



### "The Basics"

Understanding Light Non-Aqueous Phase Liquid (NAPL) Behavior in Soil

Presented at the EPA Region 3/State Corrective Action Workshop

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### What is NAPL?

NAPL stands for Non-Aqueous Phase Liquids (Chlorinated compounds or petroleum hydrocarbon products)

LNAPL refers to Light Non-Aqueous Phase Liquids (those that are lighter than water, generally petroleum hydrocarbon liquids such as gasoline)

DNAPL refers to Dense Non-Aqueous Phase Liquids (those that are denser than water). DNAPL (chlorinated compounds and PAHs) will not be dealt with in this training program.



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### The Conceptual Understanding of NAPL 1980's Pancake Model

Vertical Elevation in Soil Column



Soil Grains

Non-wetting Fluid (e.g. air or LNAPL)

~1mm

Wetting Fluid (e.g. water) preferentially contacting the soil

### The Changing Face of NAPL Research Results

- NAPL does not float on water but co-exists with water in the pore network within the aquifer
- NAPL only partially fills the aquifer pore space & NAPL saturations decrease with depth until water fills all the pores
- The degree of NAPL saturation is dependent upon the soil & fluid properties, site history & volume of NAPL released
- The variation of the NAPL saturation in the soil with depth can be predicted
- The total free NAPL volume, migration potential & recoverable volume can be predicted



### NAPL Distribution in Soil

- Porosity
- Saturation

Capillary Pressure

### **RTDF**Sharing Pore Space with Water

- Water is typically the wetting fluid in shallow aquifer.
- Air is the typically the non-wetting fluid in shallow aquifer.



**Figure 2.3** Pore-scale representation of non-wetting and wetting DNAPL residual in: a) water-saturated sand; and b) a fracture.



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### Characteristic Capillary Pressure Curves



Capillary Suction (cm)



### Movement of NAPL Into & Out of Pores





### Soil Type Determines the NAPL Saturation Distribution for The Same MW Thickness 10 ft Monitoring Well Thickness & a Diesel Fuel



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### What Volume of NAPL is Hydraulically Recoverable?

NAPL is hydraulically recoverable when the rate of recovery using conventional hydraulic methods (pumping, skimming, etc.) is technically & economically feasible at the site.

- Factors affecting hydraulic recovery:
  - Residual saturation trapped by capillary forces
  - Heterogeneity of the soil
  - Conductivity of the NAPL phase

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### **Relative Permeability**

- NAPL flows in the larger pores.
- Water flows in the smaller pores.
- The "ability" to flow is an average over the pore sizes & volume through which the fluid is flowing.
- The ability of the porous media to allow flow of a fluid when other fluid phases are present is called its relative permeability.
- The relative permeability of a fluid is a function of its saturation.

### Comparison of NAPL Conductivities in Different Porous Media



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### Effect of Viscosity & Density of Different NAPLs on Conductivity



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### **NAPL** Migration

- Affected by:
  - NAPL Fluid Properties
  - NAPL Relative Permeability
  - Conductivity of the Porous Media
  - Hydraulic Gradient
  - Pore Throat Displacement Entry Pressure
  - Fluctuating Water Table

At most sites, these factors combine to produce a plume that may be recoverable in the central portion but is not spreading or migrating

### **Remedial Methods**

- Hydraulic methods recover the liquid phase
  - Skimmers
  - Dual pumping
  - Vacuum enhanced
- Volatilization methods remove NAPL
  - SVE
  - Air Sparging
- Dual-phase methods combine hydraulics & volatilization
- Enhanced Methods
  - Steam
  - Surfactants
  - Phased soil heating
  - Chemical oxidation
  - Hot & cold water floods





### NAPL Recovery Prediction Limitations

- Model assumptions of ideal wells, spacing, and homogeneity add artificial optimism
- Volume and rate of recovery are generally over-estimated
- Time required for LNAPL removal is generally under-estimated

### **NAPL Assessment Techniques**

- Obtaining Core Samples
- Preserving Core Samples
- Laboratory Measurements
  - Soils: Saturation & Capillary Pressure
  - Fluids: Interfacial Tensions, Viscosity, Density
- Laser-Induced Fluorescence http://www.api.org/NAPL

