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

Project Number: 70035

Primary EM Problem Area: Subsurface Contamination

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Progress Report

1.0 Research objectives.

The primary hypothesis of this work is that surface-active chemicals and/or microorganisms present in the unsaturated zone can significantly alter 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.

2.0 Research progress and implications.

Research on this project began in October 1999. The present annual summary covers activities that have occurred during the period from June 2001 though June 2002.

A multi-task approach involving experimental measurements at both laboratory and field scales has been designed to meet the objectives of this research (Figure 1). Materials for this research have been chosen to be applicable to vadose zone contamination problems at the Savannah River site (SRS). Current 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. The fieldwork provides a detailed assessment of the distribution of DNAPL in the subsurface as a function of microbial populations, mineral characterization, and heterogeneous grain size distribution. Concurrent laboratory testing provides an understanding of the fundamental mechanisms governing these distributions.

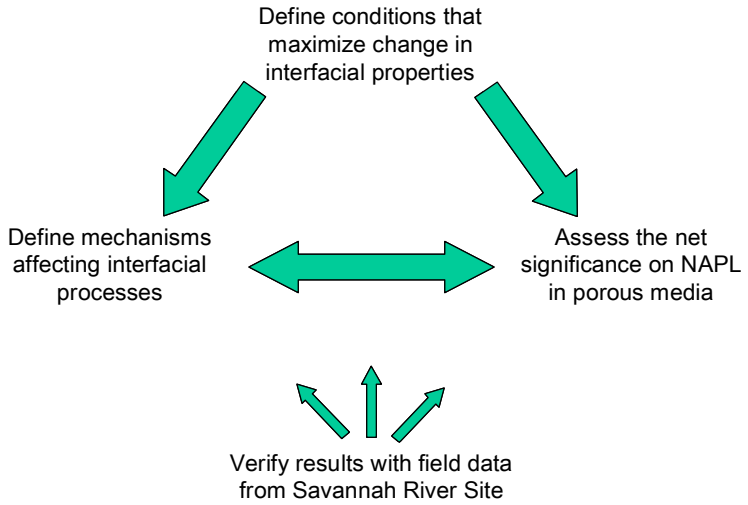

Figure 1: Approach for meeting the objectives of this research grant

Over the past year, research has focused on defining conditions that maximize change in interfacial properties and assessment of the net effect of these changes on NAPL migration and entrapment in porous media. Experimental protocols in these areas were developed and extensive data collection is on-going. Analysis of samples from a second round of fieldwork (March 2001) has also been completed to quantify the subsurface distribution of NAPL at SRS and correlate this distribution to other subsurface variables. Our progress is described below along with plans for the finishing the proposed work by the end of the project period.

2.1 Field work

2.1.1 Characterization of subsurface media

Work at the Savannah River Site has focused on characterizing subsurface soil samples from the A-14 Outfall and investigating interrelationships between soil properties that may be important to DNAPL accumulation and remediation. Extensive analyses of 2 of the 4 A-14 soil borings have been done to date. These were chosen for analysis based on their relatively high concentrations of PCE and TCE, indicating they were both in the path of migrating DNAPL. Table 1 shows a matrix of the analyses done to date.

Table 1: Matrix of soil analyses completed on soil borings MHS-03 and SB-1 from the A-14 Outfall area.

Number of Samples	**Analysis**	**Method**
32	Grain size distribution	Internal SRTC procedure
32	Surface Area	BET (nitrogen adsorption)
32	Bulk Chemistry	X-ray fluorescence
44	TCE/PCE	Soil plug/head space
20	Gravimetric moisture content	Weight difference
26	Petrographic thin-sections prepared	Standard commercial methods
9	Bulk mineralogy	Powder x-ray diffraction

Figure 1 and 2 show measured soil properties versus depth. The data for boring MHS-03 is not yet complete, but some generalizations about the soil properties can be made. Grain size is slightly coarser in MHS-03 than in SB-01, but both tend to coarsen with depth. This change in texture is reflected in other soil parameters, such as surface area and bulk chemistry. There is an abrupt change in the properties of the soils beginning at a depth of about 16 feet in MHS-03 and 18 feet in SB-01. The texture of the soils becomes coarser with a corresponding decrease in surface area and chemical indicators of clay sized minerals (Al, Fe, and Ti). Results from sieve analysis indicate a high weight percentage of small fines (<1 µm) in the top layer of the Outfall Area (Fig. 3).

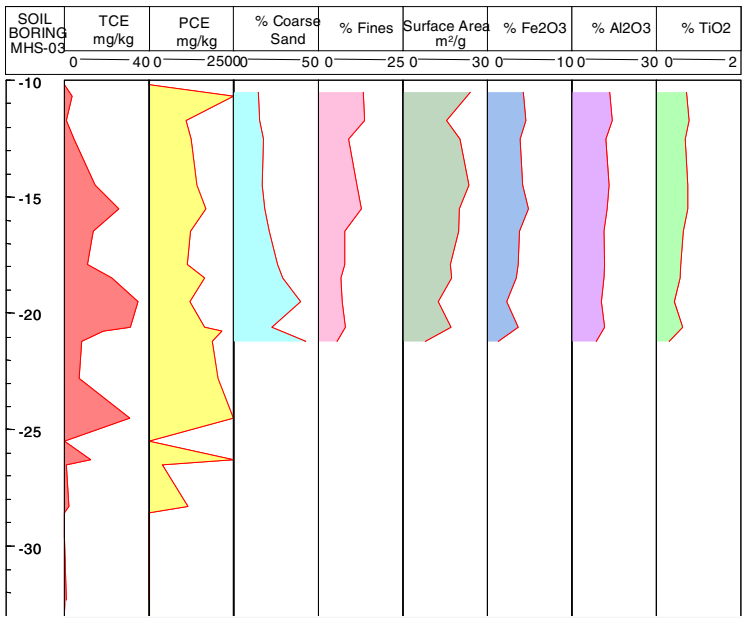

Figure 1: Soil properties of soil boring MHS-03. Sampling was done on 1 foot intervals.

