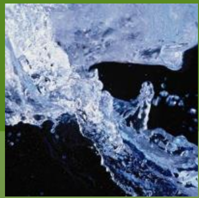
     

Impacts of Subsurface Heterogeneity

EPA
United States
Environmental Protection
Agency

Thanks to:
Steve Dyment, U.S. EPA ORD
Seth Pitkin, Stone Environmental

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

Contaminant Fate and Transport Review

United States
Environmental Protection
Agency

Advection

- **Movement at the average linear groundwater seepage velocity (v) in the direction of the hydraulic gradient**

- **$v = K(\Delta h/\Delta l)/\theta$**
  - Where:
    - K = hydraulic conductivity (L/t)
    - $\Delta h/\Delta l$ = hydraulic gradient (L/L)
    - θ = porosity (L^3/L^3)

Advection – Dispersion Equation

$$\frac{\partial c}{\partial t} + v_i \frac{\partial c}{\partial x_i} - \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial c}{\partial_{xj}} \right) = \pm \frac{G}{\theta}$$

Where:

c = Solute concentration

t = Time

v = Seepage velocity

D = Hydrodynamic Dispersion Coefficient

G/θ = Mass produced or consumed/unit volume porous media

Hydrodynamic Dispersion Coefficient

$$D = D_m + D_d$$

Where:

D = Hydrodynamic Dispersion Coefficient

D_m = Mechanical Dispersion Coefficient

D_d = Effective Molecular Diffusion Coefficient

$$D_m = ά\, v$$

Where:

ά = dispersivity (property of the medium)

v = average linear seepage velocity

$$D_d = D_o T$$

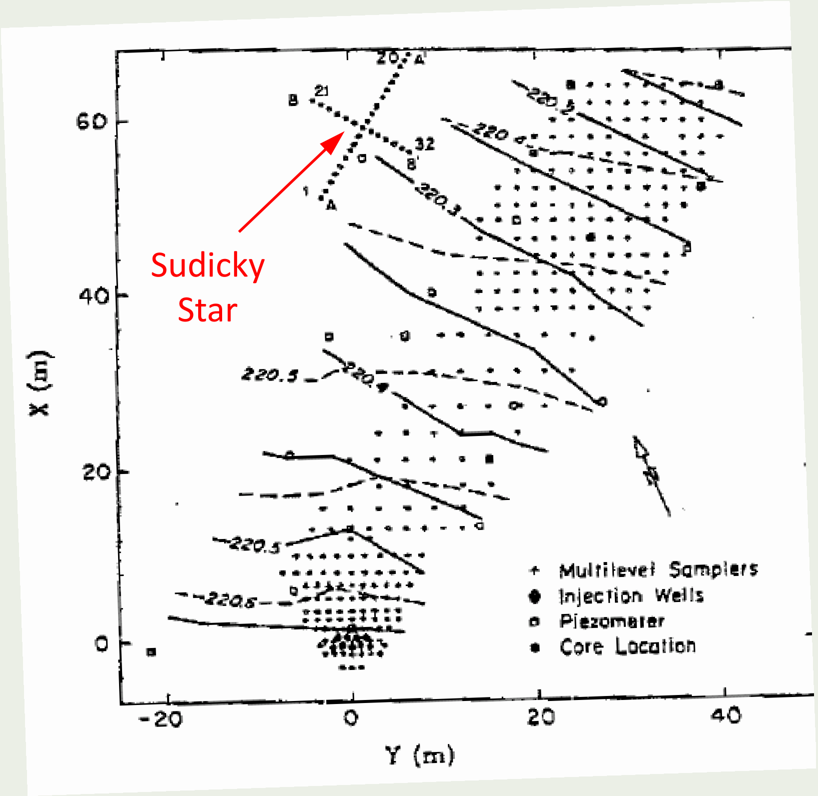
Where:

D_o = Free molecular diffusion Coefficient

T = Tortuosity

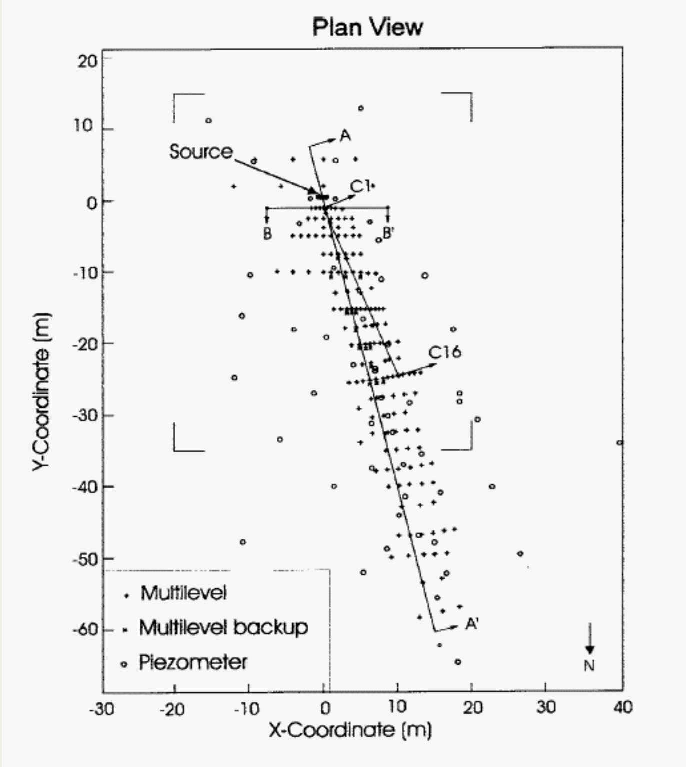
Hydrodynamic Dispersion

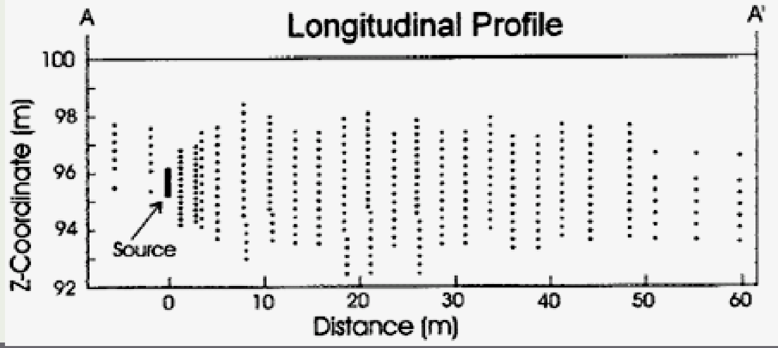
- **Natural Gradient Tracer Tests**
  - Sudicky 1979
  - Stanford/Waterloo – 1982
  - USGS Cape Cod – 1986
  - Rivett et al. 1991
- **Dispersion is scale (time/distance) dependent**
- **Transverse horizontal dispersion is weak**
- **Transverse vertical dispersion is even weaker**
- **Longitudinal dispersion may be significant**



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

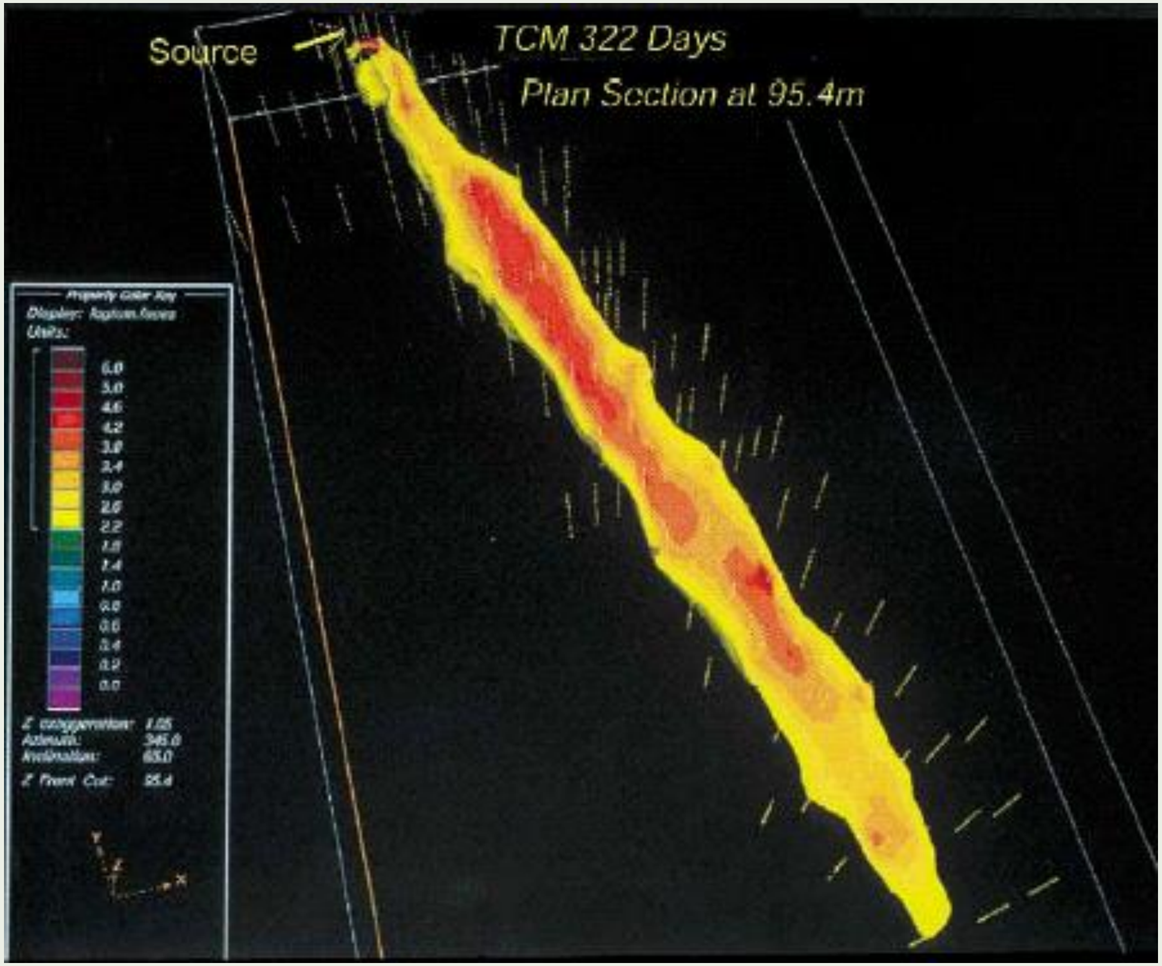
Rivett's Experiment: The Emplaced Source Site

