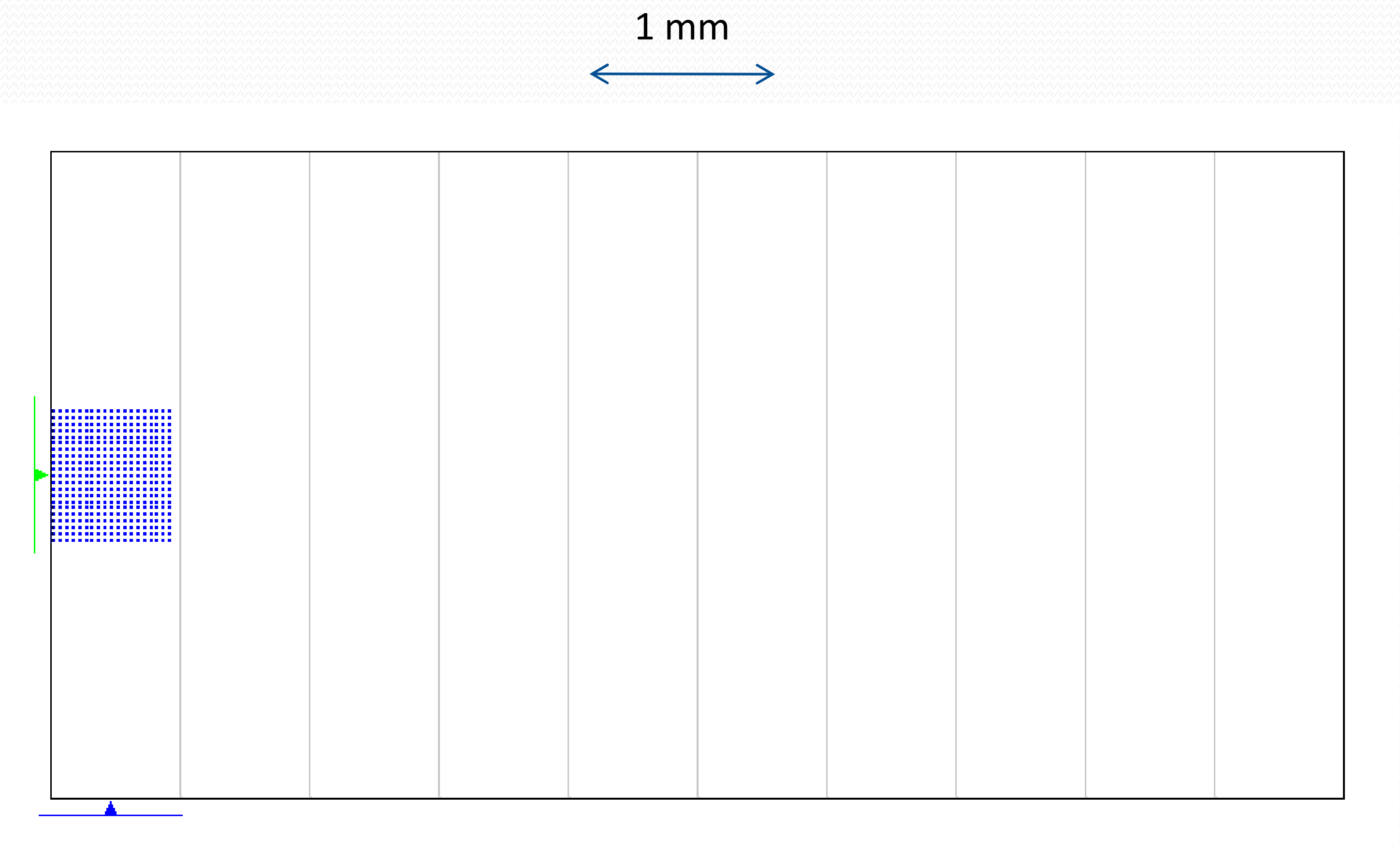
Diffusion: molecular (Brownian) motion



mouse click on figure to animate

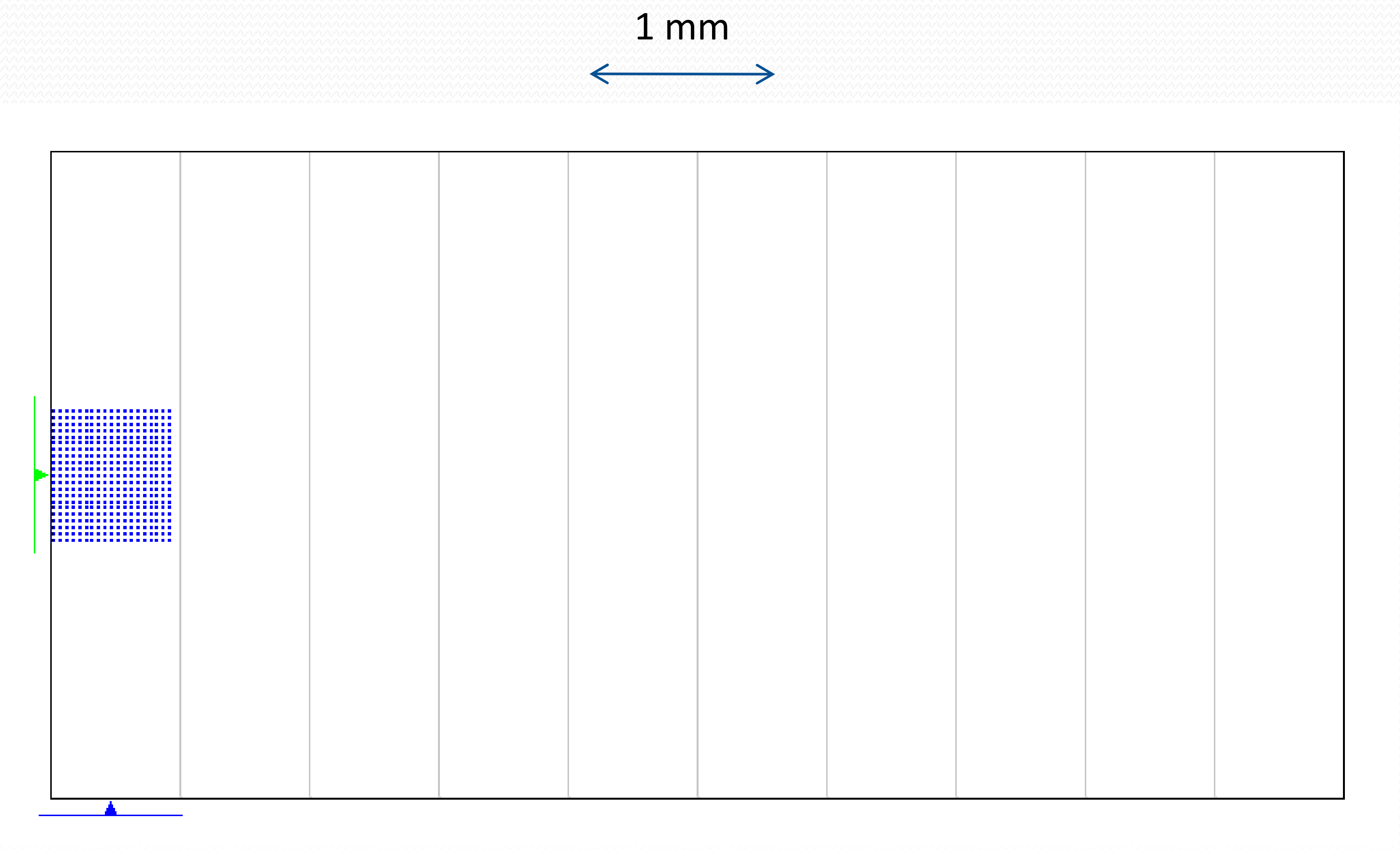
Transport Processes

Advection: transport with average flow



mouse click on figure to animate

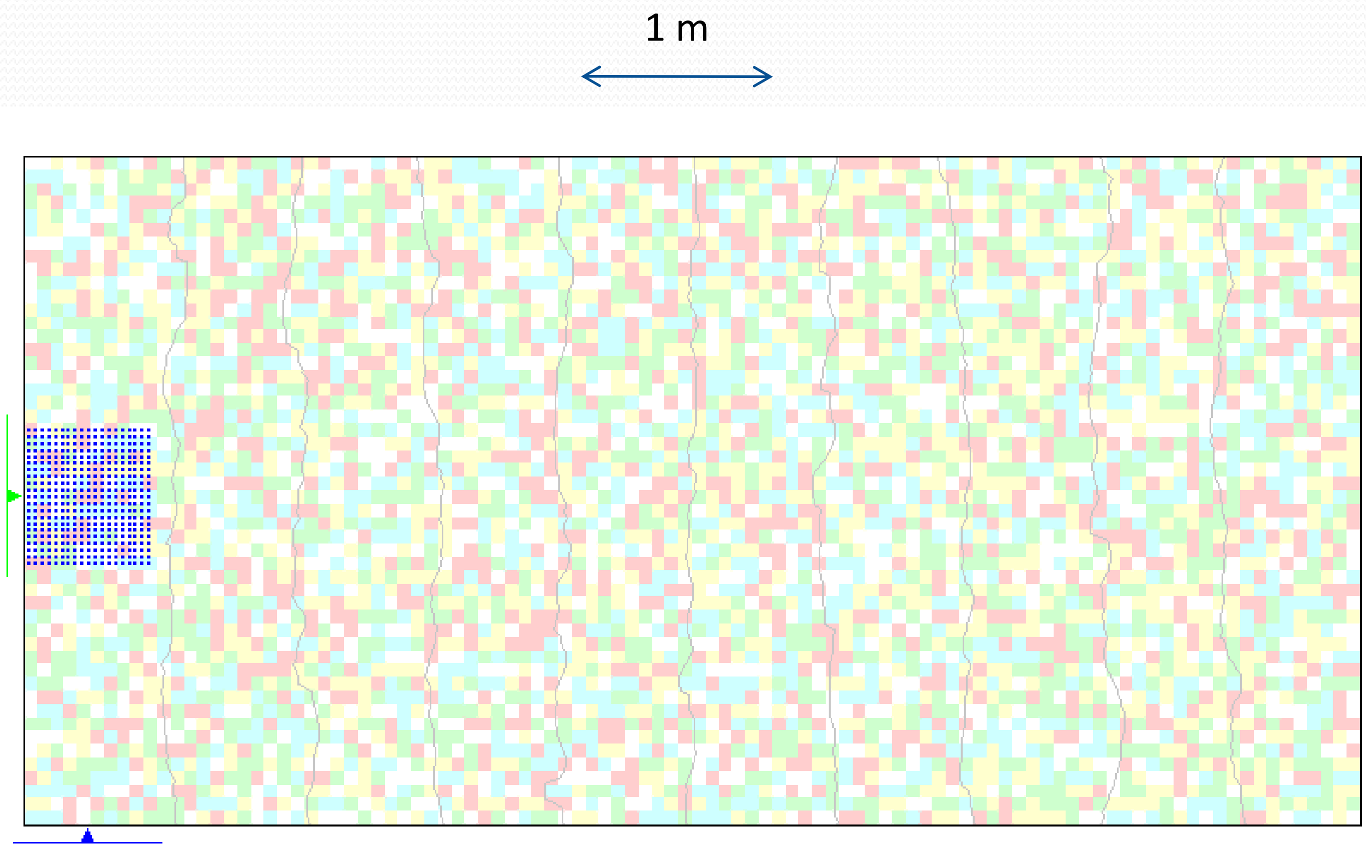
Transport Processes
Advection and Diffusion



mouse click on figure to animate

Transport Processes

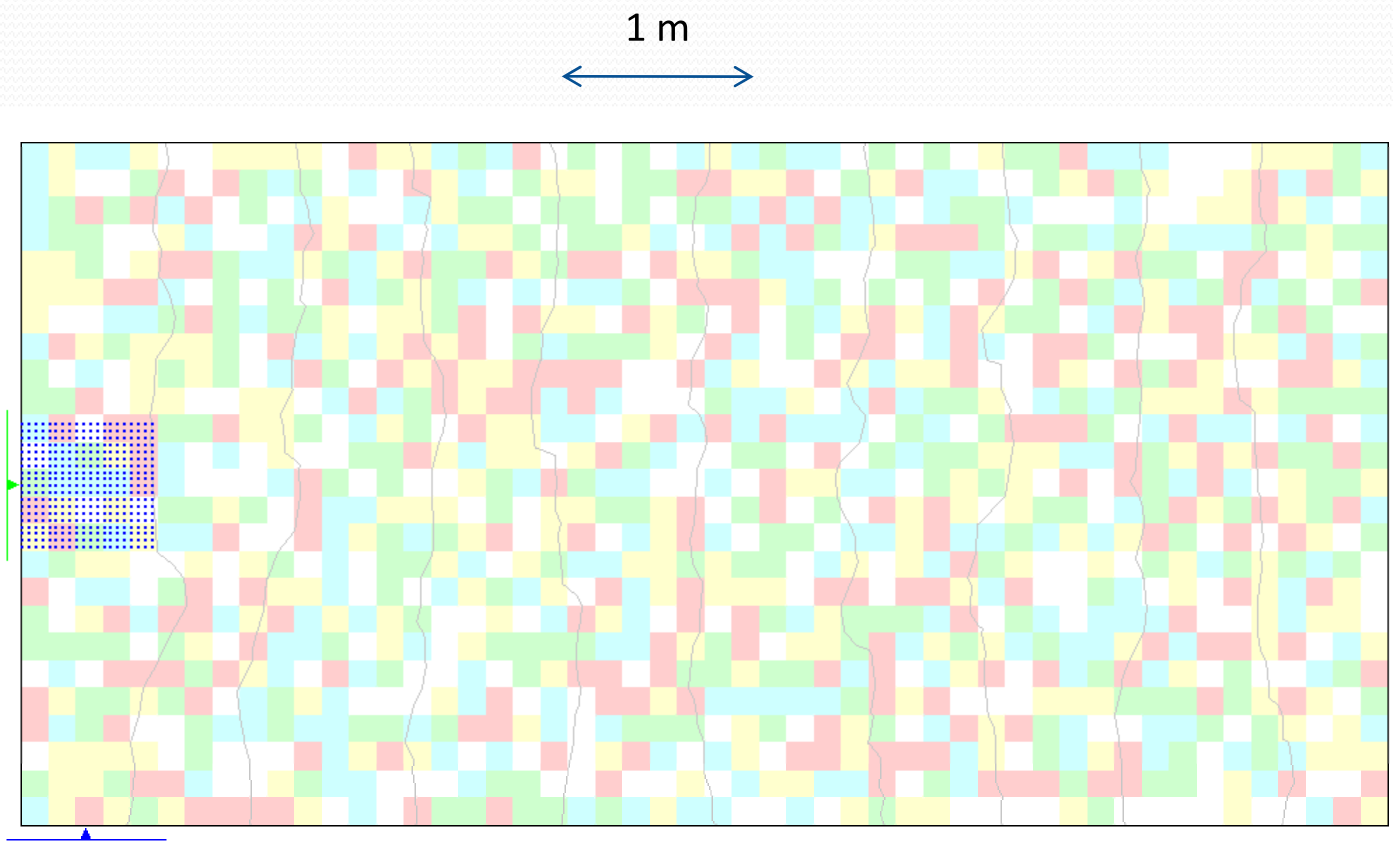
Dispersion: due to varying permeability (velocity)



