Non-Aqueous Phase Liquids
Young Environmental Professionals (YEPs) Presentation
23 February 2017

Gordon Binkhorst

Senior Hydrogeologist at ALTA Environmental Corp. 1998 - Present

Brown University, B.S. Geology 1986

UConn, M.S. Geology 1992.

   Masters Description = slug tests in typical monitoring wells bridging water table

UConn, Ph.D. Geology 1997.

   Dissertation Description = delineation and weathering of gasoline in subsurface
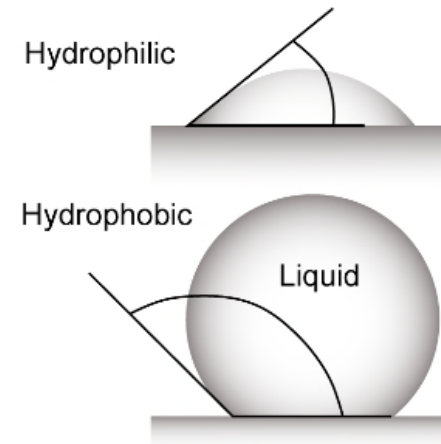
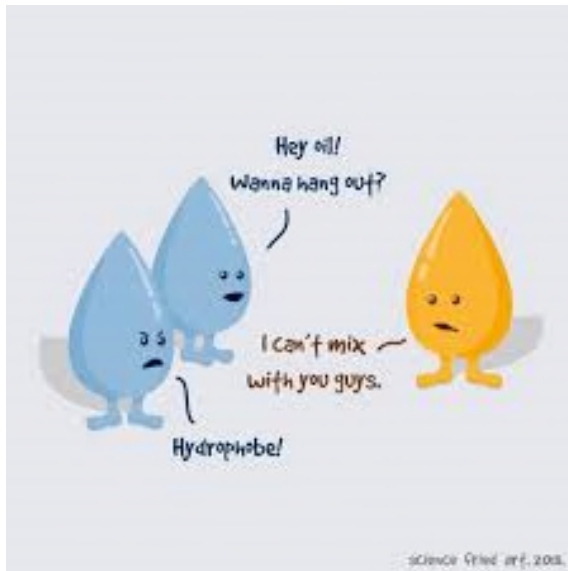Contact Info:

gordon@altaenv.com

Work: 860-537-2582

Cell: 860-573-6288

What is a NAPL

- Non-Aqueous Phase Liquid
- Polar H_2O versus non-polar NAPL make it hydrophobic (literally fear of water)
  - Surface tension and wettability

Picture 3 – "Hydrophilic" versus "Hydrophobic" contact angles – liquid / solid surface interaction.

- Sparing Soluble in Water, but still soluble...

Example Solubilities & Densities

NAPL	Solubility (mg/l)	Specific Gravity
Gasoline		0.74
Mineral Spirits		0.78
Benzene	1,790	0.88
No. 2 Fuel Oil	56	0.82 - 0.88
Kerosene		0.82 - 0.95
Motor Oil		0.87
Diesel Fuel		0.81 to 0.96
No. 6 Oil	5	0.92 - 1.08
PCE	200	1.63
TCE	1,100	1.46

Why Do We Care?

- Recalcitrant; depends on properties of NAPL
  - Solubility
  - Biodegradability (predominantly in water)
  - Vapor Pressure (volatilization)
- All of above changes composition of NAPL in subsurface (e.g., effective solubility)
- Present in Subsurface for 10s of Years
- Line-in-Sand Pre-RSRs and Cleanup Standards

Conceptual Site Model

- Predominantly Vertical Migration in Vadose Zone
  - Some lateral spreading due to dispersion in homogeneous environment
  - Lateral spreading due to lower permeability zones
  - Lateral Spreading at Capillary Fringe and at Water Table
- Small Spills of NAPLs DO NOT Reach Water Table (except as dissolved). Why?
- Migration influenced by NAPL Properties, especially surface tension, viscosity, wetting properties etc. and soil properties (permeability, moisture content, grain size).
- Volatilization and Dissolution in Vadose Zone
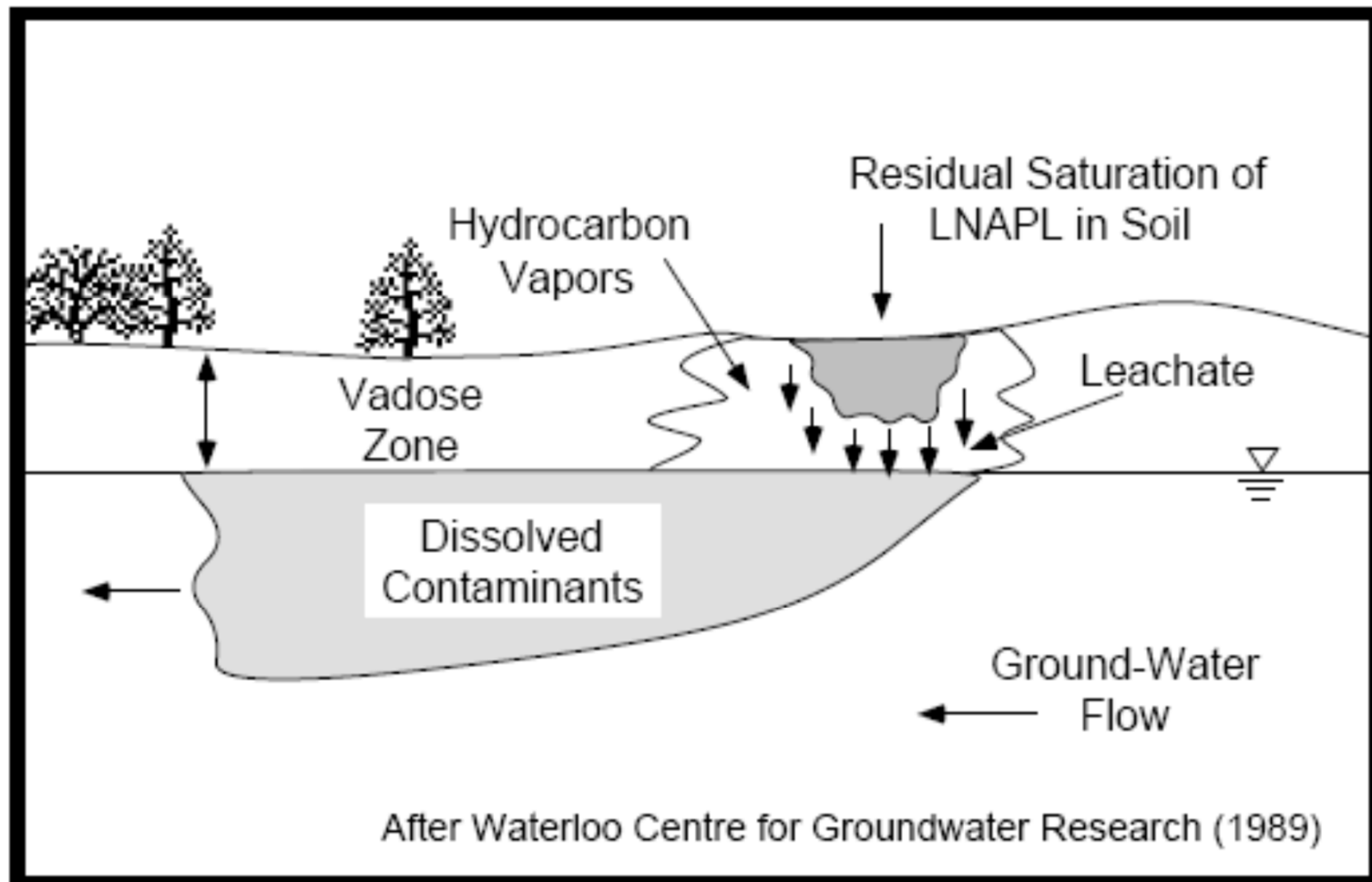
Factors affecting NAPL movement