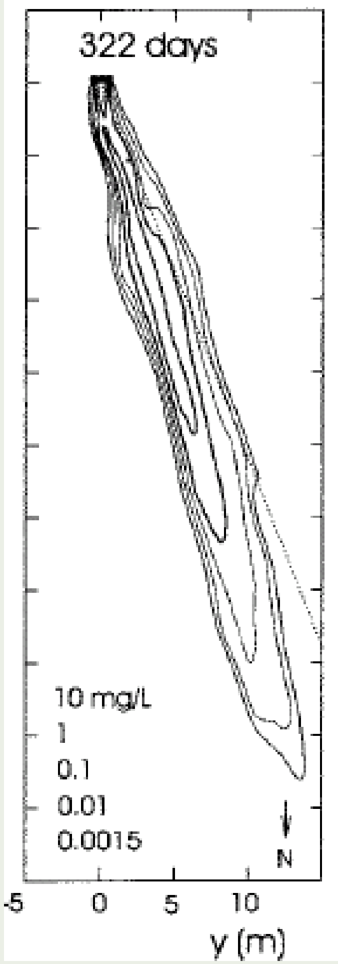




Rivett et al, 2000

TCM Plume at 322 Days; *Weak Transverse Dispersion*





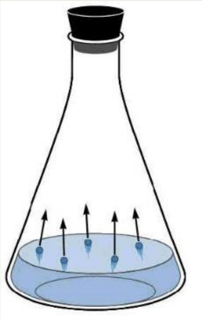
Rivett et al., 2001

Contaminant Phases

- **Non Aqueous Phase Liquid (NAPL)**
- **Gas (vapor) phase**
- **Solute (dissolved in water)**
- **Sorbed**

Volatilization (Gas Phase)

- **Creates soil gas plumes, 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: $C = X_t(P^0/RT)$



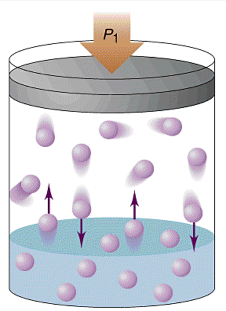
Where: **C = vapor phase concentration**

X_t = mole fraction of compound in NAPL

P^0 = Pure phase vapor pressure

R = Ideal Gas Constant

T = Temperature



- **From solute in groundwater, governed by Henry's Law**
  - Warning: many forms of Henry's constants with different units!

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

Dissolution

- **Governed by solubility**
  - Polarity
  - Molecular size
- **For a compound in a multi-component NAPL the effective solubility is a function of Raoult's law:**

$$S_{eff} = X_t S^0$$

Where: S_{eff} = effective solubility

X_t = mole fraction of compound in NAPL

S^0 = Pure phase solubility

- **Effective solubility of individual compounds change over time as more soluble compounds become depleted**

Dissolution: Rate of Mass Transfer

- **The Rate of Mass Transfer:**

$$R_{mt} = C_{mt} * \delta C * A_c$$

Where:

R_{mt} = rate of mass transfer

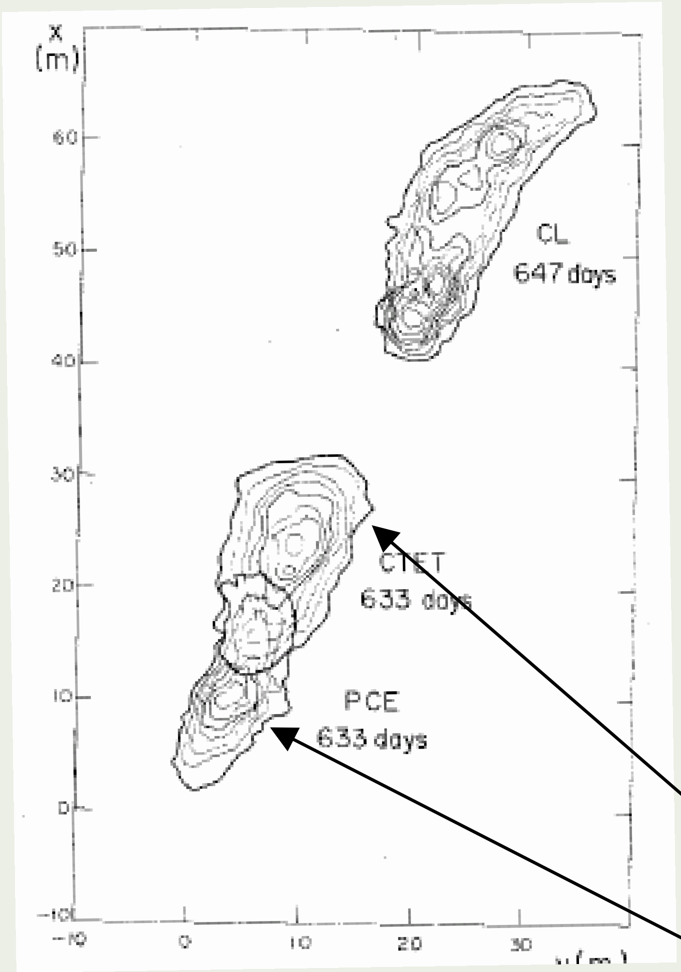
C_{mt} = mass transfer coefficient

δC = concentration gradient

A_c = Contact area

- **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

Sorption



MacKay et al., 1986

- Sorption of solutes to organic matter on the solid particles results in retardation of the plume
- Sorption is reversible
- Results in "chromatographic separation" of different contaminants in the plum
- Retardation from sorption is calculated as

$$R = 1 + \frac{\rho b}{\theta} K_d$$

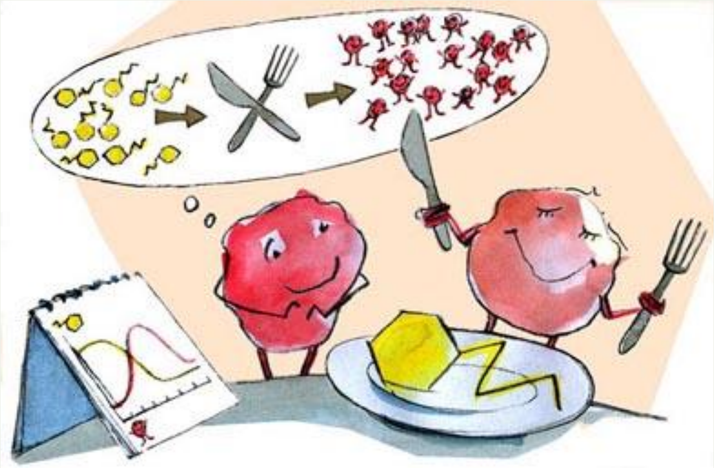
K_d can be calculated as f_{oc} * K_{oc} from K_{ow} but beware use of literature values!

R for CTET at Borden = 1.8 – 2.5

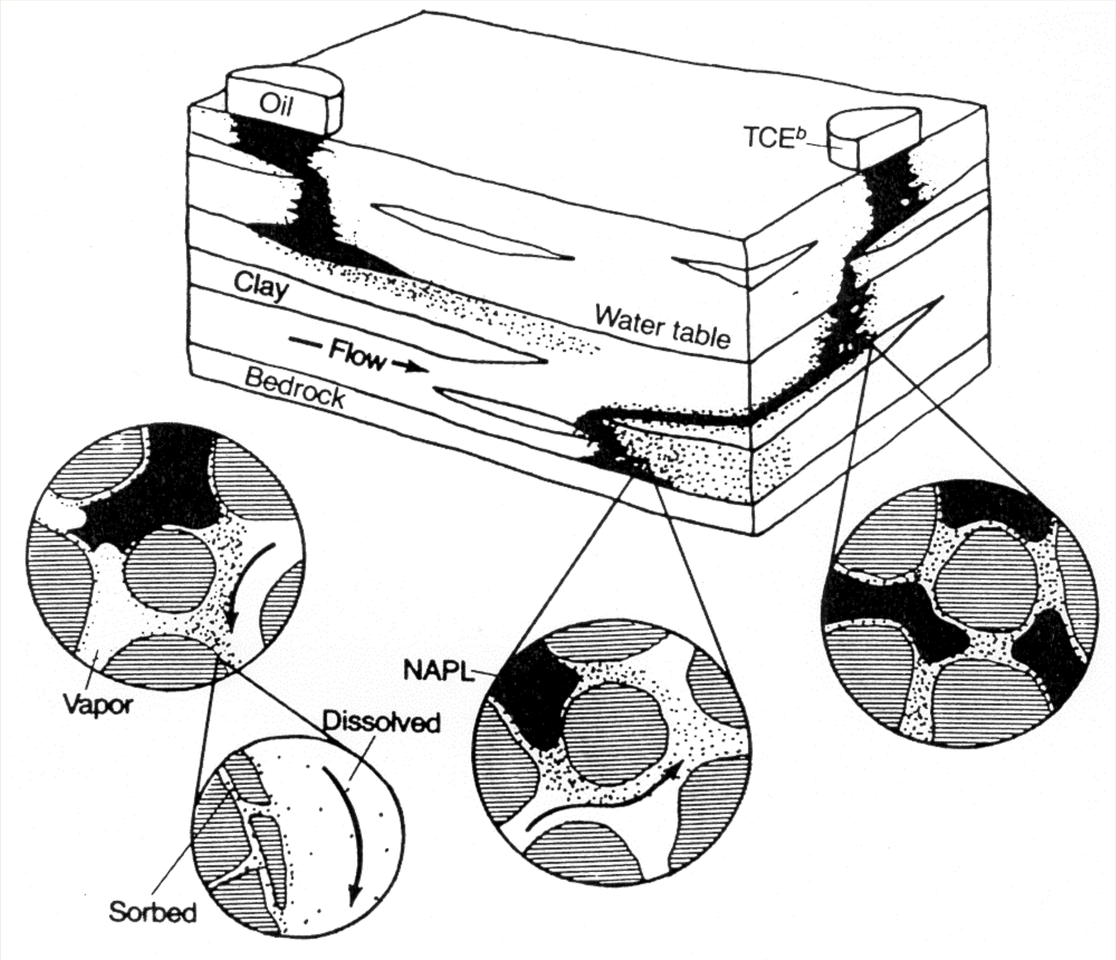
R for PCE at Borden = 2.7 – 5.9

Degradation

- **Biotic and abiotic**
- **Degradation eliminates mass**
- **Degradation rates dependent on**
  - » Presence, health of consortia of 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**



