

## **Introduction to *NAPLs***

- Review of general concepts
- LNAPL and DNAPL migration patterns
- Behavior in the subsurface
- Measurement in wells
- Emerging remediation methods
- Detailed case study - Hill Air Force Base

## **What are *NAPLs* ?**

- Immiscible hydrocarbons in the subsurface which can partially dissolve into water at very slow rates
- Can be either lighter than water (LNAPL) or denser than water (DNAPL)
- Form a visible, separate oily phase in the subsurface
- Complex migration governed by gravity, buoyancy, and capillary forces, and soil texture

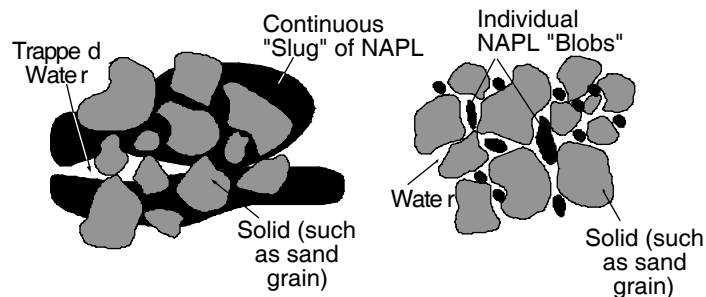
## Phase Distribution

- Free phase, aqueous, gaseous, and solid
- Distribution dictated by four processes:
  - Volatilization (Henry's Law)
  - Dissolution (solubility)
  - Sorption (tailing effects in pump/treat systems)
  - Biodegradation (aqueous phase mostly)

## LNAPL Transport Properties

- Density (LNAPL vs DNAPL)
- Viscosity (governs mobility in subsurface)
- Interfacial tension (pore scale effect)
- Wettability (affinity of soil for fluids)
- Capillary pressure (pressure across an interface)
- Saturation (fraction of pore space containing fluid)
- Relative permeability (function of saturation)

## Mobile vs. Residual NAPL



Mobile Phase NAPL or (Free-Phase NAPL) is a continuous mass of NAPL that can flow under a hydraulic gradient

Residual Phase NAPL is trapped in the pore spaces between the soil particles, and cannot be easily moved hydraulically