mouse click on figure to animate

Transport Processes

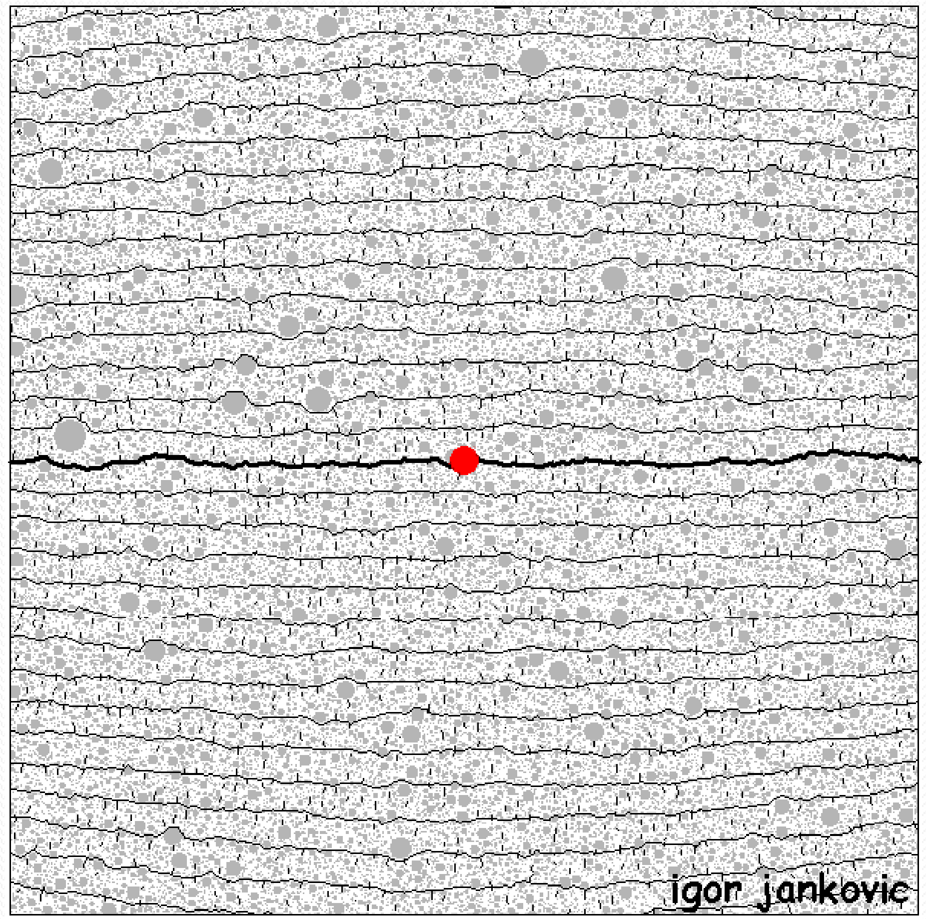
Dispersion: due to varying permeability (velocity)



mouse click on figure to animate

Matters of Scale

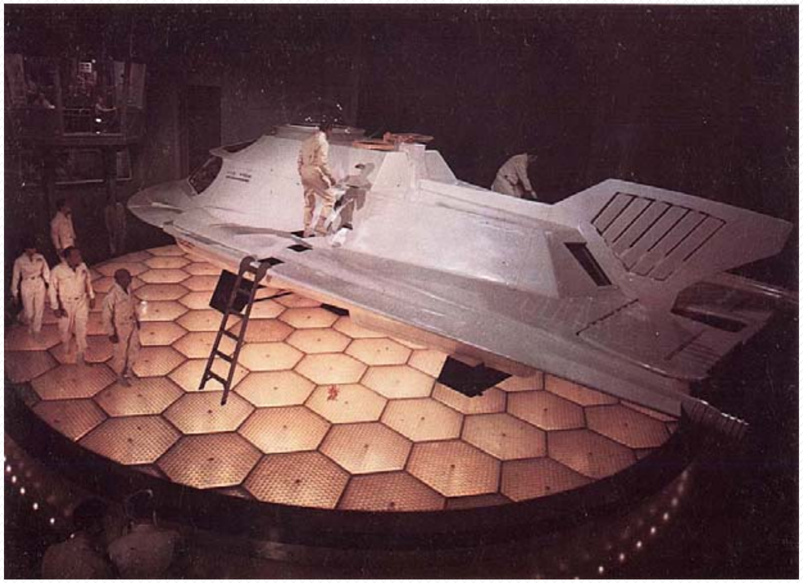
- Diffusion, advection, dispersion occur at all scales
- Not all significant at all length scales
- Measuring at one scale doesn't mean it will work at another scale



mouse click on figure to animate

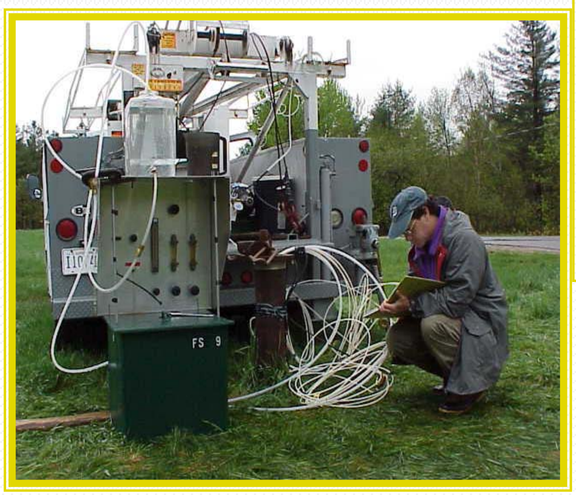
How do we know this stuff?

- Nanohydrogeophysics!?



How do we know this stuff?

- The best information we have is from field tracer tests
- We inject something with known properties and measure how it moves

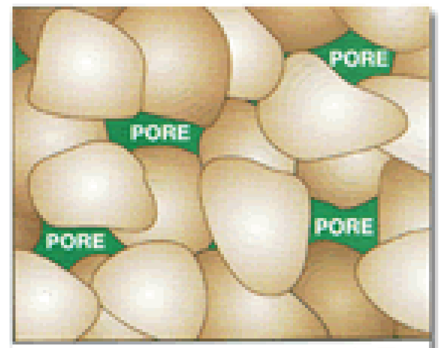


What is Special About Bedrock?

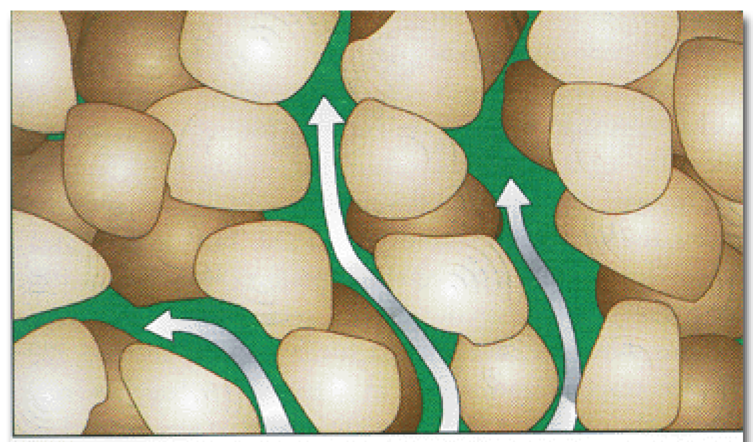
- Fractures reduce the effective porosity so water moves faster (but smaller volumes)
- Water and chemical exchange between the fracture and surrounding rock matrix
- Water flow tends to be “channeled” in fractures making water move even faster and detection even harder

Effective Porosity

- The total void space in a rock relative to the total sample volume is called "total porosity"
- Water flows only through the "effective" or hydraulic connected porosity
- Estimating effective porosity is difficult



A pore is a small open space



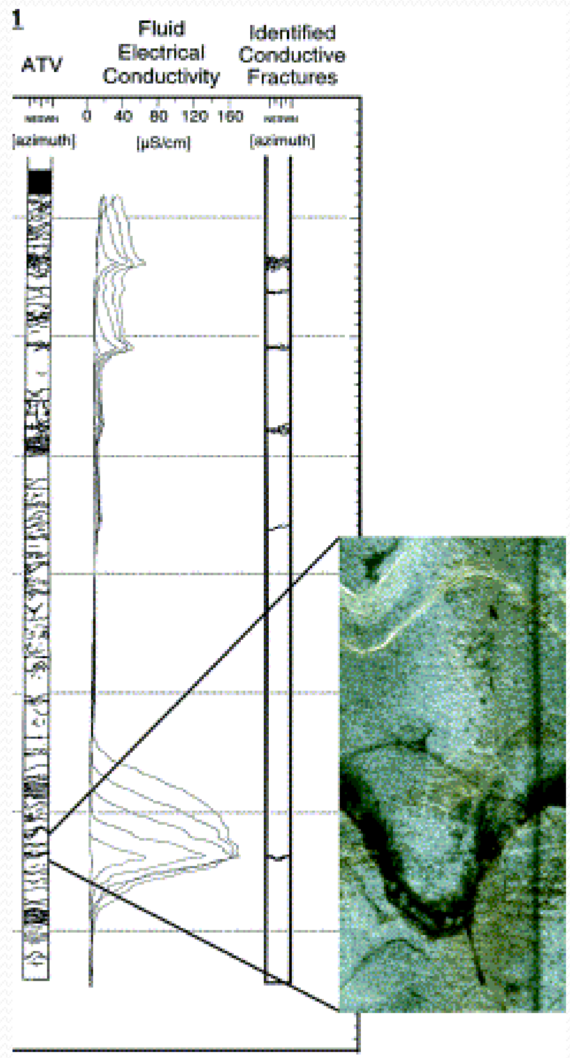
Connected pores give a rock permeability.

Effective Porosity

- This is a critical parameter for advection
- The smaller the effective pore space the faster the advective velocity.
- Fractured rock has very very small effective porosity at the field scale

Effective Porosity

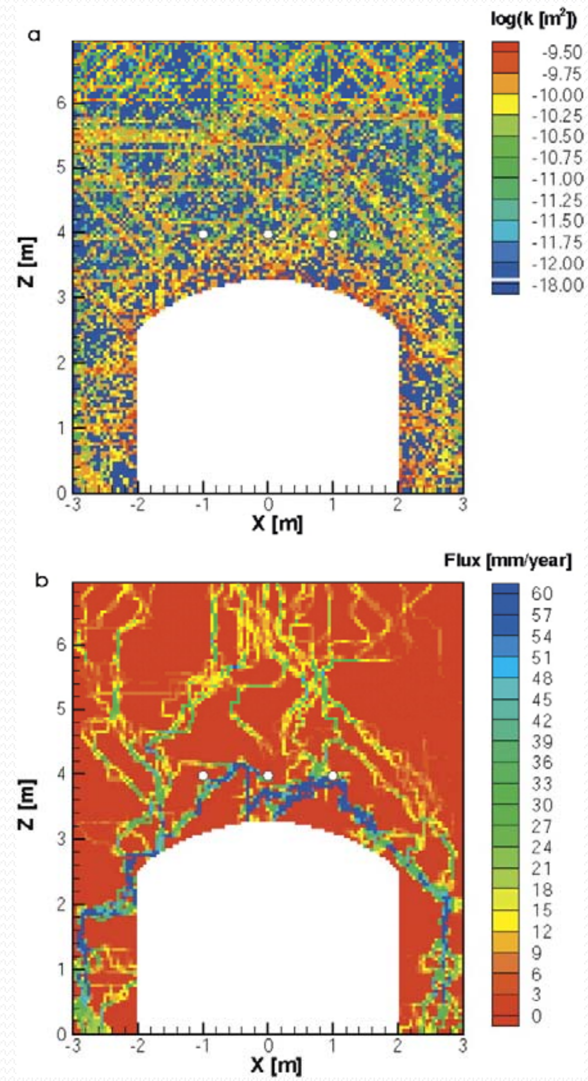
- Typically, only a fraction of observed fractures actually transmit water
- This granite has about 0.3% porosity but only 0.01% effective porosity



Cohen, A.J.B., 1995. Hydrogeologic characterization of fractured rock formations: A guide for groundwater remediation, LBL-38142, Lawrence Berkeley National Laboratory.

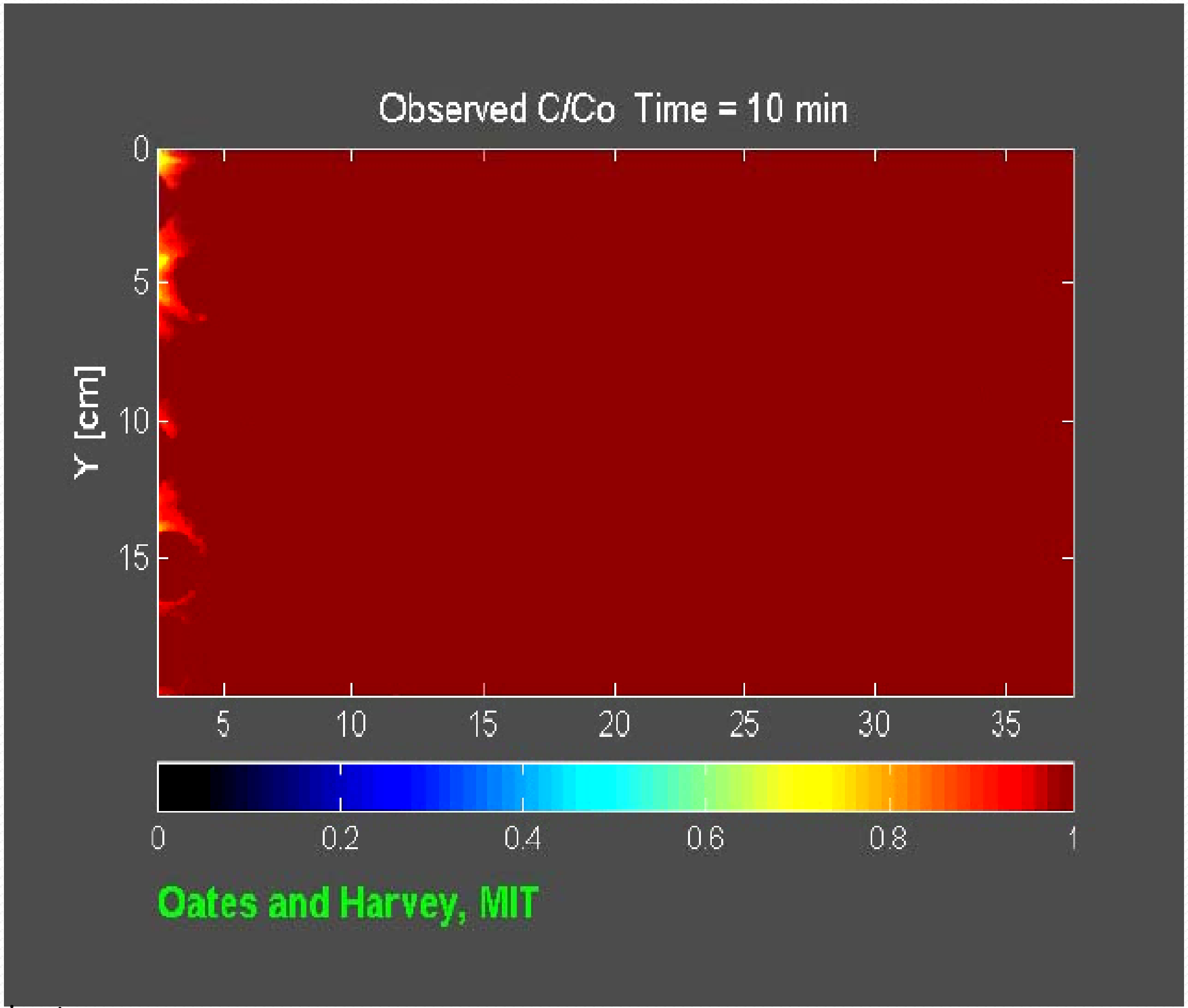
Effective Porosity in Bedrock

- Water flows only through connected fractures which tend to be widely dispersed
- Only a very small fraction of volume actually conducts fluid
- A reduction in effective porosity of 1/10 results in a 10x increase in velocity!



