



NAPLs & Their Migration in the Subsurface

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The Evolution of 'Expert' Thought on NAPLs

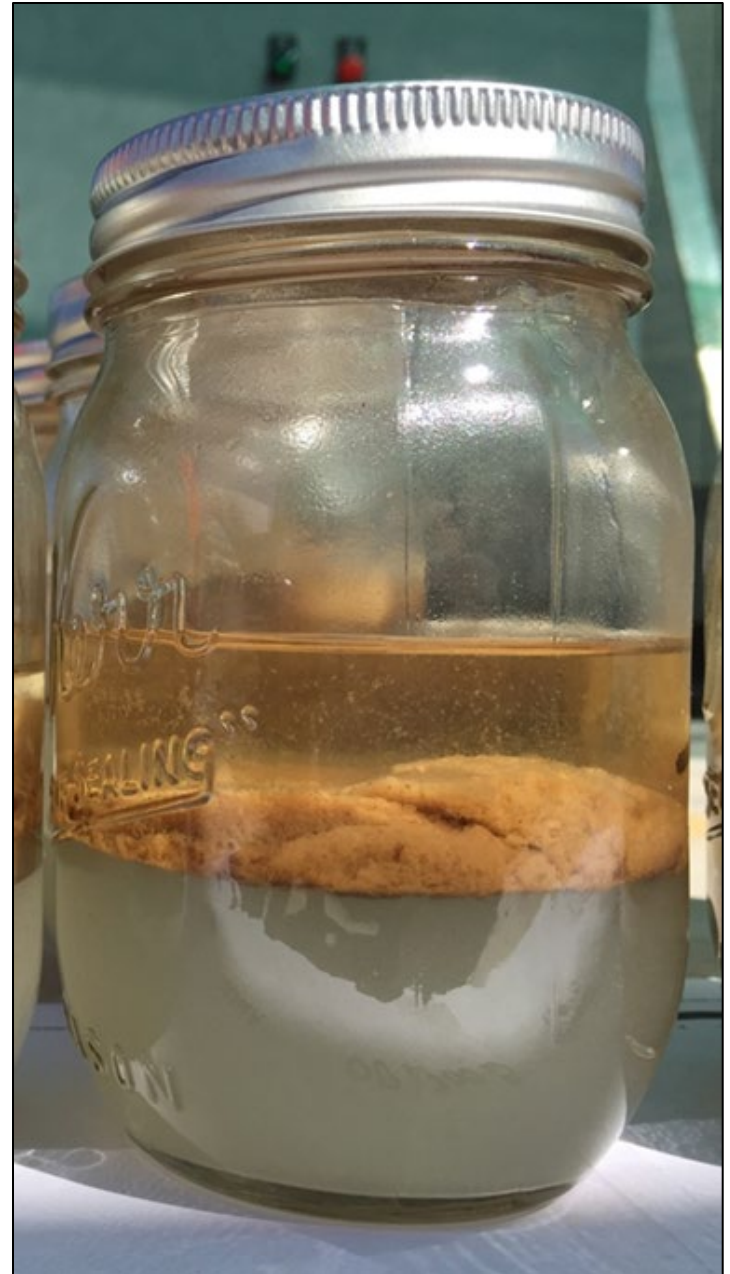
- 1980s: Nonaqueous phase liquids (NAPLs) don't exist in the subsurface
- 1990s: Maybe they exist, but you can't find them
 - Spurred development of new investigative methods
- 2000s: OK, you can find them but you can't do anything about them
 - Spurred continued development of new remedial technologies
- Back diffusion will kill you dead if you try to remediate them
 - Not if you effectively treat the low permeability media – which can be done!

Types of Sites that may have NAPLs

- Dry Cleaners – PCE
- Gas stations
- Fuel storage facilities – GATX
- Manufactured Gas Plants (MGP)
- Wood Treaters
- Waste oil recyclers
- Former Military Bases
- Manufacturing Facilities - Ball bearings, machine shops, agricultural equipment, etc, all use chlorinated solvents: TCE; PCE; 1,1,1-TCA
- Electrical shops, transformer recyclers – oils containing PCBs
- Along railroad tracks

Different types of NAPLs

- LNAPLs – lighter than water & ‘float’ on the water table
- Oils – crude oil & refined products like gasoline & diesel
- Pictured is jet fuel recovered by steam injection at former Air Force Base
- Naval fuel, Bunker C type fuels also fall in this category



Properties of Refined Fuels

- Specific gravity < 1
- Viscosity generally low
- Generally clear liquids
- Range of boiling points 80 – 140C
- Benzene may be its most soluble & volatile & toxic component – main groundwater contaminant
- ‘Float’ on the water table
- Lower molecular weight compounds generally biodegradable which limits the extent of the dissolved phase plume
- Vapors may spread in the vadose zone, cause Vapor Intrusion (VI) issues

Two General Types of DNAPLs

- DNAPLs – more dense than water, migrate downward through the water table
 - Chlorinated solvents
 - Creosote, coal tar
- Pictured is chlorobenzene/DDT DNAPL from DDT manufacturing facility
- > 400,000 lbs recovered from vadose zone by SVE



Chemical Manufacturing Superfund Site

- Specialty chemical manufacturer
- manufactured brominated, chlorinated & fluorinated compounds
- Solvents used included xylene, methylene chloride, 1,1-DCE
- ~ 3,500 gallons recovered so far
- Compounds cause odor problems



Sites may have very large quantities of NAPL



Thomas Alcamo, RPM

Chlorinated solvent properties

- Specific gravity > 1
- Volatile – significant vapor pressure, but not strong odor
- Boiling points range from 60 – 130 C
- Most neat chemicals are clear – pick up impurities while migrating in soils
- Solubility range – 100s to 1000s ug/L
- Can penetrate deep below the water table
- Difficult to see in soils
- Detect with PID
- Can form dissolved phase plumes of significant length
- MCLs – 1s to 100s ug/L