NAPL Density: LNAPL and DNAPL



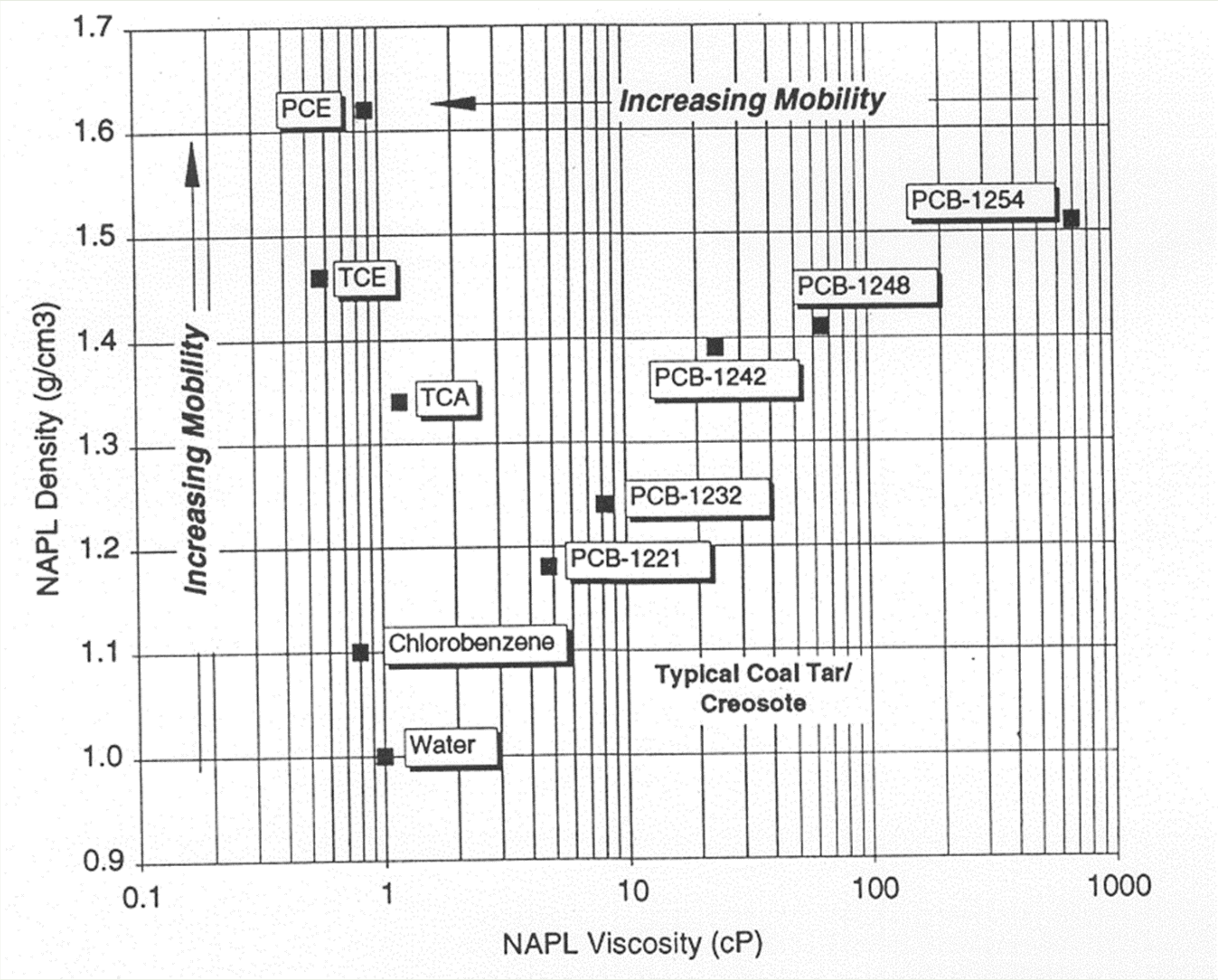
Pankow and Cherry, 1996

Density, Viscosity and Mobility

$$K = kÞg/\mu$$

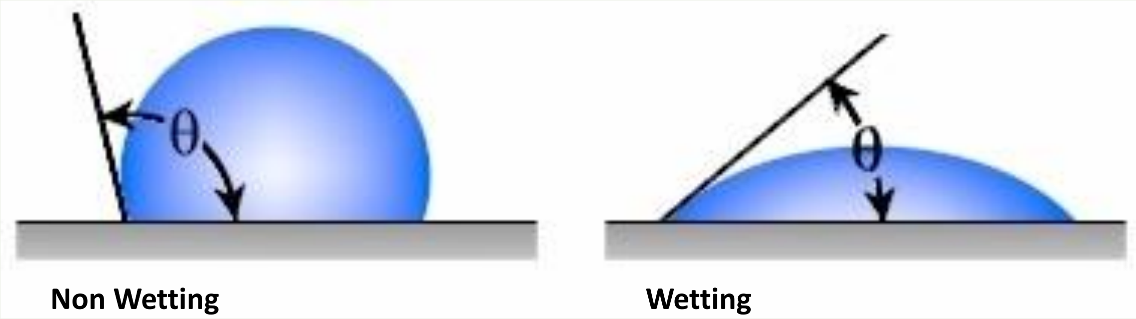
Where: K = Hydraulic Conductivity (L/t)
k = Intrinsic permeability (L^2)
Þ = density of fluid (M/L^3)
µ = viscosity ($F\text{-}t/L^2$)

Relative mobility of various liquids



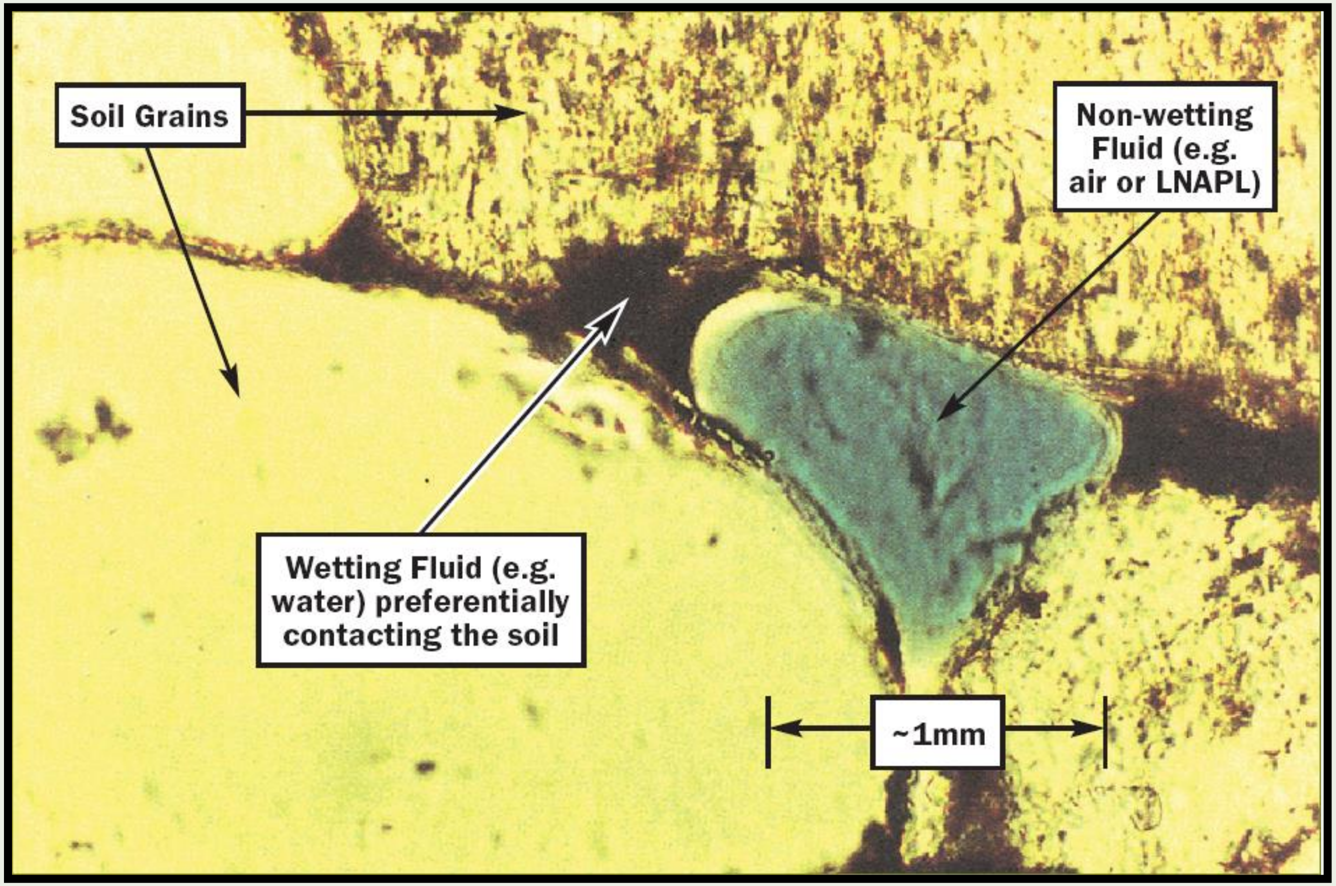
Cohen and Mercer, 1993

Multiple Fluids: Wettability



- ♦ Wettability is determined by the contact angle
- ♦ Typically aquifer materials are water wet and the NAPL is non wetting but…
- ♦ NAPL can be wetting
- ♦ Contact angle and wetting fluid can change over time

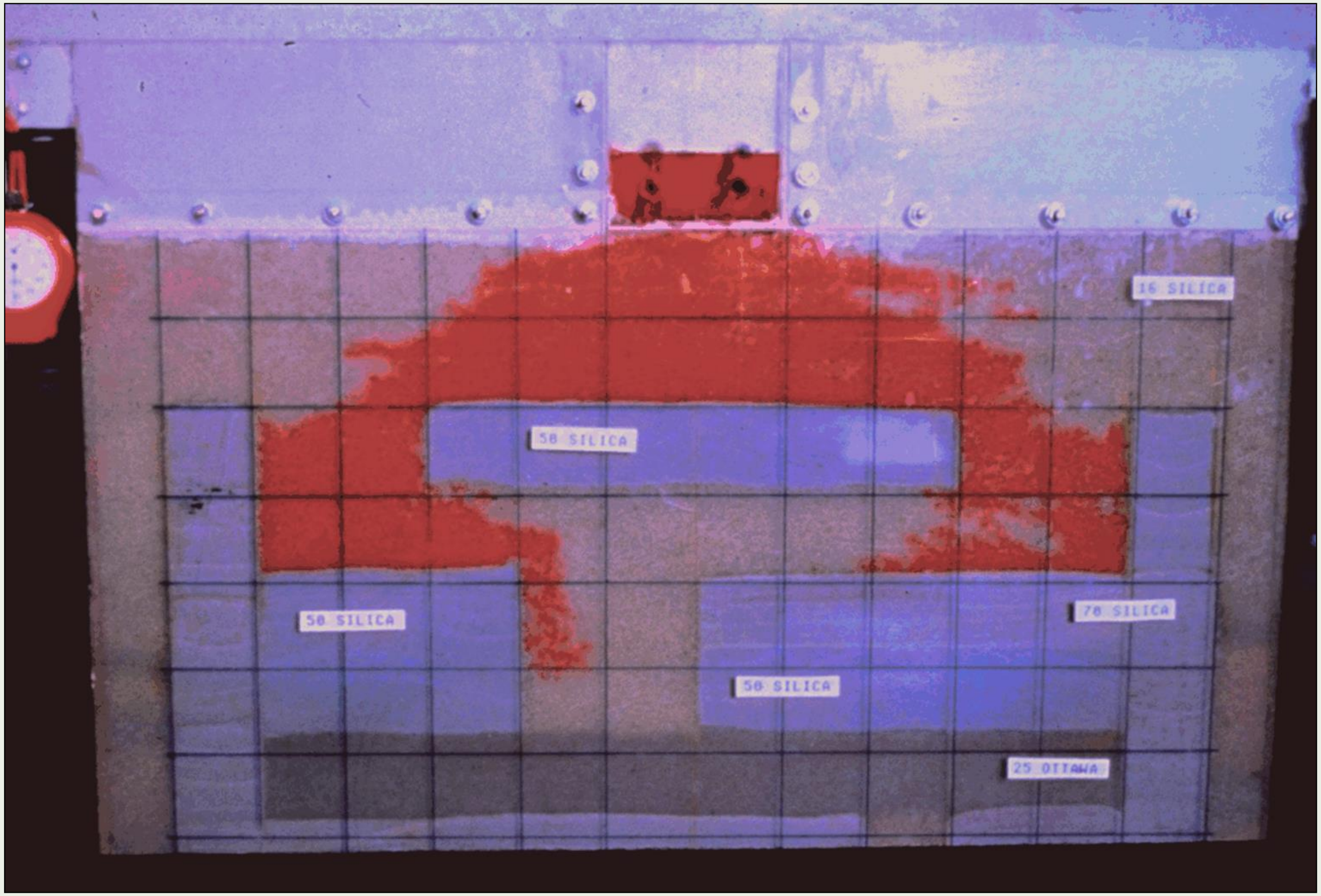
Multiple Fluids: Wettability



Source: Wilson et al., 1990.