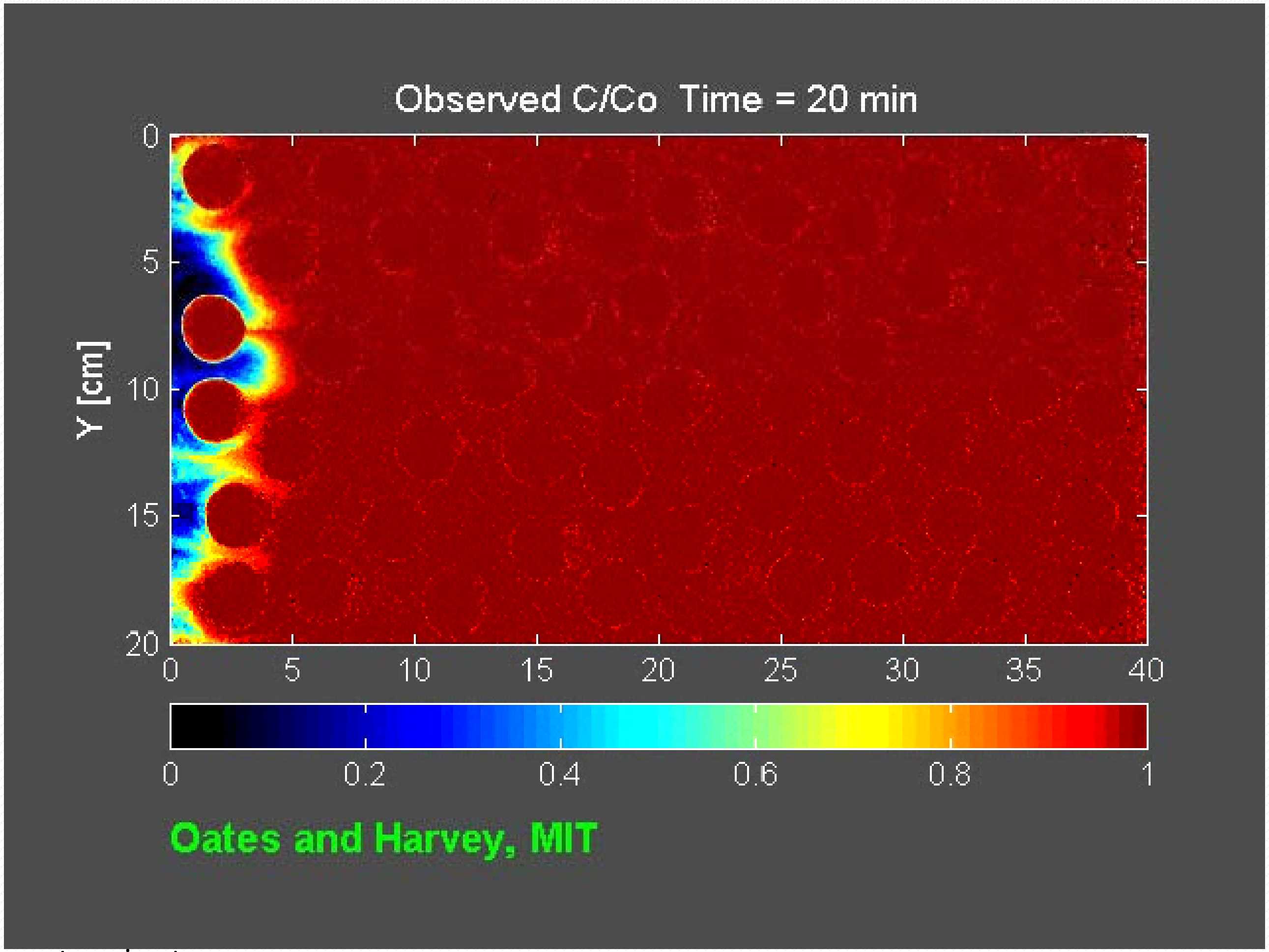
Finsterle, S. 2000. Using the continuum approach to model unsaturated flow in fractured rock. Water Resour. Res. 36:2055–2066

Dual Permeabililty



mouse click on figure to animate

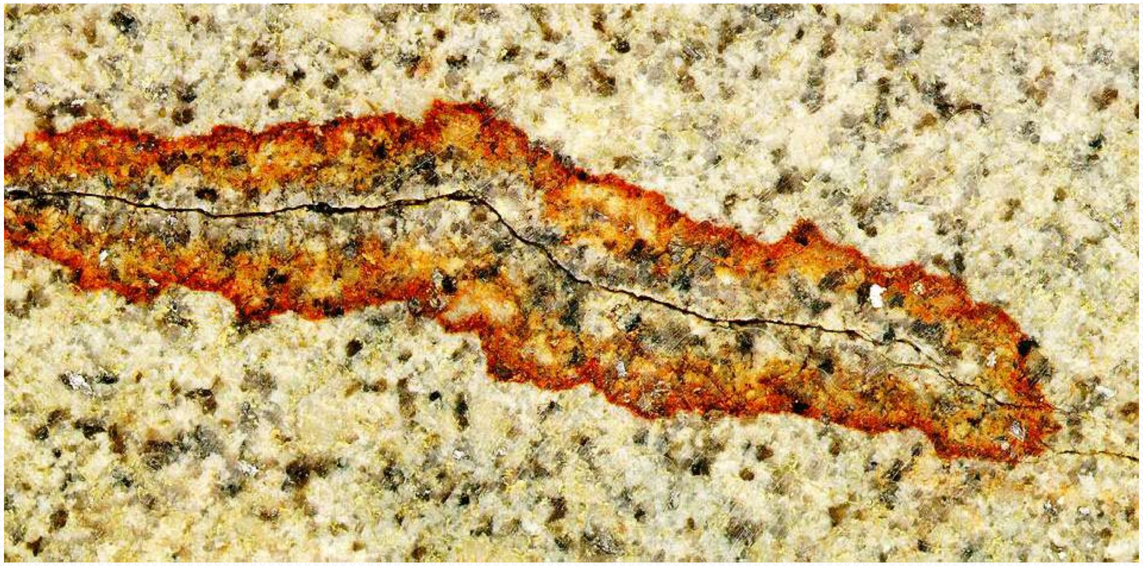
Dual Porosity



mouse click on figure to animate

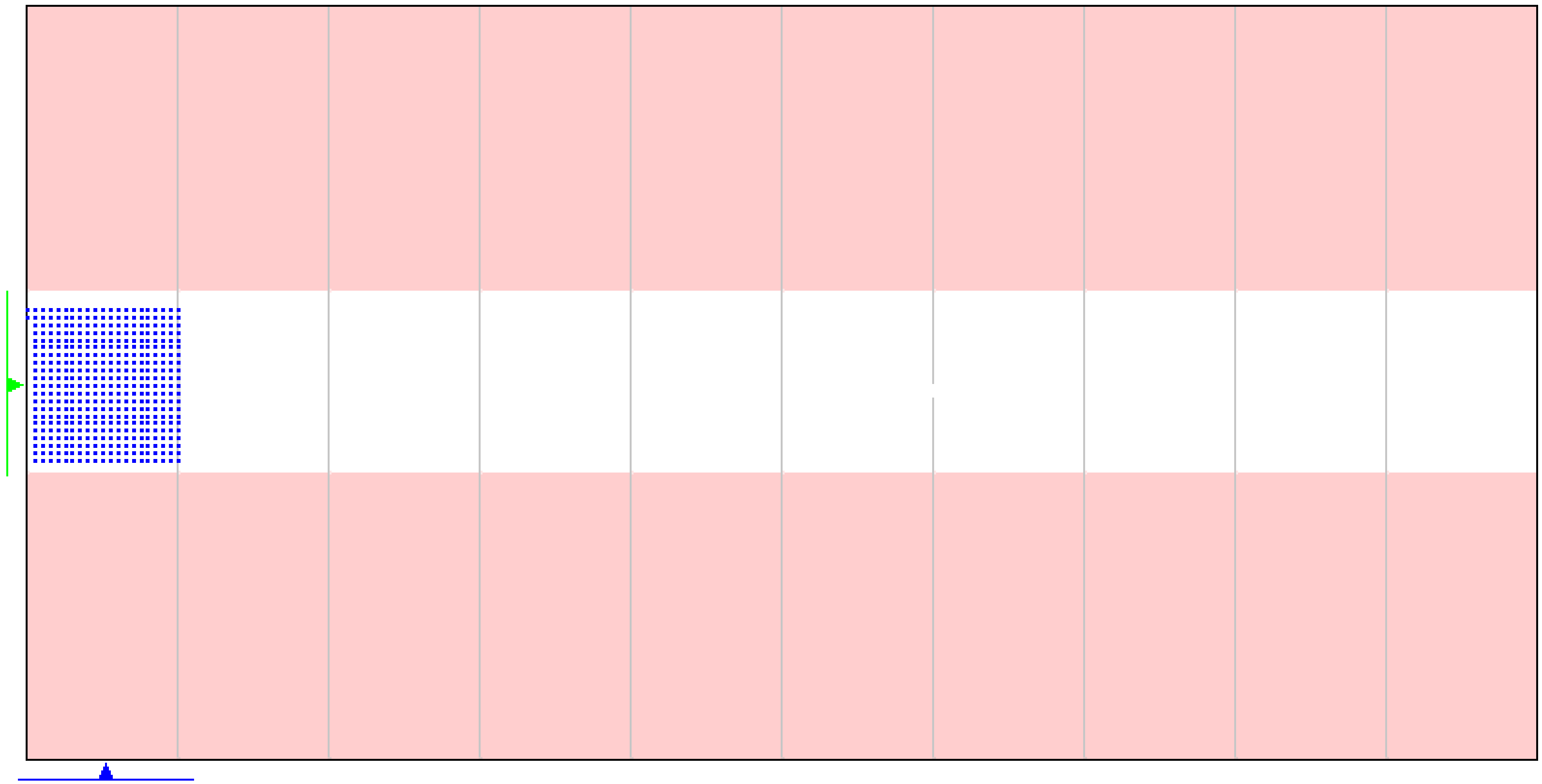
Matrix Diffusion

- Water flows mostly through fractures but can exchange through diffusion with matrix.
- Results that transport and remediation rates are slowed tremendously.