Coal Tar & Creosote

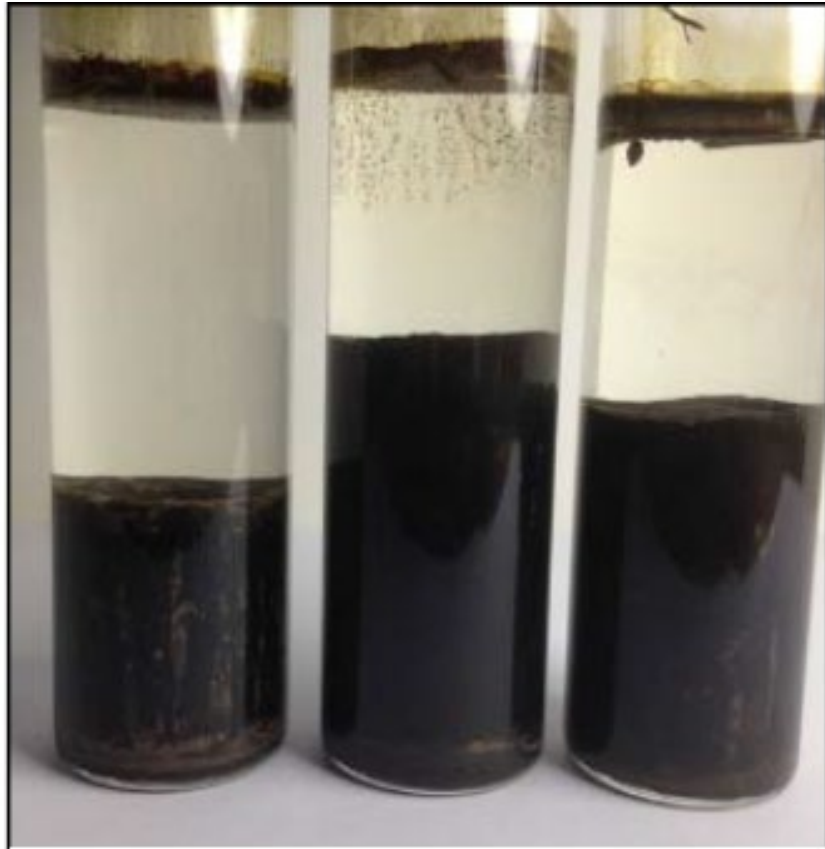


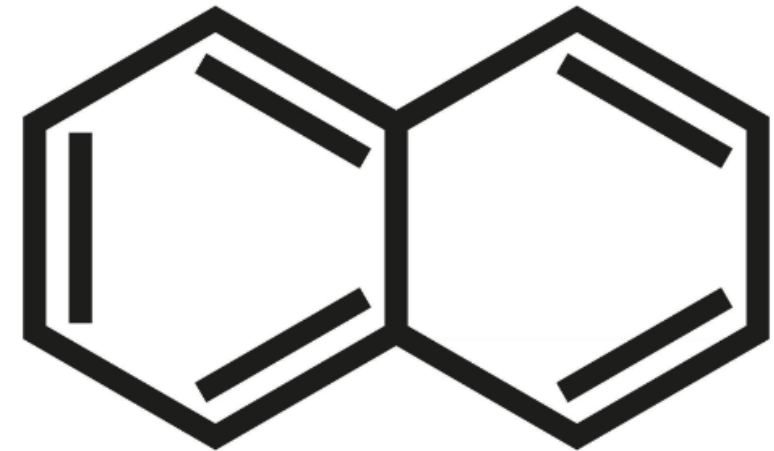
Figure 3. Centrifuged NAPL Sample from Well MW-18

- MGP & wood treater sites
- Coal tar is residual from MGP, creosote is a distillate of coal tar
- Note that there can be both LNAPL & DNAPL
- Creosote can change between LNAPL & DNAPL depending on the temperature

Coal Tar & Creosote Properties

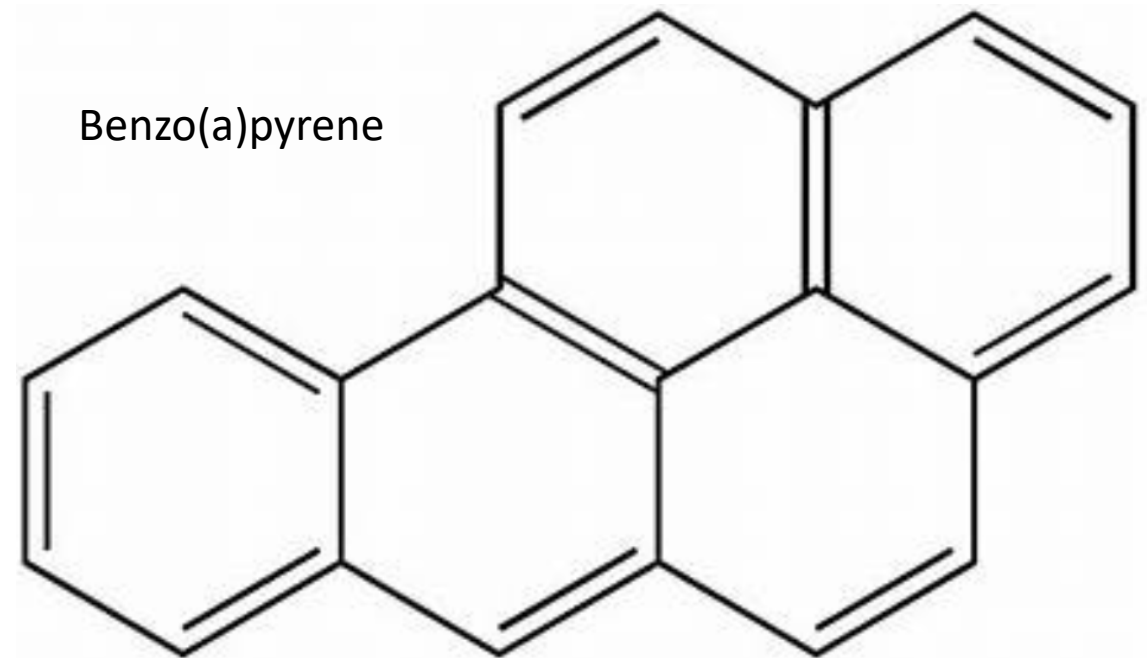
- Polynuclear Aromatic Hydrocarbons (PAHs)
- Specific gravity ~ 1
- Not real volatile however odoriferous
- Viscous liquids
- Boiling points range from 210C to 450 C
- Low interfacial tension
 - Penetrate small pores
 - Obtain high pore saturation
 - May be the wetting phase

Naphthalene



EPA considers some PAHs Priority Pollutants

- 16 Priority Pollutants are detected/quantified by EPA analytical method 8270
- Many more compounds comprise creosote & coal tar
- These compounds have a range of toxicity, B(a)p one of most toxic



Waste Oils: Petroleum Hydrocarbons & Solvents

- Varying amounts of petroleum hydrocarbons & chlorinated solvents which will determine whether it's an LNAPL or DNAPL
- May have high BTU value
- Chlorinated solvents may form dissolved phase plume



At Waste Oil Sites, NAPL properties will vary

- Wastes can contain a wide variety of chemicals
 - Petroleum hydrocarbons
 - Solvents
- Can be DNAPL or LNAPL or both
- Plume emanating from these sites usually chlorinated solvents



Young Rainy STAR, Pinellas, FL

Physical Properties of NAPLs that affect their flow in Porous Media

- Low Solubility – little dissolution in water
 - Crude oils, creosote, coal tar – very low solubility, ug/L
 - refined petroleum products – solubility 10s ug/L
 - Chlorinated solvents – solubility 100 to 1000 ug/L
- Density or specific gravity (density relative to water)
 - Refined petroleum hydrocarbons – LNAPLs, lighter than water, specific gravity ~ 0.85
 - Creosote & Coal Tar – Specific gravity ~ 1
 - Chlorinated or other halogenated organics – DNAPLs, specific gravity $\sim 1.2 - 1.6$
- Vapor Pressure – Volatility
 - Chlorinated solvents, refined petroleum products – relatively high volatility
 - Crude oils, creosote, coal tar – low volatility
- Viscosity – resistance to flow, affects how fast NAPL can migrate in a given porous media
 - Water, refined petroleum products, chlorinated solvents – low viscosity
 - Crude oils, creosote, coal tar – high viscosity

When a Liquid is spilled to the subsurface . . .