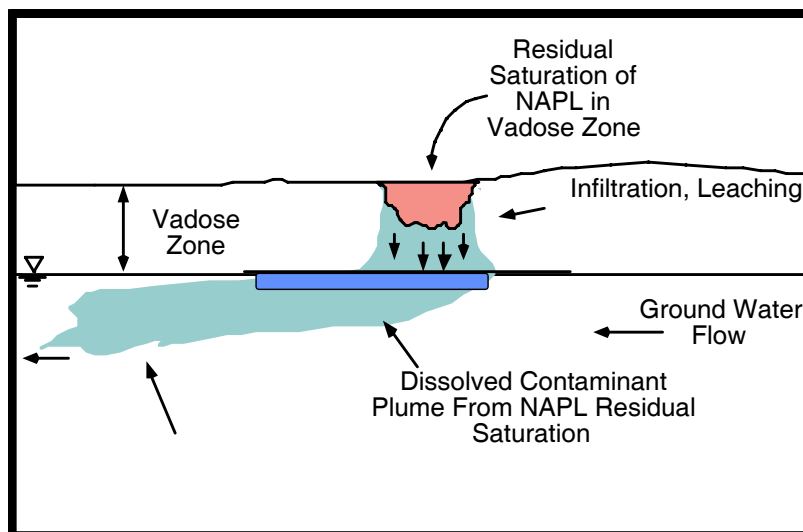
## Long-Term Sources

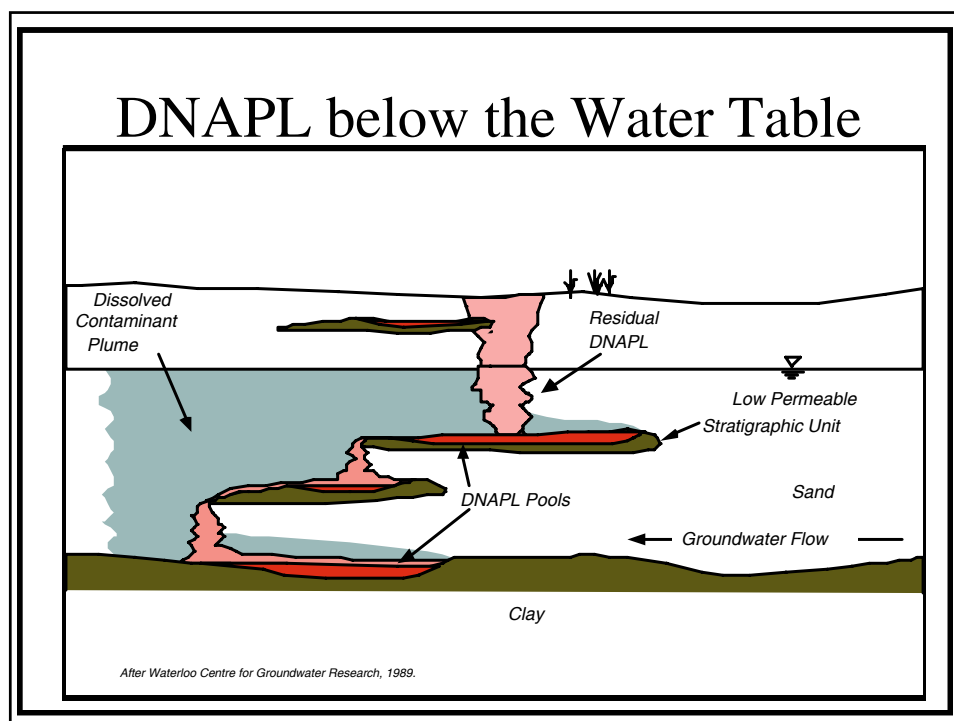
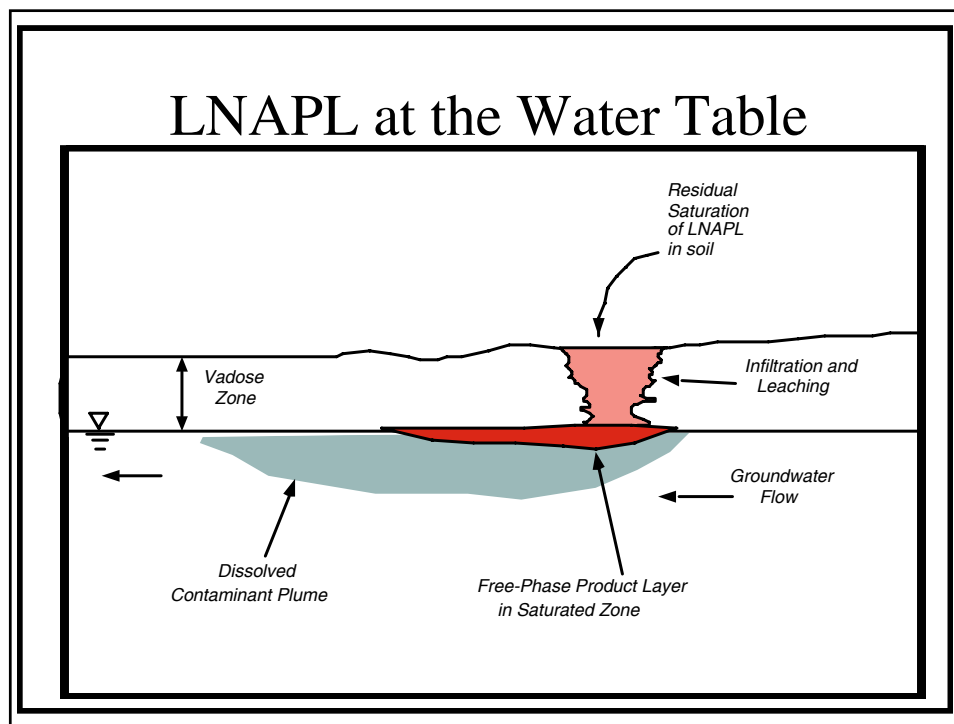
- Total mass of NAPL at a site is often many times the total dissolved mass at the same site
- The EPA in 1989 and 1992 concluded that poor performance of pump-and-treat systems was due to NAPLs acting as a continuing source
- One kg of NAPL can contaminate:
  - 100,000 L of groundwater at 10 mg/L, or
  - 100,000,000 L of groundwater at 10 µg/L
- It can take many years to dissolve a large NAPL source