Fluid properties:
- ✓ Density
- ✓ Interfacial tension
- ✓ Residual saturation
- ✓ Partitioning properties
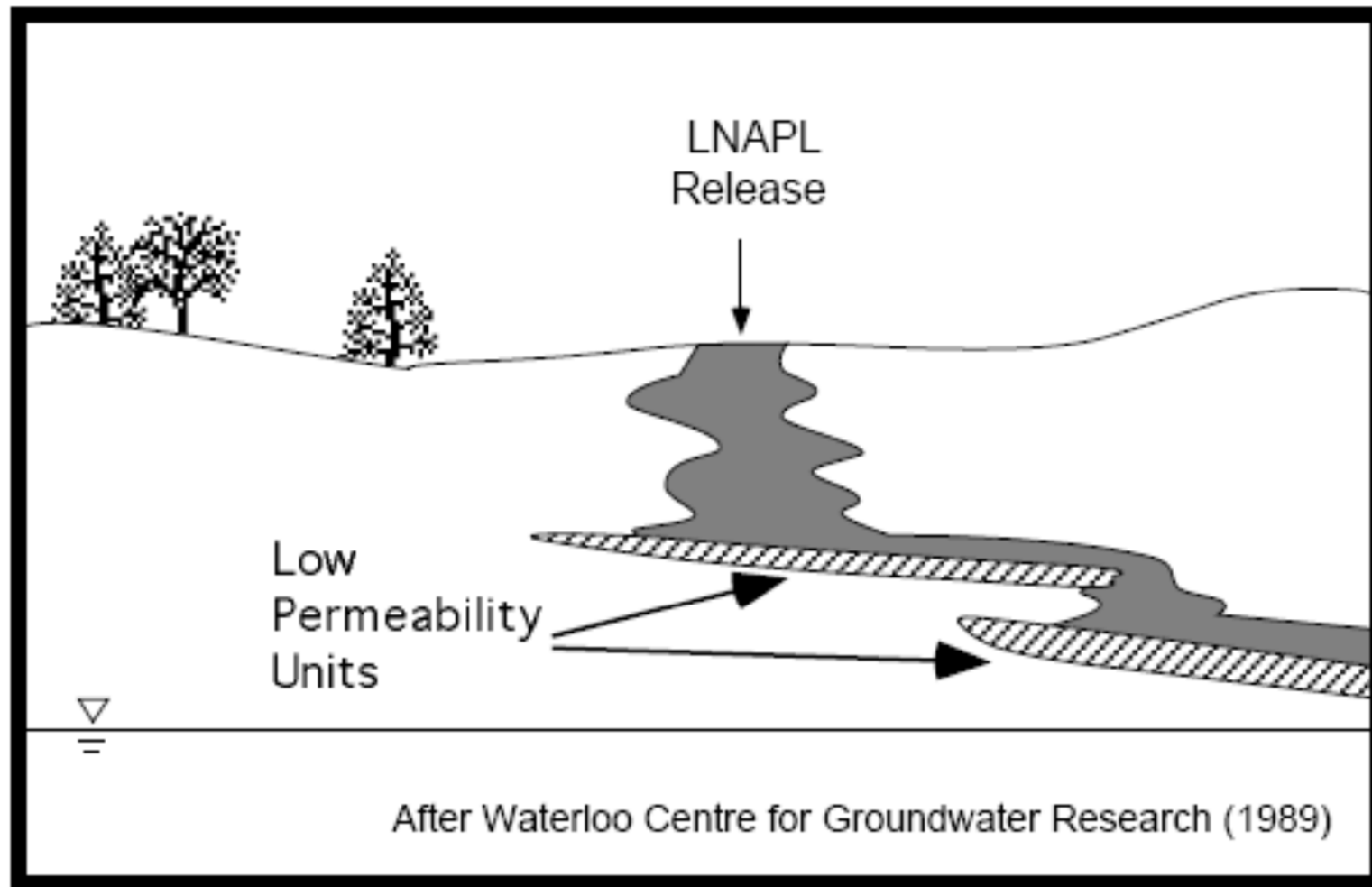- ✓ Solubility
- ✓ Volatility and vapor density

Porous medium:
- Permeability
- Pore size
- Structure

Ground water:
- Water content
- ✓ Velocity

After Waterloo Centre for Groundwater Research (1989)

LNAPL
Release

Low
Permeability
Units

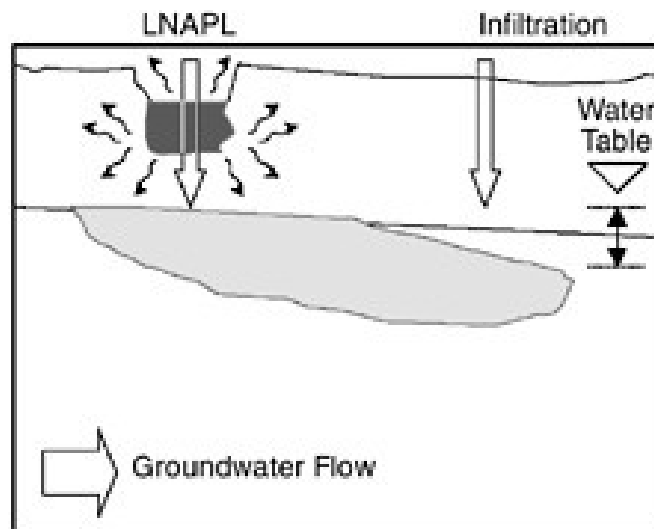After Waterloo Centre for Groundwater Research (1989)

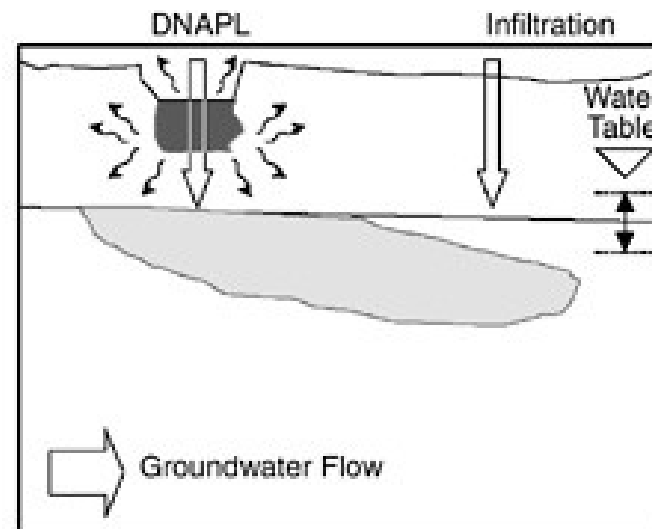Note that <u>capillary fringe</u> and water table are lower permeability horizons…
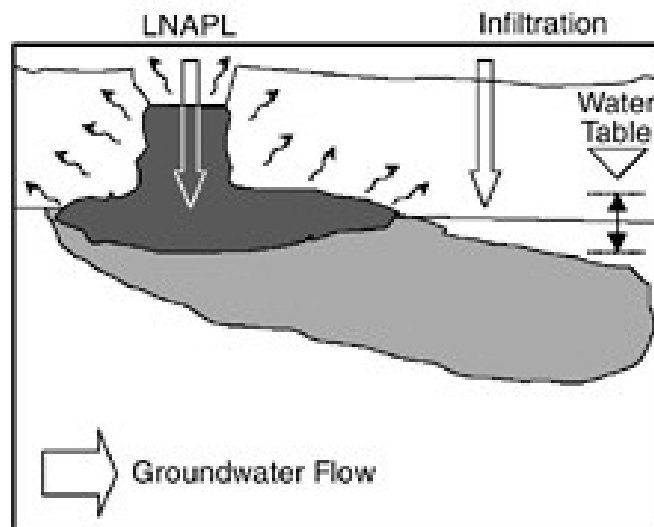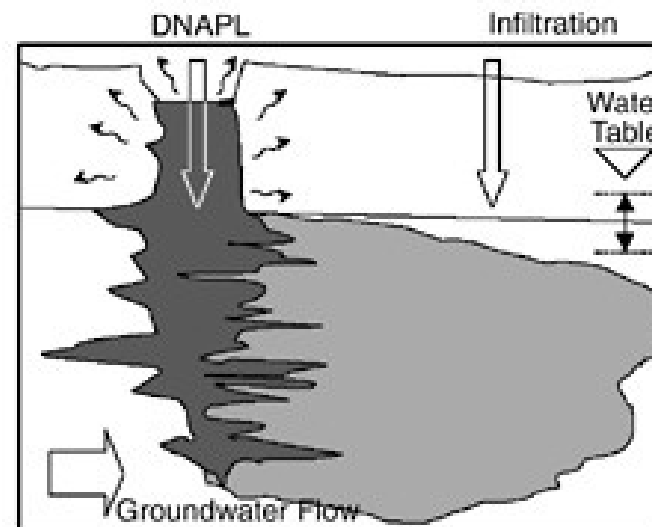
CSMs

a) Small release of LNAPL

b) Small release of DNAPL

c) Large release of LNAPL

d) Large release of DNAPL

Conceptual Site Model

- Gravity and Downward Pressure from Above
  - You need downward pressure to overcome capillary forces above water table
  - You need downward pressure to overcome capillary forces AND displace water below capillary fringe and/or water table
  - Continuous versus Discontinuous Distribution
  - Density Dependent?
- Residual Saturation

