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

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Primary EM Problem Area: Subsurface Contamination

Principal Investigators:

Lead PI: Dr. Susan E. Powers
Clarkson University
Potsdam NY 13699-5710
315-268-6542 (PN)
315-268-7985 (FN)
sep@clarkson.edu

Co-PI: Dr. Stefan Grimberg
Clarkson University
Potsdam NY 13699-5710
315-268-6490 (PN)
grimberg@clarkson.edu

Co-PI: Dr. Miles E. Denham
Westinghouse Savannah River Company
Building 773-42A
Aiken SC 29808
803-725-5521 (PN)
miles.denham@srs.gov

Co-PI: Dr. Michal Borkovec
Clarkson University
Potsdam NY 13699-5814
315-268-6621
borkovec@clarkson.edu

Researchers: Sang-Il Hwang, Post Doctoral Research Associate
Kamel Omrane, M.S. Candidate
Thomas Doty, M.S. candidate

Progress Report

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.

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 2000 through June 2001.

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 we are now beginning the phase of extensive data collection. A second round of fieldwork was also completed this spring to collect additional biological and mineral samples and to quantify the subsurface distribution of NAPL at SRS. Our progress is described below along with plans for the upcoming year.

Define conditions that maximize changes in interfacial properties

Both biotic and abiotic mechanisms have been investigated to ascertain the range of interfacial properties that we would expect in the subsurface. In the systems with microorganisms, the hydrophobicity of the cell surface and the surface tension of the culture are used to characterize changes in interfacial properties. Wettability and interfacial tension are used for this characterization in abiotic systems. Significant progress has been made in this last year to develop laboratory techniques that result in statistically significant and reproducible results that are unaffected by experimental artifacts.

Biological Components

Three PCE degrading cultures have been grown in the lab and two are currently being utilized to test the effect of nutrient amendments on cell surface properties. *Desulfuromonas chloroethinica* (ATCC #70029) was used as a model culture. One mixed culture using butyrate as a carbon source was obtained from Dr. Gossett's laboratory at Cornell University and a second well-characterized mixed culture was obtained from Dr. McCarty's laboratory at Stanford University. All cultures are currently maintained in chemostats in our laboratory. It is hypothesized that changes in the growth environment of PCE-degrading cultures may cause the culture to produce surface-active compounds. These compounds may have a significant impact on the interfacial properties of PCE, and thereby affect PCE transport. PCE degrading cultures were utilized because of their ability to withstand concentrations of PCE toxic to most organisms. Contact angles of two liquids (polar: deionized water; nonpolar: diiodomethane) on microbial lawns are used as an indicator of surface hydrophobicity and culture fluid surface tension as an indicator for the production of any surface-active compounds.

One major goal of this research is to attempt to change those interfacial properties by changing the growth environment of the culture. This new environment may stress the culture, and in turn the culture may produce biosurfactants that will change its interfacial properties. Contact angles of the two solvents (water and diiodomethane) on microbial lawns of the Cornell culture varied slightly with media ionic strength. Statistical analysis, however, revealed that these changes were not significant. The culture was

Figure 2: Effect of Ammonia Concentration on Cornell Culture Contact Angle (Ionic Strength: 0.02; error bars: standard deviation of 10 replicate measurements)

incubated at a constant ionic strength for 7 days and then 20 mL were filtered to form a microbial lawn on that filter. A second set of experiments investigated the effect of high ammonium chloride concentrations at an ionic strength of 0.02 on organisms surface properties. Results from this preliminary experiment suggest that water contact angles seemed similar for nitrogen amended and at both incubation times, however, contact angles of diiodomethane declined with increased nitrogen concentration relative to the dead control (Figure 2). Microscopic analysis of the filter revealed the presence of iron sulfide particulates (larger than 5 μm in diameter) in the unfiltered media, which could be responsible for significant scatter in the contact angles. Following this observations contact angle measurements on microbial lawns have been pre-filtered through a 5 μm filter to remove any abiotic particulates.

Cell surface contact angle for *de. chloroethinica* changed slightly as a function of growth conditions. When incubated for 7 days in the presence of 2.5 g/L ammonium chloride the contact angle of diiodomethane – a hydrophobic solvent -on the filtered culture reduced to 31 degree (compare to 45 for the control), indicating that the cell surface became more hydrophobic. Smaller changes were observed for EDTA and sodium lactate amended culture (39 and 38 degree respectively). Note that the iron precipitates problems did not interfere with these observations.