### **Obtaining Core Samples**

- Preferred Situation
  - Existing well containing product has been cored.
  - Geology & depth of likely NAPL occurrence are known.
- Data Noted in Boring Log:
  - Percent gravel, sand & fines
  - Water content
  - Odor
  - Soil structure
  - Signs of NAPL
  - PID/FID values
  - Sampling data (to 5 feet below deepest NAPL penetration or lower boundary unit)
- Further Sampling Locations Based on Data Obtained

### **Preserving Core Samples**

- To remove core from sampler:
  - If core in sleeves
    - Fill any void with plastic wrap,
    - Seal with Teflon film,
    - Tape on plastic end caps.
  - If core not in sleeves
    - Slide gently from sampler onto split PVC core supports,
    - Wrap with plastic & secure with clear box tape.
- Label each core section with top & bottom depths.
- Label multiple sleeves sequentially (A, B, C... etc.) starting with the top or most shallow sleeve.
- Immediately pack cores with ice or freeze with liquid nitrogen to minimize migration of core fluids.
- Ship cores at end of each day by overnight courier.

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### Core Testing When NAPL Present

- Photograph cores in the field in normal light & UV.
- Perform saturation analyses, typically every 4-6 inches, where there are NAPLs.
- Perform 2-5 grain size analyses, with a few Atterberg limit analyses for finegrained soils.

### Fluid Property Testing

- Field-measured interfacial & surface tensions of fluids differ from fresh product not in the soil.
- Collect NAPL & groundwater samples from a nearby well.
- Keep samples cold & measure properties ASAP.
- Measure physical properties.
- Take measurements at a temperature near the aquifer temperature.

### Laser-Induced Fluorescence (LIF)

- Tool for determining occurrence of NAPL vs. depth & lithology without sampling
- Uses fluorescence of polyaromatic hydrocarbons in NAPL phase
- LIF can be attached to cone penetrometer technology (CPT)
- LIF more successful at some sites than at others.

### **CPT-LIF** Result

LIF – Gasoline Fluorescence Intensity & Waveform

300

300

RATIO (%) 6 Silt Sand Silt Sand

**CPT** – Soil Profiling

cp-14 Waveform @ 0.15 R 0.06 0.0 70.02 0.012 10 200 Waveform @ 2.13 ft 0.06 0.037 E 10,025 -2 20 0.012 Depth (feet) 100 200 Wavjelom 😰 15,11 🕇 0.879 0.50 30 ε 3 0.336 0.159 NAPL in Sand Stringers & Not in Silty Clay

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### Core 1: NW Indiana Sand

#### 9 feet below ground surface



Dark means no

fluorescence

#### 13 feet below ground surface



#### Natural

UV Dark means no fluorescence



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### Core 2: Beaumont Clay



### Core 3: Texas Sand



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### Theory vs. Reality

#### Major Issues at Real Sites

- 1. Heterogeneity
- 2. Fluctuating Water Table (vertical equilibrium)
- 3. Site Data for Verification
- 4. Ability To Collect Site-Specific Data
- 5. Cost

### What Have You Learned?

- NAPL distribution with water & air in pore spaces determined by capillary pressure.
- NAPL distribution can be estimated.
- NAPL volume & conductivity can be estimated.
- NAPL recoverability affected by capillary forces, fluctuating water tables & relative permeability.
- Model assumptions affect recovery predictions, BUT
- Useful recovery estimates & performance goals can be set.
- Good data & good judgment lead to good site decisions.

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### NAPL Alliance

• Mission: develop improved technical approach to remediation of groundwater & soil contaminated by petroleum hydrocarbons

Goals:

- Work collaboratively to identify practicable, cost-effective solutions
- Create & test a decision-making framework for achieving cleanup goals
- Develop a procedure for cleaning up & closing large NAPL sites
- Develop a better understanding of aggressive NAPL removal technologies

Members are representatives from industry, Federal & state governments

We welcome additional state participation



### **LNAPL Decision Framework**

- Is the site secure?
- Are the appropriate stakeholders involved?
- Has an acceptable long-term vision been developed?
- Are the long-term risks & technical issues understood?
- Has a technical/administrative strategy been developed?
- Has the strategy been implemented?
- Is the plan on tract to meet endpoints, goals & long-term vision?