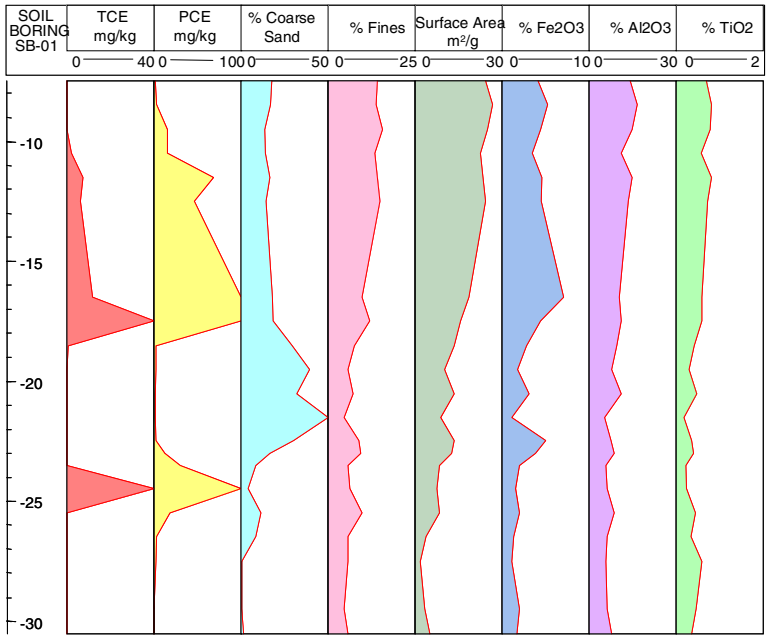

Figure 2: Soil properties of soil boring SB-01. Sampling was done on 1 foot intervals.

These are coincident with decreasing solvent concentrations. The low concentrations of PCE and TCE in this zone are likely the result of ongoing remediation efforts by soil vapor extraction. These data illustrate that heterogeneities in soil properties lead to heterogeneities in remediation efficiency.

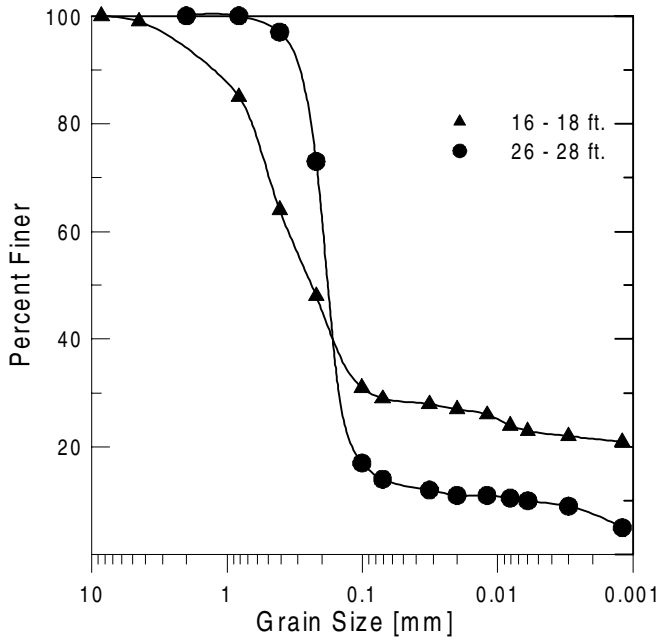

Figure 3: Grain size analysis at two depths at A-14 Outfall Area, NSB-04. In the shallower zone more than 20% of the particles are less than 1 μm.

The soil property data also suggest the importance of micro-scale heterogeneities to surface interactions of contaminants. In Figure 4, measured surface areas of soils from this study and several published studies are plotted against wt. % fine-grained material (<0.075 mm). All of the soils have the expected positive relation between surface area and wt. % fines, but the slopes of the data vary over a wide range. Two factors may contribute to this variation – the size distribution of the fine-grained fraction and the intergranular structure of this fraction. Higher slopes would result from finer intergranular material. Thus, it is possible that a sample identified as clayey by macro-scale observations may have a lower surface area than a sample that contains more sand-sized material. The thin-section photomicrographs from A-14 Outfall samples shown in Figure 5 illustrate the potential importance of intergranular structure. These samples may have similar size distributions and surface areas when disaggregated. However, the sample in Figure 5a is likely to have a higher "effective" surface area, and thus be more surface active than the sample in Figure 5b. Such micro-scale heterogeneities may have substantial influence on migration, accumulation, and remediation of DNAPL.

The samples in this study have an interesting relationship between surface area and wt. % fine-grained material (Figure 6). When the wt. % of fines is below about 7%, small changes in this parameter result in large changes in surface area. Above 7 wt. % fines, the change in surface area is less per increase in fine-grained material. This is consistent with a suite of samples in which the distribution of fine-grained material ranges from coatings on sand grains to filling pores. Coated sands may contain little fine-grained material, but have relatively high surface areas.

The results from surface area measurements and the presence of the fines in the upper region cannot be explained as natural deposits. It is hypothesized that the fines were generated during the disposal of waste solvents, which exhibited very extreme pH values (Pickett et al., 1987).