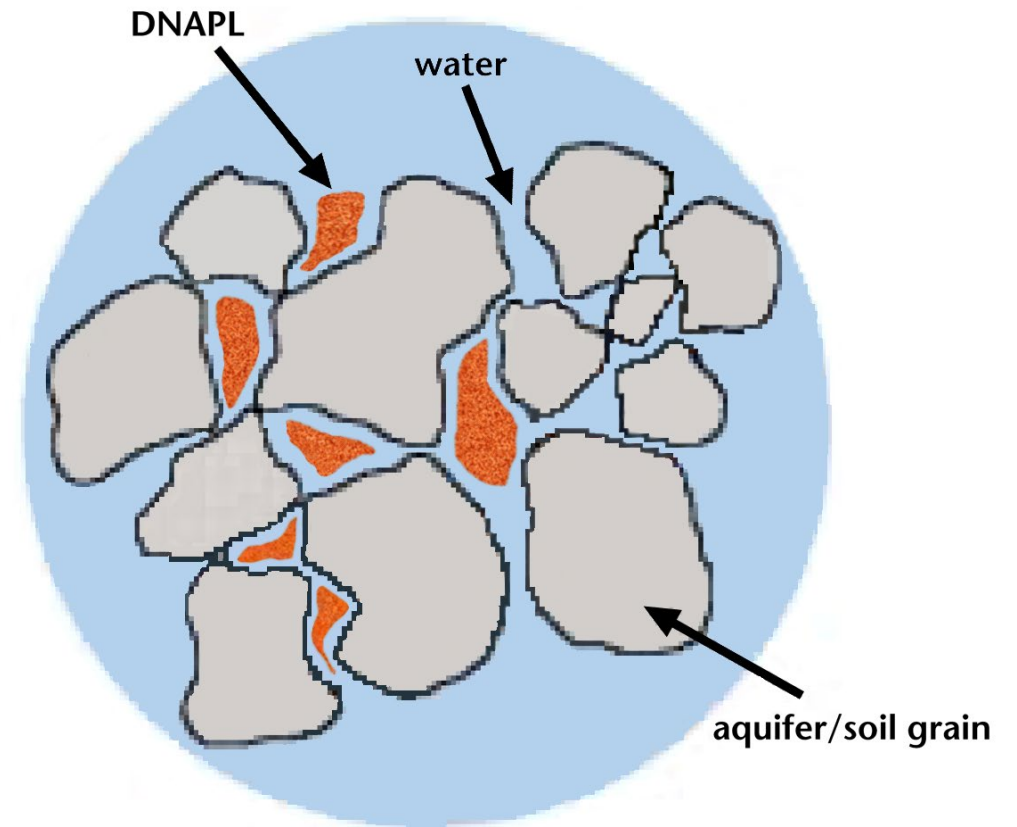
- Small spill may be completely volatilized, adsorbed, and/or solubilized so that no nonaqueous phase liquid (NAPL) remains
- When these 'sinks' are saturated, NAPL exists in subsurface in pore spaces of the soil
- In vadose zone, LNAPL & DNAPL migrate downward, leaving residual saturation in small pores it has passed through
 - Residual saturation is generally less in the vadose zone
- When the NAPL encounters pores that it cannot penetrate, flow is diverted laterally until it can migrate downward again
 - When it encounters larger pores again
 - When sufficient head builds up that it can penetrate smaller pores

When a Liquid is spilled to the subsurface . . . (con't)

- Downward migration of LNAPL is largely halted when it encounters the water table
 - LNAPL can be smeared under the water table if the water table then rises
- DNAPL can penetrate water-filled pores and continue to migrate downward until mobile DNAPL exhausted as residual saturation or it encounters small pores it cannot enter (then forms 'pools') or is diverted horizontally

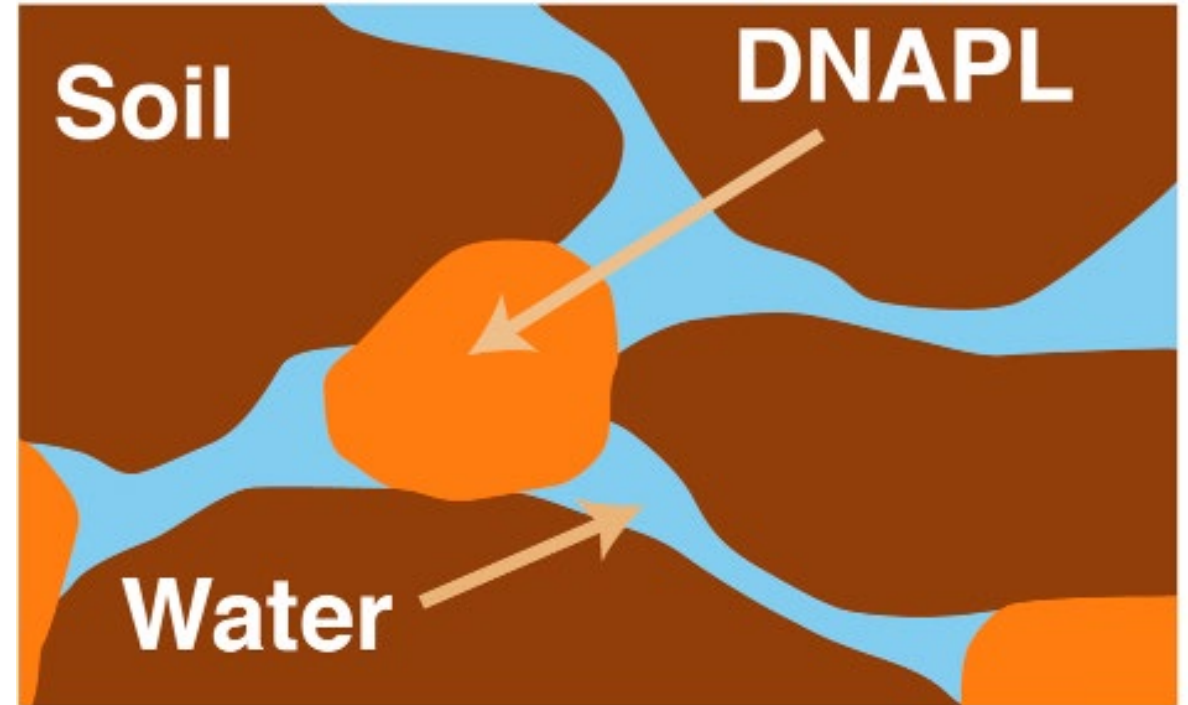
Pore Scale Concepts - Wetting and Nonwetting Phases

- Wetting phase fills small pores & coats soil grains
- Nonwetting phase fills center of large pores
- Water is generally the wetting phase relative to air or NAPL
- NAPL is generally more wetting than air



As NAPL migrates, it leaves behind an Immobile Residual Saturation

- Residual saturation: Wetting or nonwetting phase held by capillary forces and will not drain from the pore
 - Wetting phase: residual saturation 5 -10% of the pore spaces
 - Nonwetting phase: residual saturation generally 15 – 20% of the pore spaces



