DNAPL Surface Chemistry: Its Impact on DNAPL Distribution in the Vadose Zone and its Manipulation to Enhance Remediation

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DOE problems that are being addressed

The remediation of DNAPLs in subsurface environments is often limited by the heterogeneous distribution of the organic fluid. The fraction of DNAPL that is in the high conductivity regions of the subsurface can often be recovered relatively easily, although DNAPL in lower conductivity regions is much more difficult to extract

The distribution of DNAPL within the vadose zone is affected by a complex interplay of heterogeneities in the porous matrix and the interfacial properties defining the interactions among all fluid and solid phases. We need to understand these complex interactions to understand the current distribution of DNAPL in the subsurface and to plan effective remedial strategies. Results of this effort could potentially be used to increase the accessibility and, therefore, the recovery of DNAPL during vapor extraction or other vadose zone remediation efforts.

Primary hypothesis

Surface-active chemicals and/or microorganisms present in the unsaturated zone can significantly alter the interfacial phenomena governing the migration of DNAPLs, thereby affecting the accessibility of a DNAPL during remediation efforts.

The surface-active materials are present in complex NAPL mixtures and are produced through microbial metabolic processes.

The overall goal of this proposed research is to understand the role of and changes in interfacial phenomena on the accessibility of DNAPL in the vadose zone.

Research progress and implications

A multi-task approach involving experimental measurements at both laboratory and field scales has been designed to meet the objectives of this research. Materials for this research have been chosen to be applicable to vadose zone contamination problems at the Savannah River site (SRS). Initial stages of the research are focusing on well-characterized materials with a shift to site-specific media as the processes are understood. This research offers a unique opportunity to develop our fundamental understanding of the fate of DNAPLs in the vadose zone through both laboratory scale testing and evaluation of field samples collected at SRS.

Laboratory investigation

Three primary objectives are being addressed at the laboratory scale:

1. Understand and quantify the interfacial properties of DNAPLs in response to biological activity or the presence of surface-active constituents within the DNAPL mixture.
2. Characterize the transient nature of bacterial interactions at the NAPL-water interface.
3. Quantify the net effect of transient changes in interfacial properties on variables that directly affect vadose zone remediation efforts.

Variables:	**Measurements and Methods**:
NAPL composition	Interfacial tension
Aqueous phase composition	Contact Angle
Growth conditions	Capillary and packed column adhesion
Time	Micro-model flow cells for visualization
# phases present	Multi-step outflow k-S-P experiments

Preliminary findings and progress

- Quartz surfaces remain water wetting after contacting SRS NAPL over a wide range of pH values
- Technique for micro-model fabrication nearly complete
- Culturing of microorganisms on-going

The star indicates the location of one of the soil cores at the outfall area. Water containing chlorinated solvents was discharged just to the left of the present outfall. Significant contamination was found ~10-30 ft BGS (fig. 1)

The U.S. Department of Energy's (DOE) Savannah River Site (SRS) located in Aiken County, South Carolina has DNAPL contamination in both vadose and saturated zones of the subsurface. The DNAPL contains PCE (95%), TCE (5%), and impurities from its use in degreasing operations.

The Savannah River Site has a unique field situation where spent solvents containing machining oils and greases at extreme pHs were released into the SRS vadose zone at one site (M-Area) while the same solvent was released at neutral pH at another site (Outfall A-Area) in a similar geologic setting. Thus, focused characterization of NAPL distribution at these two sites can help examine the importance of pH and microbial activity on surface chemistry complexity and its evolution in the vadose zone

Field work was conducted in February 2000. Four soil cores (~35-100 ft deep) were collected at two separate areas of contamination at SRS. Duplicate sub-samples were collected in a pattern orthogonal to significant visually observed heterogeneity. Total bacterial cell concentrations were determined using the Acridine Orange Direct Counting (AODC) method (Gephardt et al. 1994). Headspace analysis was conducted by gas chromatography to measure chlorinated solvent concentrations in the soil samples. Mineralogical and grain size analyses are on-going.

The subsurface at the outfall area is characterized by a range of sand and clayey lenses (fig. 1)

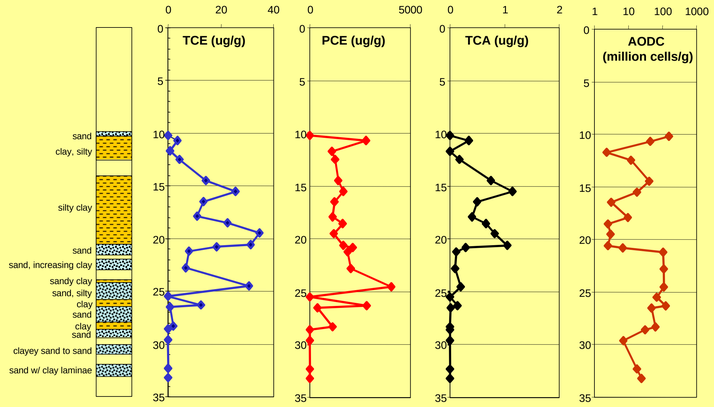

Figure 1: Solute concentrations and cell counts as a function of depth (feet below ground surface in well MHS-3). Results show consistently elevated solute concentrations in the clay layer (~10-20 ft) with highly variable concentrations at lower depths between the sand and clay lenses. Biological activity as determined by AODC illustrates the predominance of activity within the sandy strata.

Observations from field work

Data from one of the borings in the Outfall Area are presented in Figure 1.

- The concentration of chlorinated compounds and microorganisms (expressed as AODC) vary with of depth. High concentrations were observed in both the fined grained clay material as well as some of the sandy layers.
- As expected, the bacterial concentration in the silty clay layer (~10 – 20 ft) is approximately one order of magnitude lower than in the coarser material. Larger pore spaces in the sandy material allow for the more rapid exchange of nutrients for the bacteria and provide space for increased migration.
- Concentrations of TCE and PCE decline with increasing depth between 20-30 ft. Microbial concentrations, however, are relatively high in this zone.
- Bacterial concentrations below the clay layer (depth > ~ 20 ft) correlate with PCE, TCE and TCA concentrations (Figure 2). Higher substrate concentrations should induce larger microbial growth for an active microbial community at non-toxic substrate concentrations. This was observed in the boring below 20 feet. The observed TCA concentrations presented in Figure 2 correlated well with AODC counts indicating an active co-metabolic microbial community.

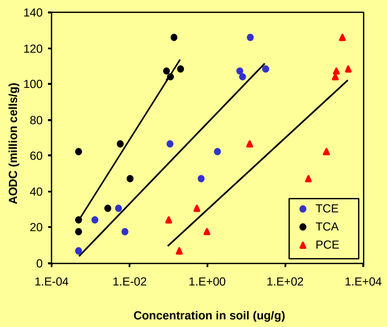

Figure 2: In the region below the clay layer (depths > ~20 feet), cell counts increase with increasing contamination levels in a statistically significant manner. The presence of TCA confirms the aerobic co-metabolism of TCE in this shallow well.

The data presented indicate that both microbial cells and solvent contamination can be found in the fine-grained material. The potential impact of the present microbial community to affect DNAPL interfacial properties that would allow for the DNAPL penetration into the fine clay lenses is currently under investigation.