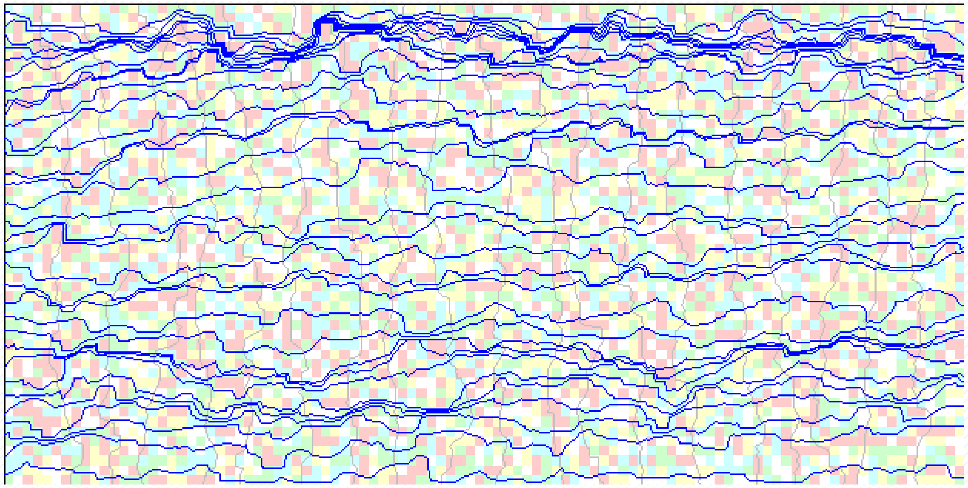
Matrix Diffusion

- Cross-section through fracture

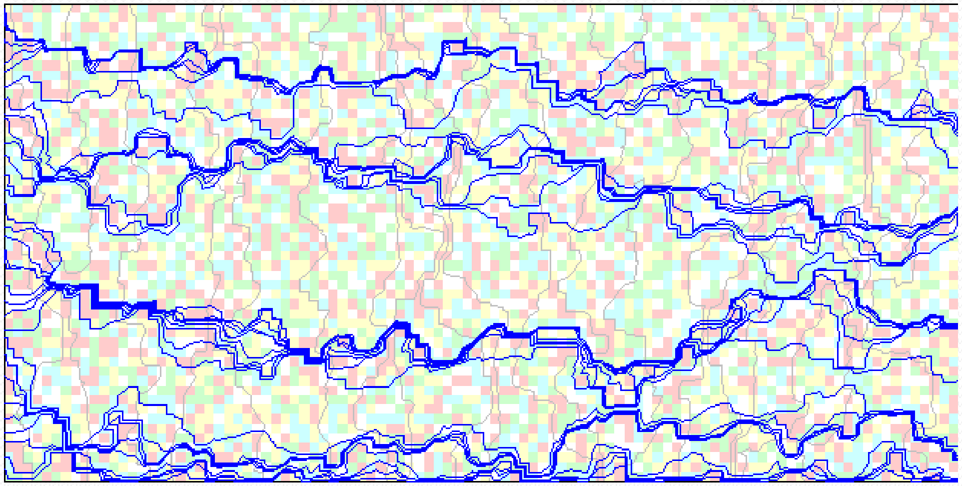


Channeling in a Fracture Plane

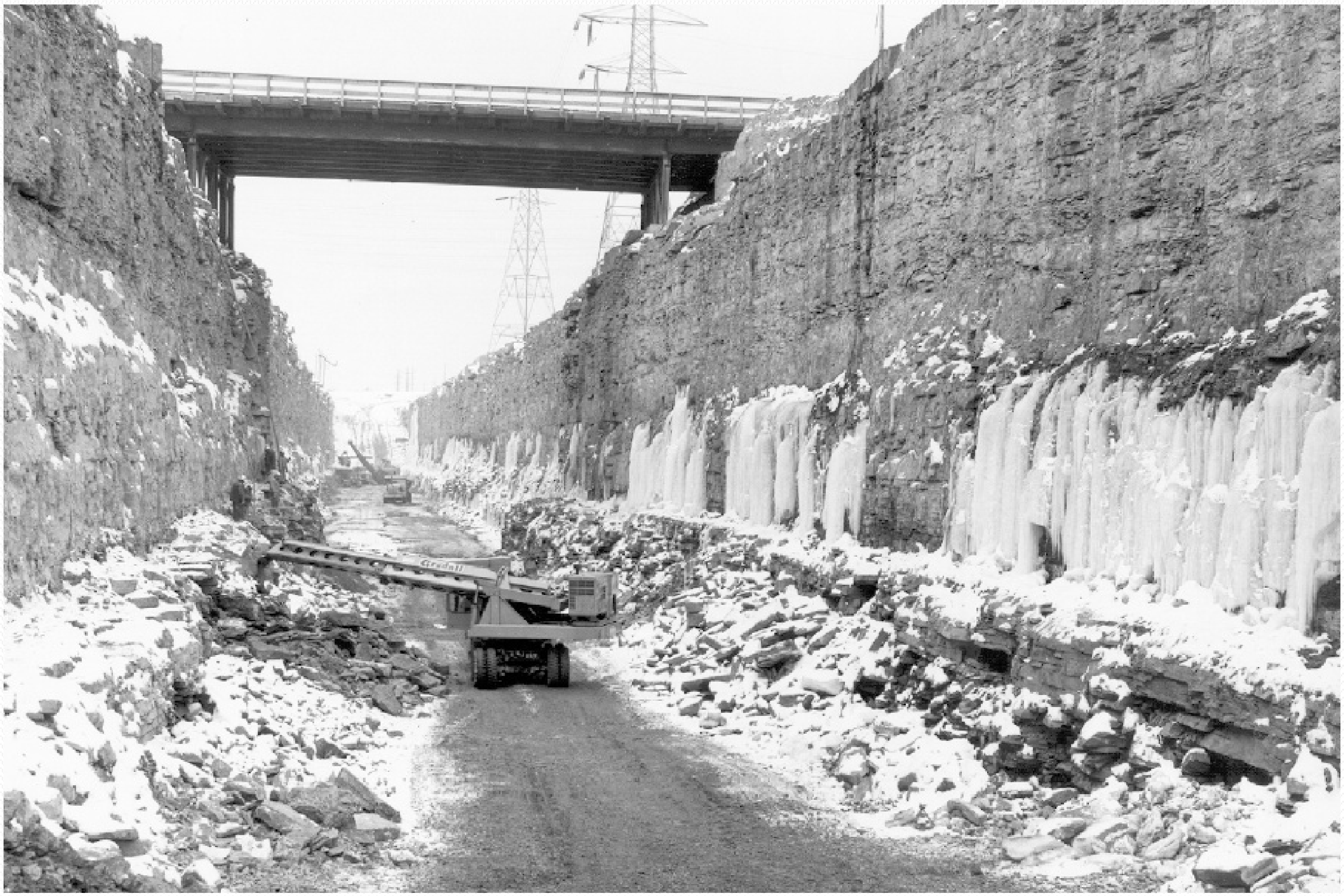
0.01 < K < 1



0.001 < K <10



Forebay Canal, Niagara Falls, NY

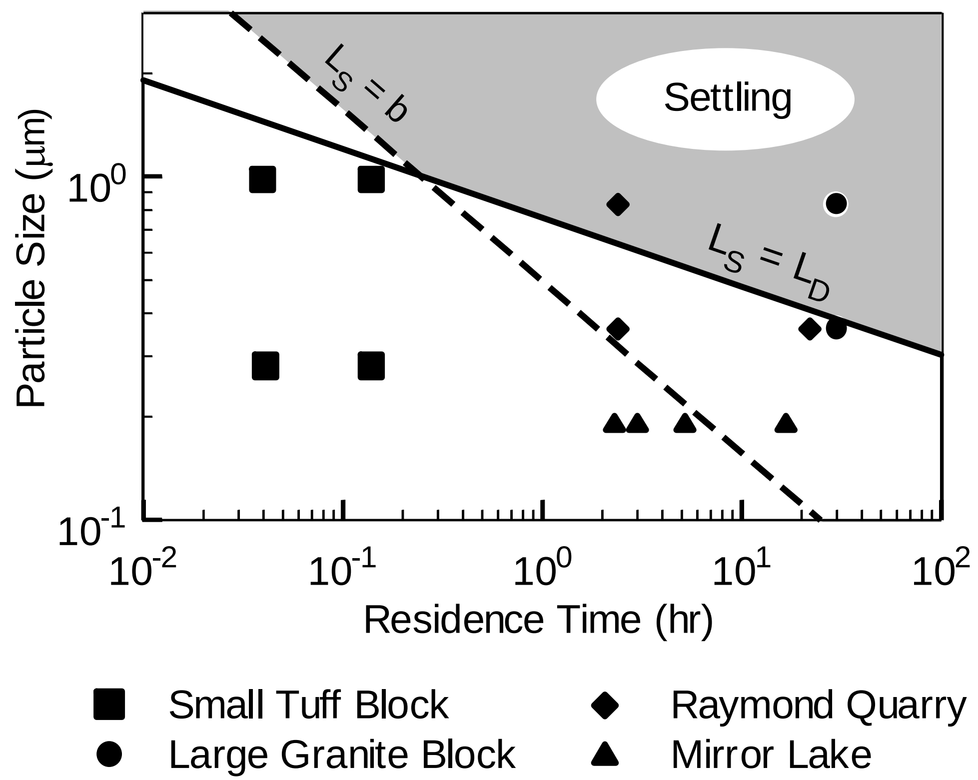


Immiscible Contaminants

- So far we have looked only at "solutes", dissolved phases
- Fuel, solvents, and particles can be separate phases
- Now we have to track transport of two phases at once

Particles and Colloids

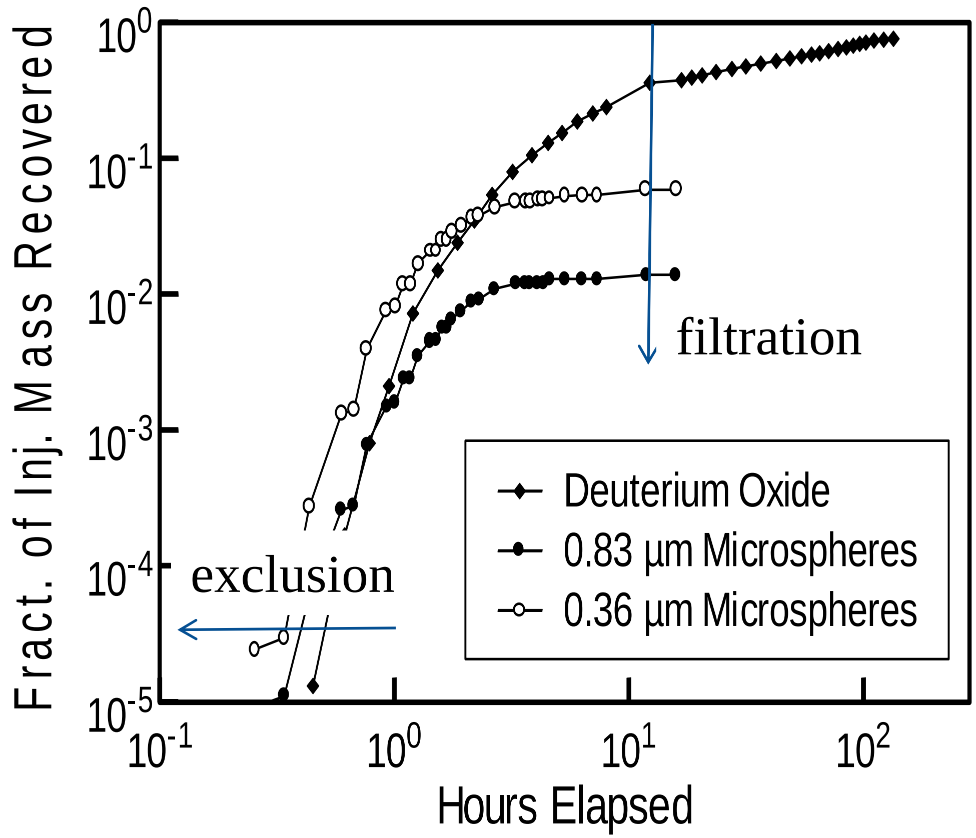
- Particles settle given enough time
- Colloids are too small to settle



Becker, M. W., P. W. Reimus, et al. (1999). "Transport and attenuation of carboxylate-modified latex microspheres in fractured rock laboratory and field tracer tests." Ground Water **37(3): 387-395.**

Pore-Size Exclusion Transport

- Colloids may migrate differently than solutes due to filtration and exclusion from small pores



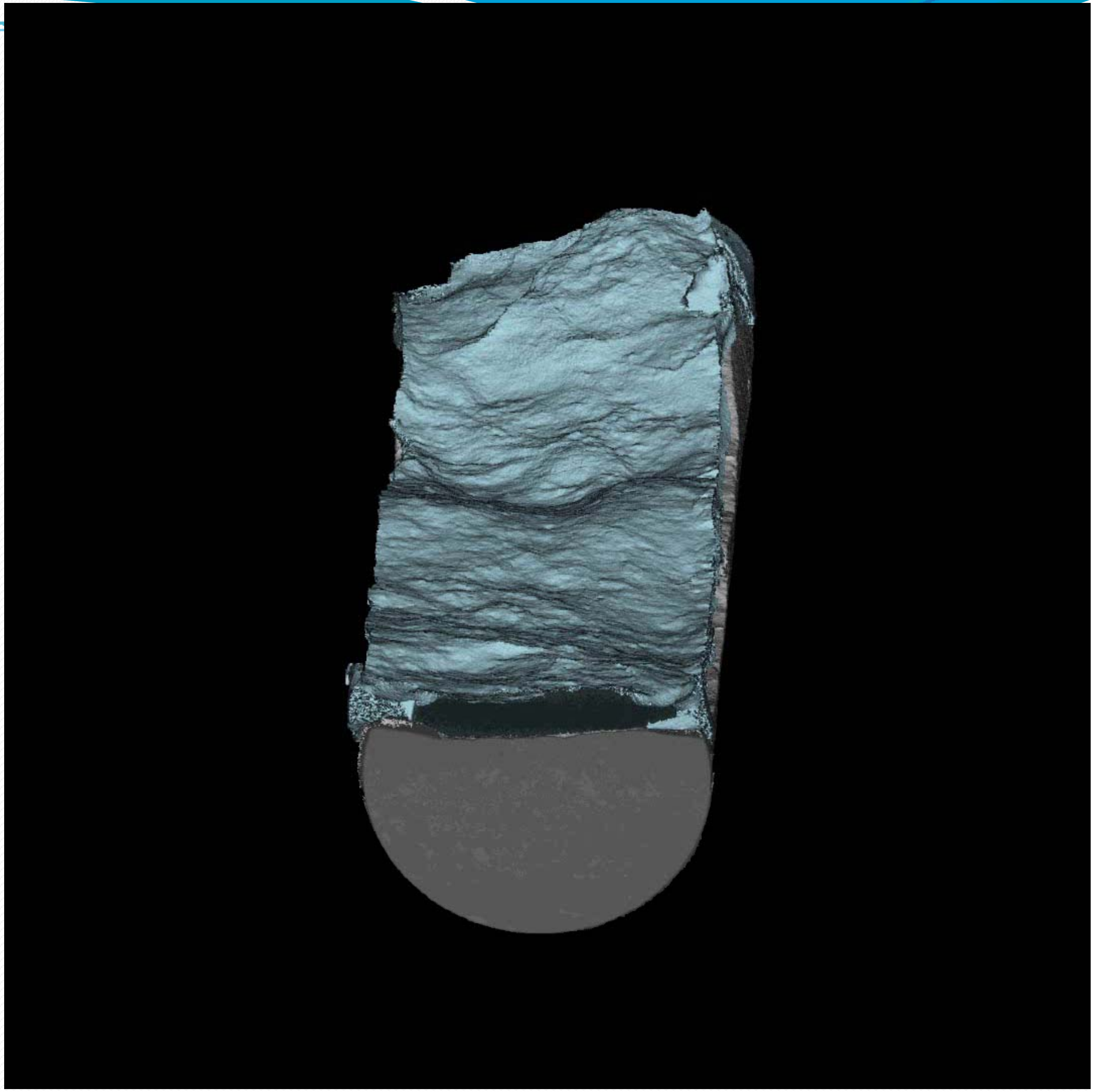
Becker, M. W., P. W. Reimus, et al. (1999). "Transport and attenuation of carboxylate-modified latex microspheres in fractured rock laboratory and field tracer tests." Ground Water **37(3): 387-395.**

“NAPL”

- NAPL = Non-Aqueous Phase Liquid
- DNAPL = NAPL denser than water (e.g. solvents)
- LNAPL = NAPL lighter than water (e.g. gasoline)
- APL = Aqueous Phase Liquid (dissolved)

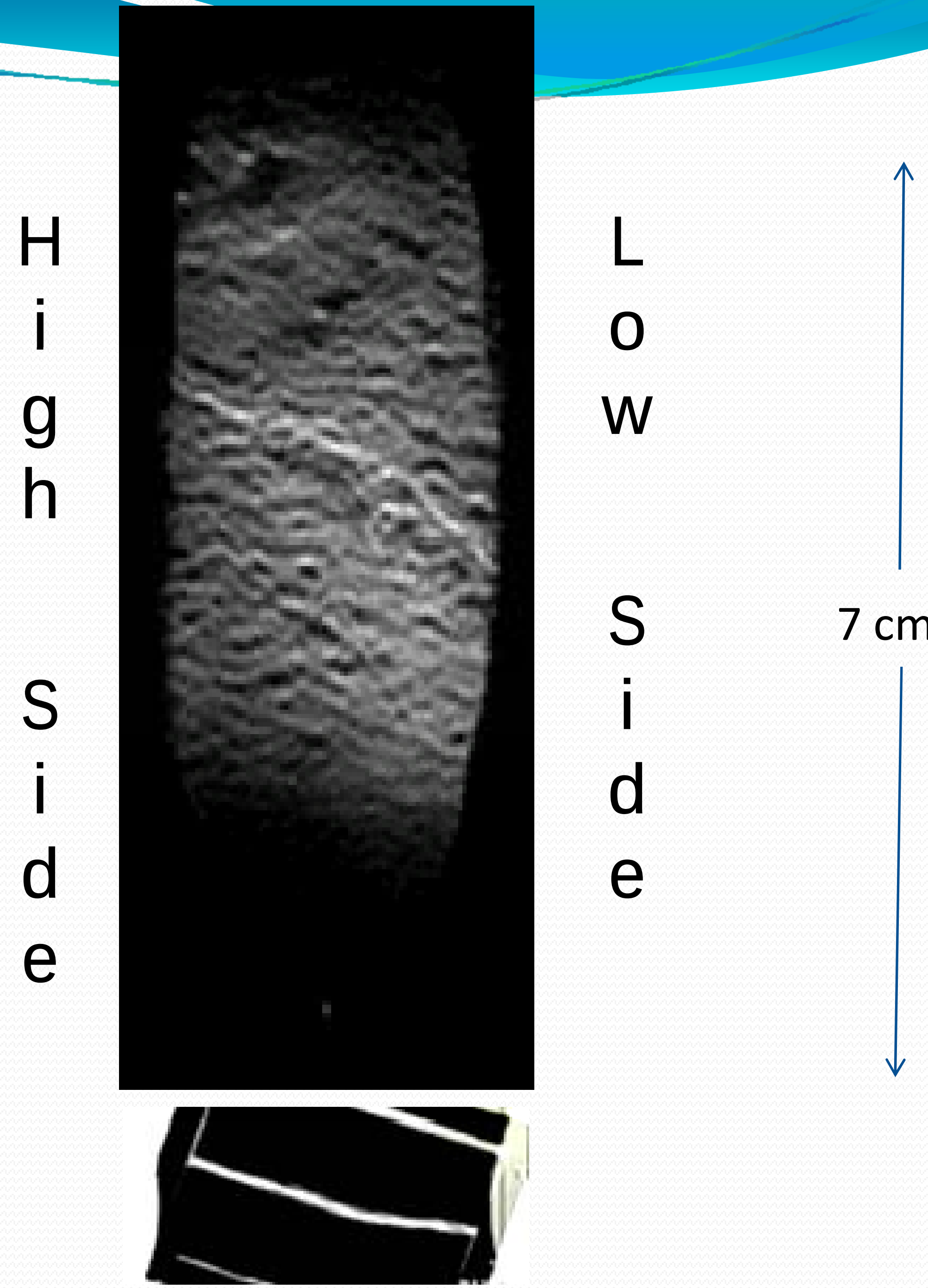
DNAPL from Well CD-2U
Hyde Park Site, Niagara Falls, NY

X-Ray CT of Natural Fracture (3x7cm)