## Smearing of LNAPL

- Seasonal fluctuation of water table
- Pump and treat system with large drawdowns - causes serious problem if wells fail and water level increases
- Trapping of LNAPL below the water table
- Trapping of LNAPL on clay lens as water table declines

## LNAPL Release to Vadose Zone





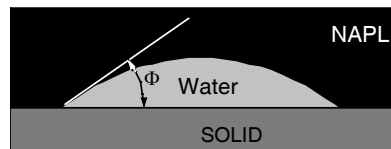
## Wettability

- Capillary pressure proportional to interfacial tension and inverse to radius of curvature
- Fluid drawn into pore is the wetting fluid
- Fluid repelled by capillary forces is the non-wetting fluid
- Water is almost always wetting when mixed with air or NAPLs in the subsurface
- NAPL is generally the wetting fluid in air but non-wetting fluid in water

## Wetting Relationships

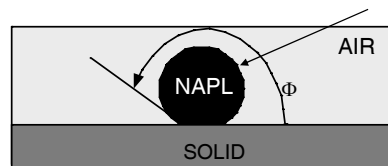
Testing fluid: water  
Background fluid: NAPL  
 $\Phi < 70^\circ$

Conclusion: Water is the wetting fluid



Testing fluid: NAPL  
Background fluid: air  
 $\Phi > 110^\circ$

NAPL is Non wetting fluid



$\Phi$  = Contact Angle

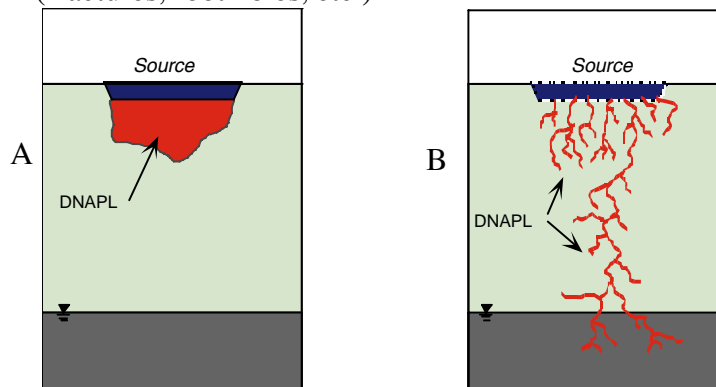
**General Wetting Relationships for Air, Water, NAPL:**

System	Wetting Fluid	Non-Wetting Fluid
air:water	water	air
air: NAPL	NAPL	air
water:NAPL	water	NAPL
air:NAPL:water	water>organic>air	air

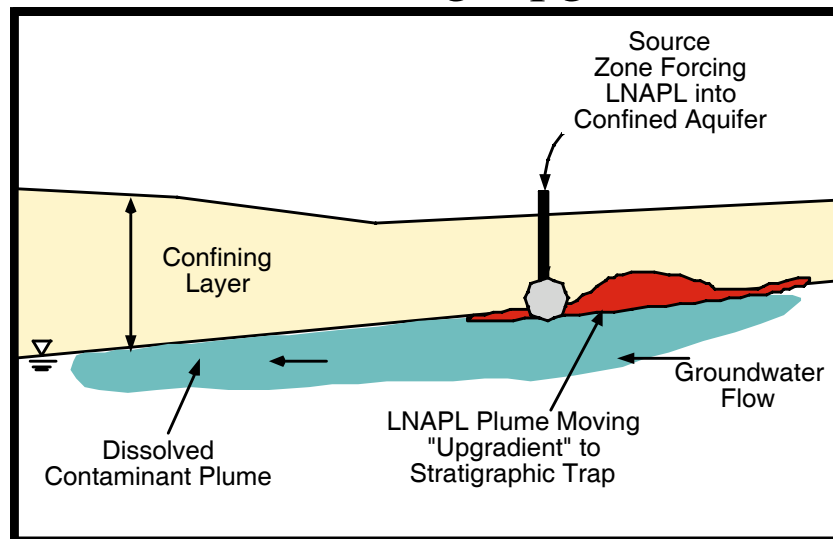
## NAPL migration in primary vs. secondary porosity.