Multiple fluids in the pore space of a granular porous media.

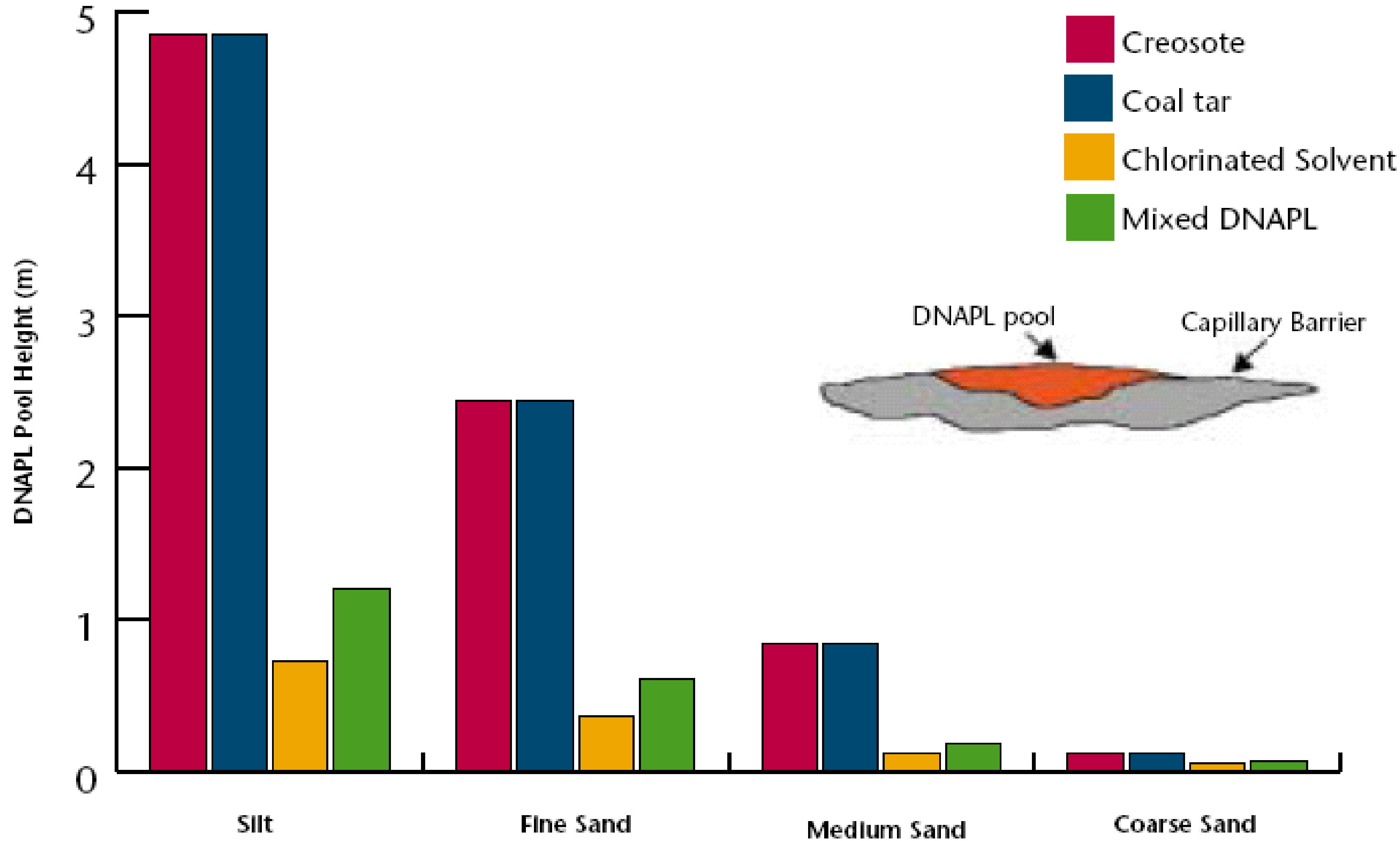
Effects of Capillary Pressure Variability on NAPL Distribution