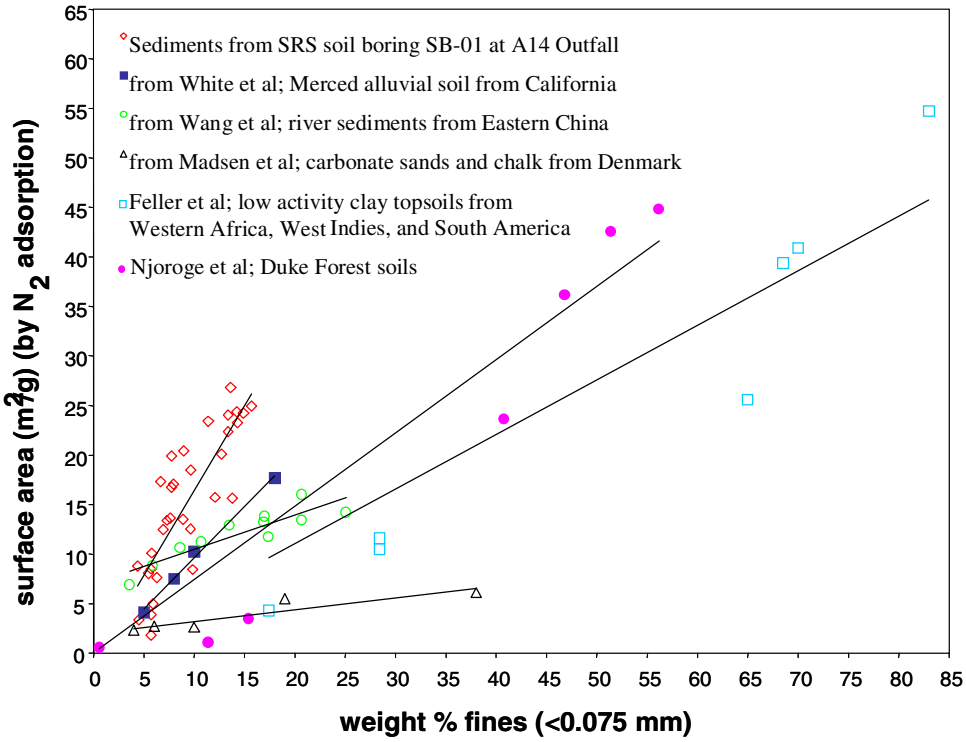

Figure 4: BET specific surface areas versus wt. % fine-grained material for soils from A-14 Outfall Area compared to data from other soil studies. Trend lines show general slope of the data, not statistically valid correlations.

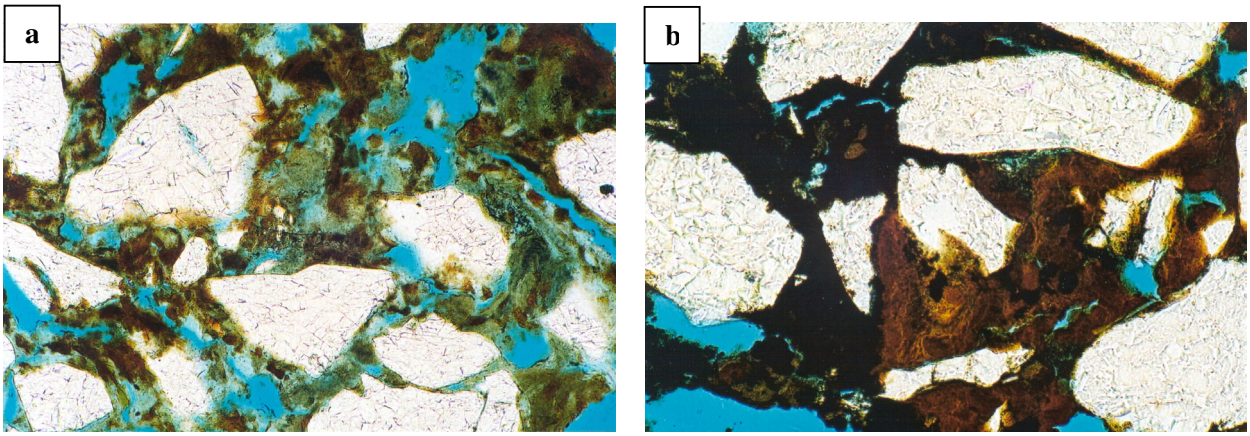

Figure 5: Thin-section photomicrograph of soil samples from the A-14 Outfall area. Quartz grains are white, porosity is blue, and intergranular material is brown. The long dimension is approximately 0.2 mm.

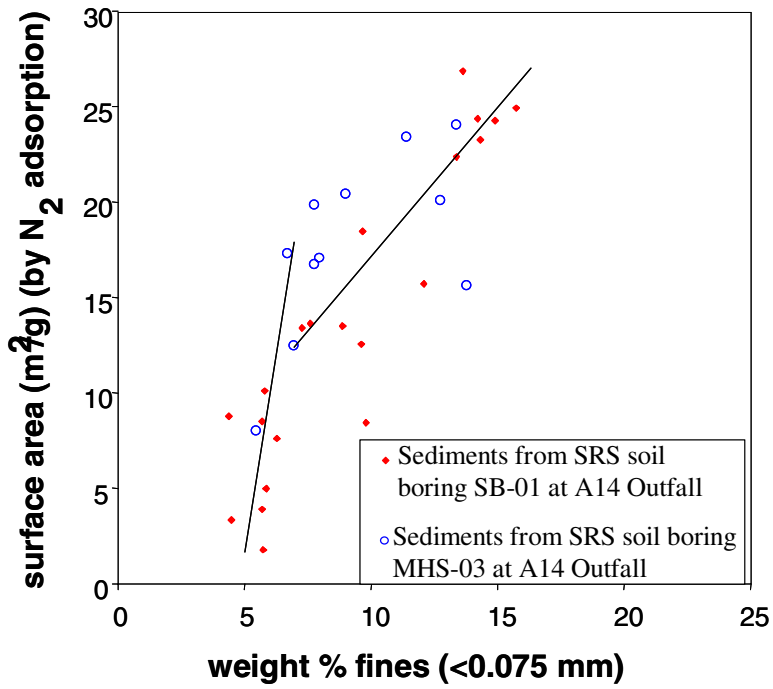

Figure 6: BET specific surface area versus wt. % fine-grained material for soil samples from borings MHS-03 and SB-01 from the A-14 Outfall area. Trend lines show general slope of the data, not statistically valid trends.