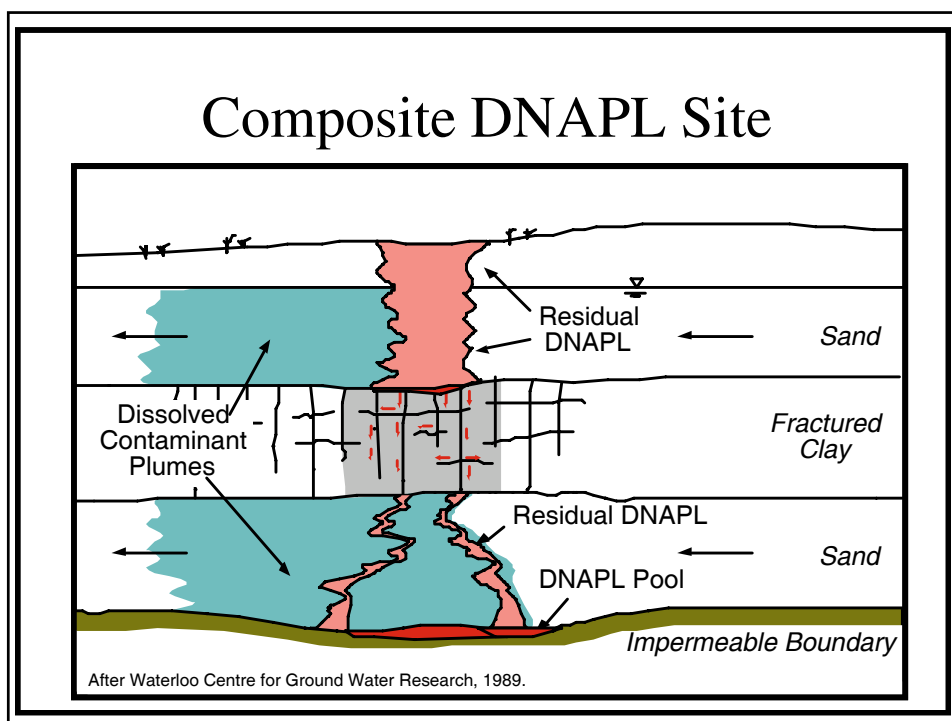
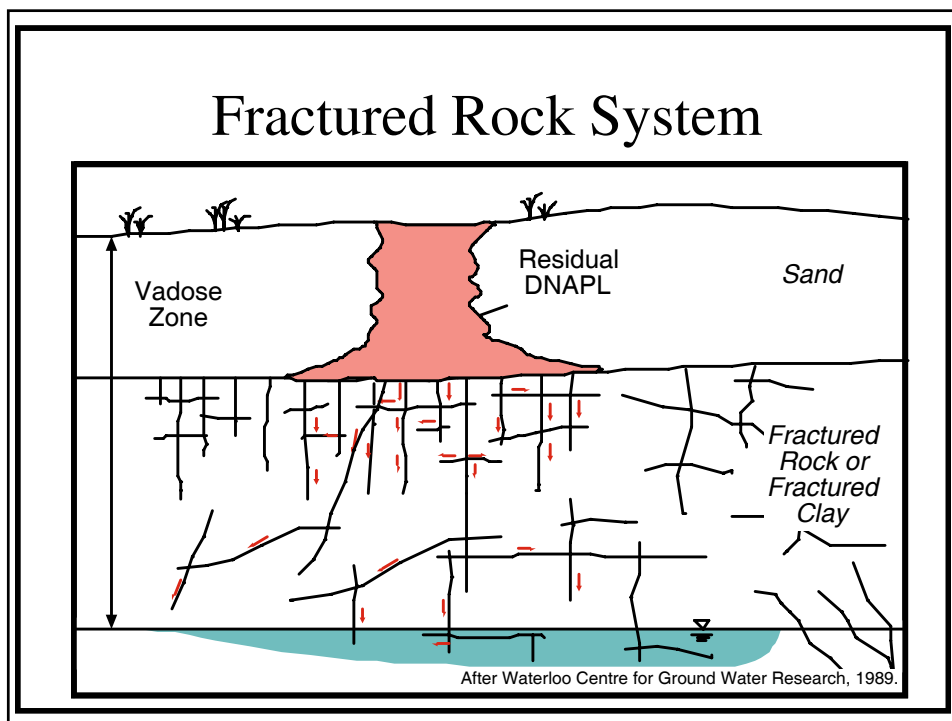
(A) NAPL migration through primary porosity.