Bernie Kueper

Variability of Entry Pressures

UK Environment Agency, Publication 133



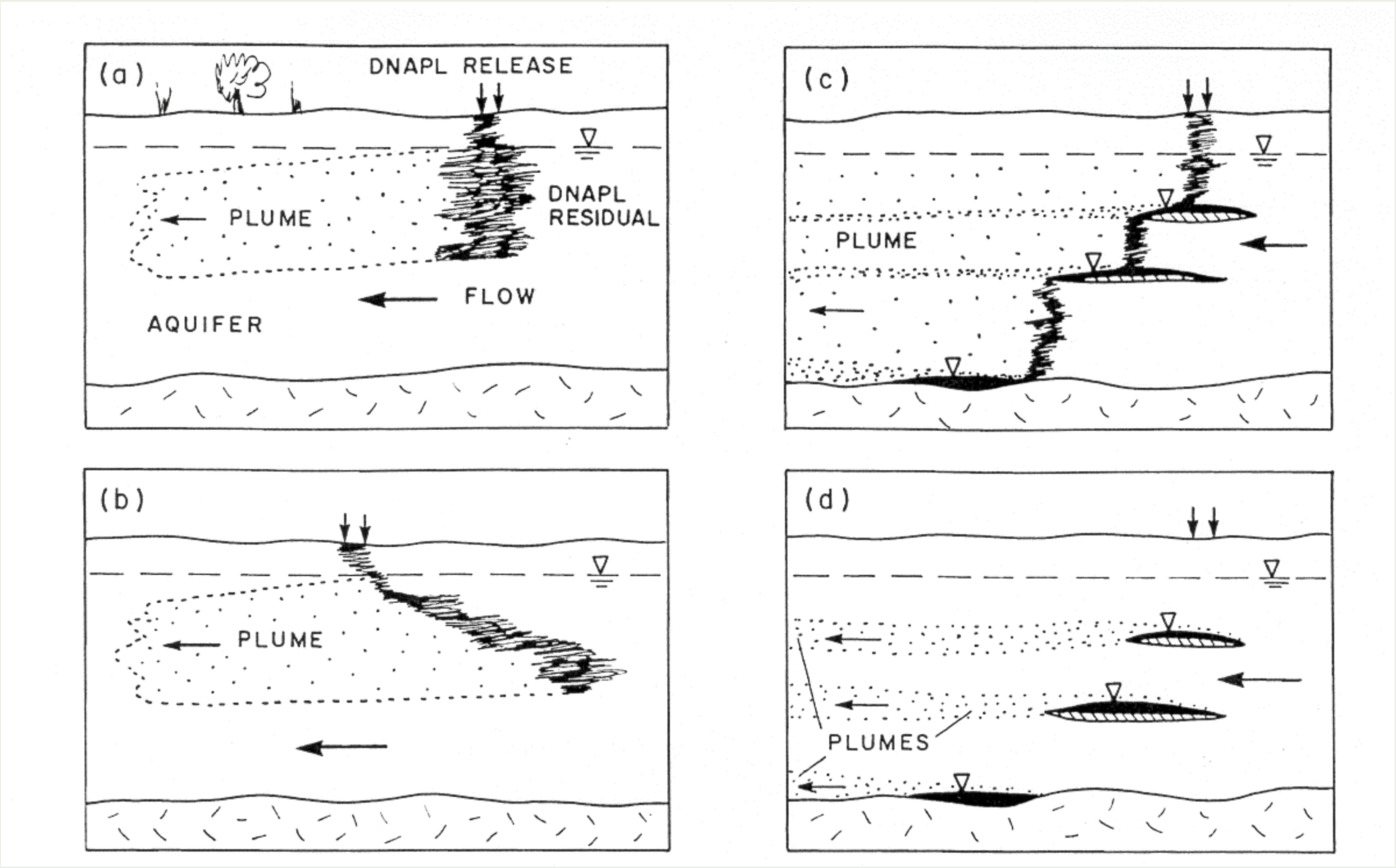
Residual NAPL

- **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)**

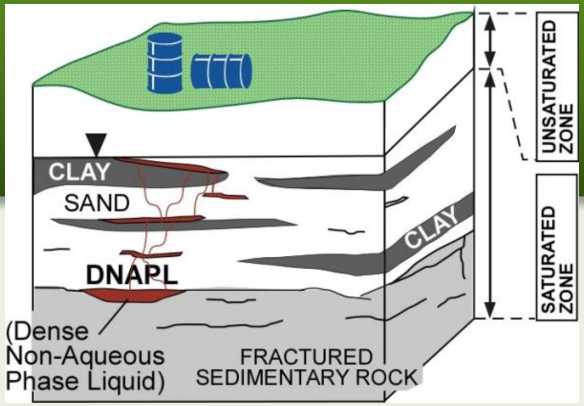
DNAPL Distribution Scenarios



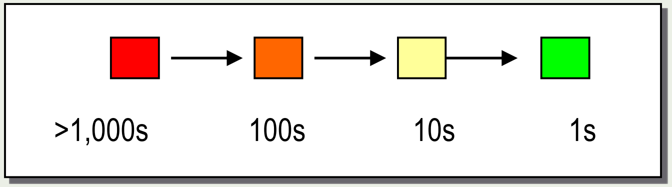
Pankow and Cherry, 1996

mm scale textural changes control DNAPL Migration

Poulsen & Kueper, 1992

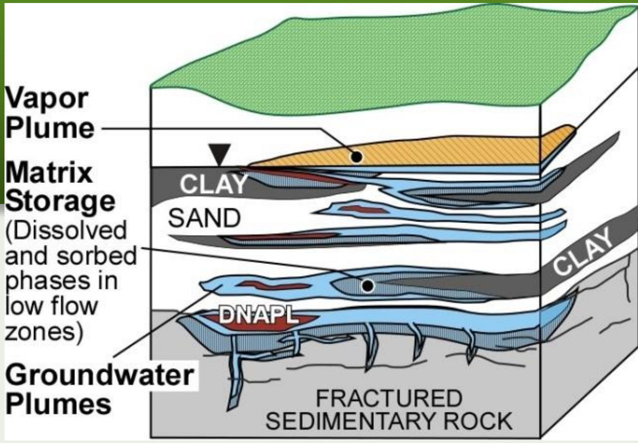


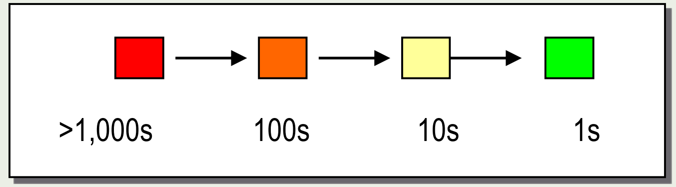
Early Stage



	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

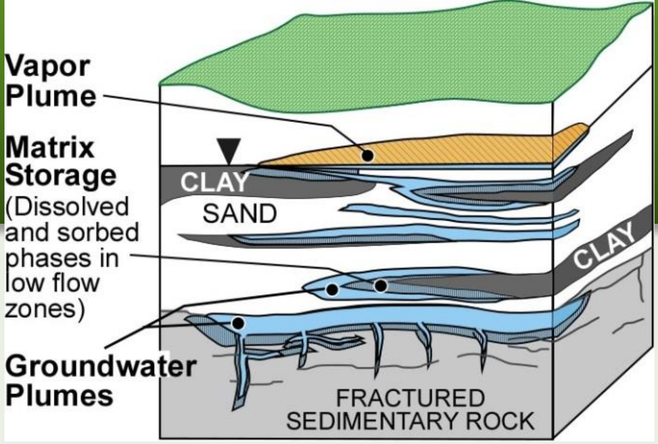
Middle Stage

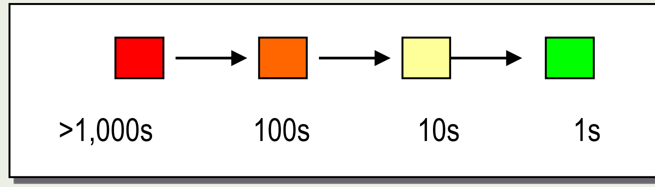


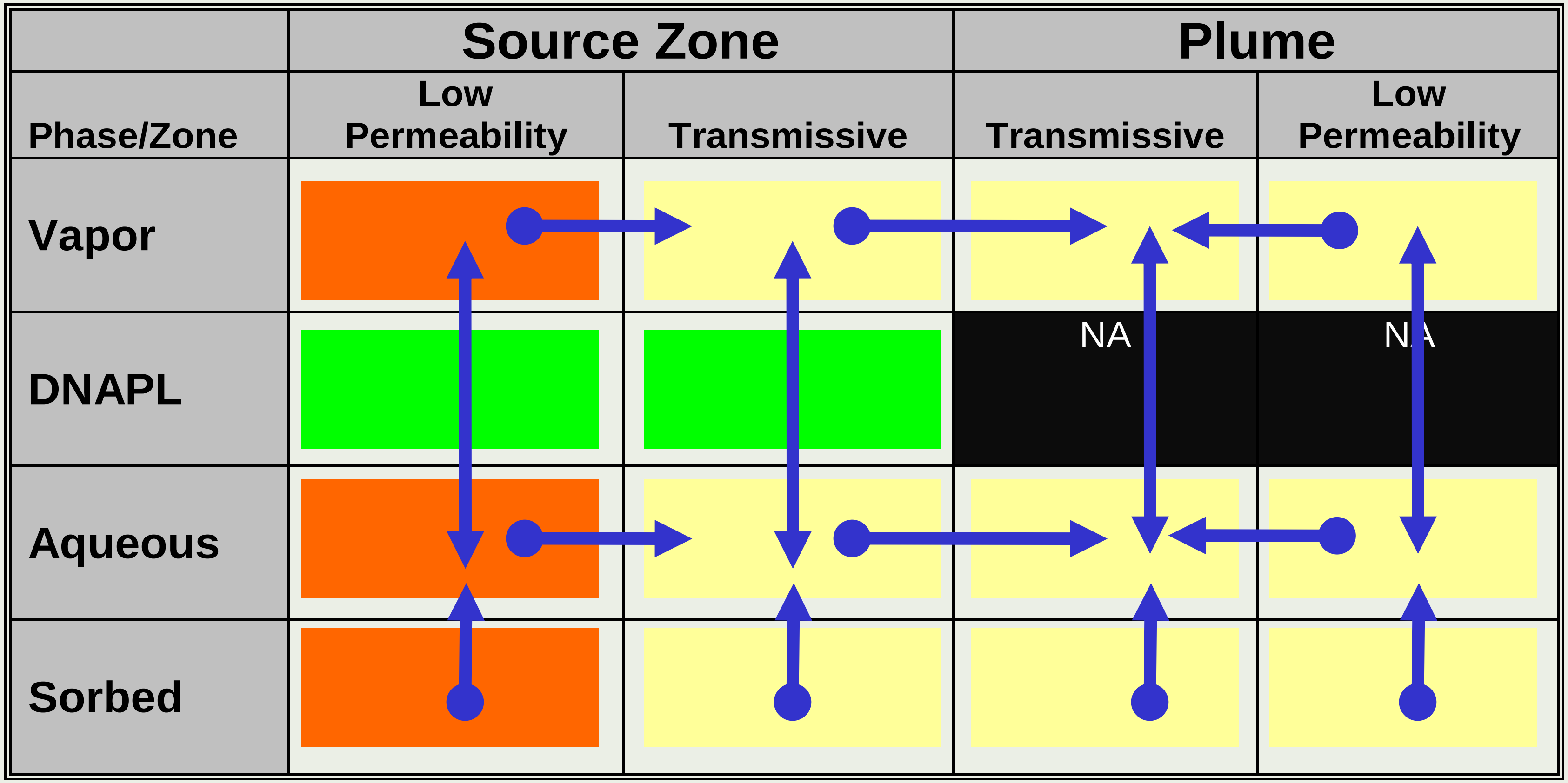


	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

Late Stage







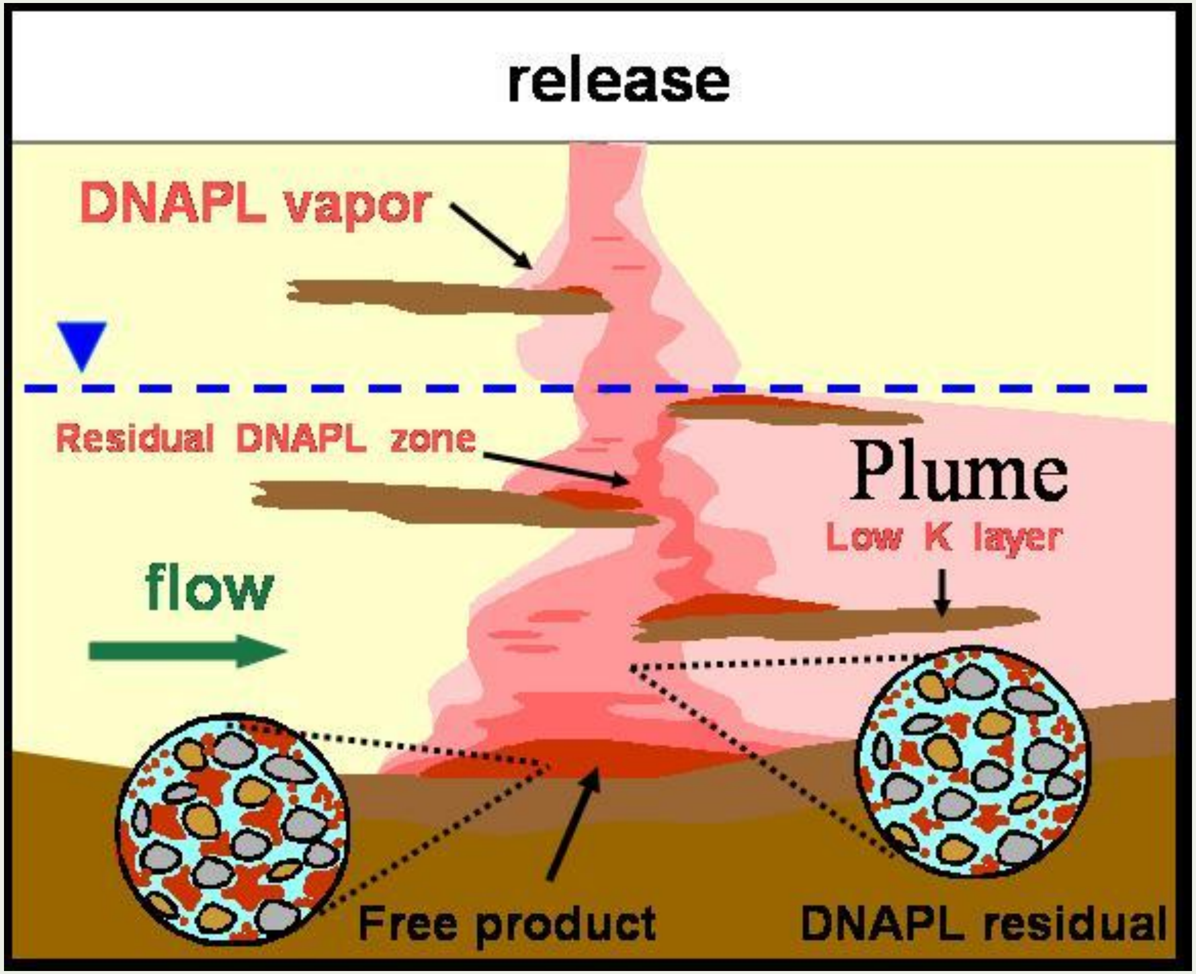
	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

What is Back Diffusion?