The inconsistencies in surface area and fines will lead to fluid flow that could be different than expected for more typical soils. Figure 7 illustrates an example of prediction of water retention curves from the PSDs using the Arya-Paris model (Arya and Paris, 1981; Arya et al., 1999a) for specific real soil data from the SRS site. Neither water retention curves predicted using the PSDs matched measured data, indicating that prediction of water retention characteristic based on the assumption of random packing of all particle size does not adequately represent real soil packing condition.

In a soil with a small fraction of fine particles (Fig. 1, 26-28 ft), the predicted water retention curve is characterized by a well-defined air-entry value, indicating narrow particle-size distribution and thus narrow pore-size distribution (Fig. 7a). However, the real water retention data showed more broad pore-size distribution. We believe that this is due to heterogeneity of colloid deposition onto solid grains, making the pore size distribution more broad.

Also, in a soil with a relatively high fraction of fine particles (Fig 1, 16-18 ft.), both predicted and observed water retention characteristic showed low air-entry values and similar shape at high water content (Fig. 5.5(b)). In the intermediate zone, however, predicted water retention showed a distinct deviation from the observed, which may be due to heterogeneity of pore-size distribution in the real soil. In the region near residual water content, the observed data showed lower capillary pressure head at the same water content than the predicted. This may indicate that fine and very fine particles would adhere to coarse particle and thus could not affect greatly pore sizes in this region.

We believe that these preliminary results show the potential for heterogeneous deposition of fine/very fine particles onto solid grains to change the pore size distribution and, thus, the related water retention characteristic to values that are different from predictions based on currently available models.

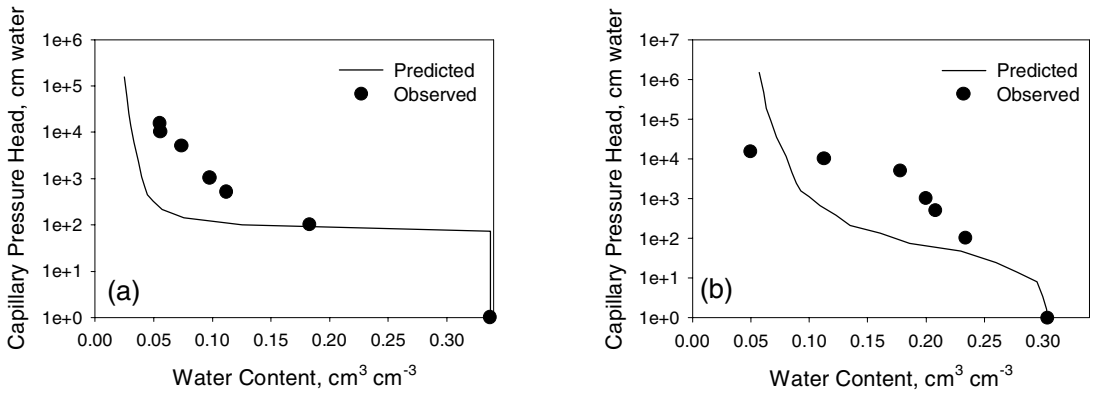

Figure 7. Comparison of experimental water retention curves for SRS soil with theoretical retention curves derived from particle size distribution measurements (Arya-Paris, 1999) (a) NSB-4 (26-28 ft) and (b) NSB-4 (16-18ft).

2.1.2 Characterization of SRS DNAPL

A small sample of DNAPL from the M-area basin at the SRS site has been tested. This DNAPL had previously been characterized as 80-95% PCE and 5-20% TCE. Based on a Ramen spectrum of the DNAPL, a hydraulic oil (bearing and circulating oil, DTE Oil Heavy Medium Mobil, Number 600163 8) has also been identified as a probable constituent in this organic phase. Recent GC fingerprints of the site DNAPL relative to a mixture of PCE, TCE and this hydraulic oil, however, illustrate that there are many additional constituents in the site DNAPL that are not present in the surrogate mixture.

The complexity of the site DNAPL has also been confirmed based on its low interfacial and surface tension (Table 2). Based on the relative PCE/TCE concentrations, Looney et al. (1992) predicted the IFT to be on the order of 40 dynes/cm. Adding the hydraulic oil or the surfactants used in the Purex process (TBP or DBBP) to a mixture of PCE and TCE reduced the IFT to ~ 21 dynes/cm, but not as low as the site DNAPL. The very low IFT at low and high pH is similar to the trends seen in our laboratory for coal tar samples that contain colloidal asphaltene materials (Zheng and Powers, 1999). These materials contain acidic and basic functional units that are protonated or deprotonated at these pH extremes. Contact angle measurements in a system of quartz, DNAPL and DI water (pH=7, 10), showed that this system is water wetting.

Table 2: Surface and interfacial tension for SRS DNAPL

pH	ST	IFT
3.0	--	1.8±0.3
6.3	36.4±0.5	6.8±1.0
10.3	--	2.6±0.5

2.1.3 Characterization of microbial population at SRS

Significant bacterial concentrations were observed throughout the core (Fig. 8). As expected, bacterial concentrations were somewhat lower in the zone of finer soil (<17 ft), where the smaller pores limit the transport of nutrients and bacteria. Interestingly, lowest cell concentrations were observed in the zone that is influenced by the ongoing remediation. Possibly, the low VOC concentration in combination with low moisture content (< 20%) limited the growth of organisms in that region. In regions of medium pore size bacterial concentrations correlate well with contaminant levels (Fig. 9)