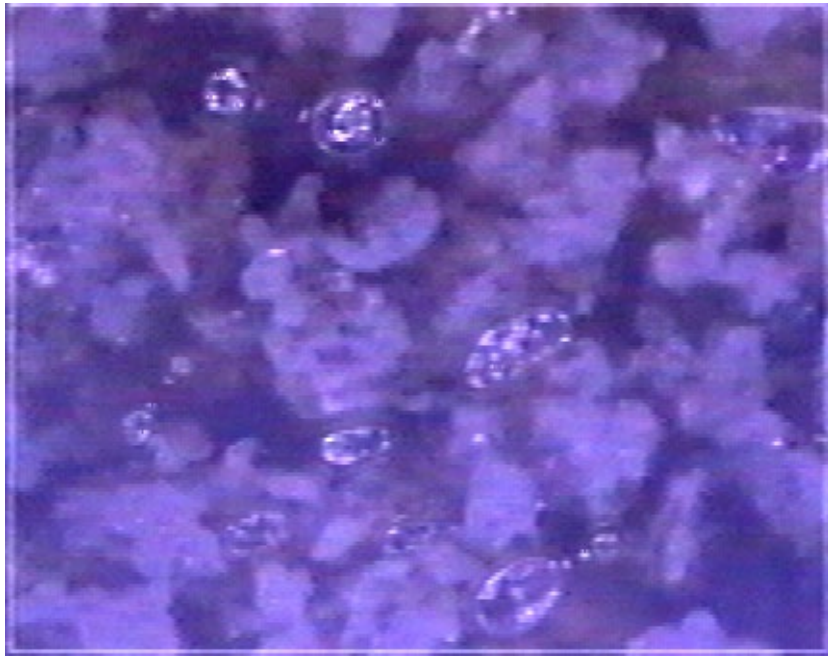
Residual saturation is a source for dissolved phase plume!

Properties of the Porous Media that Affect NAPL Migration

- Heterogeneity – diverts flow
 - Pore Scale
 - Formation scale
- Average grain/pore size – smaller grain sizes reduce fluid flow rate & can limit entry by non-wetting phase
- Grain surface area – affects adsorption onto grain surface
- Natural organic matter – affects absorption into organic matter ‘matrix’ – desorption may be slow

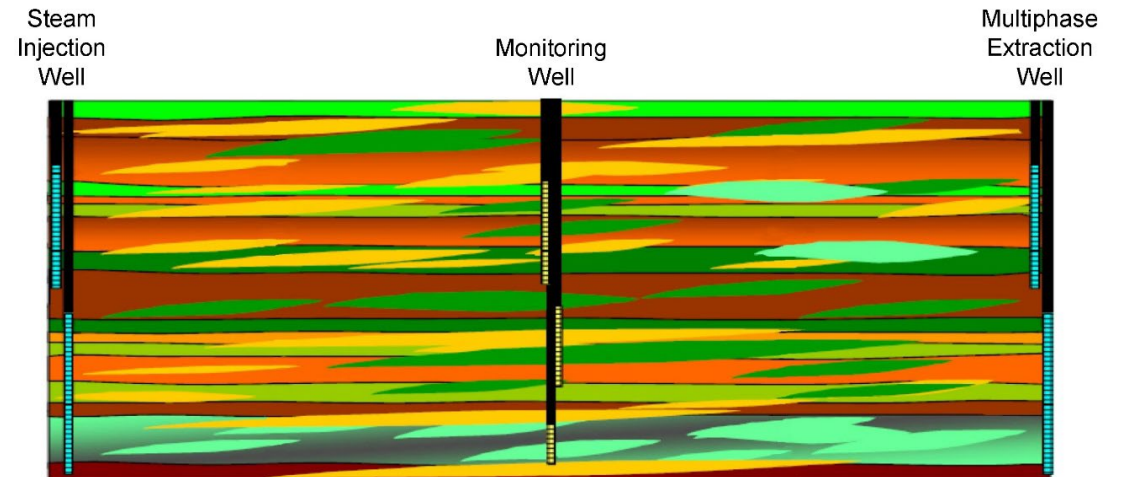
Scales of Heterogeneity

Pore Scale Heterogeneity



GeoVis picture of NAPL & air in pore spaces

Formation Scale Heterogeneity



Small Scale Heterogeneity Controlling NAPL Flow

- Coal tar & creosote



Photograph 30. Boring RI-B7. Discrete tar impacted zone at 153 ft bls. Partially saturated pore spaces of fractured hard limestone unit.



NAPL Flow controlled by the Formation

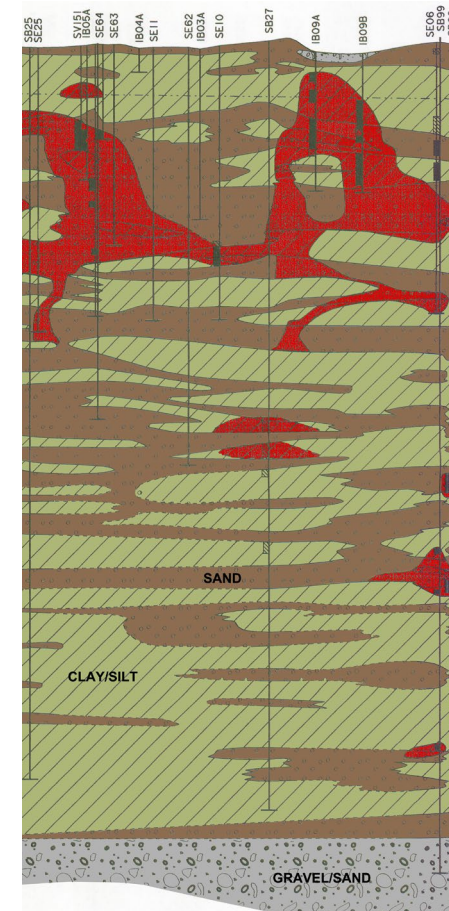
- FLUTE ribbon shows NAPL in sandy layer between silty layers
- DNAPL was also found in the silty layers
- Chlorobenzene/DDT DNAPL