Initial variables investigated for the butyrate fermenting culture (Cornell culture) were ionic strength ($I = 0.2$ to 0.01) and the ammonia concentration in the growth media. Surface tension of unfiltered culture media under all growth conditions was slightly lower than filtered culture fluid at all growth conditions (60 vs. 68 dyn/cm). Since a similar trend was observed in the killed control microcosms, the change in surface tension could also be linked to the presence of iron sulfide precipitates present in the growth media.

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.

Quartz surfaces remained water wetting under all concentration and pH conditions tested. This suggests that the TBP and DBBP remain neutrally charged over the pHs tested. Additional tests with goethite-coated sands will provide an assessment of potential wetting conditions for mineral surfaces that have very different surface charge characteristics. Wettability experiments will also be conducted with sand and clay samples collected from SRS.

Assess net significance on NAPL migration and entrapment

Micromodel Experiments

Fingering is caused when immiscible fluids search for the least restrictive path when traveling through the subsurface. It is believed that the dynamics of these fingers will have a profound impact on the quantity of trapped fluids in the subsurface. Using two-dimensional glass bead micromodels, we are assessing the effects of various physical and chemical parameters that influence the pore scale flow phenomena. Such parameters will include surface and interfacial tension (IFT), wettability, and viscosity. The effects are observed visually and image analysis software will be used to quantify the observations. The project began with two-phase air/water systems, followed by two-phase NAPL/water systems, and will ultimately include three phase Air/Water/NAPL systems.

The experimental setup consists of a horizontally mounted glass bead micromodel on an under lit microscope base. Suction head is applied with the use of a 1ml x10 burette horizontally mounted on a jack stand. A SONY color video camera is mounted on an Olympus SZX12 microscope. An analog image is captured and converted to a digital signal that is then sent to the computer. Epix software is used for the image capture and Scion Image is used for image analysis. Micromodels are constructed using 0.5mm glass beads that are sandwiched between 2 pieces of 1/8" glass. The area occupied by the glass beads is approximately 5cm X 6 cm. Teflon and Stainless steel strips are used to confine the glass beads as well as act as capillary barriers.

The initial air-water systems studied are comprised of fluids with varying surface tensions. The different surface tensions are accomplished by using de-aired/de-ionized water (DDI), 10% ethanol, and 50 % ethanol in water mixtures as the model fluids. Organic dyes were added to the aqueous phases to facilitate image analysis. The surface tensions of the dyed fluids were 68, 52, and 38 dynes per cm respectively.

OBSERVATIONS:

The right picture below (Figure 3) illustrates the initial entry of air into a DDI system. The finger is readily developed and advancing into the model. The left picture demonstrates a very uniform air entry in a 50% ethanol system. These results are consistent with expectations because of the lower surface tension and, therefore, reduced influence of capillary forces in the system containing ethanol.

Figure 3: Fingering patterns with DDI water (right) and 50% ethanol (left). Looking at a larger scale (Figure 4), it is apparent that fingering is more extensive in the DDI model. The ethanol model drained more completely. The “Active Front” of the DDI model is more dispersed along the direction of flow (left to right). The drainage of the ethanol model is more direct. The capillary barrier failed in the example presented in these photos. Recent advances in the design of the micromodels have greatly reduced the experimental artifacts associated with these capillary end effects.

(a)

(b)

Figure 4:

Final distribution of fluids (aqueous phase is dark) in DDI (a) and 50% ethanol (b) systems

QUANTITATIVE RESULTS:

The data presented in Figure 5 is a collection defines characteristics of the fingers illustrated in Figure 4. Measurements were normalized with respect to the water system to allow a comparison of both systems. These characteristics suggest that:

- The liquid/air interface was shorter in the systems with a lower surface tension. This was apparent in the meandering nature of the water system fingers.
- The Ethanol/Water system yielded longer lengths along the direction of drainage. This indicates that the fingers follow a more direct path to the drainage point when compared to that of the DDI of which the fingers meander towards the drainage point.
- The Ethanol/Water system was comprised of shorter finger lengths and wider fingers. The overall finger area is comparable between the two systems

Figure 5: Measured finger characteristics (red- 50% ethanol, blue – DDI)

DISCUSSION

Changing the interfacial properties of the system influences the fingering phenomena and dynamics. With decreasing interfacial tension, we observed an increase in the drainage efficiency of the different systems. The finger area does not seem to be significant but rather the finger width and length, or the ratio between, appear to be the controlling factors in the model drainage.