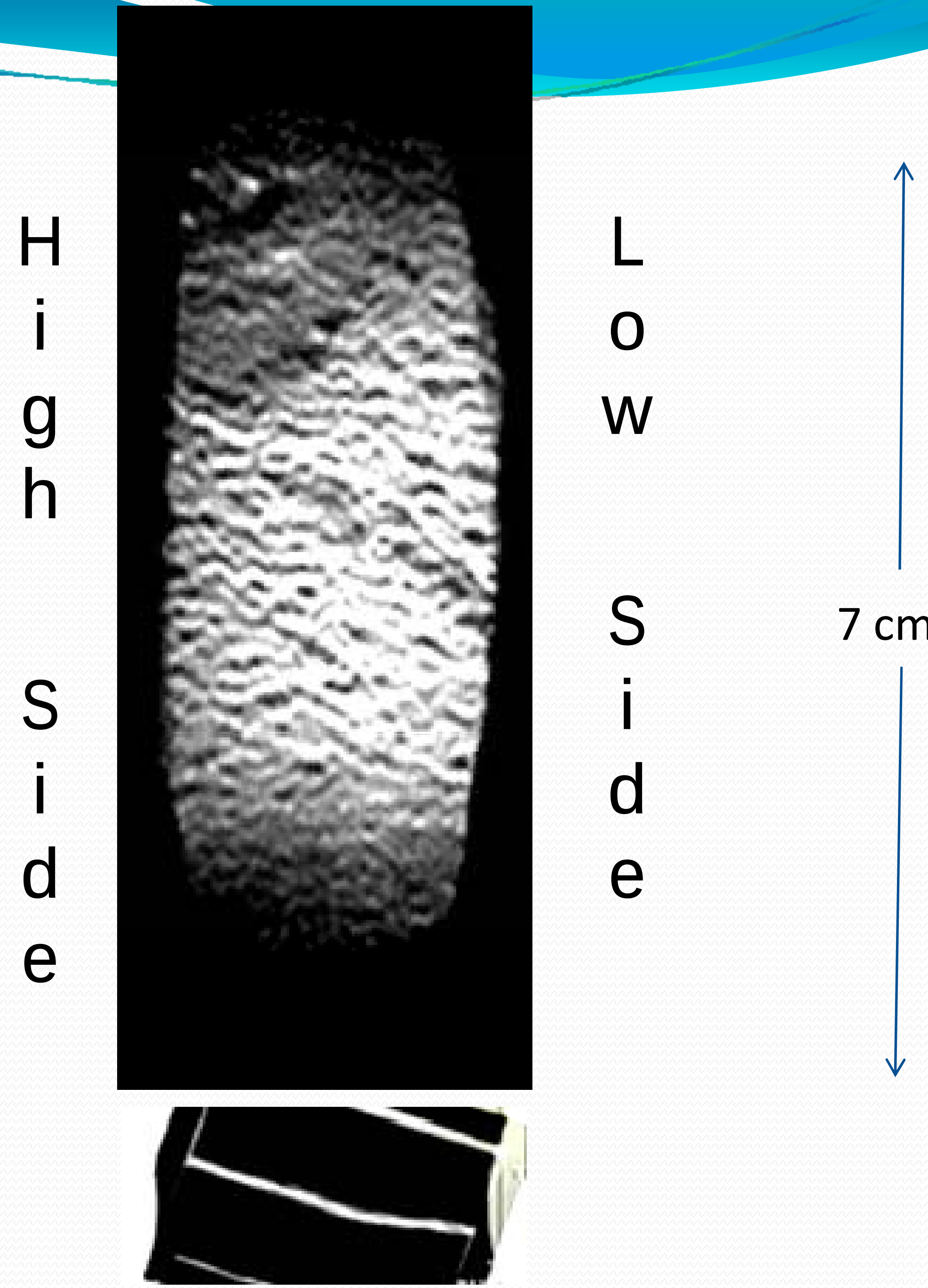
mouse click on figure to animate

Dodecane (LNAPL) Infiltrates Water



mouse click on figure to animate

FC-75 (DNAPL) Infiltrates Water

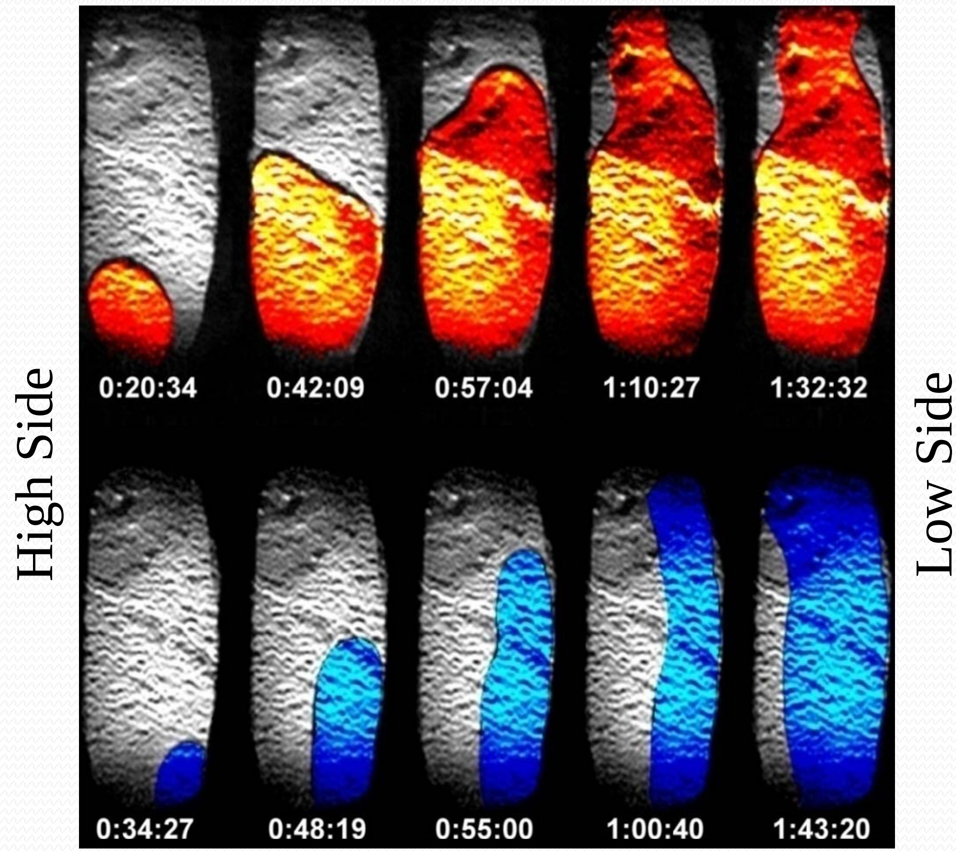


mouse click on figure to animate

LNAPL vs DNAPL

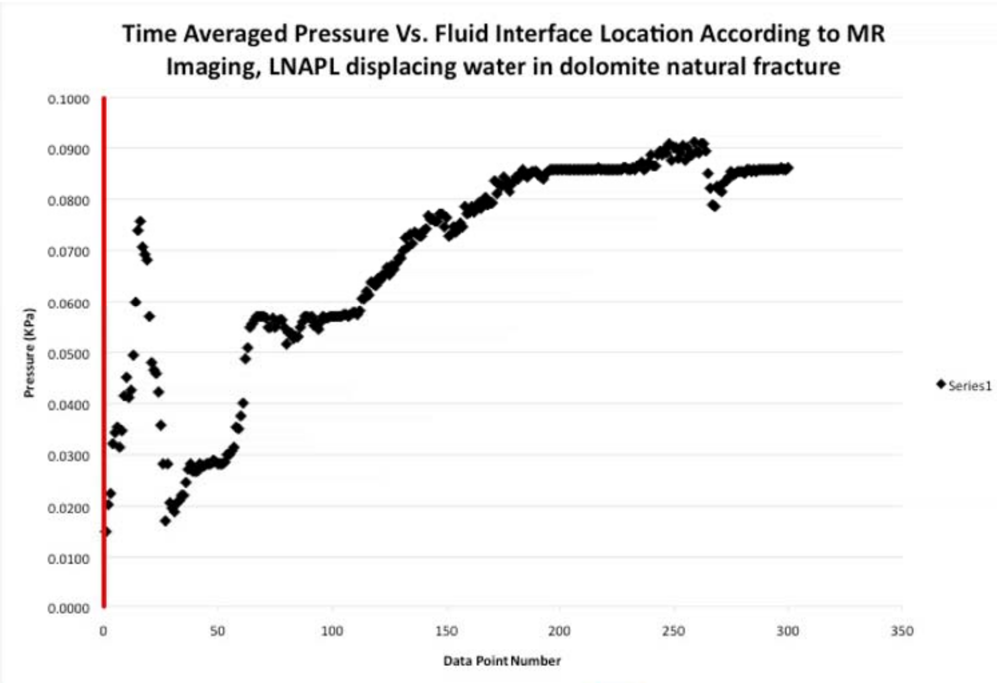
LNAPL

DNAPL



After Becker, M. W., M. Pelc, R. V. Mazurchuk, and J. Spernyak (2003), Magnetic resonance imaging of dense and light non-aqueous phase liquid in a rock fracture, *Geophysical Research Letters, 30(12).*

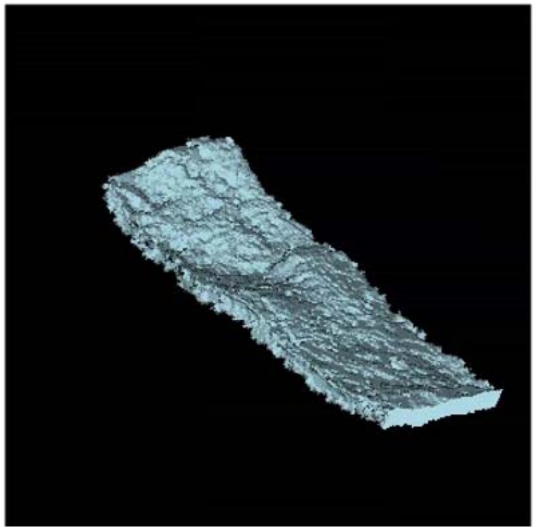
Pressure Resistance Due to Topography

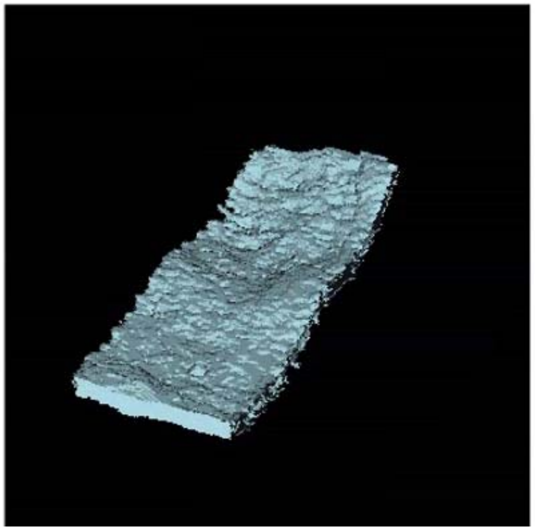


Measured pressure in reference to dodecane slug's location in rock fracture

Dodecane Slug

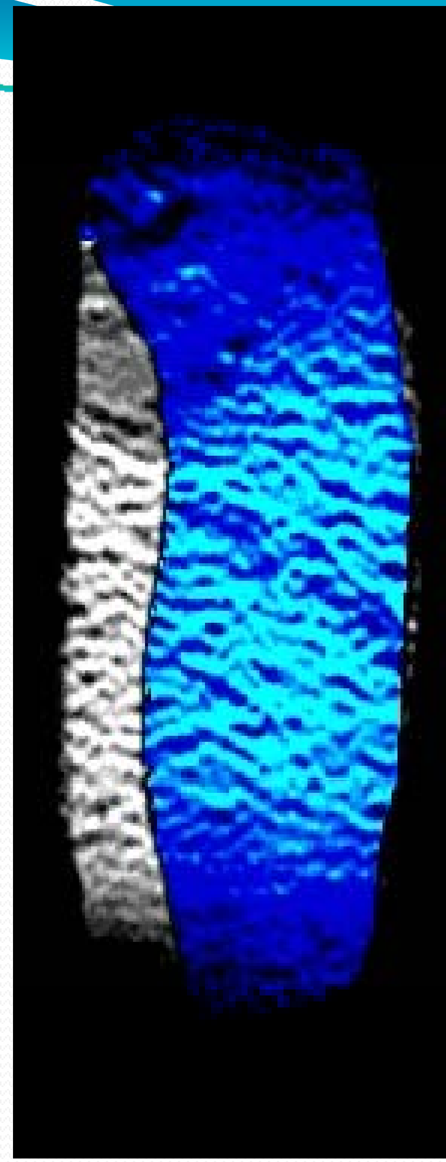
Water Saturated Rock Fracture





Water Infiltrates FC-75 (DNAPL)

High Side



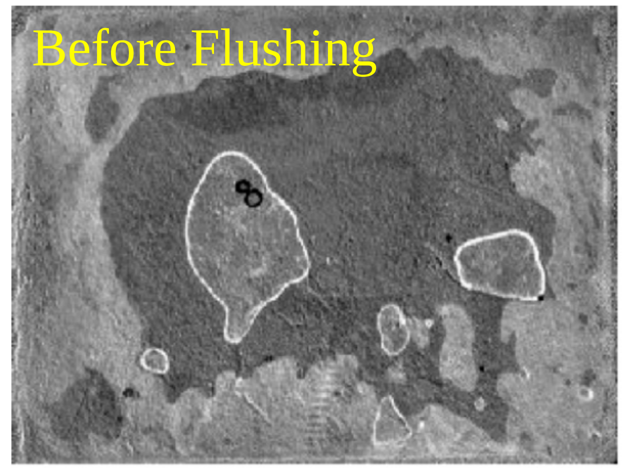
Low Side

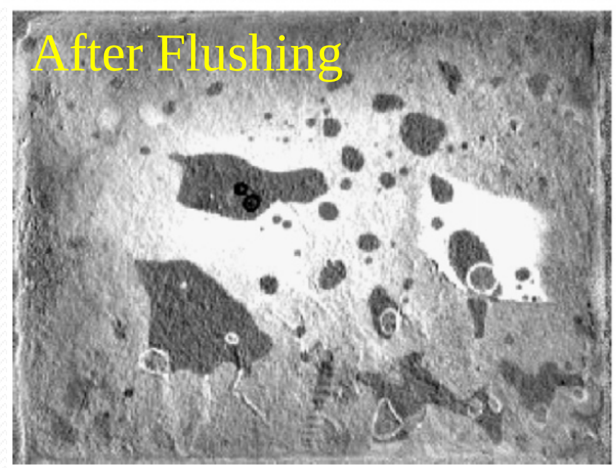
7 cm

mouse click on figure to animate

“Ganglia” of NAPL

- Trying to flush NAPL from fracture leaves residual “ganglia”
- Ganglia cannot be forced from fracture but must be dissolved
- Dissolution is slow because surface area is slow

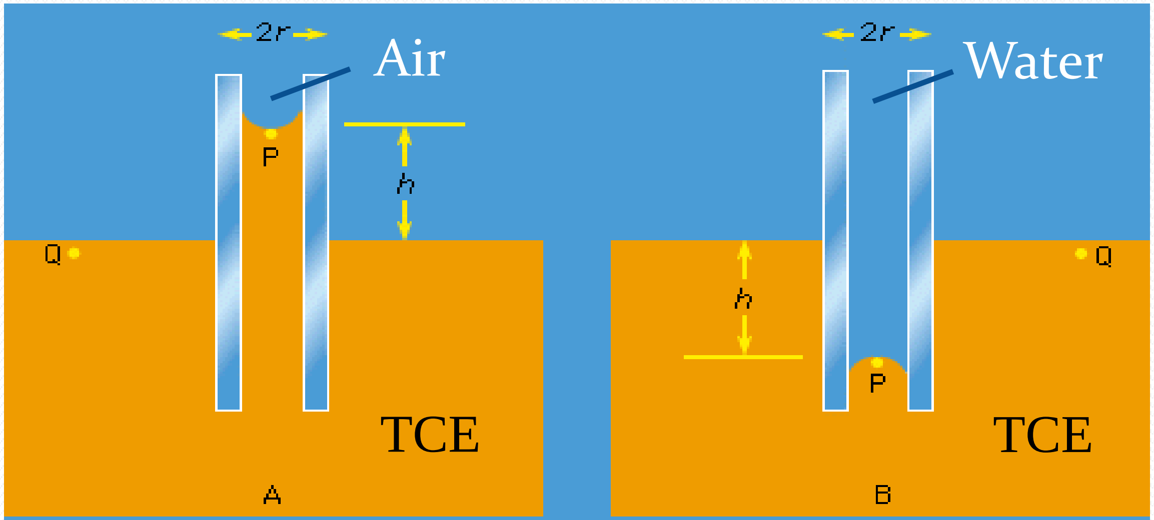




Bergslien, E., Fountain, J., 2006. The effect of changes in surface wettability on two-phase saturated flow in horizontal replicas of single natural fractures. Journal of Contaminant Hydrology, 88(3-4): 153-180.