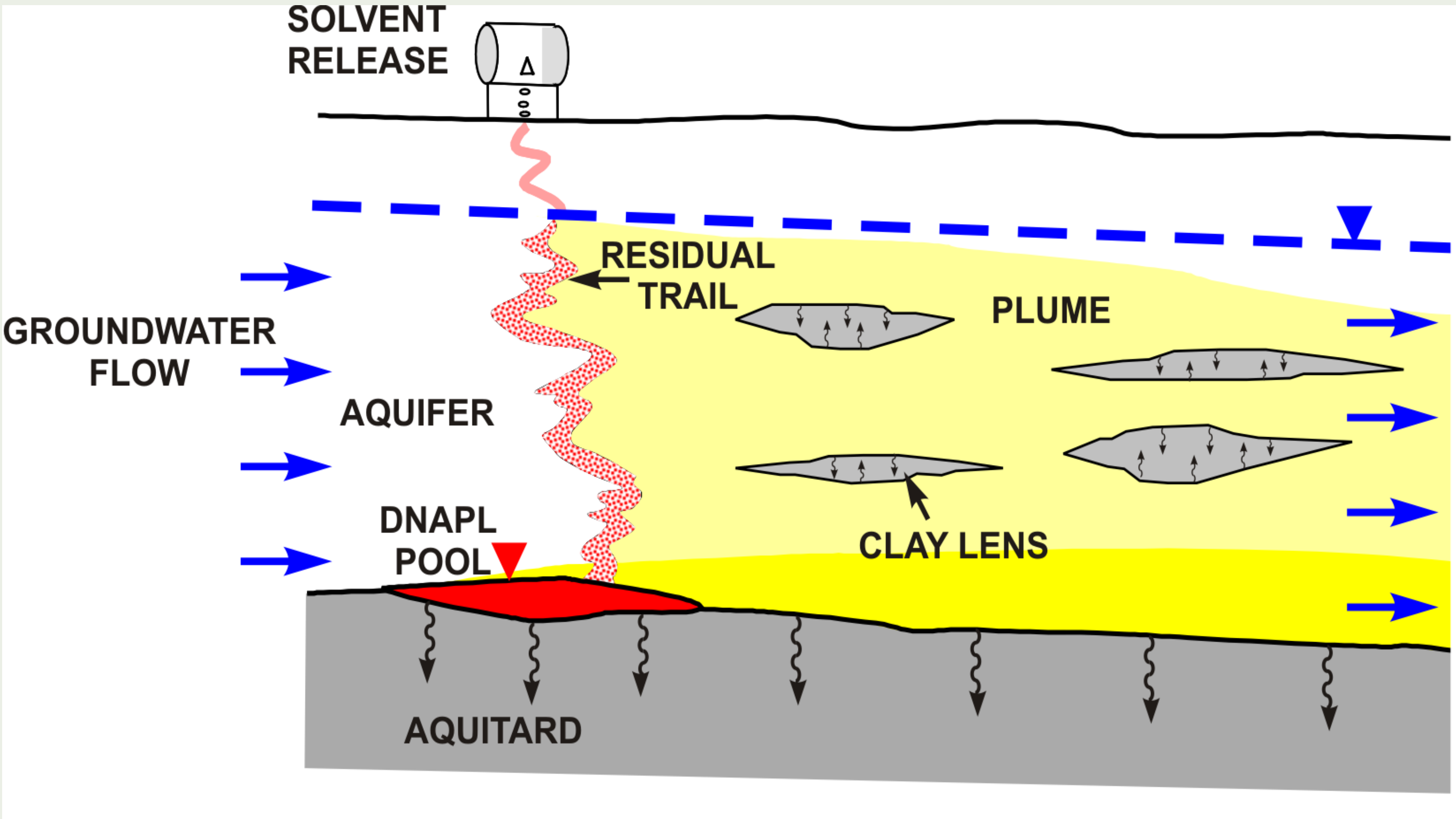
- **Slow release of contaminants stored in lower K zones (dissolved and sorbed phase) back to higher K zones**
- **Occurs when concentrations at interfaces between high-low K zones decline**
  - natural source depletion
  - Source and plume zone remediation
- **Can be primary cause of long-term plume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

Stronger Back-Diffusion Effects Expected at Sites with DNAPL Releases

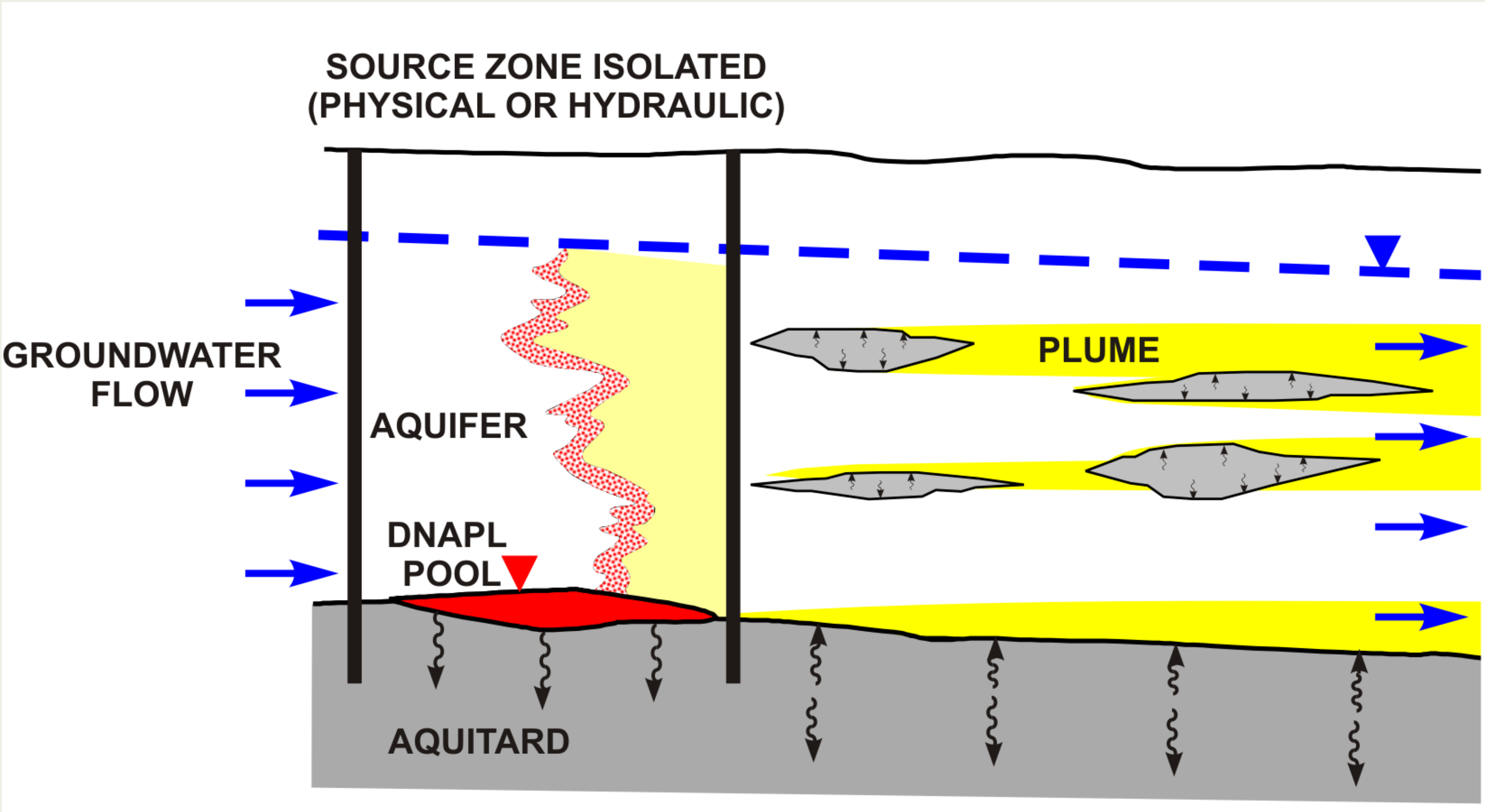
- DNAPL and high plume [VOCs] proximate to low K zones
- Most sites contaminated for decades (significant inward diffusion)
- Sorption increases low K zone mass storage
- 4-5 OoM between solubility and MCLs for most chlorinated solvents



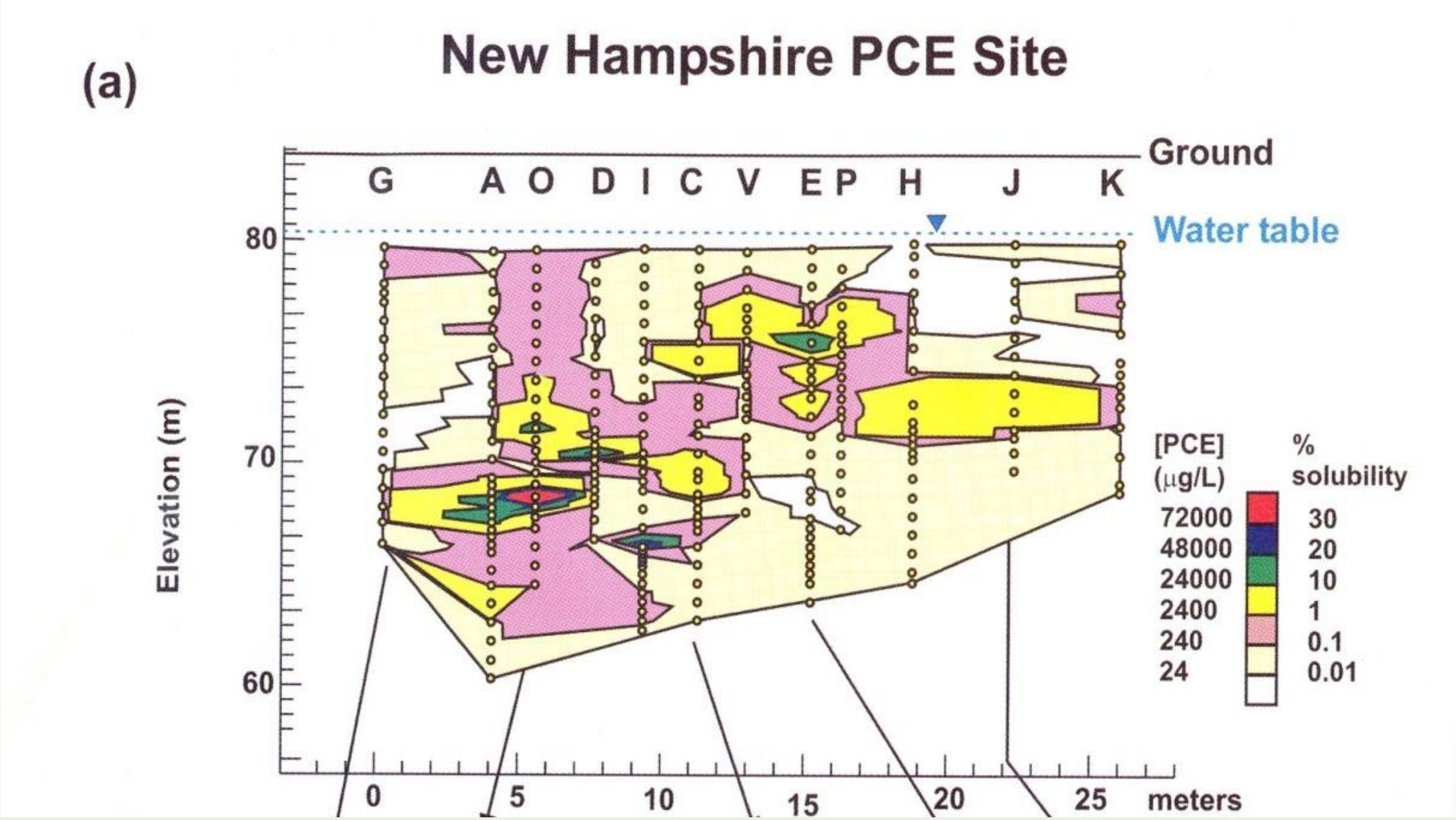
Sand Aquifer with Clay Lenses and Underlying Aquitard



Persistent Plume after Source Isolation due to Back Diffusion from Aquitard and Clay Lenses