The image analysis software has provided a means to accurately quantify the observed finger parameters. It is felt that as more systems are examined, the relationships between finger parameters and overall drainage will become clearer. This understanding will ultimately allow for better fluid removal from the models.

CONTINUING WORK:

Research will continue using the water and ethanol/water models. The reproducibility of the measurements and model construction will be considered. Once results from the surface tension experiments are completed, variable wettability and NAPL/water systems will be introduced to the models.

Capillary Pressure – Relative Permeability Constitutive Relationships

BACKGROUND AND OBJECTIVE

Constitutive relationships between relative permeability, capillary pressure, and saturation (k-S-P) are necessary for mathematically quantifying the migration of DNAPLs in the subsurface. In this research, we will be measuring k-S-P relationships for a wide range of interfacial properties to define the range of parameter values that we could expect in the subsurface. However, prior to completing this analysis, we need confidence that the multi-step outflow experiments and inverse modeling will work well for the porous media and fluid systems of interest. Problems finding a unique set of parameters for k-S-P constitutive relationships commonly occur using these techniques. It is known that sandy soils have greater uniqueness problem than other soils (Inoue et al., 1998), but the effect of different k-S-P functions

or variability in the surface tension on the uniqueness problem is not understood. The objective of research conducted over the past year was to examine the influence of surface tension on the performance of different k-S-P functions to ensure that we can provide unique parameter estimates using multi-step outflow technique in sandy soils.

RESEARCH APPROACH

A numerical investigation was initially employed to determine which k-S-P function is best for sandy soil. We selected six k-S-P functions including the van Genuchten-Mualem (VGM), van Genuchten-Burdine (VGB), Brooks and Corey-Mualem (BCM), Brooks and Corey-Burdine (BCB), Lognormal Distribution-Mualem (LDM), and Gardner-Mualem (GDM) functions. Multistep outflow data were initially generated numerically for a typical sandy soil to assess the ability of these functions to uniquely and accurately predict known parameter values.

Additional k-S-P data were generated experimentally to verify that the selected function uniquely estimate k-S-P parameter values as a function of surface tension. Three aqueous phases with a range of surface tensions were generated by the addition of ethanol to water as described for the micromodel experiments.

The one-dimensional, two-fluid flow model TF-OPT of Hopmans et al. (1998) was used for both numerically generating k-S-P data sets and inverse modeling to estimate parameter values.

RESULTS AND DISCUSSION

The best function for sandy soils was determined based on results of the numerically generated data. Functions were compared by their ability to fit the data, accuracy, and reliability. It was previously determined that the best model fits for all 6 k-S-P functions required the use of three flow variables (cumulative outflow (Q), capillary pressure head (h), and initial water content). The VGM, LDM, and GDM had lower root mean square (RMS) values than VGB, BCM, and BCB. The BCM and VGB functions did not converge for some initial estimates. The LDM function was defined as best based on the RMS criterion. Normalized values very close to one showed that the LDM function resulted in correct solutions. The coefficient of variation for each parameter was used to understand the reliability of the function in determining the correct solution. The LDM again was the most stable one among the functions investigated. Therefore, among the k-S-P functions, the LDM performed best and had unique solutions for a sandy soil. This function has two fitting parameters, $\mathbf{s}$ and h_m , where $\mathbf{s}$ is related to the pore size distribution and h_m related to the bubbling pressure. Its functional form is defined as:

$$S_e = F_n[\ln(h_m / h) / \mathbf{s}] \quad F_n(x) = \frac{1}{2} \operatorname{erfc}\left(\frac{x}{\sqrt{2}}\right)$$

$$k_{rn} = (1 - S_e)^l \left\{ 1 - F_n \left[F_n^{-1}(S_e) + \mathbf{s} \right] \right\}^2$$

$$k_{rw} = S_e^l \left\{ F_n \left[F_n^{-1}(S_e) + \mathbf{s} \right] \right\}^2$$

Based on the above numerical investigation, we used the LDM function as the most appropriate for our experimental investigation. Low RMS indicates LDM performed well for our experimental data for all surface tensions considered (Table 1). Overall, the optimized simulations showed an excellent match with the corresponding measurements, indicating that the optimized parameters captured the main features of

the measured flow data (Fig. 6). As expected, lower surface tension of aqueous phase correlated to reduction in fitted h_m values (Table 1, Fig 7). The use of this model does not predict any differences in the relative permeability curve as a function of surface tension. This unexpected result is currently being examined further.