(B) NAPL migration through secondary porosity features (fractures, root holes, etc.).



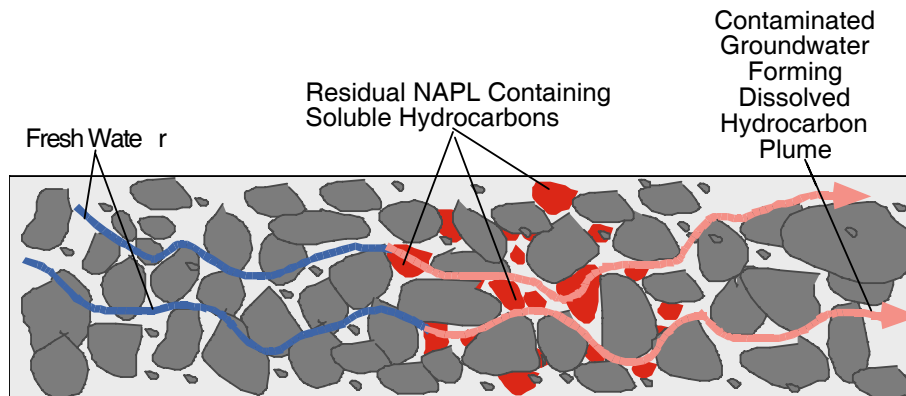