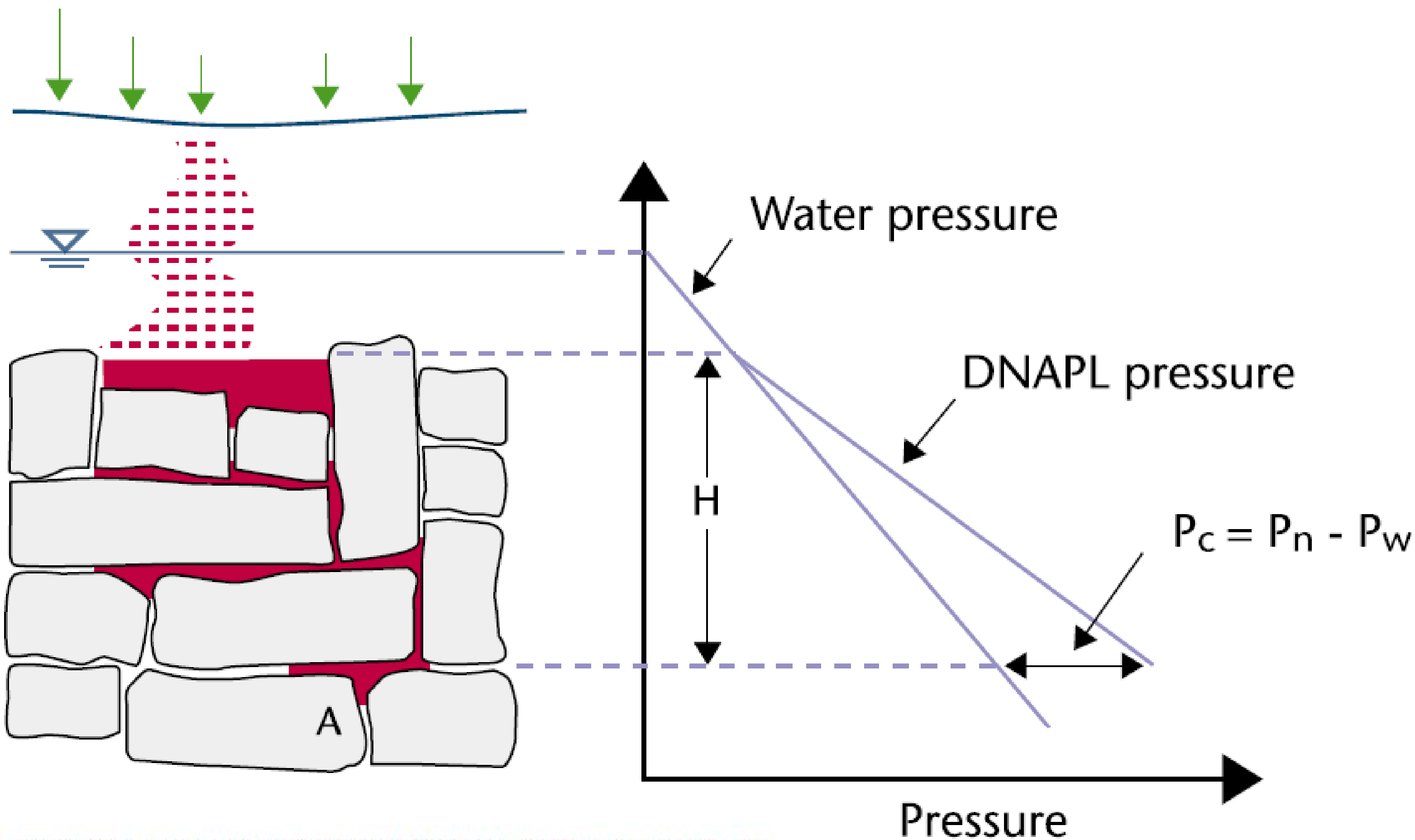
Capillary Effects on NAPL

- Phases will enter pores depending upon their affinity for the solid walls versus resident fluid
- Wetting fluid displaces non-wetting fluid



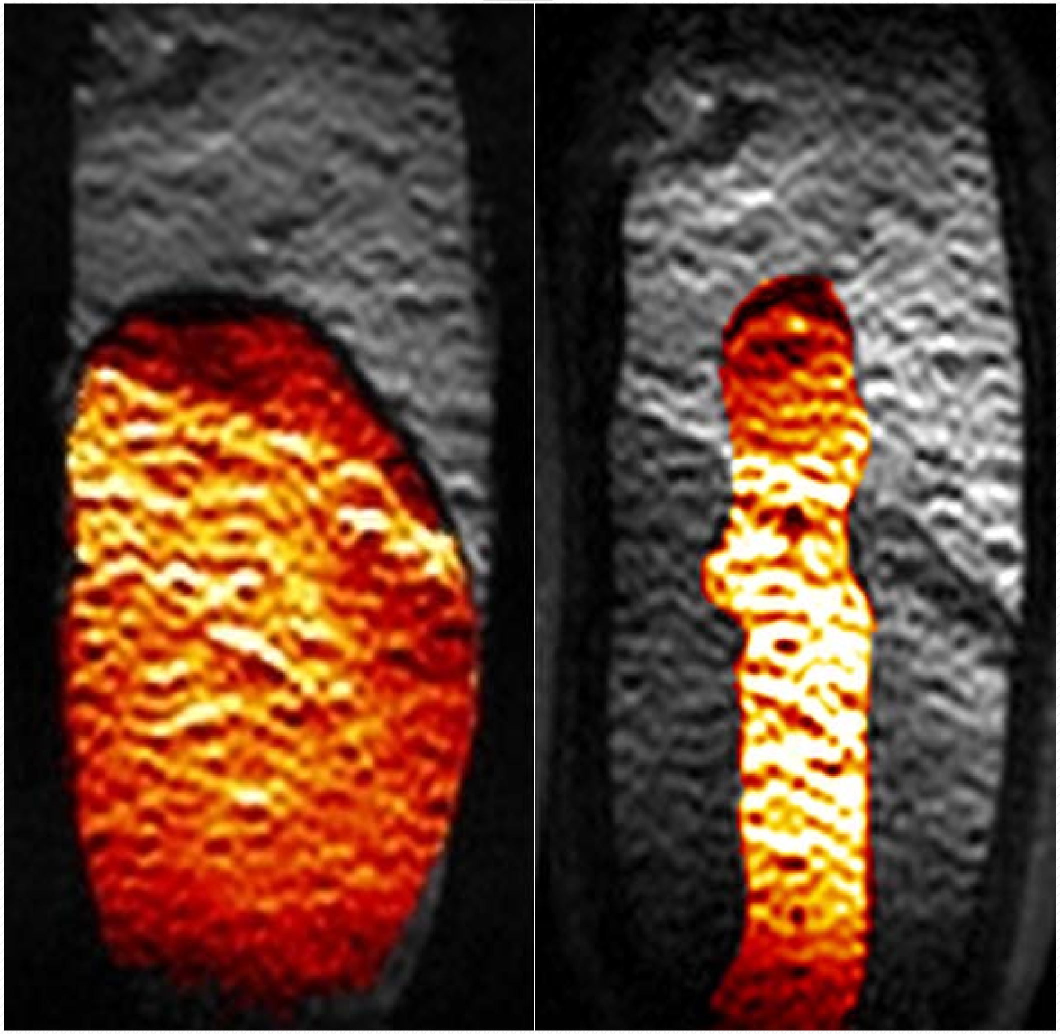
(A) The liquid wets the tube and rises up in it. (B) The liquid does not wet the tube and is depressed.

DNAPL Overpressure



Environment Agency Illustrated handbook of DNAPL transport and fate in the subsurface

Dodecane Infiltration Water: Effect of Surface Chemistry



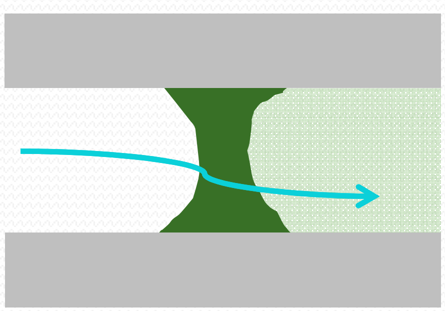
Before Saturation with Dodecane

After Saturation with Dodecane

Miscible versus Immiscible

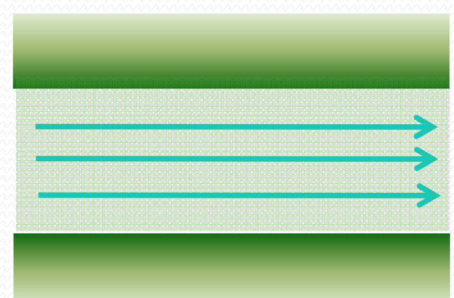
Immiscible

- Mass mostly in fractures as ganglia or pools
- Surface area small

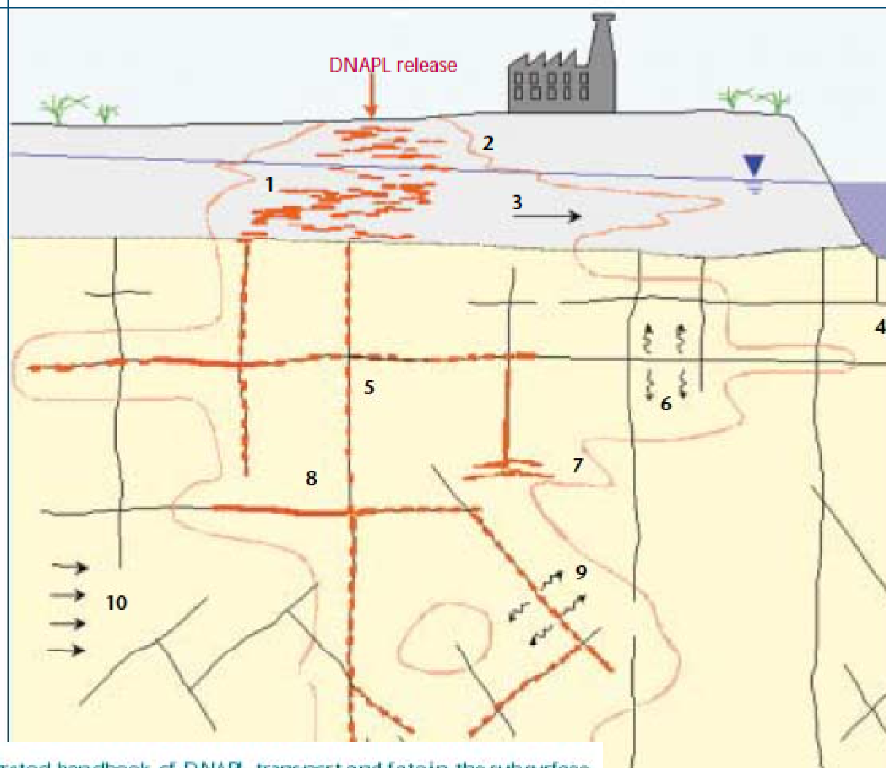


Miscible

- Mass mostly in matrix
- Surface area large



The Overall Picture

Features	Release of chlorinated solvent DNAPL into Triassic Sandstone	Domain
1 Residual and pooled DNAPL in drift 2 Vapour 3 Aqueous phase plume migration 4 Aqueous phase plume migration in fracture 5 Residual DNAPL in fractures 6 Aqueous phase matrix diffusion 7 DNAPL penetration into coarse grained matrix 8 Pooled DNAPL in fractures 9 Matrix diffusion adjacent to DNAPL 10 Groundwater flow direction 11 DNAPL migration to depth		**Surface** **Drift** (unsaturated) **Drift** (saturated) **Bedrock** (saturated)

Environment Agency Illustrated handbook of DNAPL transport and fate in the subsurface

EPA 129 Priority Pollutants

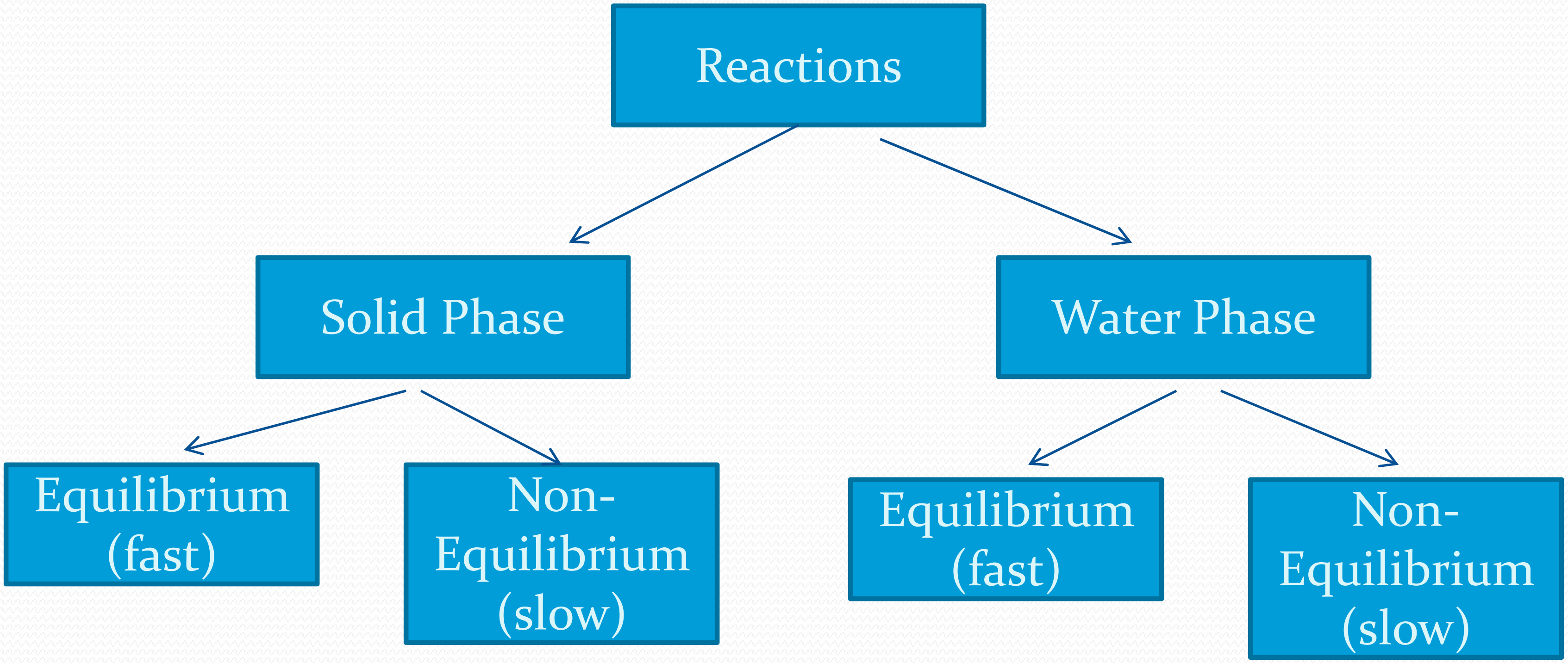
- Acenaphthene
- Acrolein
- Acrylonitrile
- Benzene
- Benzidine
- Carbon tetrachloride
- Chlorobenzene
- 1,2,4-trichlorobenzene
- Hexachlorobenzene
- 1,2-dichloroethane
- 1,1,1-trichloreothane
- Hexachloroethane
- 1,1-dichloroethane
- 1,1,2-trichloroethane
- 1,1,2,2-tetrachloroethane
- Chloroethane
- REMOVED
- Bis(2-chloroethyl) ether
- 2-chloroethyl vinyl ethers
- 2-chloronaphthalene
- 2,4,6-trichlorophenol
- Parachlorometa cresol
- Chloroform
- 2-chlorophenol
- 1,2-dichlorobenzene
- 1,3-dichlorobenzene
- 1,4-dichlorobenzene
- 3,3-dichlorobenzidine
- 1,1-dichloroethylene
- 1,2-trans-dichloroethylene
- 2,4-dichlorophenol
- 1,2-dichloropropane
- 1,2-dichloropropylene
- 2,4-dimethylphenol
- 2,4-dinitrotoluene
- 2,6-dinitrotoluene
- 1,2-diphenylhydrazine