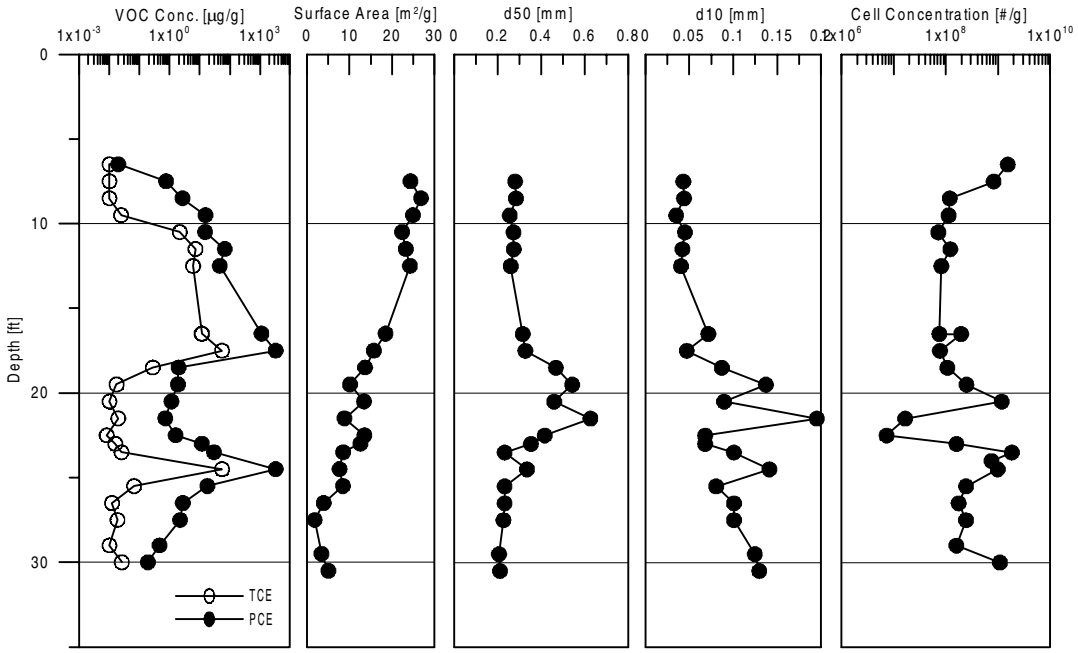

Figure 7: Bacterial concentrations in boring SB-01 in A-14 Outfall Area of SRS as a function of depth and porous media properties

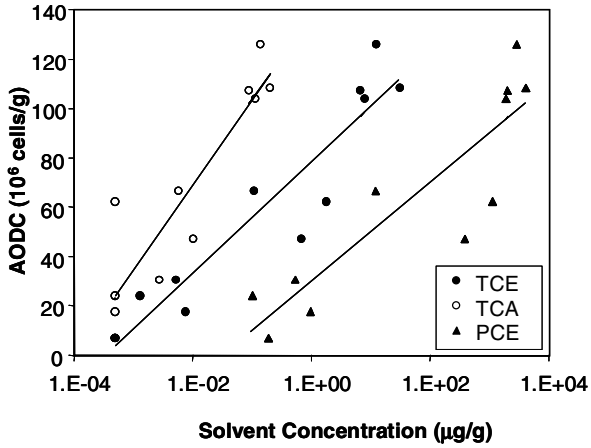

Figure 8: Total bacterial concentrations increased with increasing contaminant levels.

2.2 Laboratory - Characterization of interfacial properties

2.2.1 Bacterial processes

Microcosm experiments were conducted to assess the impact of colloidal material and biologically produced compounds on NAPL interfacial properties. A simultaneous reduction in surface and interfacial tension was used as a screening tool for surfactant production. However, since particles predominantly settle at the DNAPL/water interface an interfacial effect due to the presence of particles should induce a reduction in interfacial tension only.

Among the variables investigated for the butyrate fermenting culture (Cornell culture) were ionic strength (I = 0.2 to 0.01), the ammonia concentration in the growth media, the presence of elevated PCE concentrations and the presence of dissolved oxygen. Surface tension of unfiltered culture media under

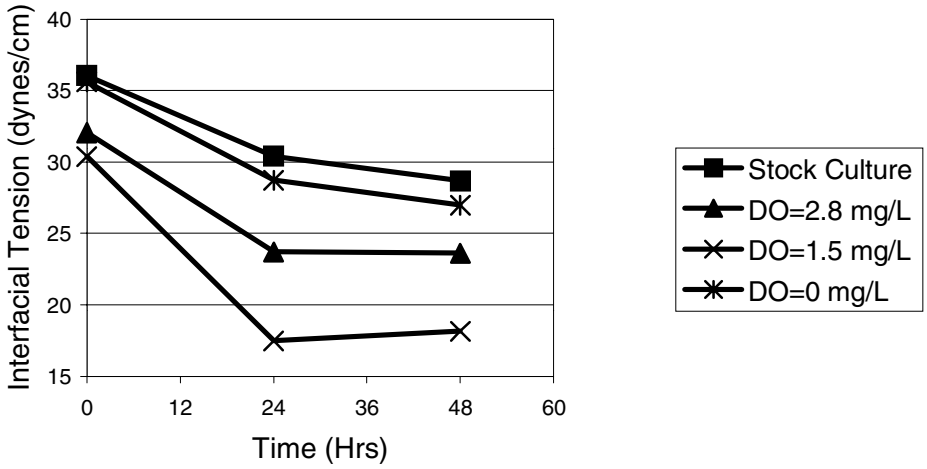

Figure 9: Effect of dissolved oxygen on IFT for butyrate fed culture, filtered through 1 μm to remove inorganic particulate.

all growth conditions was slightly lower than filtered culture fluid at all growth conditions (60 vs. 68 dyn/cm). Interfacial tension, however, changed significantly upon inducing stresses to the enrichment culture. For example upon exposure of the culture to oxygen, followed by a one-week incubation IFT declined up to 43% relative to the unstressed stock culture (Figure 9). IFT measurements were conducted over a 48 hrs period to determine the dynamic processes of particulate settling and the absorption of surface-active compounds at the TCE/water interface. IFT tension in all samples declined as a function of time, which could be attributed to particulate settling. The extent of IFT decline relative to the non-stressed culture (Stock Culture) however was dependent on the "stressor" concentration. Abiotic controls at similar dissolved oxygen levels did not exhibit any effects on IFT suggesting that the decrease in IFT was due to biological activity. The difference in IFT increased over the first 24 hrs of the analysis. At the beginning of the IFT measurement the difference between TCE and the stock culture versus oxygen stressed organisms was less than 5 dyn/cm. After 24 hrs of equilibrating the two phases this difference increased to 14 dyn/cm or approximately 50% (Figure 9).