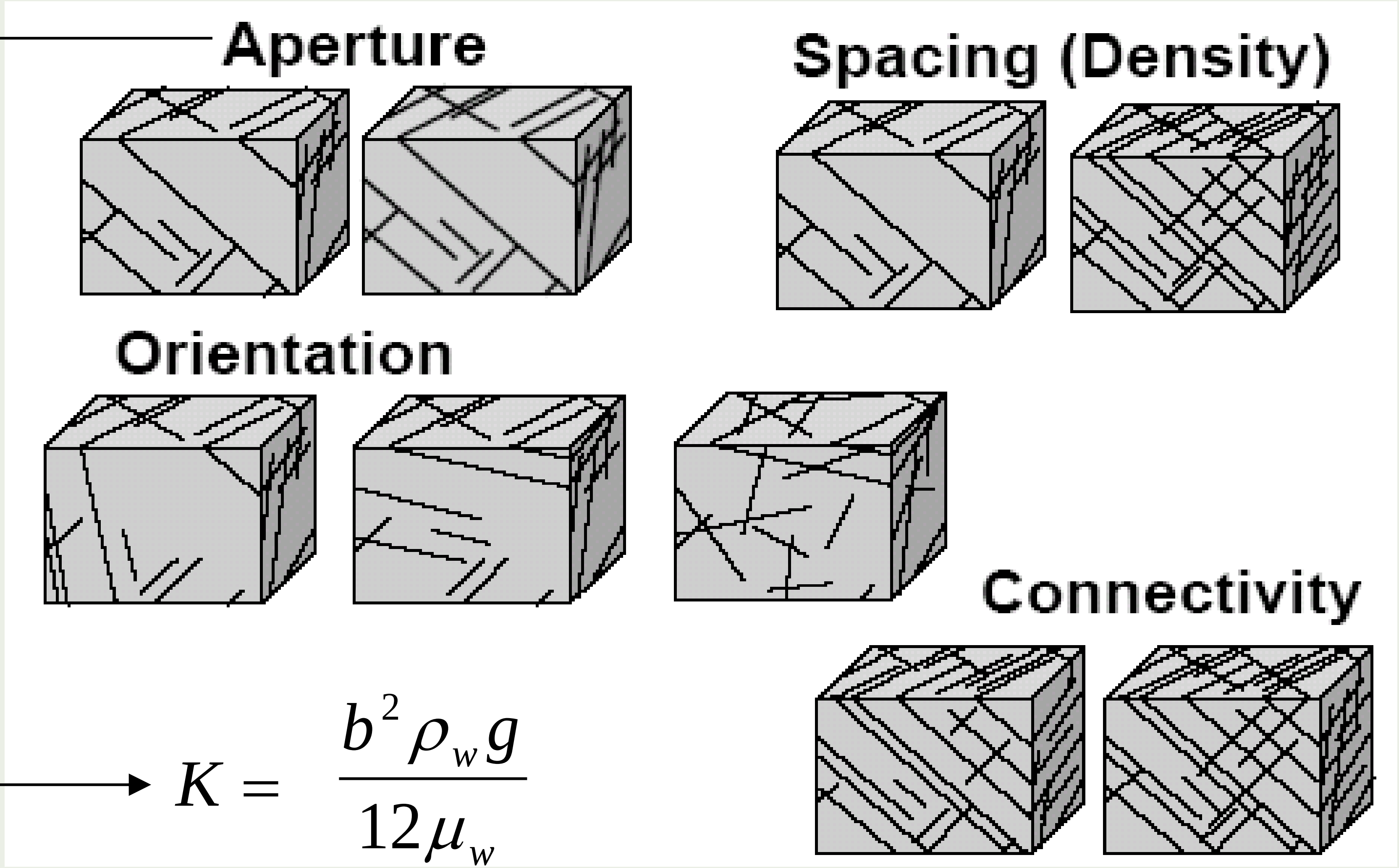
Mass Flux Distribution



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

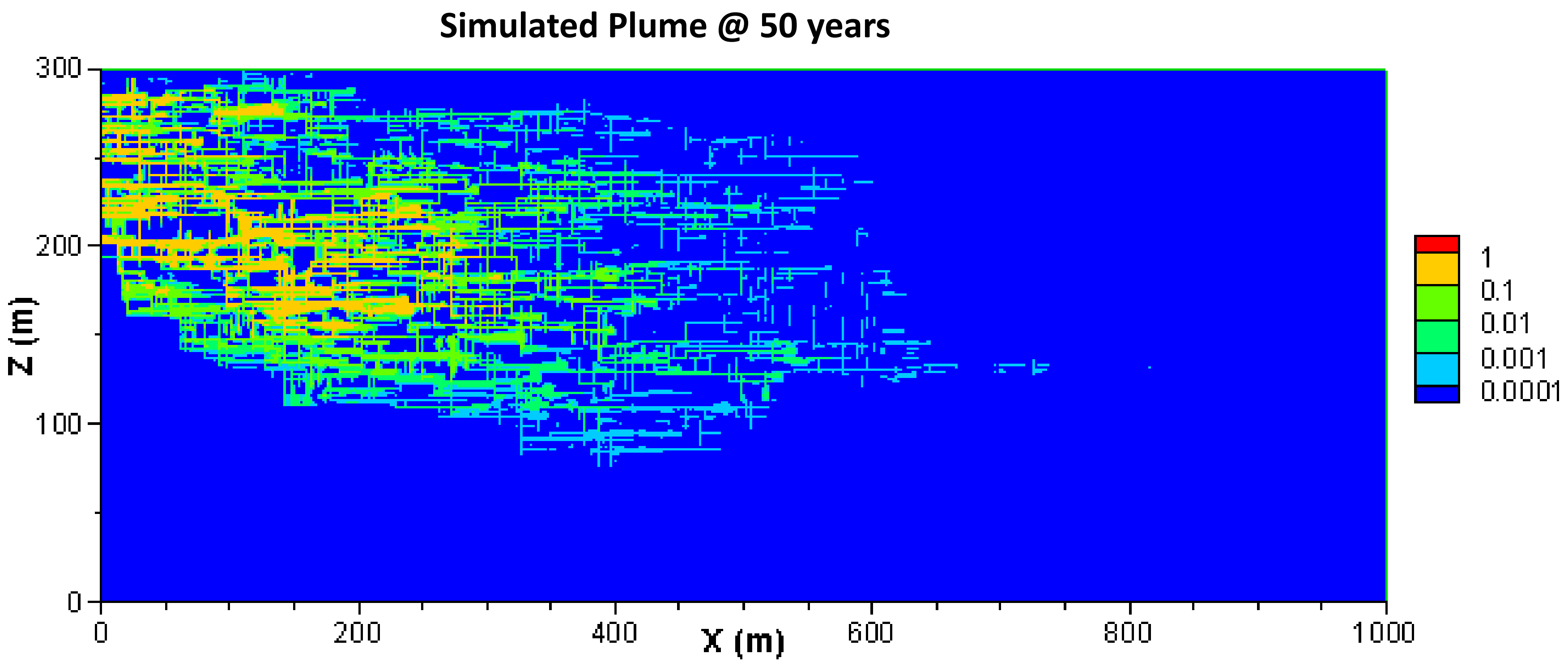
Optimal Spacing is ~0.5 m

Factors Governing Flow in Fractured Media

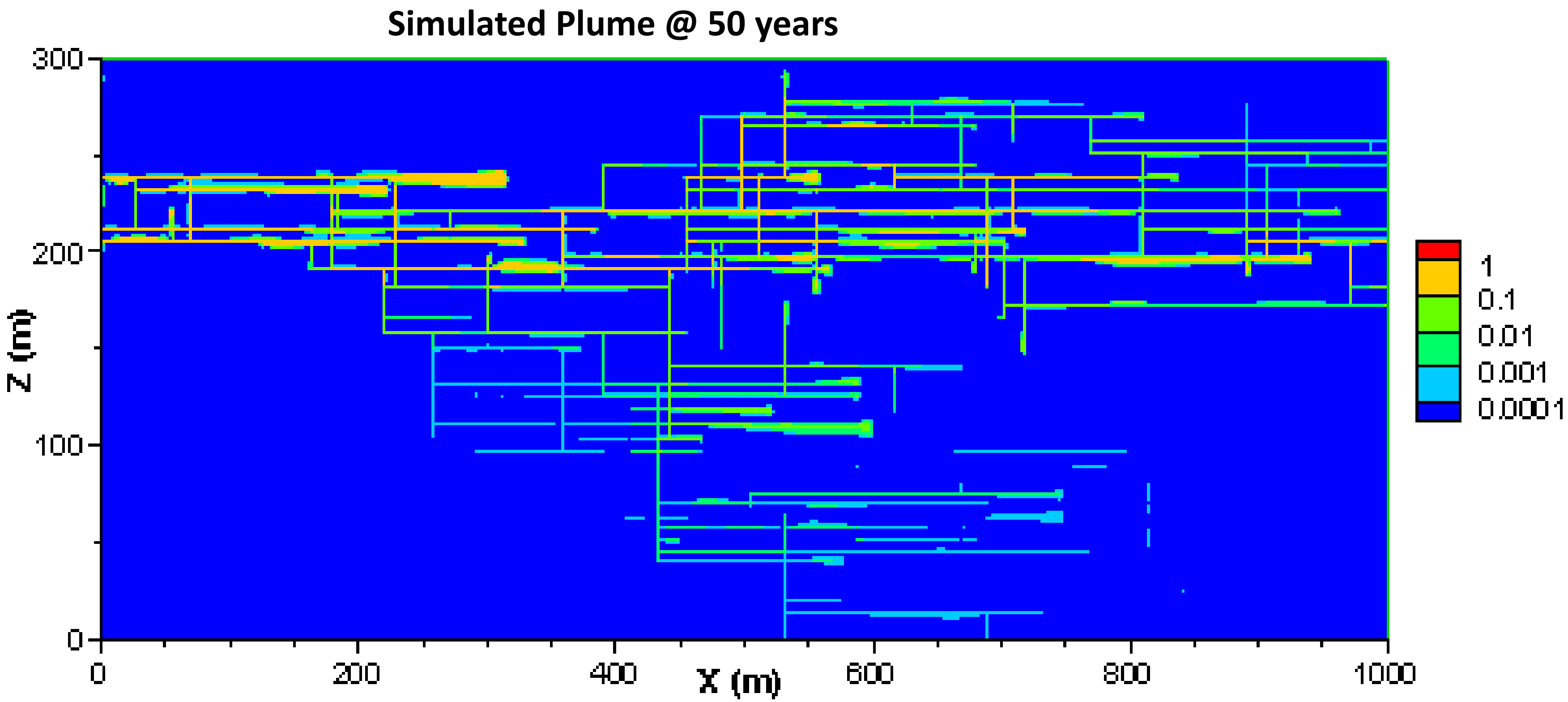


$$K = \frac{b^2 \rho_w g}{12 \mu_w}$$

Dense, Well Connected Fx Network

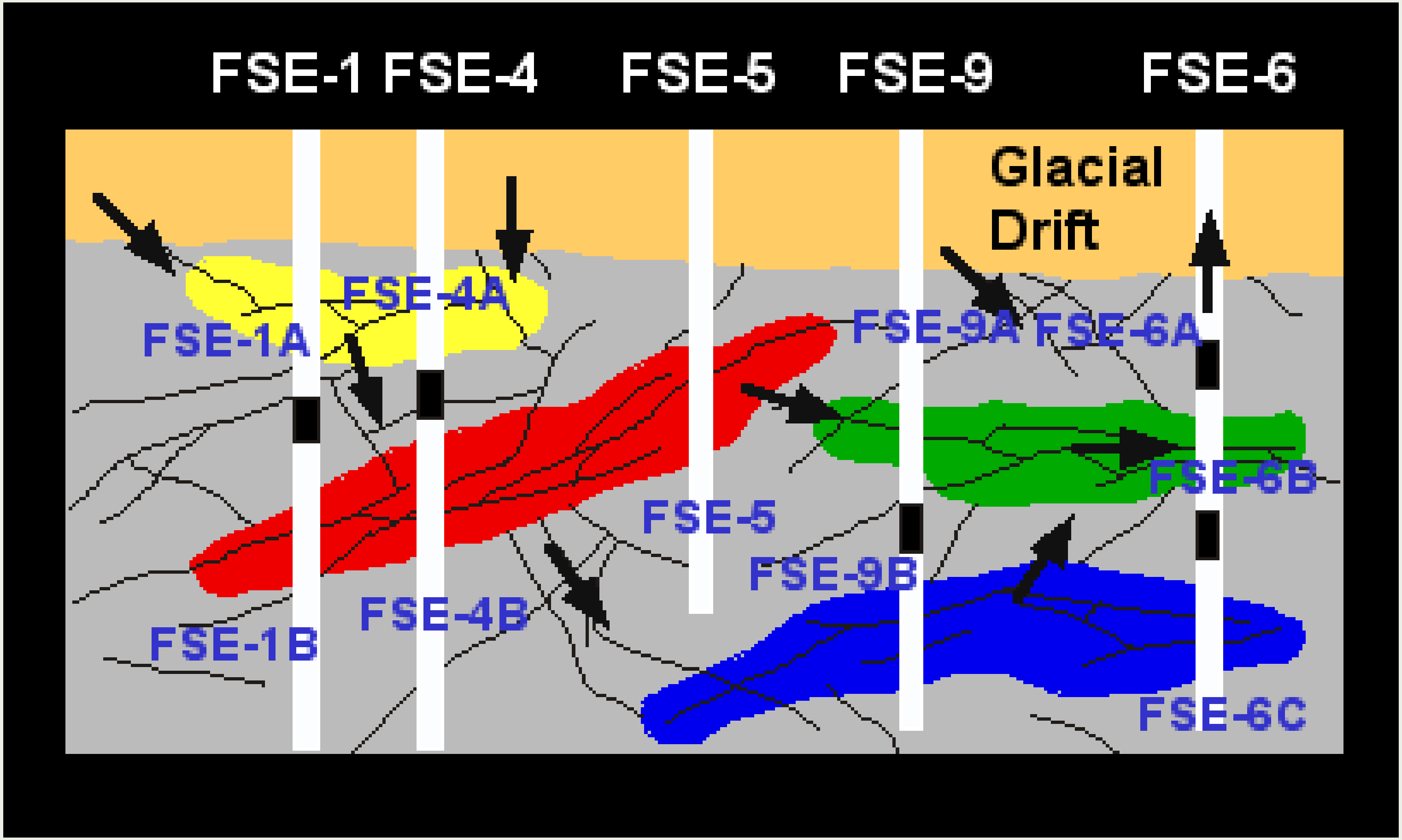


Sparse Network of Major Fractures



