“The Basics”

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

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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.
The Conceptual Understanding of NAPL
1980’s Pancake Model

Vertical Elevation in Soil Column

“Pancake Layer” Conceptualization

NAPL

Water
Soil Grains

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

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

~1mm
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
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.
Characteristic Capillary Pressure Curves

- **Clay**
- **Silty Sand**
- **F-M Sand**
- **Coarse Sand**

**Y-axis:** Capillary Suction (cm)

**X-axis:** Water Saturation (%)
Movement of NAPL Into & Out of Pores
What Do Lab Data Show?
Soil Type Determines the NAPL Saturation Distribution for The Same MW Thickness

10 ft Monitoring Well Thickness & a Diesel Fuel
Idealized Conceptualization of NAPL in a Well & Adjacent Formation

1) Continuous non-wetting LNAPL in the Formation

2) Monitoring well
   - LNAPL in a well
   - LNAPL-water interface in well
   - Water pressure
   - LNAPL pressure

3) LNAPL saturation

Pressure

LNAPL saturation
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
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

- Sand, $K = 2.24 \times 10^{-3}$ cm/sec
- Silty Sand, $K = 3.52 \times 10^{-5}$ cm/sec
- Sandy Silt, $K = 5.19 \times 10^{-7}$ cm/sec

Conductivity (cm/sec) vs. Monitoring Well NAPL Thickness (ft)
Effect of Viscosity & Density of Different NAPLs on Conductivity

![Graph showing the effect of viscosity and density on conductivity]

- Gasoline
- Diesel
- Oil

Effective Conductivity (cm/sec)

Saturation (%)
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.
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 fine-grained 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

CPT – Soil Profiling

LIF – Gasoline Fluorescence Intensity & Waveform

NAPL in Sand Stringers & Not in Silty Clay
Core 1: NW Indiana Sand

9 feet below ground surface

13 feet below ground surface

Natural

UV

Dark means no fluorescence

Natural

UV

Dark means no fluorescence
Core 2: Beaumont Clay
Core 3: Texas Sand

% benzene saturation

% fines
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.
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?