## LNAPL Moving Upgradient



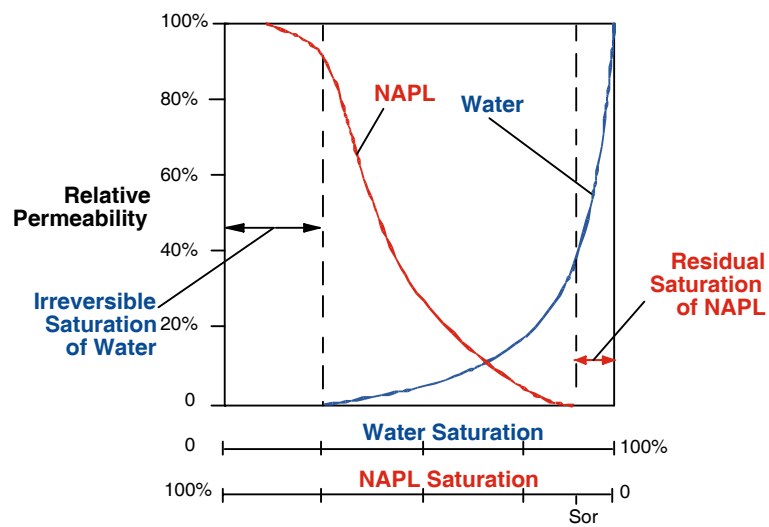


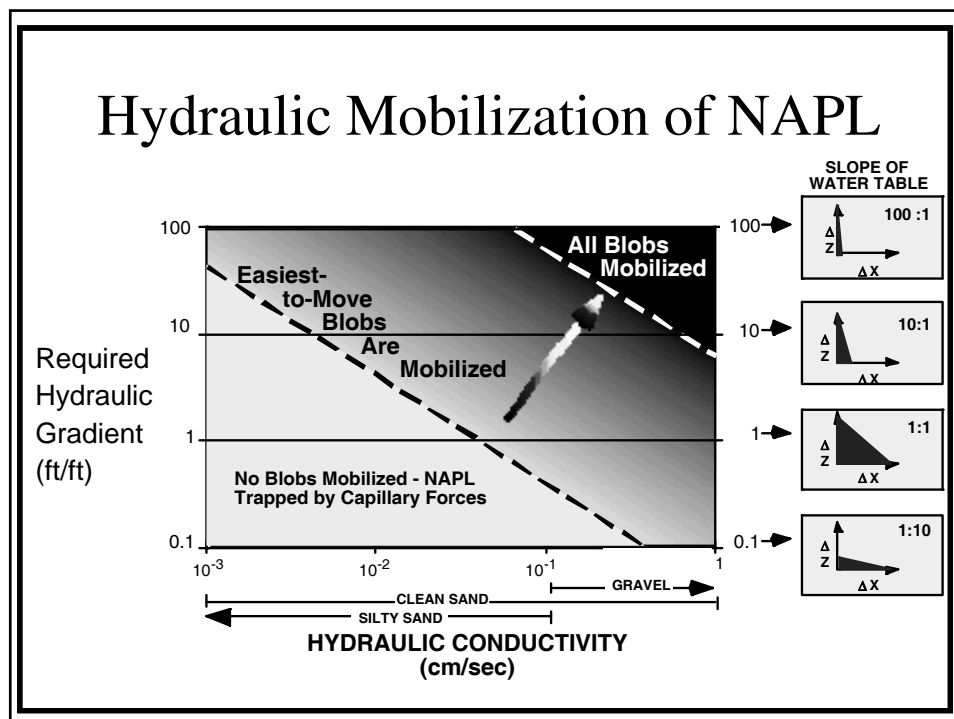
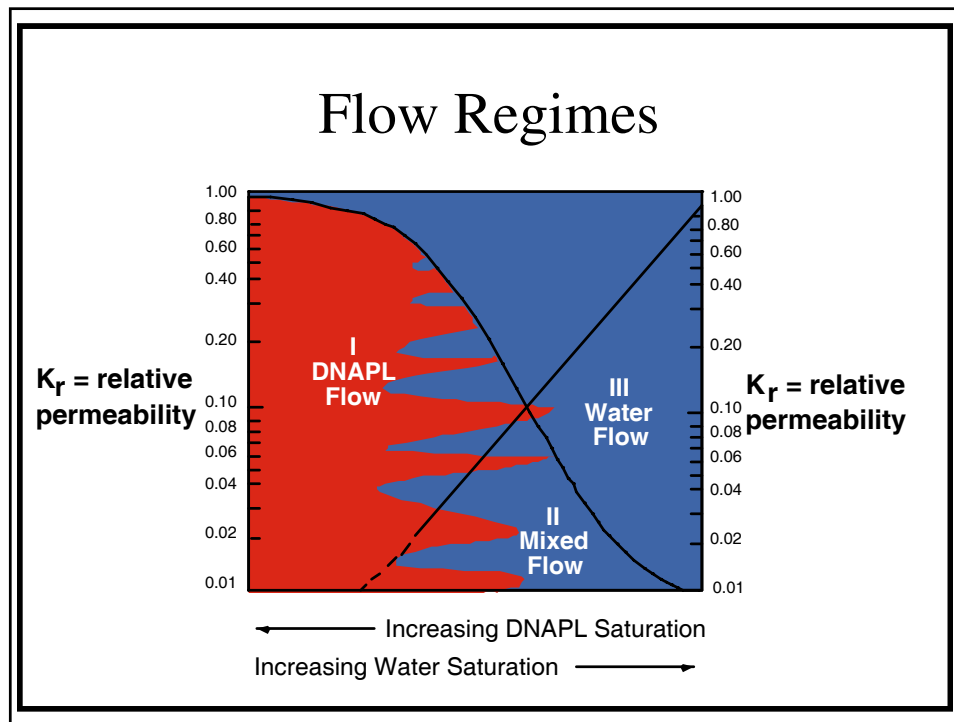