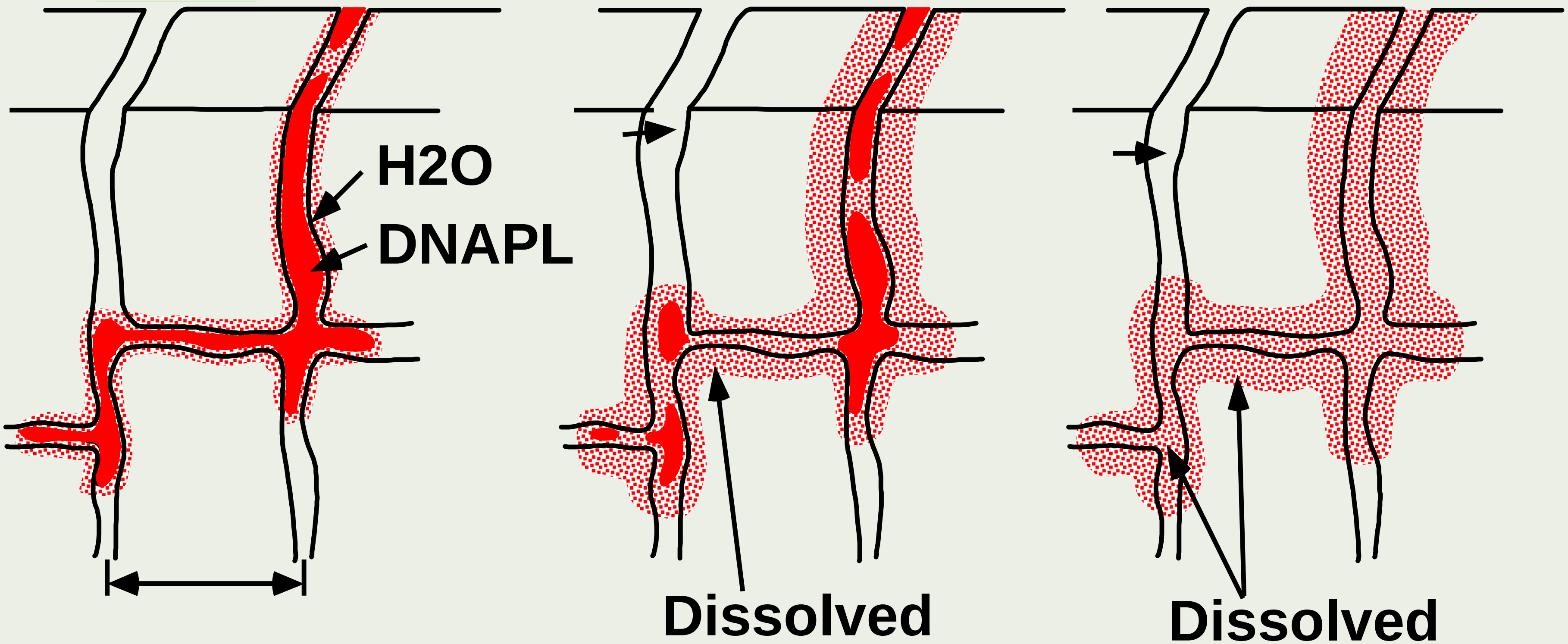
Fracture Interconnectedness

Mirror Lake, NH (Granite)



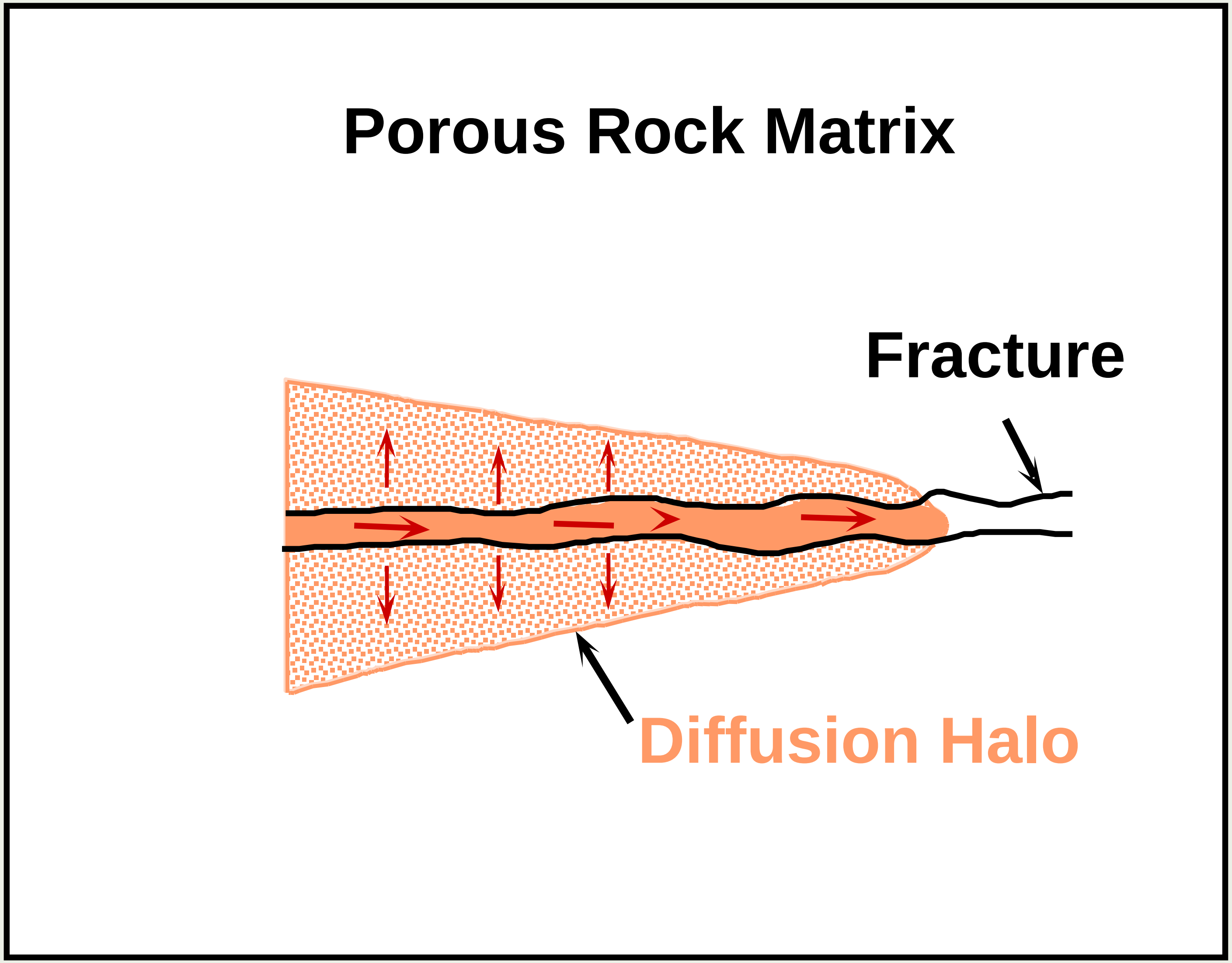
Shapiro, A. M., and P. A. Hsieh, 1994

DNAPL Disappearance from Fractures by Diffusion



Early Time **Intermediate** **Later Time**

Diffusion Into Rock Matrix



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**

Questions?

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