Another Example of Formation Controlling NAPL Flow

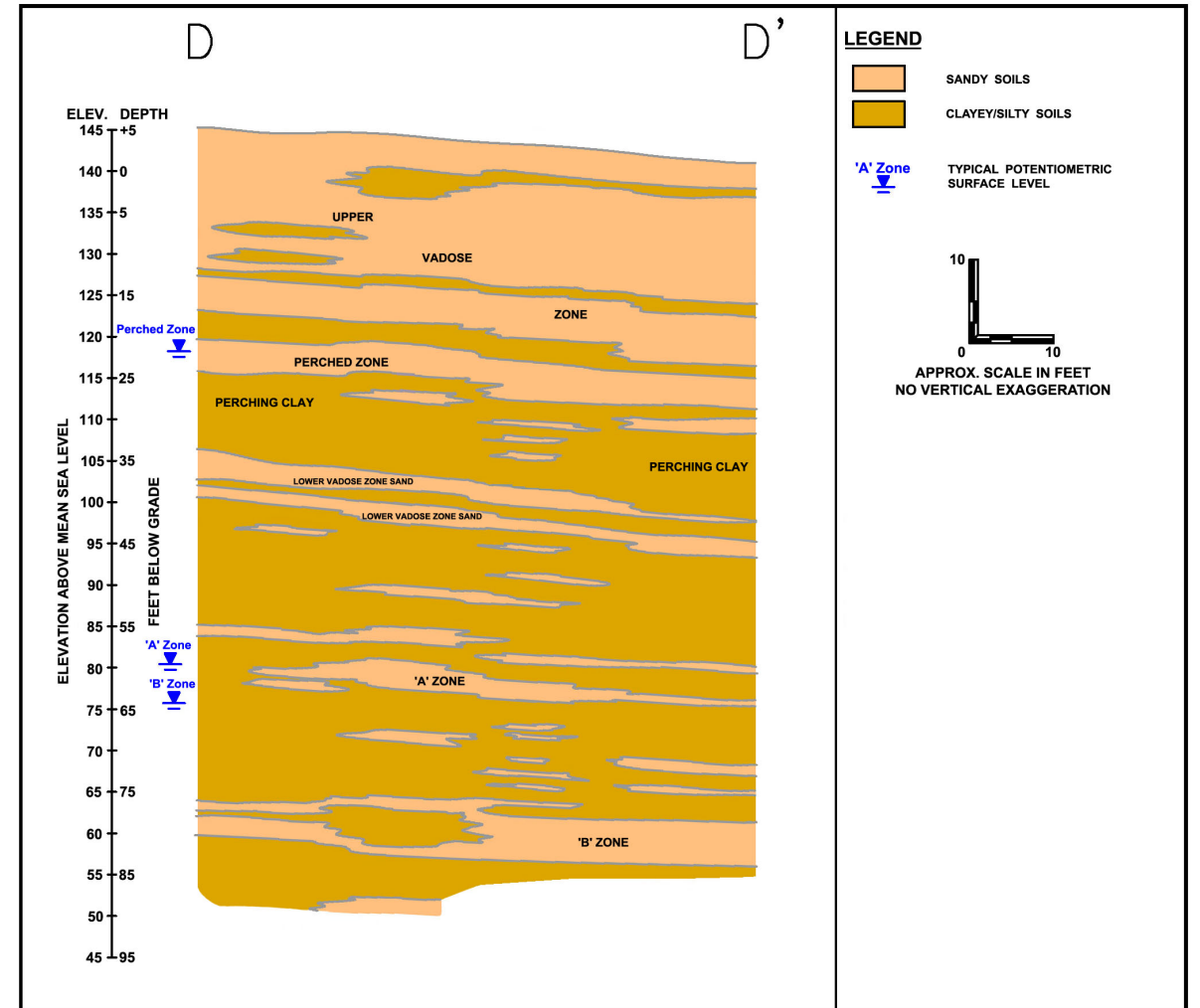
- Formation described as ‘inter-fingering and layering of three depositional environments’
 - Closed lagoon environment
 - Flood plain & overbank deposits
 - Channel bedload deposits

Creosote mostly migrating through more permeable sand lenses but also through low permeability soils



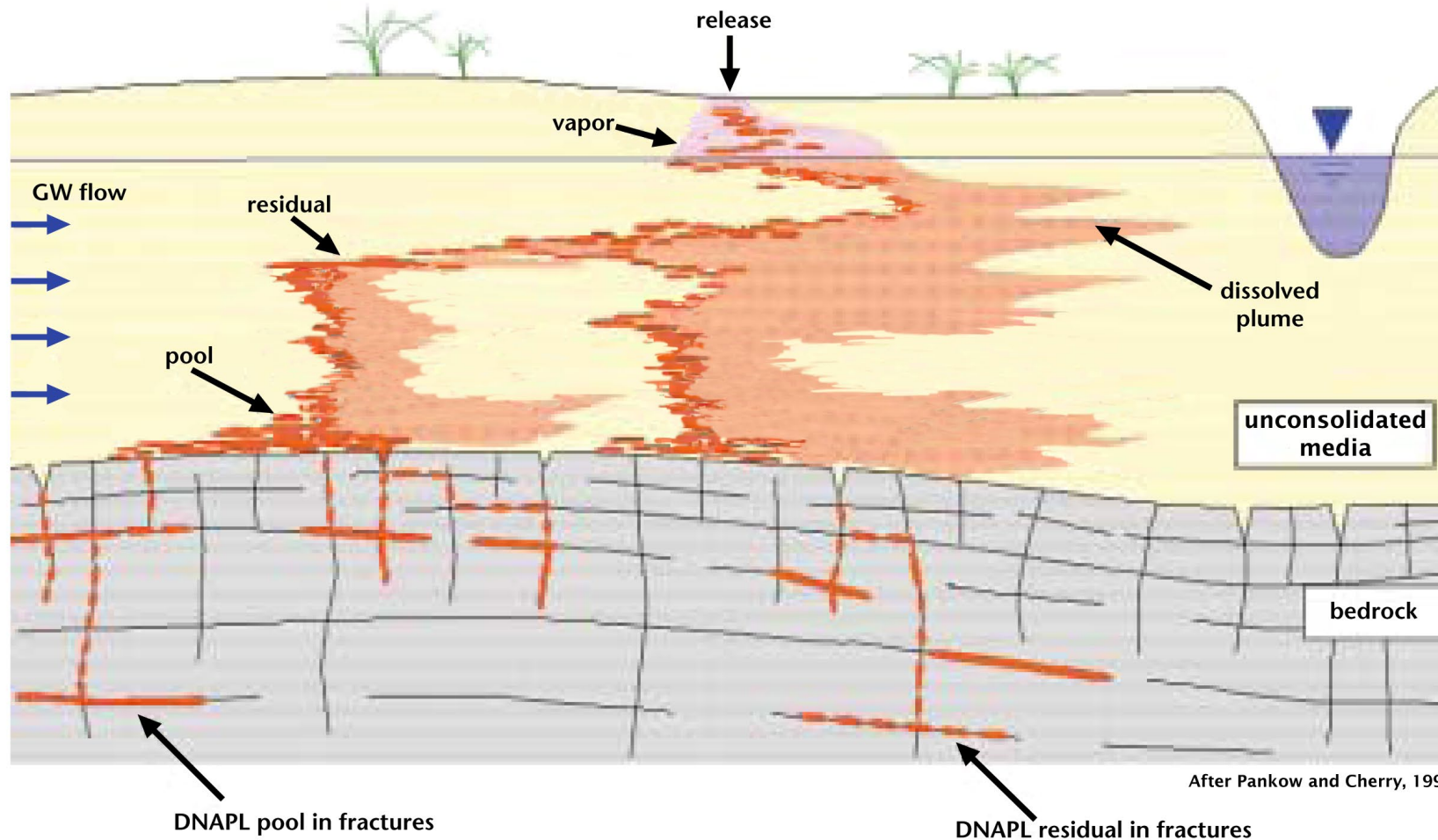
Layered Heterogeneity with a Dip

- When low permeability materials are encountered, NAPL may spread laterally on top of the low permeability unit
 - NAPL may follow a downdip in the low permeability unit – even if groundwater flow is a different direction



Effects of Heterogeneity on DNAPL Distribution

Subsurface geologic heterogeneity largely controls DNAPL migration



Are NAPL 'Pools' Stable?