Percent of Void Spaces Filled with LNAPL in a Coarse Soil
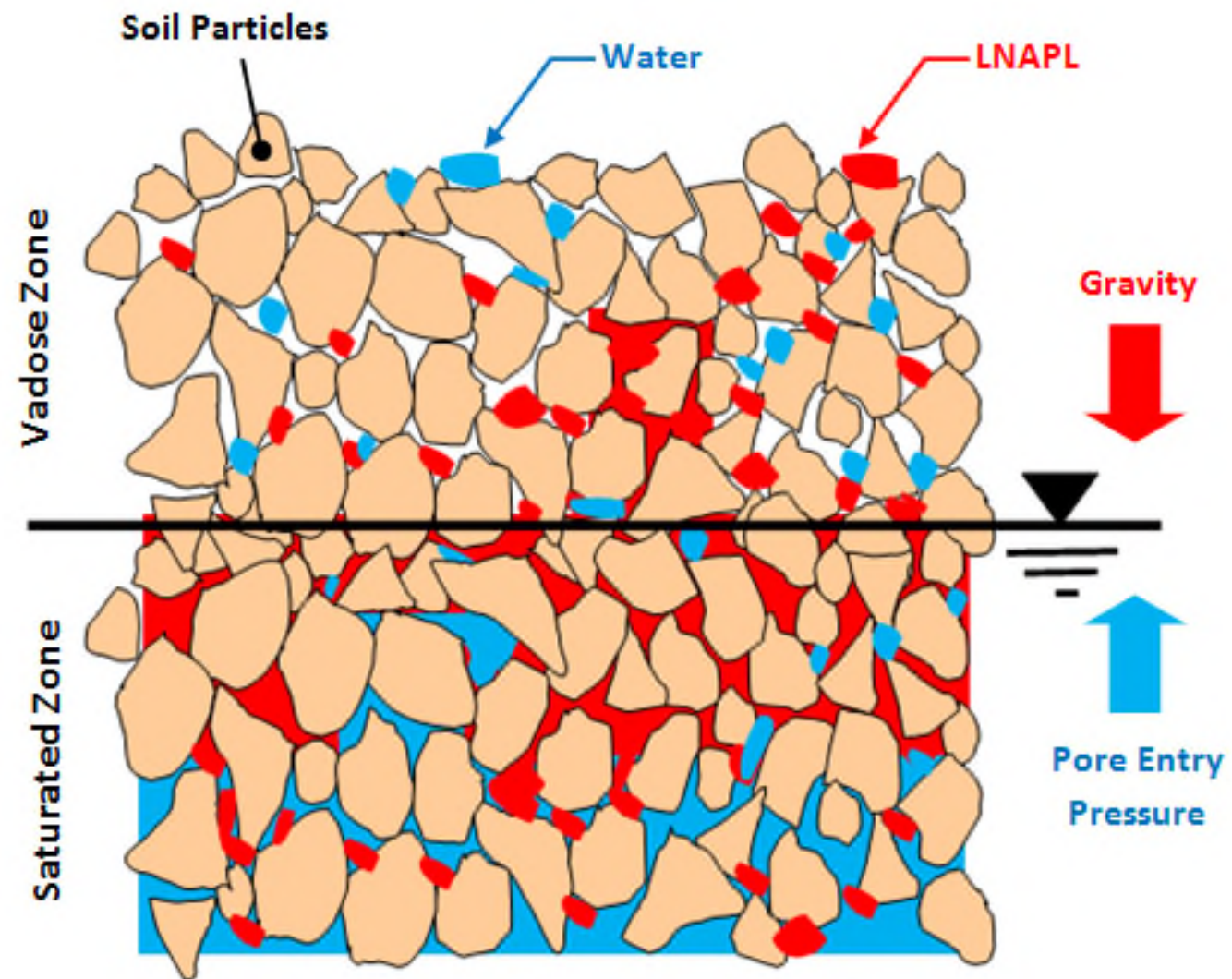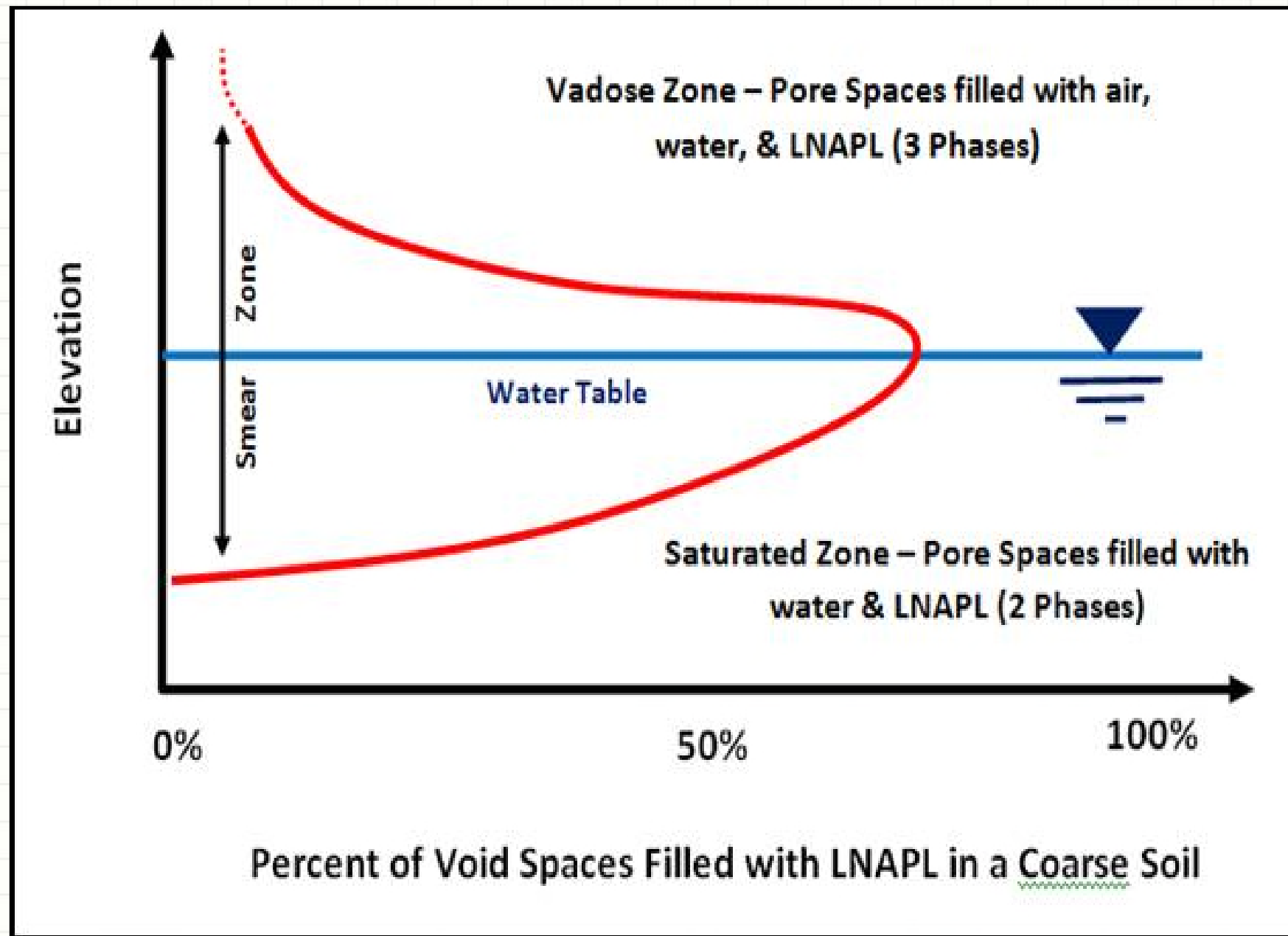
Prior to Rise in Water Table
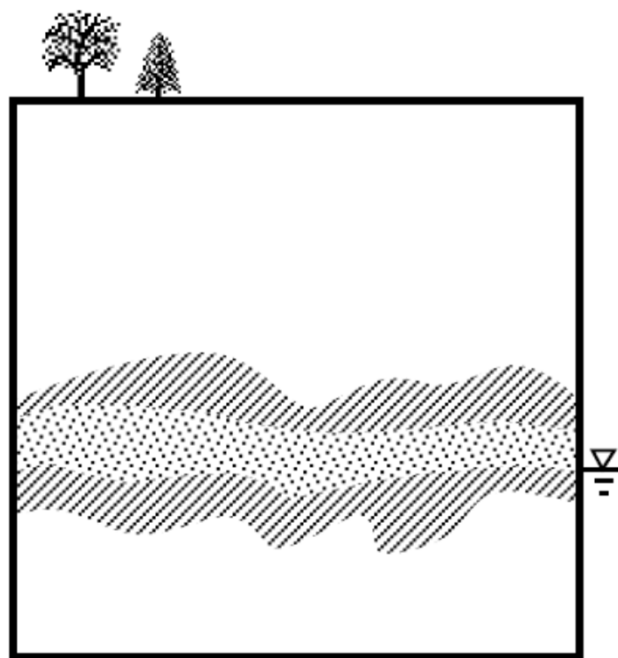
Following Rise in Water Table
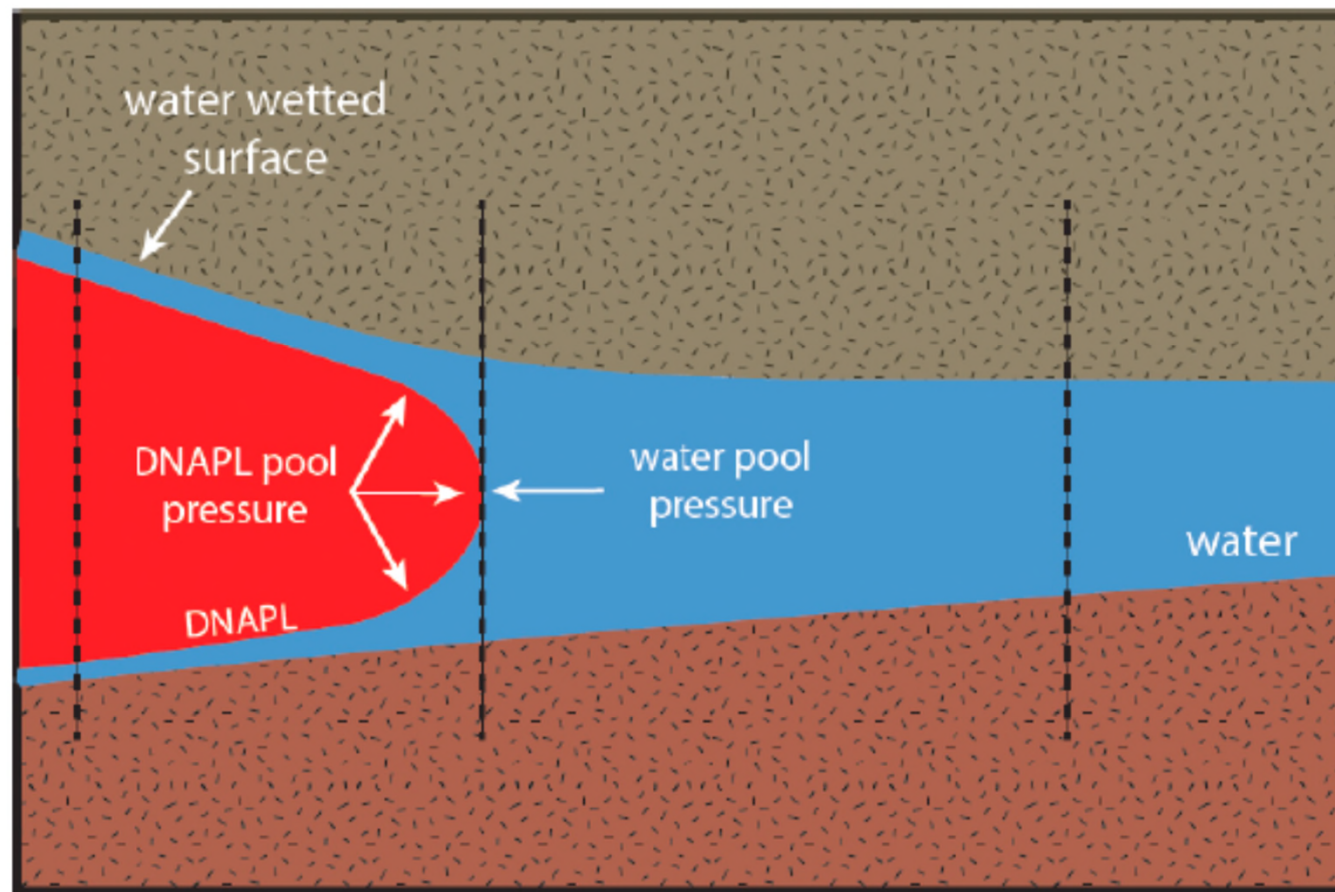
Figure 2-6. Typical conditions in an aquifer with DNAPL present when water is the wetting fluid.
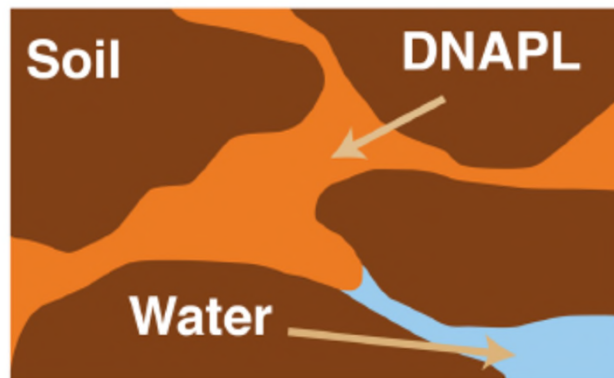
Mobile DNAPL
DNAPL body is continuous and its capillary pressure is high enough to exceed groundwater pore entry pressure, displace groundwater, and migrate through the subsurface.