Similar reductions in IFT were observed when the culture was grown in the presence of 190 mg/L PCE, which is a concentration approximately 10 times higher that is used to grow the stock culture (Figure10). Noteworthy for this set of results are that surface tension decreased slightly (from 70 to 60 dyn/cm) and was not a function of equilibration time. Since TCE is heavier than water, a reduction in surface tension can only be explained through the presence of dissolved surface-active compounds. Due to gravity all particulate matter would be expected to settle to the TCE/water interface rather than accumulate at the water/air interface. IFT for the PCE stressed culture at t=0 was 24 dyn/cm compared to 36 dyn/cm for the un-stressed culture (Figure 10). This difference is indicative of the presence of surfactants in the stressed culture. The further decline in IFT for both stressed and non-stressed cultures could be explained by the accumulation of microorganisms at the TCE/water interface. As shown earlier this resulted in a decline in IFT.

In summary, among the growth conditions tested (elevated concentrations of EDTA, ammonia, PCE and several levels of dissolved oxygen) induced stresses affected interfacial properties. Most significant effects for the butyrate using enrichment culture were obtained in the presence of oxygen. Table 3 summarizes the percent reduction in surface tension (ST) and interfacial tension (IFT) after 24 hrs for

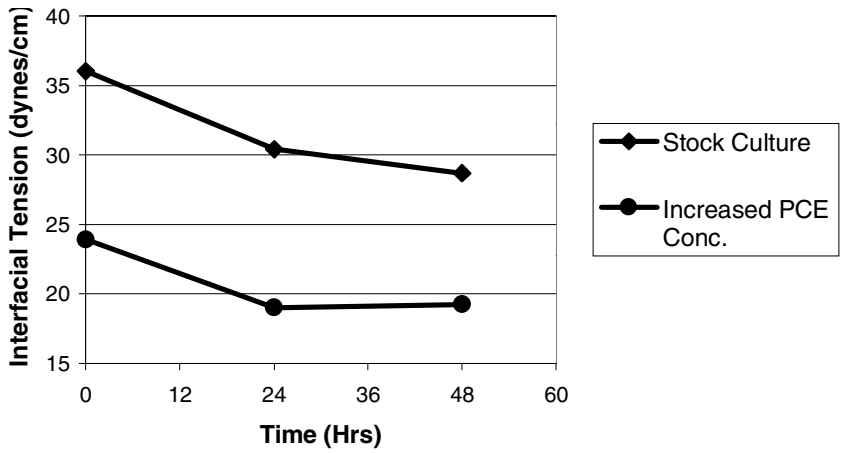

Figure 10. IFT of butyrate enrichment culture. Effect of elevated PCE concentration on IFT.

particle-free media and media that contained bacteria (particulate). ST declined up to 15 % for the media that contained bacteria while ST for the particle-free fraction was not affected. Reduction in IFT was observed for both particle-free and particulate fractions. However IFT for the particulate fraction decreased to a greater extent. A reduction in IFT for a particle-free solution would be indicative of the presence of dissolved biosurfactants, which should also induce a reduction in ST. No significant reduction in ST for the particle-free fraction, however, was observed. The particle-free media was generated through filtration through 0.2 µm filters. Particles smaller than 0.2 µm particles could have passed through the filter and accumulated at the TCE/water interface. We are currently in the process of investigating this phenomenon.

Time = 24 hours	Particulate		Particle Free	
Variable	**ST**	**IFT**	**ST**	**IFT**
DO = 0 mg/l	2.80	5.53	-1.01	10.16
DO = 1.5 mg/l	11.47	42.53	3.47	33.75
DO = 2.8 mg/l	4.04	22.05	-0.84	14.13
PCE = 190 mg/l	15.31	37.48		

Table 1. Summary of surface tension (ST) and interfacial tension (IFT) assays. Presented in the percent decline in ST of IFT relative to the stock culture.

Significant IFT reduction can be attributed to both, the accumulation of bacteria at the DNAPL interface and the production of biosurfactants. However, low IFT of the SRS DNAPL could not be reproduced in any of the laboratory experiments. We are currently in the process to determine whether microorganisms from two SRS sites could induce interfacial property changes in response to environmental stresses such as the presence of oxygen or elevated PCE concentrations. Results from this research phase should be expected within the next two months.

2.2.2 Abiotic mechanisms

Microbial consortia are not the only source of surface-active materials that can affect interfacial properties. Experiments have been conducted to assess abiotic factors as well. Interfacial tension measurements and wettability characterization are being used to identify ranges of interfacial properties that may be encountered in the subsurface. At this point, we have considered only variable DNAPL

compositions. Two chemicals used by the DOE in conjunction with chlorinated solvents that are of interest are tributyl phosphate (TBP) and di-butyl, butyl phosphonate (DBBP). These chemicals were added to PCE or TCE for investigation. Water at a range of pH values was considered.

At a neutral pH, the addition of these chemicals dropped the interfacial tension of TCE from 34 dynes/cm to ~25 dynes/cm at 4% TBP or DBBP (by mass). Higher concentrations resulted in only marginal additional decreases in the IFT. The addition of abiotic colloids to the system did not substantially reduce the interfacial tension (Figure 11).