- 'Pool' implies that the DNAPL saturation is above residual saturation, thus 'mobile'
- Force gradient can cause movement of NAPL pool
- Calculation by Sitar et al. determined that TCE in fine sand under typical groundwater conditions can form a stable pool 92 meters in length
 - 100 fold increase in gradient (ie, by pumping) will reduce the stable pool length by 100, mobilizing a large pool
- Hydraulic gradients can mobilize pools laterally and vertically

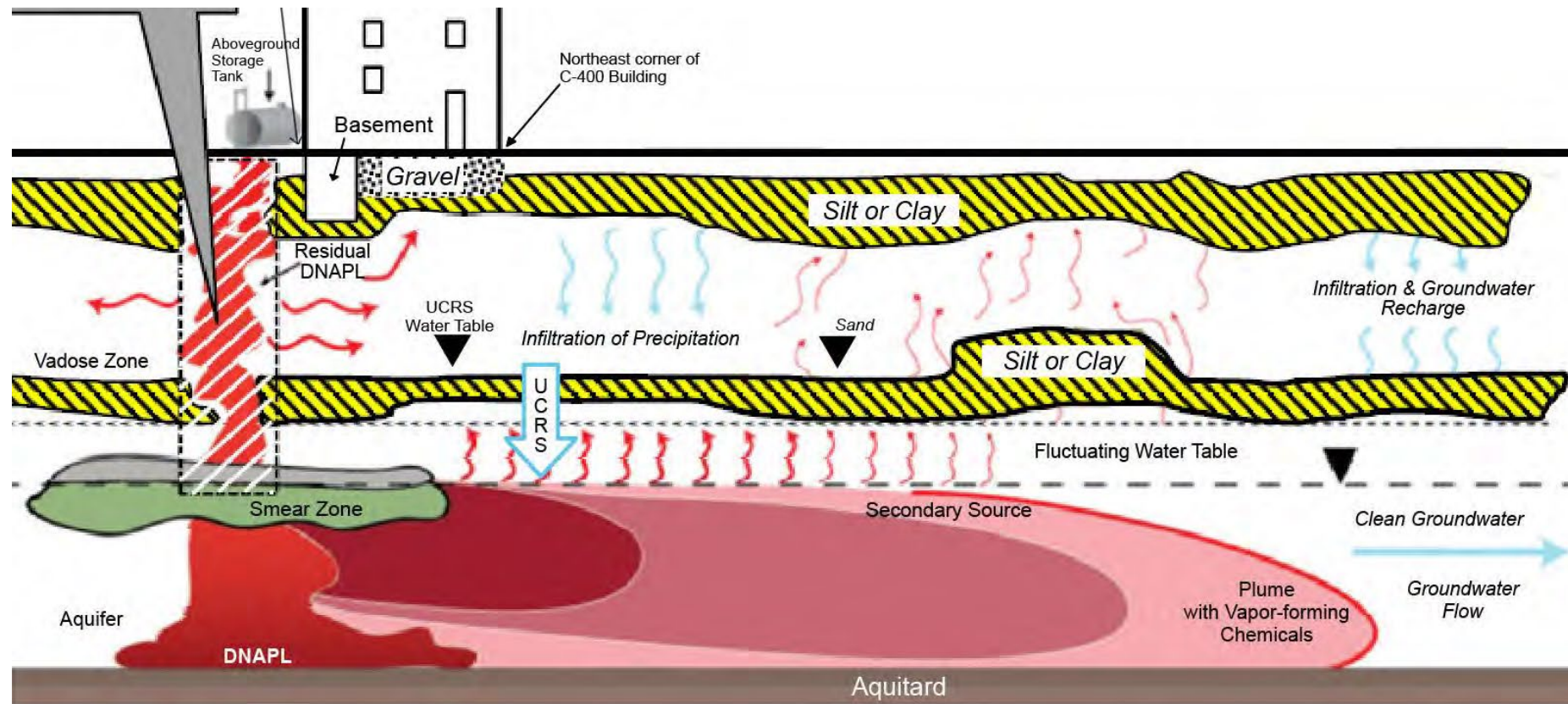
'Stable' DNAPL pools can be remobilized by:

- Changing hydraulic conditions
 - Rising or declining groundwater level
 - Pumping of well
 - Freeze/thaw
- Changes in properties of multi-component NAPL
 - As the more soluble component dissolves away and the density and interfacial tension of the remaining NAPL changes

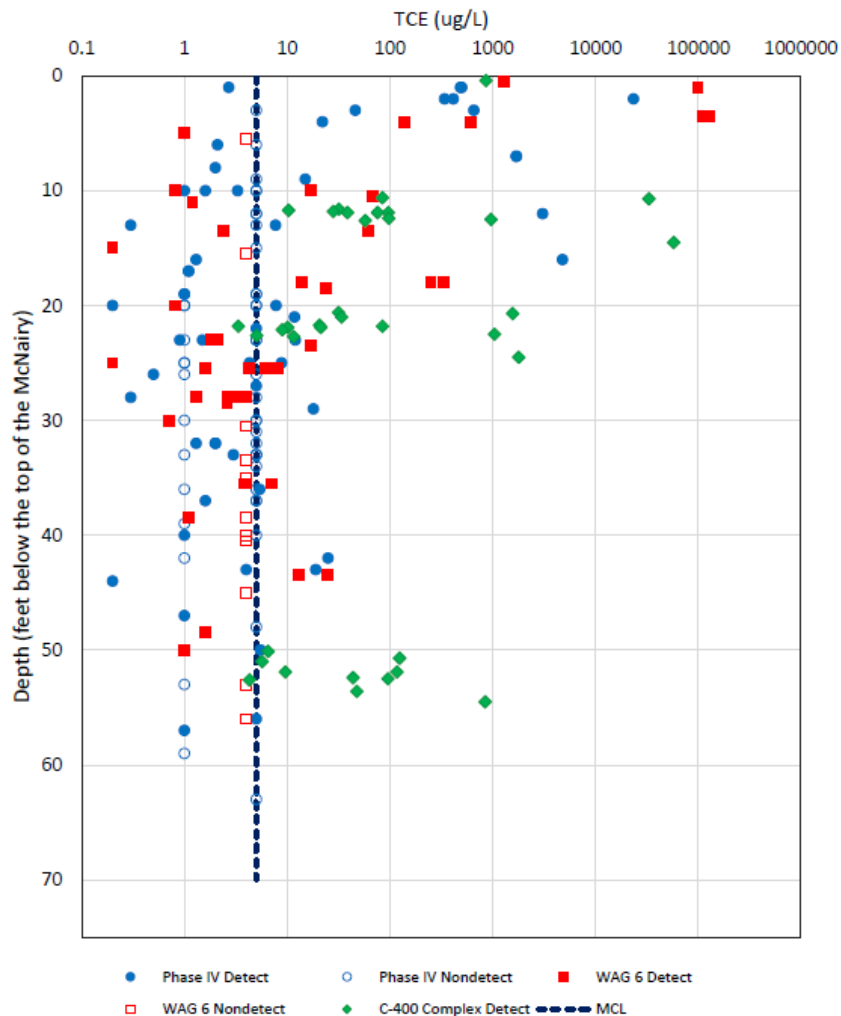
If NAPL accumulates in a well, it is Mobile

- Mobile NAPL is above the residual saturation, can migrate
- Even when mobile NAPL is present, it may not migrate into a well
- Pumping & drawing down the water table may produce sufficient force to draw NAPL into a well
- A well that does not have a sump may allow DNAPL to migrate through it without it being detected

Typical Conceptual Site Model predicts DNAPL 'Pooling' on top of Aquitard



DNAPL & dissolved phase contaminants penetrate into the low permeability aquitard



- Groundwater concentration data from the 1990s (red squares) show DNAPL concentrations of TCE in the top 5 ft of the ‘aquitard’
- 2020s concentration data (green diamonds) show DNAPL concentrations penetrating deeper into the ‘aquitard’
- In 1990s, TCE exceeded MCL ~45 ft into ‘aquitard’
- By 2020s, TCE exceeded MCL > 55 ft into ‘aquitard’

What that 'aquitar' actually looks like . . .