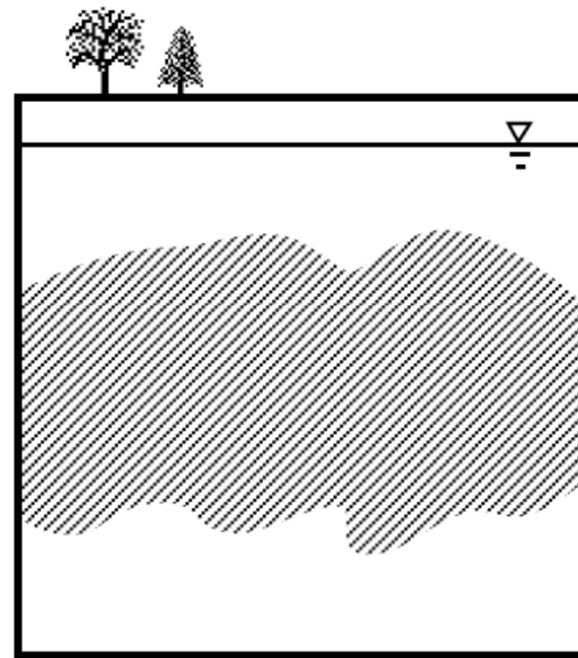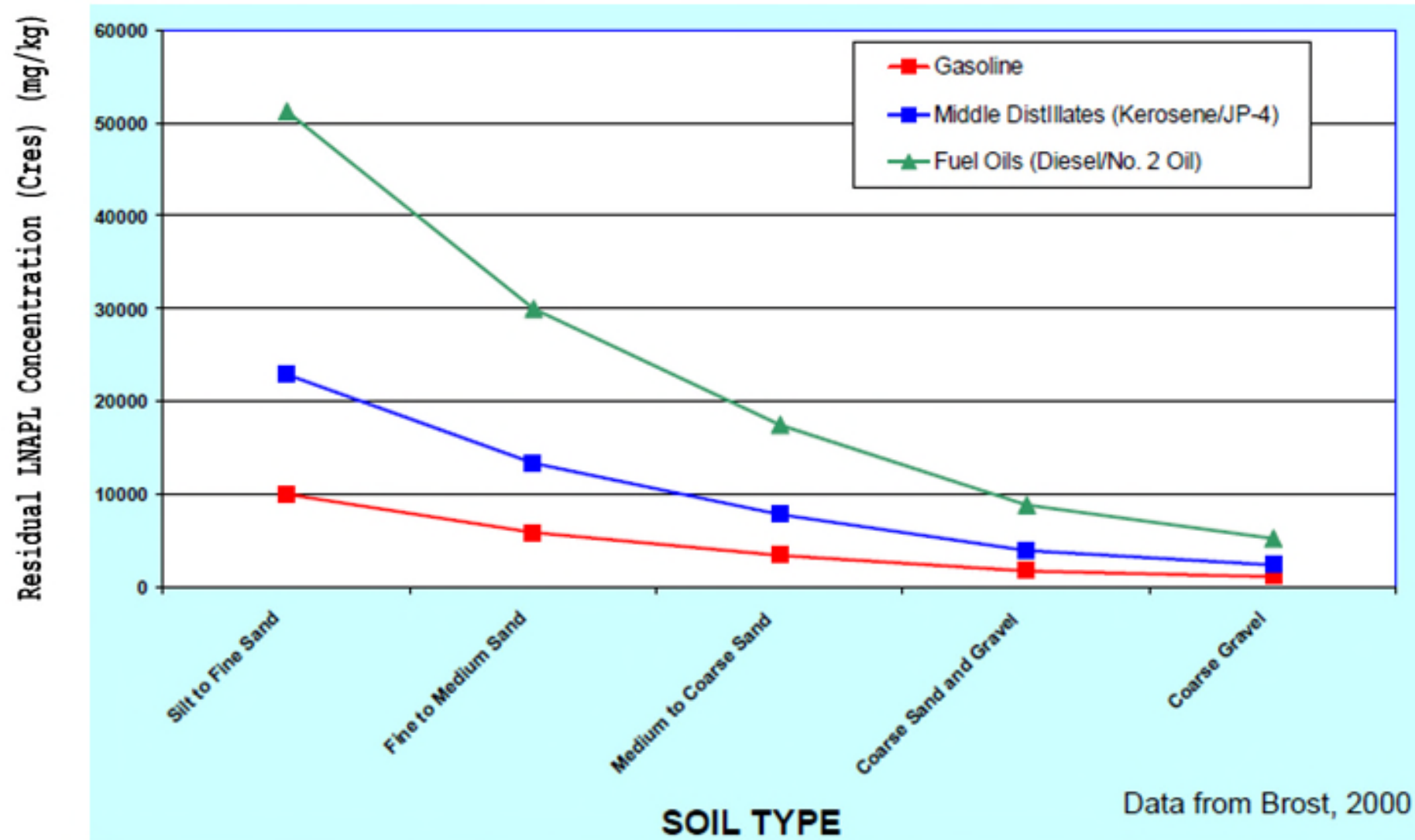**Potentially Mobile DNAPL**
DNAPL body is continuous, but its capillary pressure is not high enough to exceed groundwater pore entry pressure; under current conditions, it will not displace groundwater and migrate. If conditions change (for example, drilling through a potentially mobile DNAPL body, soil fracturing), potentially mobile DNAPL may mobilize and begin migrating.
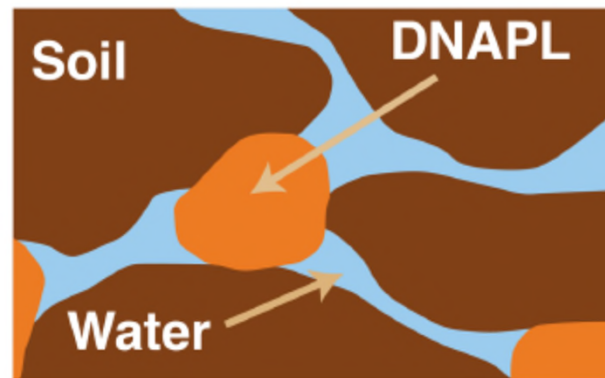
Immobile Residual Phase DNAPL
"Droplets" of DNAPL called ganglia are present in the pore spaces but are not connected to other DNAPL ganglia. They are immobile because they cannot exceed the capillary pressure and displace groundwater in the formation.