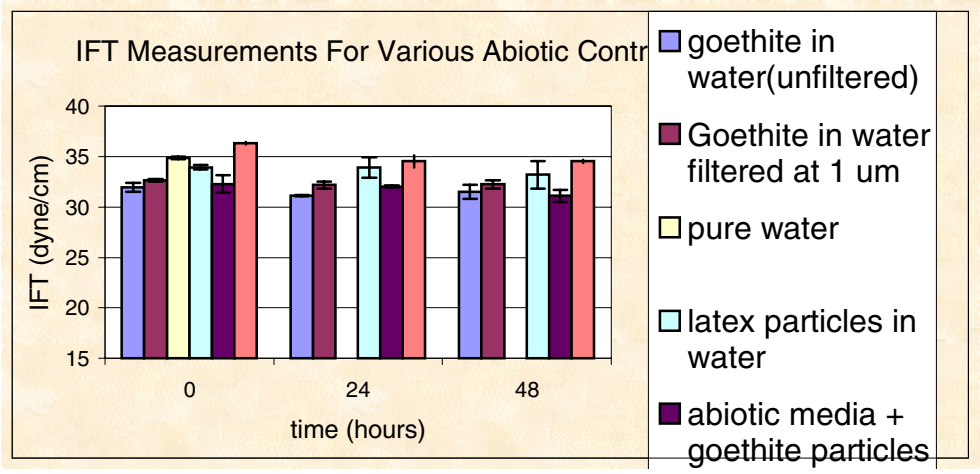

Figure 11: Interfacial tension of TCE with water as a function of the presence of abiotic colloids

2.3 Laboratory analysis of the impacts on multiphase flow

Two different sets of experiments and associated analyses have been completed to define the significance of variable interfacial properties on multiphase flow. Micromodel experiments illustrate the pore-scale flow and distribution of fluids through a simplified porous medium. Results of these experiments help to better define conceptual models and understanding of the flow processes. Multistep outflow experiments provide a means of quantifying constitutive relationships for capillary pressure and relative permeability as a function of fluid saturations (k-S-P). Significant numerical modeling is required for the inverse modeling of data from these experiments.

2.3.1 Micromodel Experiments

Micromodel experiments and the associated image analysis have shown significant differences in the fluid distributions as a function of several of the variables tested. These variables included surface/interfacial tension, orientation of the model, and drainage versus imbibition pathways. Altering the fluids considered varied the surface and interfacial tensions. We've used air-water, air-ethanol, TCE-water, and SRS DNAPL-water in the experiments conducted to date.

Figure 12 illustrates the distribution of water (blue) and air in the ~4 cm x ~7 cm micromodels during drainage and imbibition. Image analysis allowed the identification of the interface between the two fluids. This interface was divided between that part created by the bulk fluid flow and that resulting from the retention of entrapment of fluids within the porous medium due to the immiscible displacement process. Fractal analysis was used to characterize the fractal dimension (D) and fractal coefficient (b) for each of the experiments. Statistical analysis showed that there were statistically significant differences in these parameters, most notably between drainage and imbibition for most cases, and as a function of surface / interfacial tension during drainage of the wetting phase. S/IFT has less impact on the fractal parameters during imbibition of the wetting phase.

New advances we've made in the application of fractal analysis to images of the flow processes have enabled the interfacial area of the residual fluid to be quantified – in a relative sense - in these systems. There were significant reductions in the residual wetting phase surface area as the surface tensions decreased and increases in the surface area of the residual nonwetting phase (Fig. 13). These differences in surface area could have a significant impact on the accessibility of fluids to remediation efforts based on mass transfer processes.

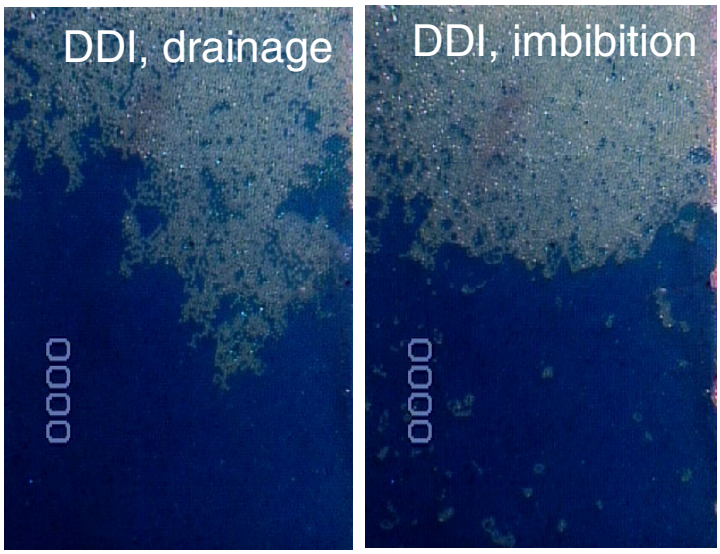

Figure 12: Photographs from glass bead micromodels illustrate the significant differences in the nature of the air-liquid (liquid is dark) interface in drainage versus imbibition.

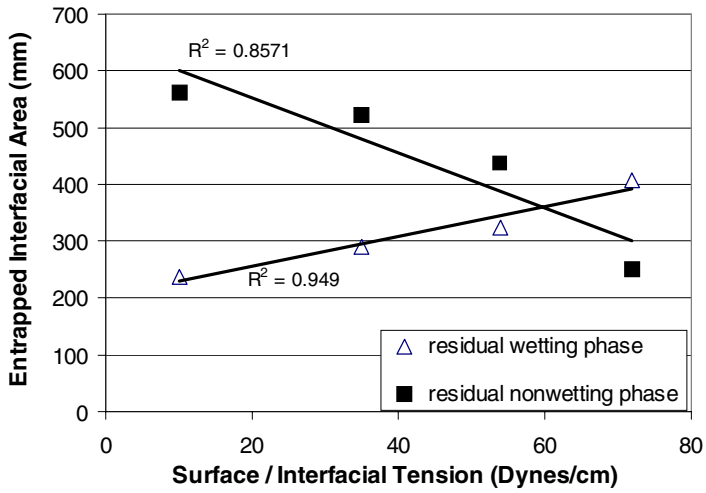

Figure 13: Results of a new application of fractal analysis quantify trends in the interfacial area of fluids at their residual saturation. Note: the lowest IFT values represent results of experiments with the SRS DNAPL

Micromodel experiments with variable wetting properties are on-going. Experiments with bacteria – both stressed and not stressed - will be initiated soon.