- Soil cores from the 'aquitar' show interbedding of sandy soils with clayey soils
- The 'aquitar' is not a monolith
- NAPLs can migrate slowly into low permeability soils

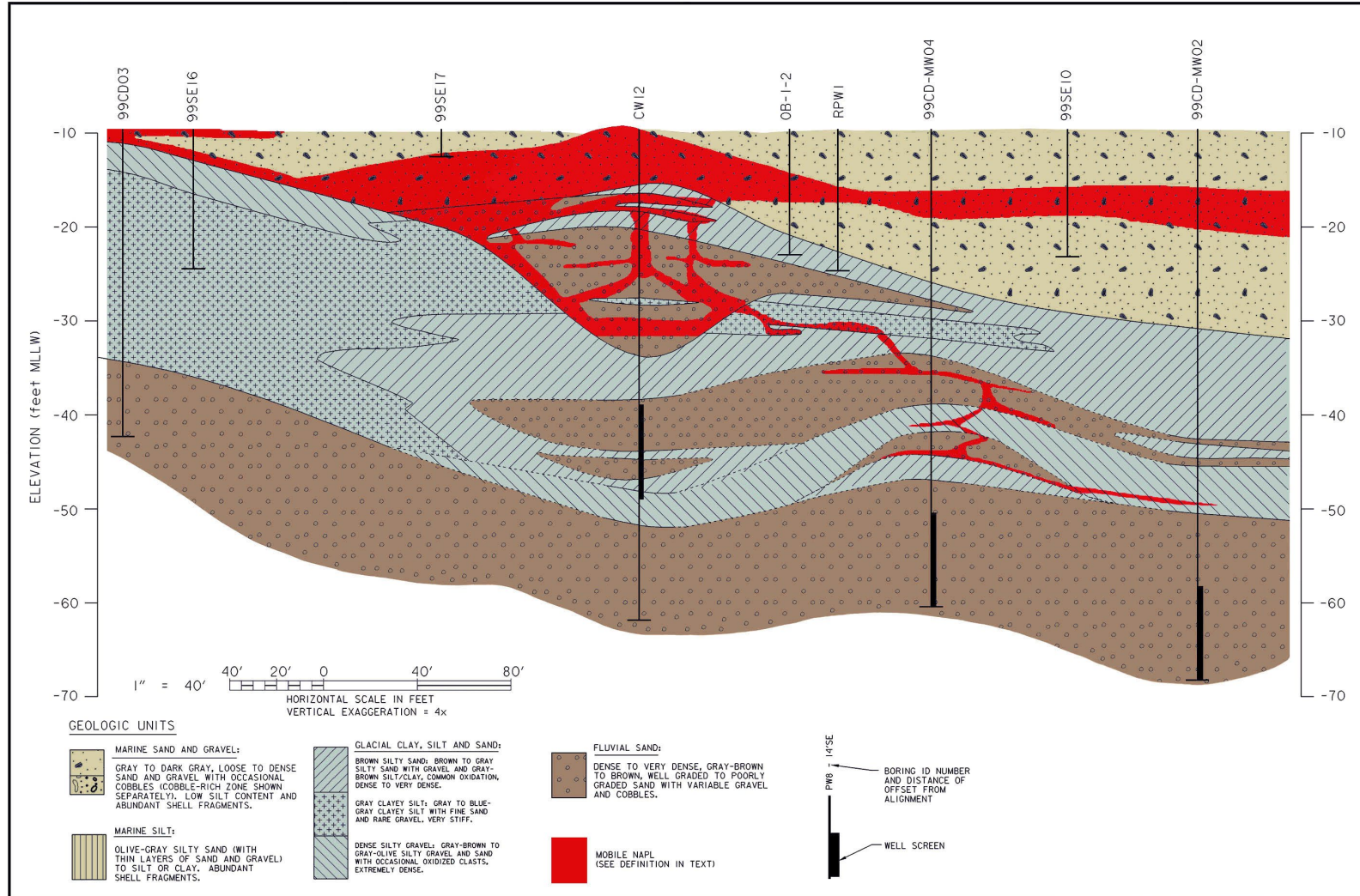
 FOUR RIVERS NUCLEAR PARTNERSHIP, LLC		PHOTOGRAPHIC RECORD	
Project: PGDP, C-400 Complex RIFS, Kevil, KY		Geologist: Ken Davis	Plate Number: 400-S1A-03
Client: US Department of Energy		Driller: Cascade – Sonic Rig	Photo Date: 3/23/2021
			
97' 102'			
Notes: core run from 97 to 102 ft bls. Photo is top of run.			
			
102' 107'			
Notes: core run from 102 to 107 ft bls. Photo is bottom of run.			

UCRS = Upper Continental Recharge System RGA = Regional Gravel Aquifer

'Aquitards' & Downward Migration of NAPL

- Most (if not all) low permeability media have fractures or lenses of more permeable media that NAPL can penetrate
- An aquitard that limits groundwater flow may not protect an underlying aquifer from DNAPL contamination!
- Fracture bedrock: DNAPL has been found to penetrate very small fractures
- Flow into fractured bedrock controlled by fracture aperture just as flow in soils is controlled by pore size