Figure 2-1. Mobility characteristics of DNAPL: mobile, potentially mobile, and immobile.

How Do We Find NAPLs

- "Floating": atop water table in wells or at bottom of wells
  - Interface probes & bailers and their issues
- High & sustained concentrations in groundwater and % levels of solubility/effective solubility
- Sheens/blebs in soil or purge water
- Sudan IV (oil soluble dye)
- UV Light
- Soil-Water Test
- Soil Concentrations (e.g., C_{nap})

Free Product in Monitoring Wells

Light Non-Aqueous Phase Liquid (LNAPL) Distribution at the Pore Scale - Sand
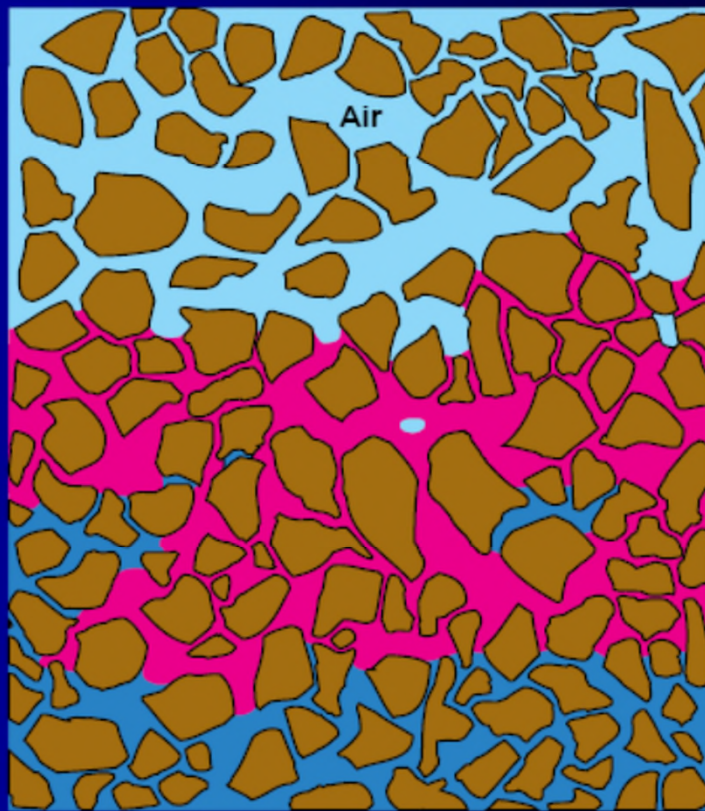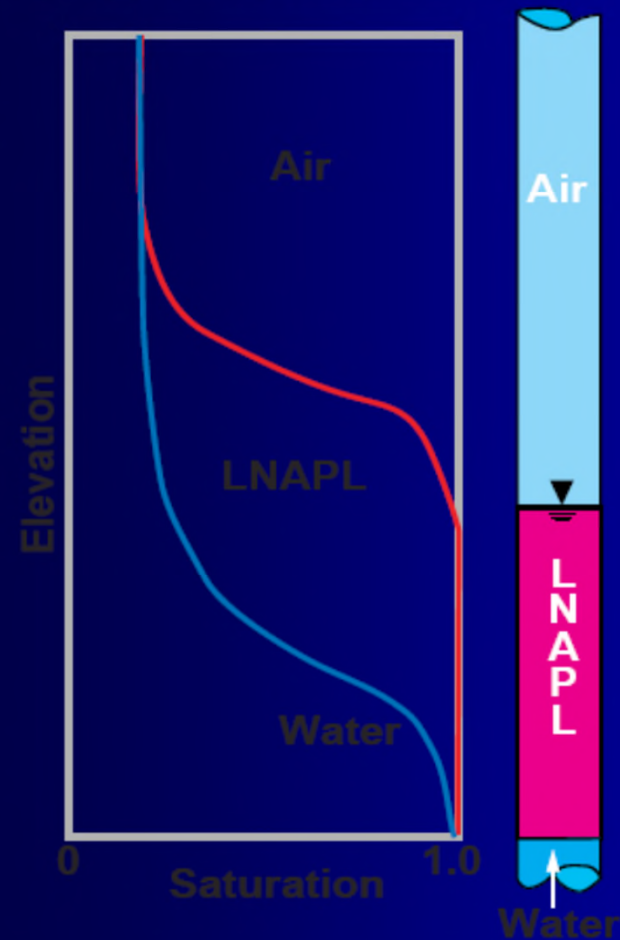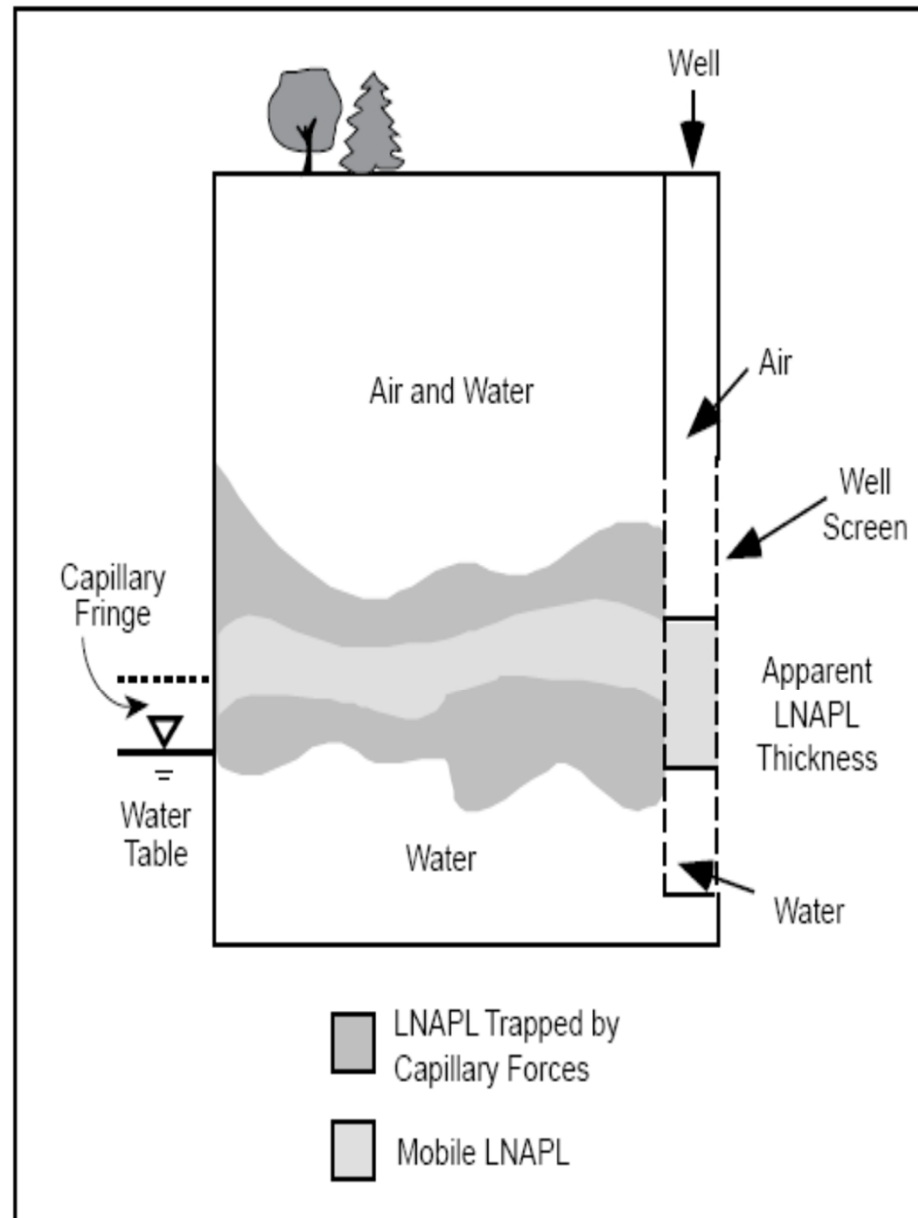
Figure 10. Simplistic conceptualization of LNAPL thickness measured in well and LNAPL distributed information.