- Ethylbenzene
- Fluoranthene
- 4-chlorophenyl phenyl ether
- 4-bromophenyl phenyl ether
- Bis(2-chloroisopropyl) ether
- Bis(2-chloroethoxy) methane
- Methylene chloride
- Methyl chloride
- Methyl bromide
- Bromoform
- Dichlorobromomethane
- REMOVED
- REMOVED
- Chlorodibromomethane
- Hexachlorobutadiene
- Hexachlorocyclopentadie ne
- Isophorone
- Naphthalene
- Nitrobenzene
- 2-nitrophenol
- 4-nitrophenol
- 2,4-dinitrophenol
- 4,6-dinitro-o-cresol
- N-nitrosodimethylamine
- N-nitrosodiphenylamine
- N-nitrosodi-n-propylamine
- Pentachlorophenol
- Phenol
- Bis(2-ethylhexyl) phthalate
- Butyl benzyl phthalate
- Di-N-Butyl Phthalate
- Di-n-octyl phthalate
- Diethyl Phthalate
- Dimethyl phthalate
- benzo(a) anthracene
- Benzo(a)pyrene
- Benzo(b) fluoranthene
- Benzo(b) fluoranthene

- Chrysene
- Acenaphthylene
- Anthracene
- Benzo(ghi) perylene
- Fluorene
- Phenanthrene
- Dibenzo(,h) anthracene
- Indeno (1,2,3-cd) pyrene
- Pyrene
- Tetrachloroethylene
- Toluene
- Trichloroethylene
- Vinyl chloride
- Aldrin
- Dieldrin
- Chlordane
- 4,4-DDT
- 4,4-DDE
- 4,4-DDD
- Toxaphene Alpha-endosulfan
- Beta-endosulfan
- Endosulfan sulfate
- Endrin
- Endrin aldehyde
- Heptachlor
- Heptachlor epoxide
- Alpha-BHC
- Beta-BHC
- Gamma-BHC
- Delta-BHC
- PCB–1242 (Arochlor 1242)
- PCB–1254 (Arochlor 1254)
- PCB–1221 (Arochlor 1221)
- PCB–1232 (Arochlor 1232)
- PCB–1248 (Arochlor 1248)
- PCB–1260 (Arochlor 1260)
- PCB–1016 (Arochlor 1016)
- 2,3,7,8-TCDD

Antimony
Arsenic
Asbestos
Beryllium
Cadmium
Chromium
Copper
Cyanide, Total
Lead
Mercury
Nickel
Selenium
Silver
Thallium
Zinc

Reactions in Groundwater

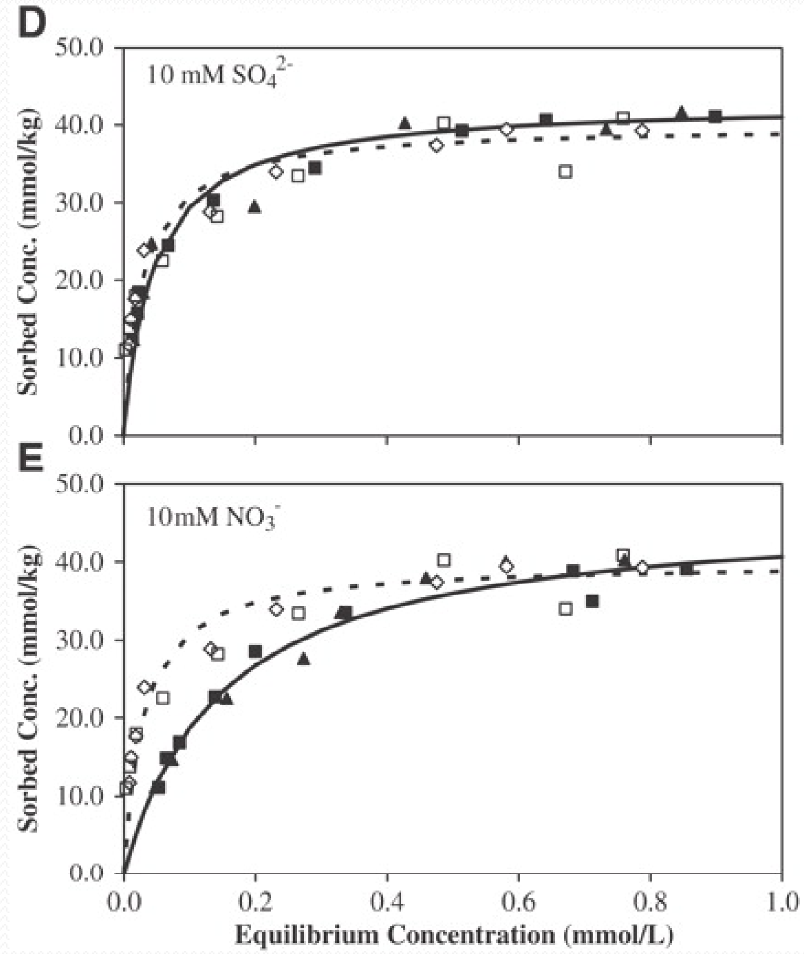


Reactions with Solids

- Ionic contaminants (e.g. heavy metals) tend to adsorb to minerals
- Hydrophobic contaminants (like solvents) tend to absorb to hydrophobic organic material
- Surface and bulk retention are called generally "sorption"

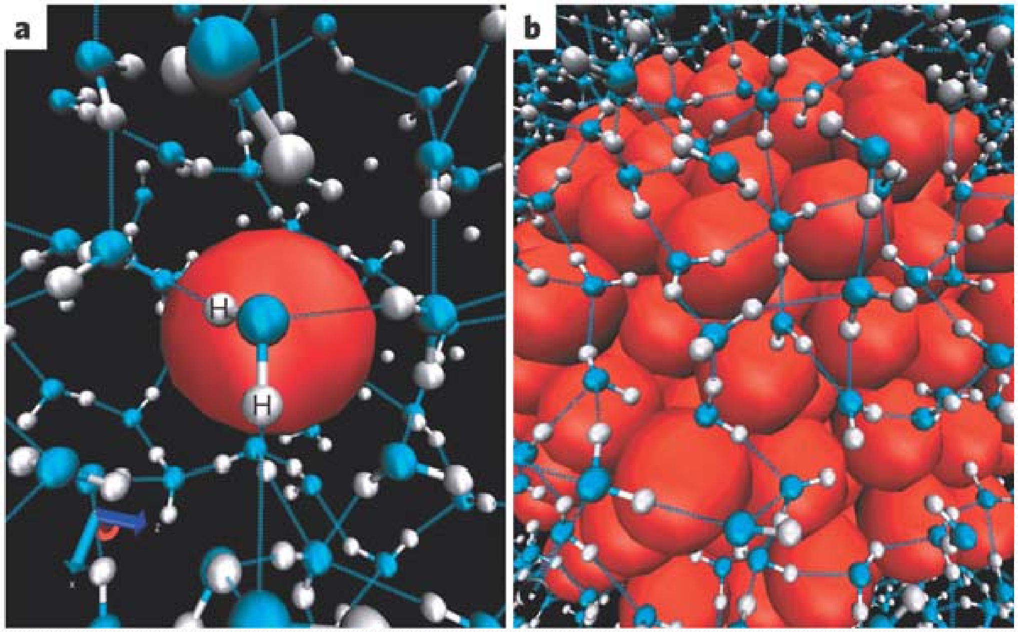
Sorption Isotherms

- The propensity for a solute to bind to a mineral is determined by mixing the solute with a mineral, and measuring the amount still in the liquid.
- Repeating this measurement at the same temperature results in an adsorption isotherm.



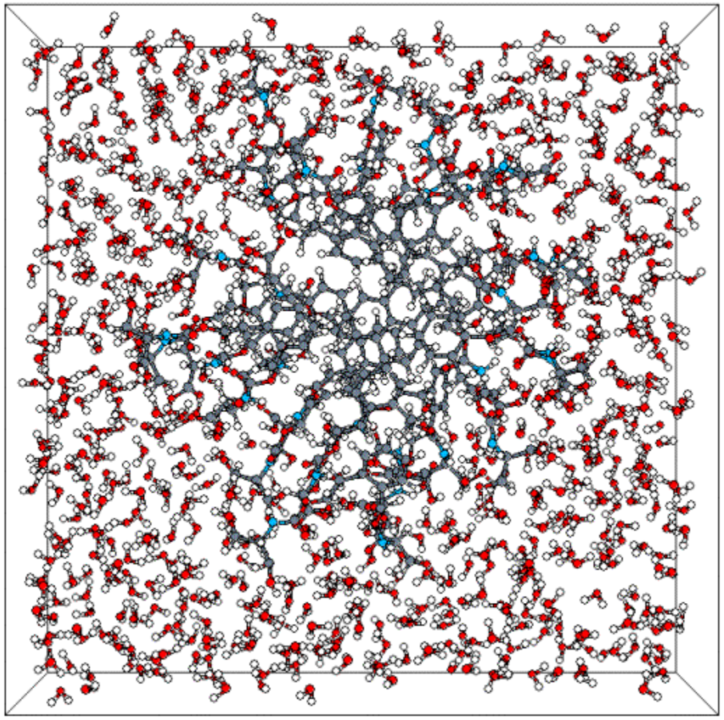
Non-Polar Organic Molecules

- Water molecules are attracted to one another and try to expel non-polar molecules
- Non-polar molecules will partition to other non-polar organic material



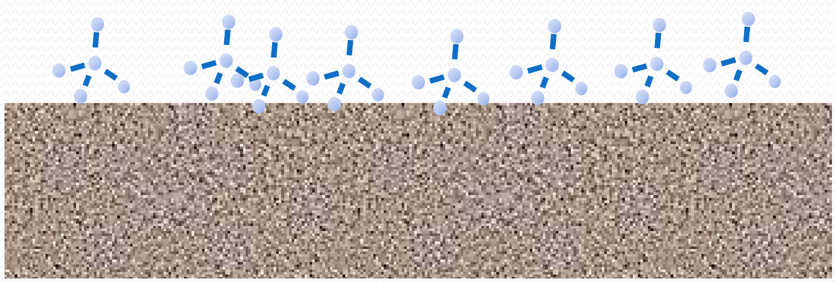
Natural Organic Material (NOM)

- Plants and animal remains decompose into complex organic molecules
- NOM is made of large, complex, non-polar molecules
- Also serves as a food source for bacteria that degrade organic contaminants



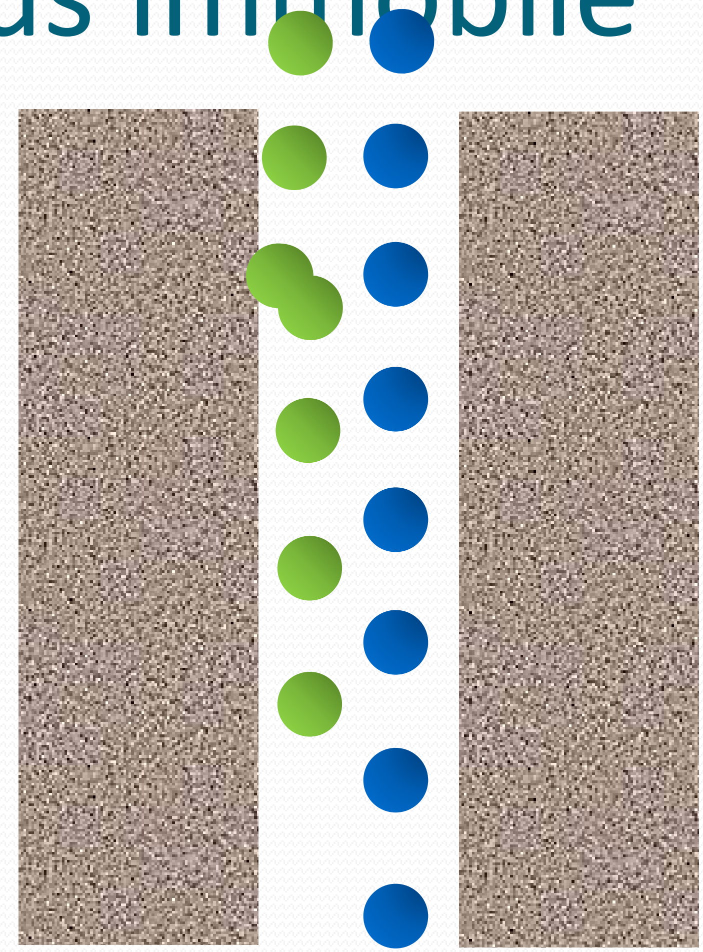
Adsorption vs. Partitioning

- Adsorption: takes up surface space, molecules compete for space
- Partitioning (absorption): diffuses through entire solid, molecules live by thermodynamics



Retardation: Solids Immobile

- Refers to the slowing of a contaminant with respect to water flow
- Due to reversible chemical reactions or adsorption to surface
- Over-simplified as a predictive tool but a useful concept

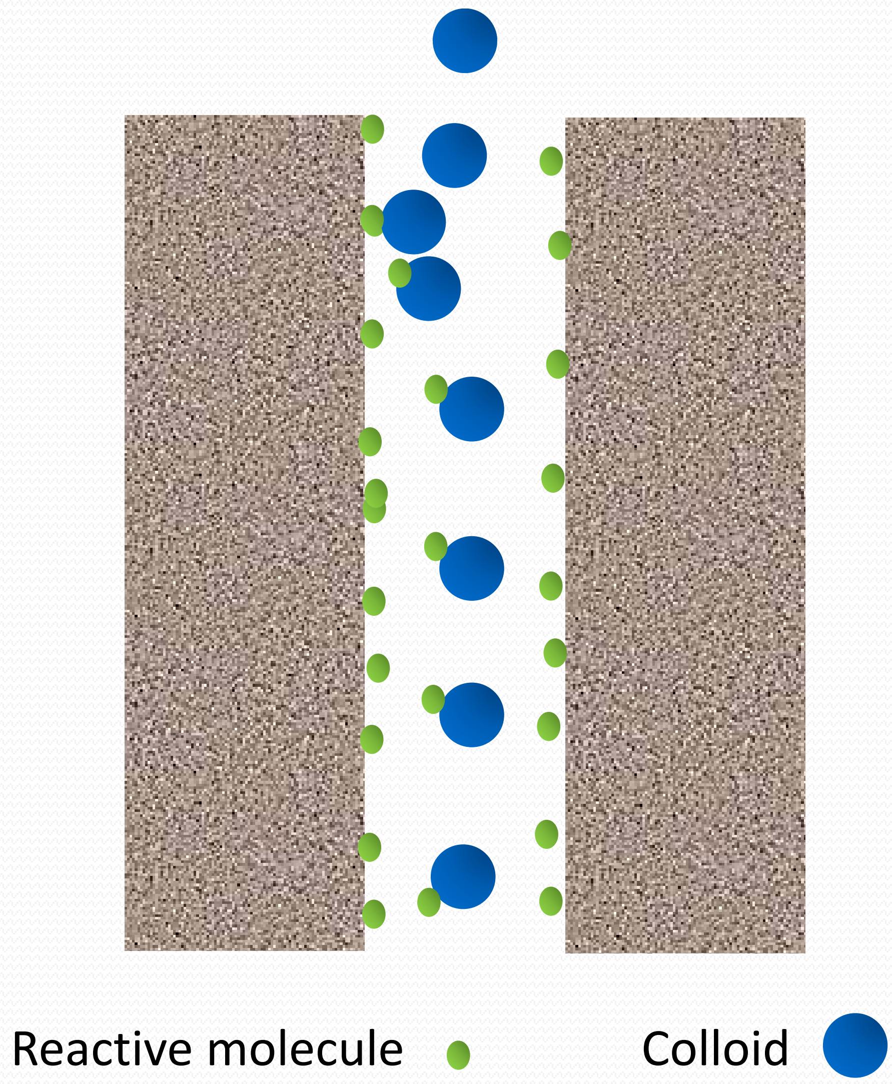


Reactive molecule   Nonreactive molecule

mouse click on figure to animate

Facilitated Transport: Solids Mobile

- When solids move as particles they can mobilize adsorbed contaminants
- Important consideration for sampling, be careful with filtering!



mouse click on figure to animate

Important Compounds at SSFL

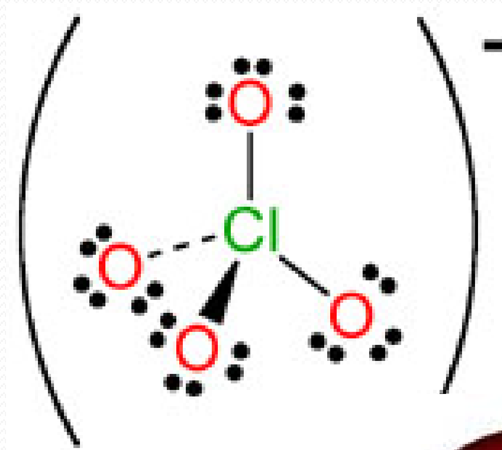
- Perchlorate
- Tritium and Strontium-90
- TCE and related products