## Dissolving NAPL

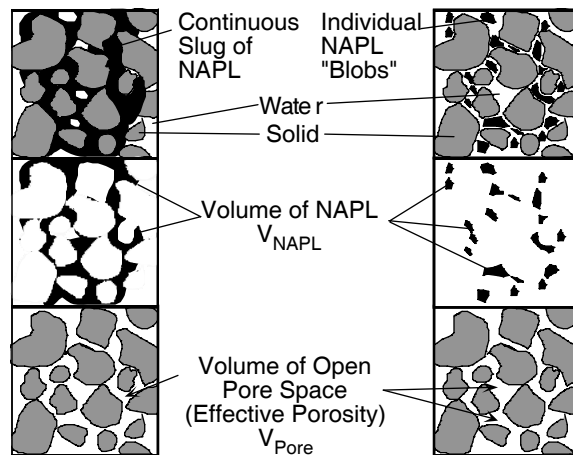


## Relative Permeability





## Calculating Saturation



$$S_{NAPL} = \frac{V_{NAPL}}{V_{Pore}}$$

Can be estimated in the lab via the following:

$$S_o = \frac{\rho_b \cdot TPH}{\rho_n \cdot n \cdot 10^6}$$

Where:

$\rho_b$  = soil bulk density [g/cm<sup>3</sup>]

$\rho_n$  = NAPL bulk density [g/cm<sup>3</sup>]

n = porosity

TPH = Total Petroleum Hydrocarbons  
[mg<sub>NAPL</sub>/kg<sub>dry soil</sub>]

## Partitioning Tracer Test for $S_N$

- Chemicals are introduced consisting of conservative and partitioning tracers (PTT)
- NAPL - Water Partition Coefficient  $K_N$ .
- $K_N = C_N/C_w$  where  $C_N$  is the conc. in NAPL and  $C_w$  is water conc.
- At steady state, the effect is to delay or retard the PT transport rate according to a retardation factor
- $R = 1 + (K_N S_N)/(1 - S_N) = t_p/t_n$

## Partitioning Tracer Test for $S_N$

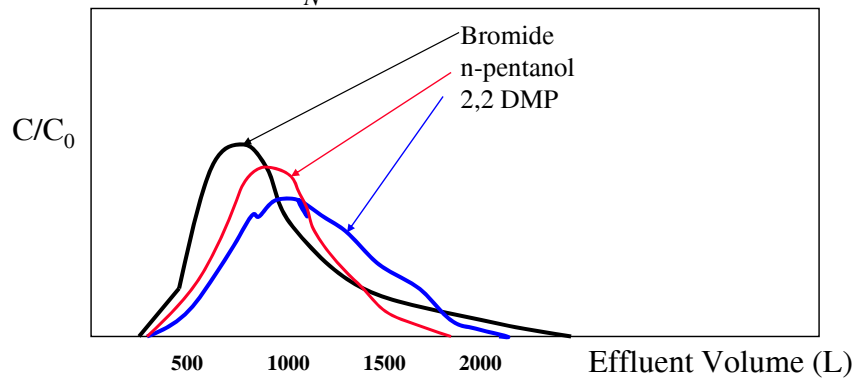
- $T_p$  is travel time for the Partitioning tracer
- $T_n$  is the travel time for the conservative tracer (Br-)
- Sorption is assumed insignificant
- PT compounds often used include alcohols such as
  - ethanol (0.1)  $K_N$  values in parentheses
  - n-pentanol (1.4)
  - n-hexanol (4.6)
  - 2,2 dimethyl-3-pentanol (12.9)
  - n-heptanol (20.0)