Figure 3-4
Microscopic capillary pressure-saturation relationship for two-fluid system in porous media
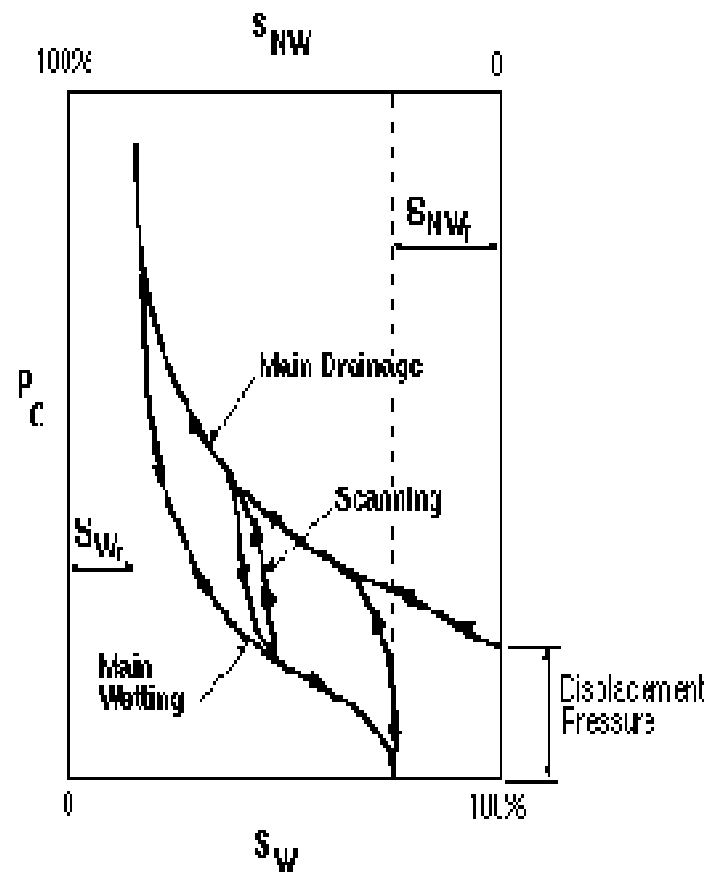
S_W – Wetting Phase Saturation S_{W_r} – Residual Wetting Phase

S_{NW} – Nonwetting Phase Saturation S_{NW_r} – Residual Nonwetting Phase
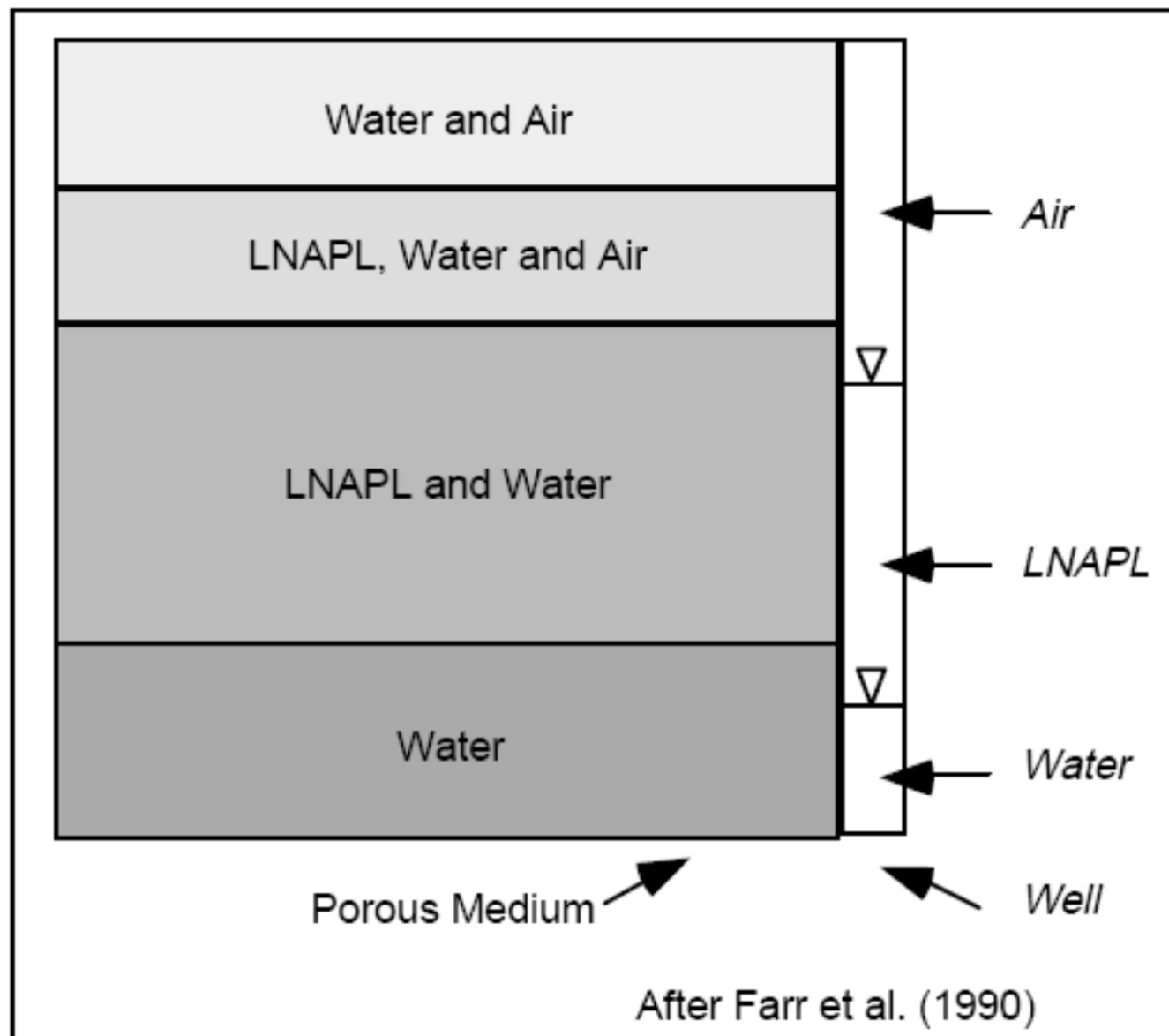
Figure 7. Conceptualization of a multiphase fluid distribution in porous medium and monitoring well screened within the medium.

LNAPL in Wells

- Well must be screened across water table…
- LNAPL thicknesses can be wrong!!!
  - Measurement errors
  - Rising/Falling Water Tables
  - Product on Capillary Fringe (draining into well)
  - Stuck In Wells
  - Does not include product in formation that is below residual saturation!
- Bail down tests at a minimum; correlation with soil concentrations etc.

Correction for LNAPL in Wells

- Well must be screened across water table...

Diagram showing depth to product, depth to water DTW$_a$, and corrected depth to water DTW$_c$, with correction:

$$DTW_c = (DTW_a - DTP)\rho_{prod} + DTW_a$$
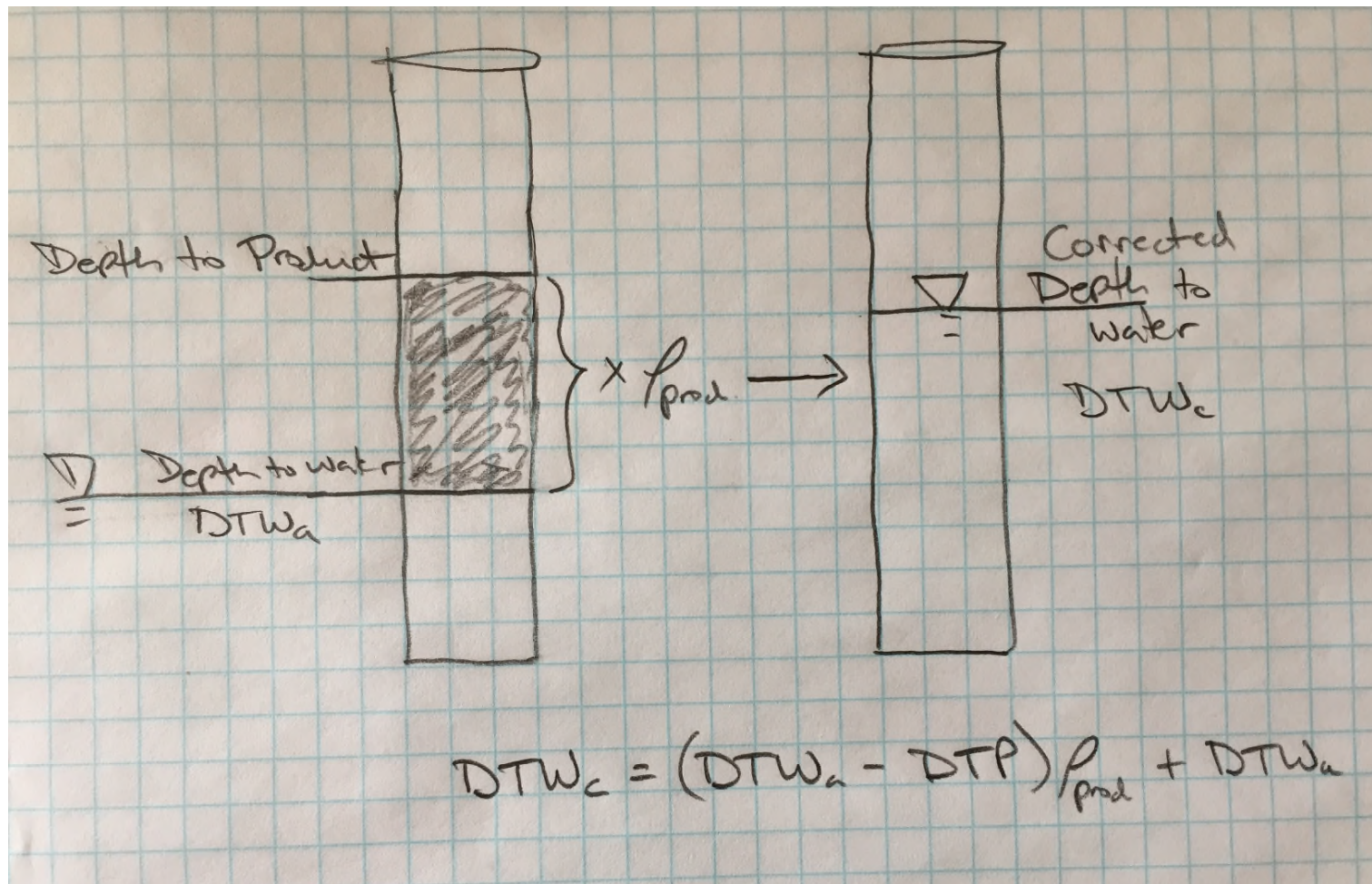
REGULATION

OF

DEPARTMENT OF ENERGY AND ENVIRONMENTAL PROTECTION

(3) Determining the Presence of Non-aqueous Phase Liquids in Soil.

For the purpose of this subsection, the presence of non-aqueous phase liquids in soil shall be determined using the following equation: $C_{nap} = (S/2\rho_b)(K_d \rho_b + \theta_w + H'\theta_a)$, where:

C_{nap} = the concentration of an organic substance at which or above which such substance may be present in a non-aqueous phase

S = the effective solubility

ρ_b = dry soil bulk density

K_d = soil-water partition coefficient, which may be approximated by $K_{OC} \cdot f_{OC}$

K_{OC} = soil organic carbon-water partition coefficient

f_{OC} = fraction organic carbon of soil

θ_w = water-filled soil porosity (L_{water}/L_{soil})

θ_a = air-filled soil porosity (L_{air}/L_{soil})

H' = Henry's law constant (dimensionless)

H = Henry's law constant (atm-m^3/mol)

Total Soil Concentration Components

$$C_{it} = C_{iw} + C_{ia} + C_{iv} \ (+ \ C_{in})$$

<u>Total Soil Concentration of i</u> =
Concentration of i in the water in sample +
Concentration of i that is adsorbed to soil +
Concentration of i that is in the vapor in your sample +
?Concentration of i that is in the NAPL in your sample?

Maximum Total Soil Concentration without NAPL Present

$$C_{in} = C_{iw} + C_{ia} + C_{iv}$$

If You Calculate Maximum in Water, Adsorbed and in Vapor Phases, then…

Anything Left = NAPL

$$C_{nap} = (S_e/\textbf{2}\rho_b)(K_d\rho_b + \theta_w + H'\theta_w)$$

$$C_{nap}\ (\frac{mg}{kg}) = \textbf{0.5} \times (S_eK_{oc}f_{oc} + \frac{S_e\theta_w}{\rho_b} + \frac{S_eH'\theta_w}{\rho_b})$$

Factor of 2 means you are calculating ½ of C_{nap}, i.e., conservative)

$S_e = effective$ solubility

θ_w/ρ_b = water filled porosity/dry bulk density = moisture content (e.g., 0.2 or 20%)
θ_a/ρ_b = air filled porosity/dry bulk density = vol. air per mass of soil
H' (unitless) = H (atm-m^3/mol) x 41 at 20 deg C

C_{nap} Examples

- Cnap for TCE = 660 mg/kg
- Cnap for PCE = 115 mg/kg
- Cnap for benzene = 700 mg/kg

Water saturated sample;

organic carbon content of 0.006 or 0.6%;

dry bulk density of 1.5 kg/l

Effective Solubility

$$C_{iw} = S_{iw}X_{in}$$

The mole fraction of each constituent is calculated from its mass concentration in the NAPL (C_{in}), its molecular weight, and the average molecular weight ($\overline{mw_n}$) of the NAPL:

$$X_{in} = C_{in}\frac{\overline{mw_n}}{mw_i} = \frac{m_{in}}{m_n}\frac{\overline{mw_n}}{mw_i}$$

The approximate molecular weight of fresh and weathered gasoline is 95 and 111 grams/mole, respectively (Johnson et al., 1990b).

$$C^s_{iw} = S_{iw}X_{in}\theta_w$$

Effective Solubility - Gasoline

Compound	Concentration Range (Wt%)	Average Concentration (Wt%)	Molecular Weight (g/mole)	Mole Fraction X_{in}	Pure Solubility (mg/l)	Effective Solubility (mg/l)
MTBE	0-15	7.5	102.18	0.07	48,000	3,360
Benzene	0.7-3.8	2.25	78.11	0.027	1,790	48
Toluene	4.5-21	12.75	92.15	0.131	520	68
E. Benzene	0.7-2.8	1.75	106.17	0.016	140	2.2
m,p-Xylene	1.1-3.7	2.4	106.17	0.021	187	3.9
o-Xylene	3.7-14.5	9.1	106.17	0.081	215	17.4
n-Propylbenzene	0.13-0.85	0.49	120.2	0.004	52.2	0.21
1,3,5-Trimethylbenzene	0.6-1.1	0.85	120.2	0.007	48.2	0.34
Naphthalene	0.2-0.5	0.35	128.17	0.003	30.6	0.09

Solubility vs. What We Encounter in GW

- Effective Solubility
- Contact with NAPL/dead end pores/discontinuous
- Mass flux limited by contact time
- 1 to 10% of solubility can be indicative
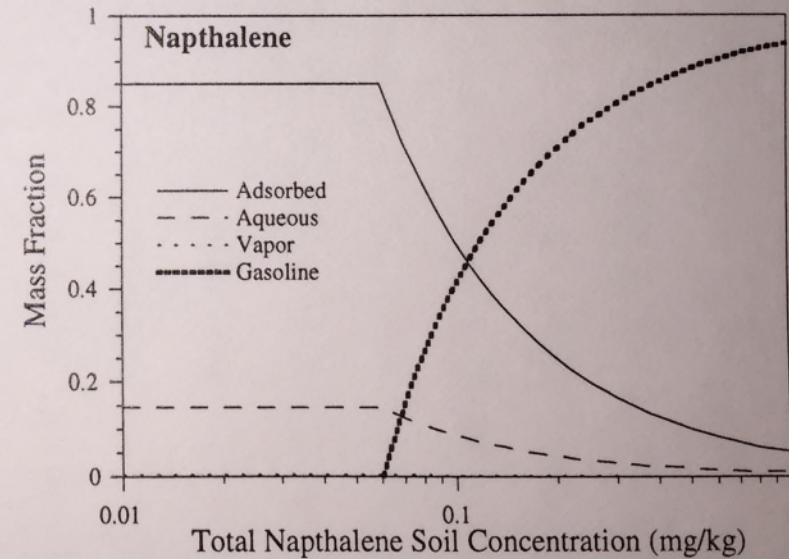- High and Sustained