2.3.2 Multistep outflow experiments

Multistep outflow experiments and associated numerical analysis have been developed and applied to understand the significance of interfacial tension and wettability on k-S-P relationships. Variable ST and IFT had the expected pressure lowering impact on P-S curves, but no effect on k-S curves for the conditions tested. Fig. 14 illustrates the effect of fractional wettability on these curves. In contrast to theoretical models that predict that the capillary pressure curves would be lowered with a decrease in water wettability, the results presented below illustrate that the nature of capillary fluid flow is not that easily described. At low capillary pressures, the decrease in water wetness causes some pores to drain more readily, where as more water is retained in other pores at higher pressures. The net result of these changes is an increase in the relative permeability of water in the system.

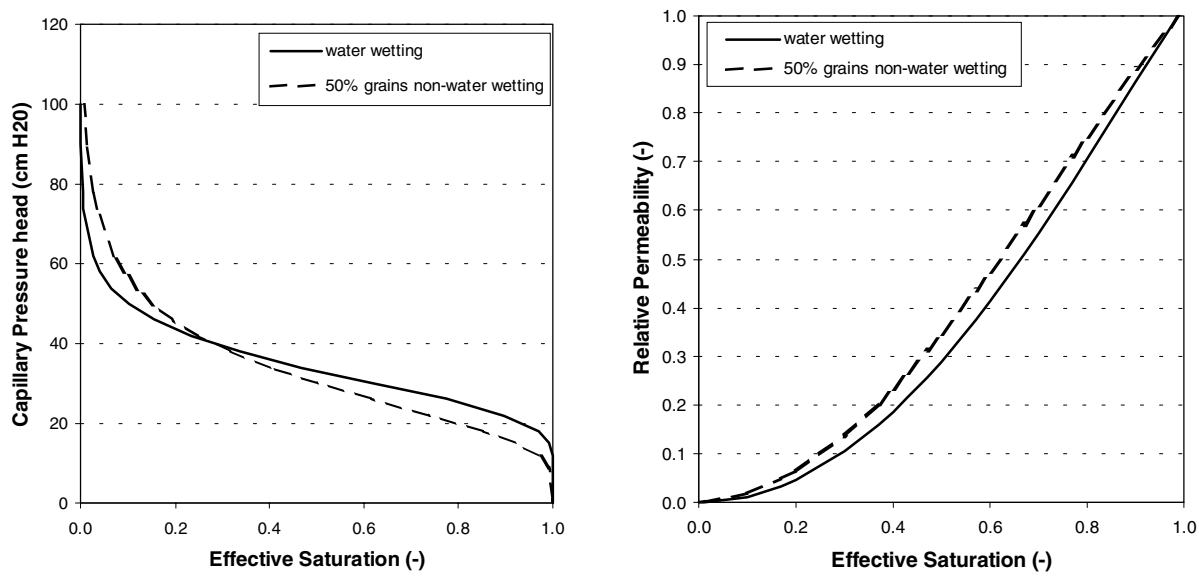

Figure 14: Results from multi-step outflow experiments and inverse modeling for medium sands as a function of wettability. The P-S curve for heterogeneous wetting conditions is different than those expected for a system with homogeneous wetting sand grains. The relative permeability in the fractional wetting system is higher than in a water wetting system due to the increased presence of water in larger pore spaces.

Experiments and mathematical analysis of the results is on-going for a wider range of fluid systems and wettability conditions.

3.0 Information Access.

Project webpage: http://www.clarkson.edu/~doe

3.1 Presentations

Powers S.E., "Mechanisms affecting the wetting conditions in environmental systems contaminated by nonaqueous phase liquids." *Presented* at the Gordon Conference on Modeling Fluid Flow in Permeable Media, Andover NH, August 9, 2000.

Grimberg, S.J., S.E. Powers, M. Denham, K. Chen, "Field Study to Correlate Chlorinated Solvent Concentrations and Microbial Distributions in the Unsaturated Zone." *Presented* at the ACS Summer Meeting, Division of Environmental Chemistry, Washington DC, August 2000.

Hwang, S.I., S.E. Powers (2001) Using a Multi-Step Outflow Technique to Estimate k-S-P Parameters for Contaminated Solutions. *Presented* at the Annual AGU Conference, Boston, MA, May 29 - June 1, 2001

Cianci, J., S.I. Hwang, S.E. Powers (2001) Photo-visualization Study Illustrating the Effects of Interfacial Properties on Multiphase Flow in Glass Bead Micromodels. *Presented* at the Annual AGU Conference, Boston, MA, May 29 - June 1, 2001.

Hwang, S.I., and S.E. Powers, "Using a Multi-Step Outflow Technique to Estimate Unsaturated Hydraulic Conductivity Function for Quartz Sands With Variable Interfacial Properties." Presented at the AGU Fall Meeting, San Francisco CA, December 2001.

Hime, J., A. Crandall, S.J. Grimberg**,** "Optimal Conditions for TCE Bioremediation". Presented at the 74th Annual Meeting of the New York Environment Association, New York, NY, February 4-6, 2002.

Doty, T., S.J. Grimberg (2002) "The Role of Microorganisms on DNAPL Interfacial Properties and Transport." *Presented* at the 3rd International Conference on Remediation of Chlorinated and Recalcitrant Compounds*,* Monterey, CA, May 20 – 23, 2002.

Omrane, K.

3.2 Papers

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Note 4-5 additional papers will be completed in the next 6 months.

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