## Typical Values of $S_N$

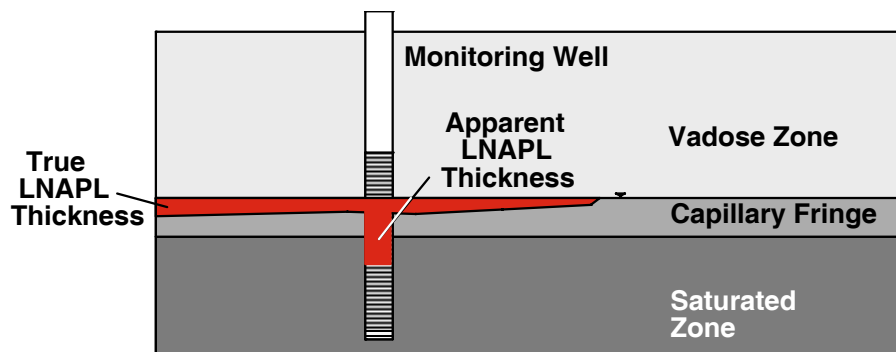
- |                            |   |
|----------------------------|---|
| • EW1 from UF test cell    | 0.031                                   |
| • EW2 from UF test cell    | 0.049                                   |
| • EW3 from UF test cell    | 0.088                                   |
| • Total or Avg for UF cell | 0.054 or about 5.4 %<br>NAPL Saturation |

## Partitioning Tracer Test for $S_N$

- Measured BTC for PTT with bromide
- Time difference between different chemicals allows calculation of  $S_N$



## Apparent LNAPL Thickness

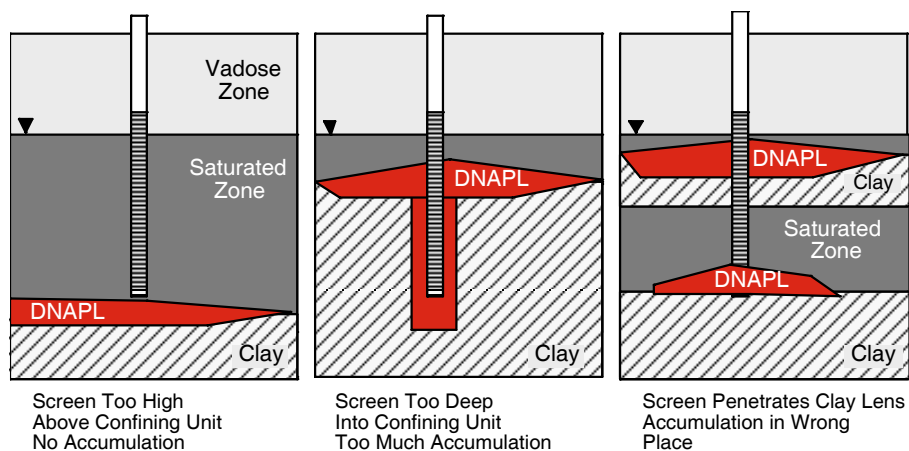


$$h_f \approx h_w \frac{\rho_w - \rho_{\text{LNAPL}}}{\rho_{\text{LNAPL}}}$$

## Apparent LNAPL Thickness

- Thickness in screened well casing only indicator of actual thickness in the unit
- Thickness in the well may be 2 to 10 times larger than actual thickness of mobile LNAPL in the surrounding aquifer
- No methods exist to improve these estimates

## DNAPL Detection Problems



## Remediation of LNAPL

- Excavation
- Trenches, drains, and wells
- Soil vapor extraction (SVE)
- Air sparging
- Enhanced oil recovery (water, steam, cosolvents, surfactants, etc)
- Bioremediation
- Physical barriers

## Hill AFB in Utah

Largest Remediation Project for  
NAPL in a Source Zone -

Joint project with several  
universities, U.S. EPA, U.S. Air  
Force, and private industry

1994 - 1998