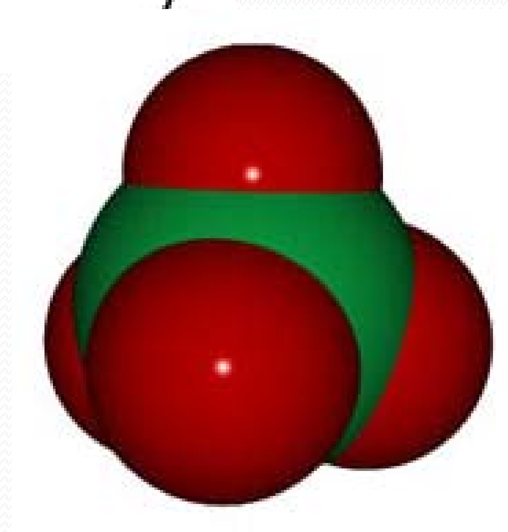
Perchlorate

- Naturally occurring and man made
- First observed after 1997 when an analytical method was developed to detect it (<4 ppb)
- Since then, detection of the contaminant in soil, surface water, and/or drinking water wells has been reported in 49 states.
- Highly mobile and persistent in groundwater

Perchlorate

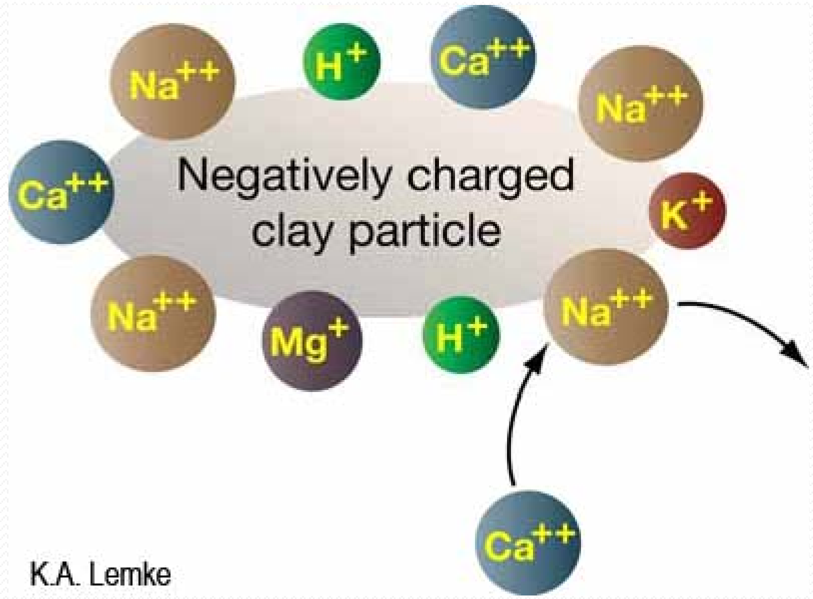
- Charge makes the soluble in water
- Perchlorate is an ionic contaminant
- Perchlorate is a "salt" meaning it bonds with a cation to form compounds





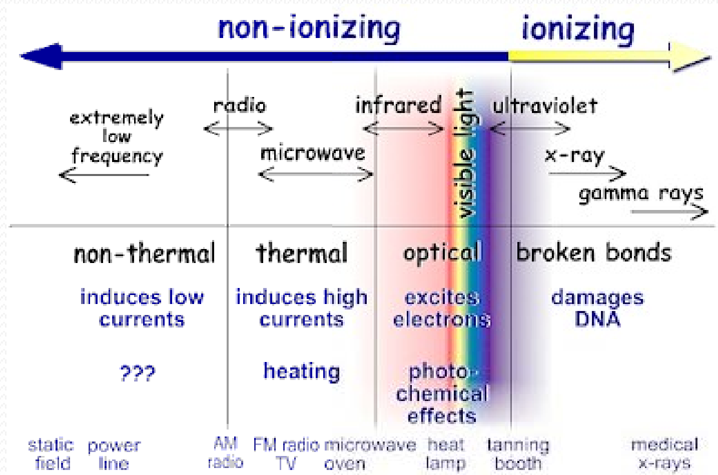
Ion Exchange

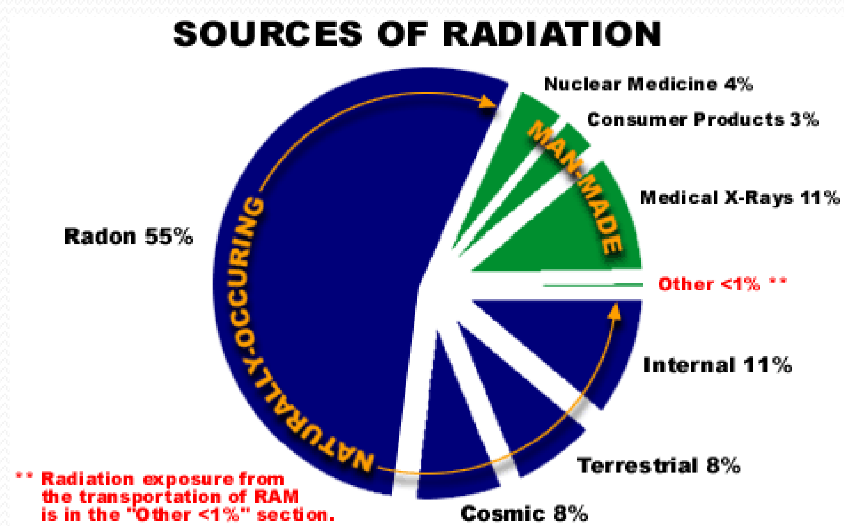
- One ion replaces another on a surface
- Ions are retained in order of their decreasing affinity for the surface chemistry
- Ion exchange leads to a retardation of the transport of ionic contaminants



Radionuclides

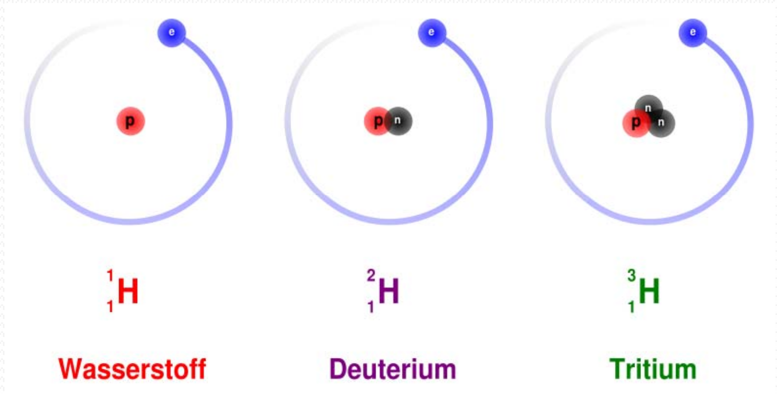
- Radionuclides are unstable atoms that give of particles or photons that can damage cells
- Atoms generally have chemical properties of their more stable cousins

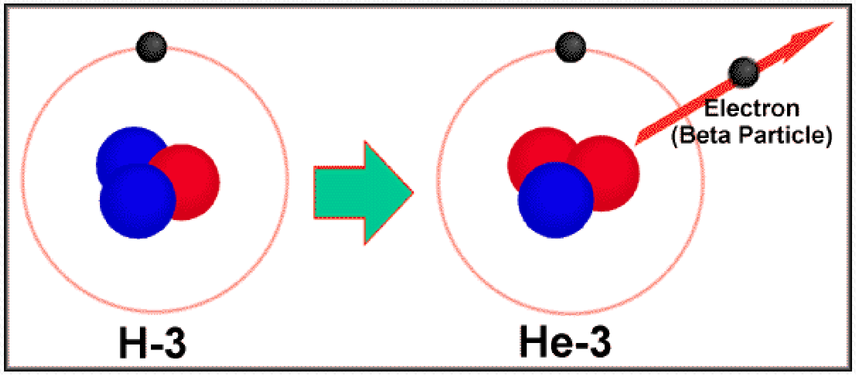




Tritium

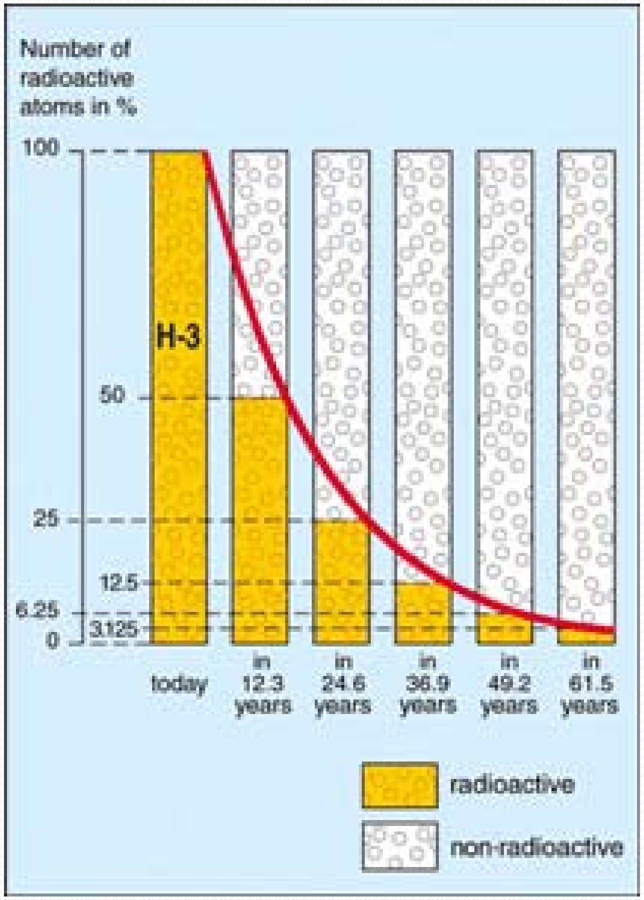
- "Normal" Hydrogen has one proton, Tritium has one proton and two neutrons
- Tritium releases an electron to become ^{3}He
- This beta particle cannot penetrate skin but is a hazard if inhaled or ingested





Tritium Transport

- Most hydrogen (and tritium) atoms are in water
- In general, moves with water
- Half-life of 12.3 yrs means it decays rapidly



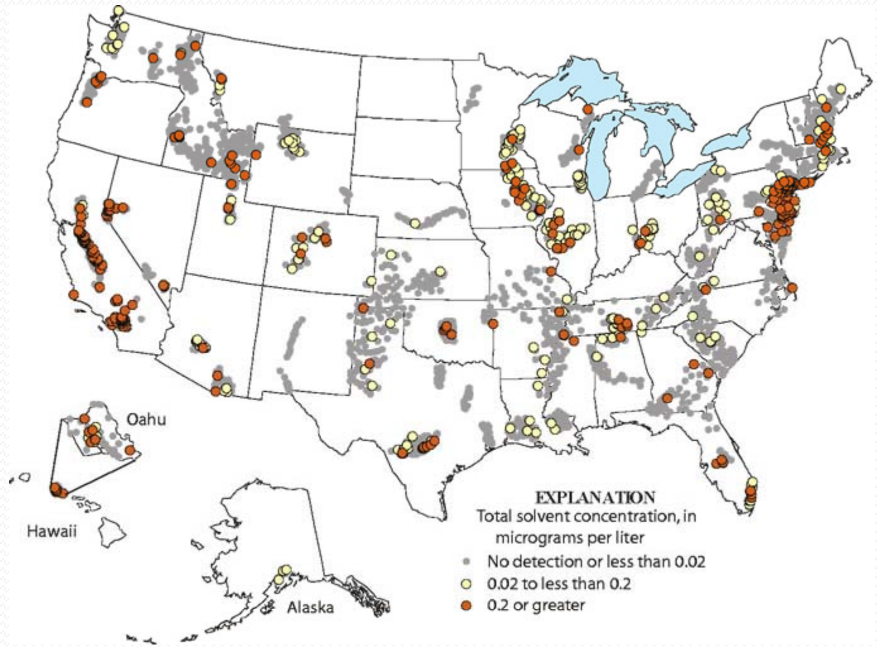
Stontium-90

- Beta emitter
- Similarity to Calcium makes it a “bone seeker” so it is a greater health hazard than tritium
- Also exchanges with ions in rocks so tends to move slowly in rock

Strontium-90 Full table	
General	
Name, symbol	Strontium-90, ^{90}Sr
Neutrons	52
Protons	38
Nuclide data	
Half-life	28.8 years
Decay products	^{90}Y
Decay mode	Decay energy
Beta decay	0.546 MeV

Chlorinated Solvents

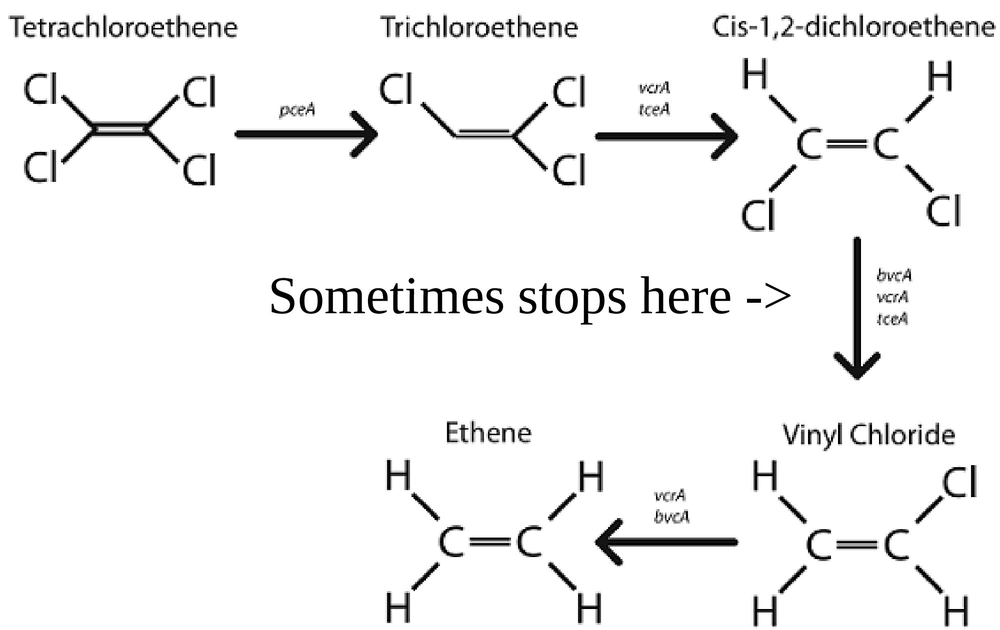
- Chlorinated solvents useful for degreasing
- Examples:
  - dichloromethane,
  - tetrachloroethene,
  - trichloroethane,
  - tricholoroethene.
- Over 320 million lbs of TCE produced in the US in 1991.
- Chlorinated Solvents found in about 20% of US groundwater supply(USGS)



Biodegradation of Chlorinated Ethenes

- Reductive Dechlorination
  - Chlorine atoms are replaced by electrons coupled to hydrogen atoms
- Aerobic Cometabolism
  - Oxygen transferred to organics and accidently degrade TCE with same enzymes
- Direct Oxidation
  - DCA, DCE, and VC can serve as electron donors for bacteria

Reductive Dehalogenation



Abiotic Transformation

- Some evidence that chlorinated organics can be transformed without bacteria
- Iron, sulfur, seem to be important to these processes
- Most of our understanding comes from laboratory rather than field tests

Take Home Lessons

- The physics of transport are well understood, the geology is not
- Miscible (APL) and immiscible (NAPL) fluids transport in entirely different ways
- Most contaminants are unstable and want to become benign, but this can take a long time.
- Contaminant hydrogeology isn't rocket science…

… IT'S HARDER!