Table 1. LDM Fitted Parameters

	% Ethanol		
	0	10	50
h_m (cm)	32.5226	26.8216	18.1083
σ	0.3173	0.3066	0.2915
$\Theta_{a,r}$	0.0131	0.0190	0.0190
k (cm ²)	1.44E-08	1.74E-08	6.09E-09
RMS	0.552	0.506	0.744

Figure 6: Comparison of the observed and optimized h_c and Q values of a sand

Figure 7: Optimized k-S-P functions corresponding to the parameters listed in Table 1: (a) individual capillary pressure function, (b) relative permeability function

CONCLUSIONS

Of the 6 k-S-P functions considered in the numerical investigation, the LDM function performed best and had unique solutions for a sandy soil. Using LDM function, we were able to estimate k-S-P relationships in sand as affected by variable surface tensions.

CONTINUING WORK

The analysis described above provides confidence that the experiments and analysis of multiphase outflow experiments provide unique, accurate, and reliable estimates for the parameters needed in the LDM model for k-S-P relationships. We are currently in the process of generating data sets for analysis of the net effects of interfacial properties on multiphase flow. Variables include: surface tension (A/W systems), DNAPL IFT, wettability, and bacterial presence. The data generated will then provide ranges of possible parameters for the LDM model that will be incorporated into a numerical model to assess multiphase flow at field-scale scenarios.

Fieldwork

In May 2001, additional field work was performed at SRS to obtain samples for laboratory experimentation and characterize the distribution of DNAPL as a function of the grain size heterogeneity in the vadose zone. Two soil borings at the A-14 outfall at SRS were drilled to a depth of 30 feet and sampled. A 1.5 inch diameter continuous core in an acetate sleeve was obtained using a small direct push

rig. Samples were obtained from a total of 45 locations in the 2 cores. Clarkson University personnel collected samples for microbiological analyses, while Savannah River Technology Center personnel collected complimentary samples for analysis of chemical and physical properties. This site was sampled last year for PCE/TCE NAPL contamination and for microbial activity.

Funding for the borings was provided through collaboration between two EMSP projects (this one and Dr. Bradford from the Department of Geology and Geophysics at the University of Wyoming). Dr. Bradford is currently an EMSP investigator to study the potential of ground penetrating radar (GPR) methods to locate NAPL contamination. For his project GPR scans were verified using actual field borings. Funding from his project was used for two borings, organic and moisture content analysis while funds from this project was used for microbial soil sampling and soil characterization. The location of the two borings was selected based on prior information on DNAPL contamination and to confirm prior measurements that correlated microbial counts with contaminant concentration.

Samples are being tested for both biotic and Abiotic characteristics. Bacterial counts in the soil have been determined using the Live/Dead BacLight Assay (Molecular Probes, Inc.). This method allows for the discrimination of viable and dead (membrane-compromised) organisms, which is a significant improvement over the prior used Acridine Orange Direct Count (AODC) method. A subset of soil samples will be analyzed using both the AODC and the Live/Dead BacLight methods to correlate prior sampling efforts to this spring's data set. Analyses of TCE and PCE concentrations have been completed and are currently being reviewed. They suggest that DNAPL was encountered at depths of about 23 feet in both soil borings. Soil moisture content analyses have also been completed. Sample preparation for inorganic chemical analyses, surface properties, mineralogical analyses, and textural analyses is underway. These analyses will be completed on bulk samples this fiscal year. Specific analyses include x-ray fluorescence analyses of Fe, Ti, and Mn, surface area measurements, and grain size distributions. More detailed analyses of the mineralogy and chemistry of selected samples will be completed next year (FY2002). Uncontaminated soil samples collected from this site will be used to characterize the wetting properties of soil-NAPL-systems and will be used in column experiments. These soils will be split with the EMSP research group at the University of Michigan where Dr. Linda Abriola and her colleagues will conduct related tests.

Planned activities.

A three-pronged approach is planned for the next year of this project. These concurrent activities include:

1. Continued analysis and interpretation of field results.
2. Identification of conditions that lead to alteration of interfacial properties and, therefore, capillary flow. Adhesion and interfacial tension will be used as preliminary screening properties. The techniques for these experiments are fully tested, allowing a wide range of experimental matrices now be tested.
3. Continued experimentation and significant analysis of the implications of altered interfacial properties on multiphase flow behavior in micro-models and capillary pressure-relative permeability columns.

Information Access.

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

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