		Soil Equivalent Concentrations					Total	Percent of Total		
	K_d	C_{iw}	C_{iv}	C_{ia}	C_{iw}	C_{iv}	$C_{ia}+C_{iw}+C_{iv}$	Soil Equivalent Concentrations		
Compound	(l/kg)	(mg/l)	(mg/l)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	C_{ia}	C_{iw}	C_{iv}
MTBE	0.006	3347.035	95.670	19.369	366.082	10.464	395.915	4.89%	92.46%	2.64%
Benzene	0.044	48.984	8.886	2.153	5.358	0.972	8.483	25.38%	63.16%	11.46%
Toluene	0.150	68.285	14.602	10.267	7.469	1.597	19.333	53.11%	38.63%	8.26%
E. Benzene	0.380	2.192	0.644	0.834	0.240	0.070	1.144	72.88%	20.96%	6.16%
m,p-Xylene	0.442	4.005	1.066	1.771	0.438	0.117	2.326	76.15%	18.84%	5.01%
o-Xylene	0.231	17.507	3.119	4.052	1.915	0.341	6.308	64.24%	30.35%	5.41%
n-Propylbenzene	1.273	0.202	0.064	0.257	0.022	0.007	0.286	89.84%	7.72%	2.44%
1,3,5-Trimethylbenzene	0.941	0.324	0.081	0.305	0.035	0.009	0.349	87.32%	10.15%	2.53%
Naphthalene	0.638	0.079	0.002	0.051	0.009	0.000	0.060	85.06%	14.58%	0.36%

Parameters

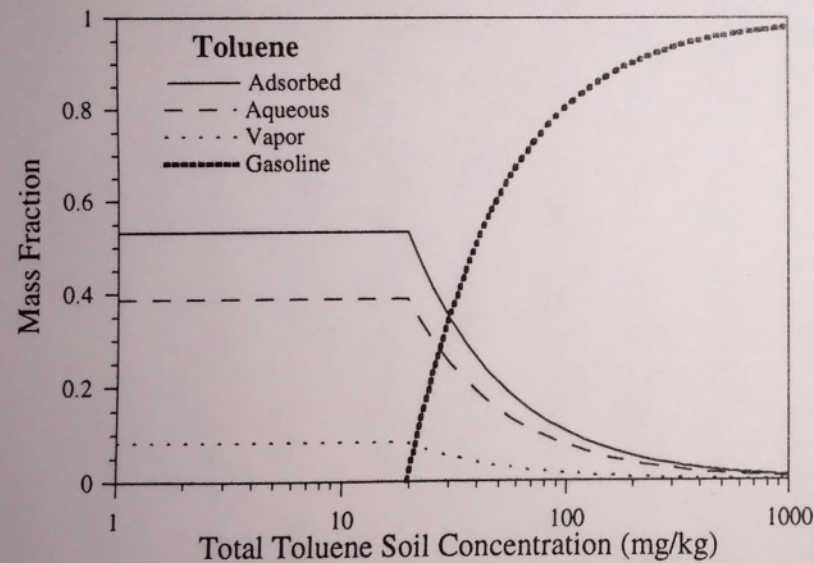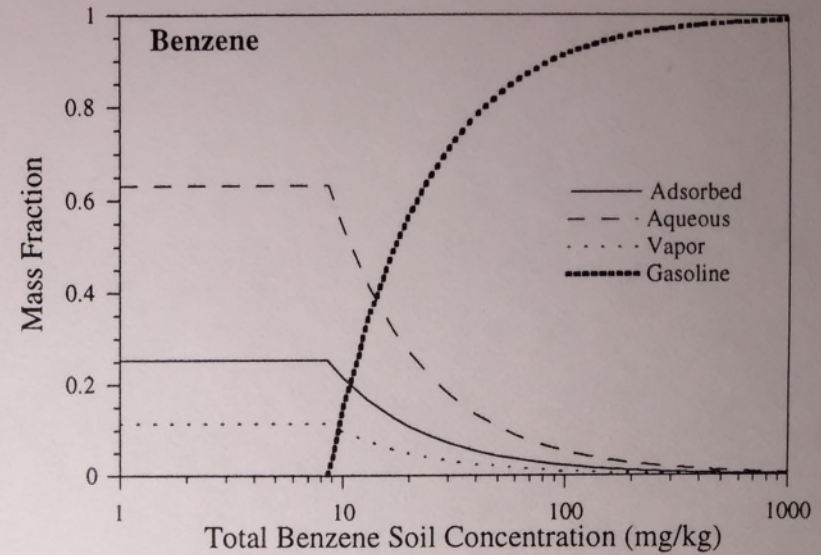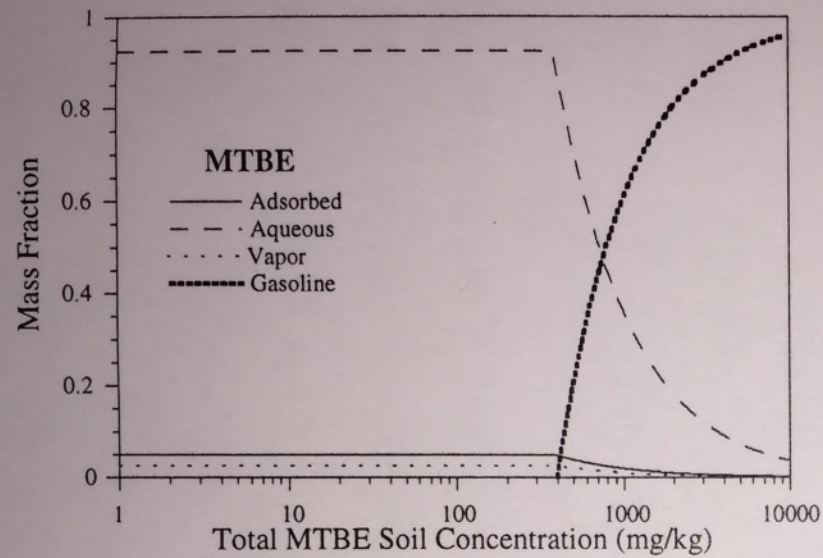|	
f_{oc} =	0.0005
Void Content (l/kg) =	0.219
Water Content (l/kg) =	0.109
Air Content (l/kg) =	0.109

Figure 2-1. Relative contributions to total soil concentrations for the low organic, partially saturated, vadose zone sample depicted in Table 2-2(c).

Phase III Investigations for NAPL per DEEP SCGD (2007)

Non-Aqueous Phase Liquids
- If the CSM indicates a potential for NAPLs, the Phase III sampling and analysis plan should be designed to evaluate if NAPLs are present.
- NAPL may be present at the site either as mobile, separate-phase product, relatively immobile interstitial separate-phase product, or sorbed onto soil grains.
- Special care should be taken to ensure that cross-contamination does not occur when evaluating the presence of NAPLs. If NAPL is present, the Phase III investigation should identify the source and evaluate the spatial distribution.
- If DNAPL is present, permeability contrasts in unconsolidated materials, saturated and unsaturated flow characteristics, and/or the topography of the bedrock surface may play a crucial role in the migration of contaminants.
- The environmental professional must take into consideration cross-media contaminant transfer and potential impacts to receptors when conducting investigations that may encounter NAPLs and DNAPLs in particular.

Dense Non-Aqueous Phase Liquids (DNAPL)

- DNAPL must be contained or removed from soil and groundwater to the maximum extent <u>prudent</u>

- "Prudent" means reasonable, after taking into consideration cost, in light of the social and environmental benefits. *From 22a-133k-1(a)(54) – the definitions in RSRs*

22a-133k-2(g) and 22a-133k-2(c)(3)

Light Non-Aqueous Phase Liquids (LNAPL)

- LNAPL must be removed in accordance with RCSA 22a-449(d)-106(f) (UST regs)

- This means to the maximum extent practicable (e.g. cost not a consideration)

- Chlorinated solvents, coal tars, etc. can under some circumstances be LNAPLs

22a-133k-2(g) and 22a-133k-2(c)(3)

22a-449(d)-106(f) & -106(d)(1)(F)

- (f): At sites where investigations under subdivision 22a-449 (d)-106 (d) (1) (F) of these regulations indicate the presence of free product, owners and operators shall remove free product to the maximum extent practicable <u>as determined by the implementing agency</u>…
  - Note: (F) Investigate to determine the possible presence of free product, and begin free product as soon as practicable and in accordance with 22a-449(d)-106(f) of these regulations.
- In meeting the requirements of this section, owners and operators shall: (see next 2 slides)

(a) Conduct free product removal in a manner that minimizes the spread of contamination into previously uncontaminated zones by using recovery and disposal techniques appropriate to the hydrogeologic conditions at the site, and that properly treats, discharges or disposes of recovery by-products in compliance with applicable local, State and Federal regulations;

(b) Use abatement of free product migration as a minimum objective for the design of the free product removal system;

(c) Handle any flammable products in a safe and competent manner to prevent fires or explosions; and

(d) Unless directed to do otherwise by the implementing agency, prepare and submit to the implementing agency, within 45 days after confirming a release, a free product removal report that provides at least the following information:

(1) The name of the person(s) responsible for implementing the free product removal measures;

(2) The estimated quantity, type, and thickness of free product observed or measured in wells, boreholes, and excavations;

(3) The type of free product recovery system used;

(4) Whether any discharge will take place on-site or off-site during the recovery operation and where this discharge will be located;

(5) The type of treatment applied to, and the effluent quality expected from, any discharge;

(6) The steps that have been or are being taken to obtain necessary permits for any discharge; and

(7) The disposition of the recovered free product.