Cross Section of Creosote in Subsurface

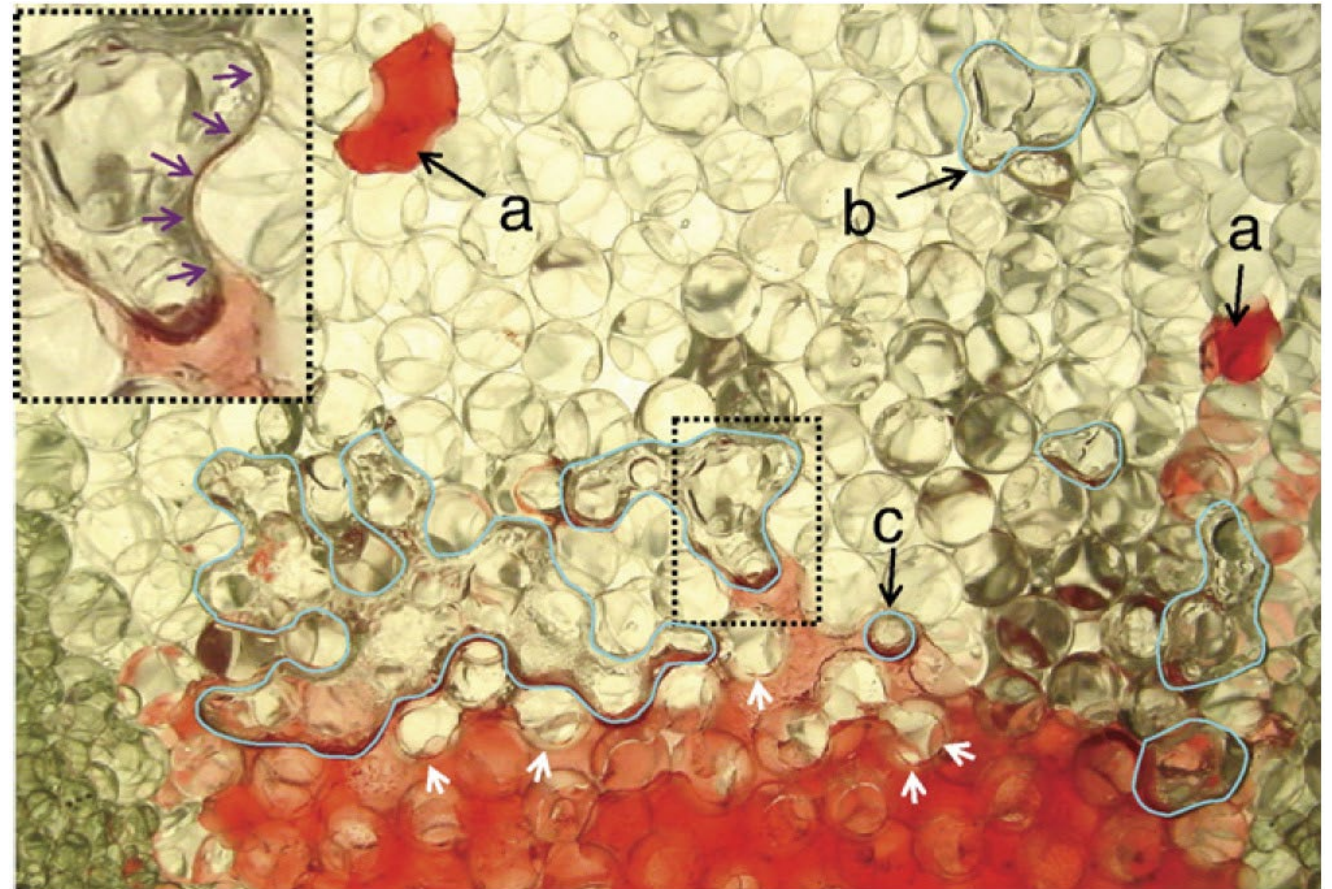


Vapor Migration from Volatile NAPLs

- Vapors of volatile compounds such as chlorinated solvents, BTEX can migrate long distances from NAPL source
- Very high concentrations can form under buildings
- Vapor Intrusion (VI) when it enters building
- Additional groundwater contamination

2D Model filled with glass beads, TCE DNAPL (dyed red) injected at bottom, then air injected beneath it

- a) residual TCE DNAPL blobs,
- b) gas bubbles trapped above the pool
- c) a seed bubble remaining behind after gas bubble mobilization.
- d) The inset picture clearly shows DNAPL spreading along the gas bubble interface, though it does not appear to completely surround it.
- e) Mumford et al.

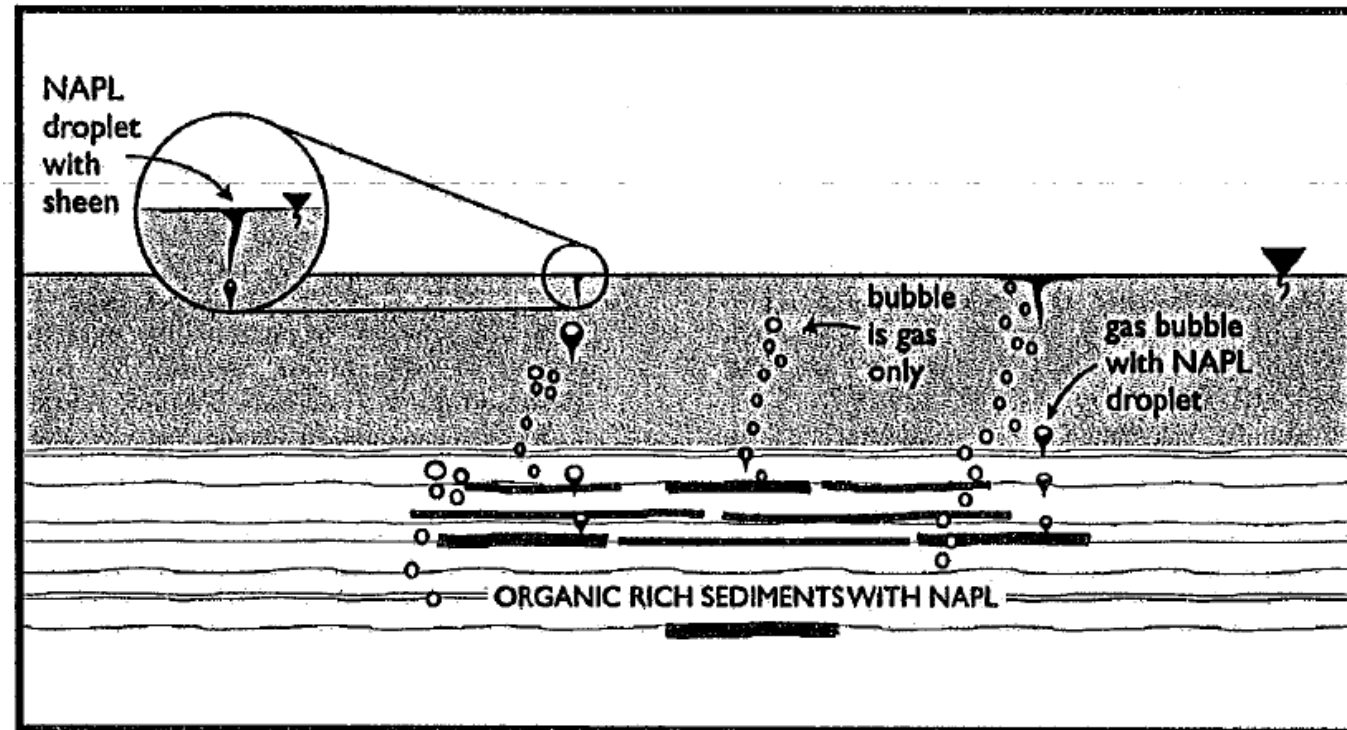


Air bubbles can carry DNAPLs up through porous media as a liquid & carry nonvolatile compounds with it

- Observed with chlorobenzene & DDT in 1D experiment
- 'Dissolved air flotation' in water treatment industry
- Contaminated aquifers generally have dissolved gases that can cause this phenomenon to occur
- Same process as solvent sublation which can be used to separate slightly soluble compounds (PCP) from water

Ebullition transports hydrophobic liquids upward attached to vapor bubbles

- Biogenic gases methane & carbon dioxide can cause ebullition
- Anything dissolved in the liquid – dyes, metals, DDT, PCBs, sediments, ions will rise with liquid
- Occurs in peat soils as organic matter degrades
- Ebullition is a natural process observed at a significant number of Superfund sites, including McCormick & Baxter Superfund Site in Portland, Oregon & Pine Street Superfund Site, Vermont



In Summary . . .

- There are numerous sources/types of NAPLs from many different activities & they migrate in the natural environment as a separate phase liquid, dissolved in water, as a vapor, & as a liquid attached to a vapor bubble
- Understanding the properties of NAPLs & how they migrate in the natural environment determines proper approach for investigating NAPL distribution in the subsurface
- The properties of NAPLs in the natural environment determines how they can best be remediated