Research Objective

Nearly all Department of Energy (DOE) facilities have landfills and buried waste areas. Of the various contaminants present at these sites, dense non-aqueous phase liquids (DNAPL) are particularly hard to locate and remove. There is an increasing need for external or non-invasive sensing techniques to locate DNAPLs in the subsurface and to track their spread and monitor their breakdown or removal by natural or engineered means.

G. Olhoeft and colleagues have published several reports based on laboratory studies indicating that strong electrical signatures are produced when organic solvents, notably toluene, PCE, and TCE, reside in clay-bearing soils. According to Olhoeft, these electrical signatures are apparently characteristic of and unique to the particular organic solvent involved. The experiments are performed by packing the contaminated soil in a sample holder and a 4-electrode complex electrical resistivity measurement is made, where two of the electrodes are used to impose a sinusoidal electric current and the remaining two electrodes are used to sense the response voltage of the specimen. The relative phase (or time delay) between the source and the response signals at low excitation frequencies is a particularly sensitive measure of electrochemical processes occurring within the specimen. This suggests the basis of an ideal new measurement technique for geophysical characterization of NAPL pollution. Despite the promising laboratory results, attempts to measure these effects in the field for characterizing polluted sites, including studies supported by DOE funding, seldom have been successful.

Encouraged by the aforementioned laboratory results we had proposed to bring the field measurement of complex resistivity as a means of pollution characterization from the conceptual stage to practice. For this purpose we intend to document the detectability of clay-organic interactions with geophysical measurements in the laboratory, develop further understanding of the underlying physical and chemical mechanisms, and then apply these observations to develop field techniques to monitor the remediation of organic pollutants.

Research Progress and Implications:

This was originally a 3-year project which had been extended by 9 months to allow completion of certain technical tasks delayed by changes in personnel. This report summarizes work performed during the final calendar year of this 3 year 9 month period and is not the final report.

- **New England Research** A primary task of this work is to determine the magnitude and robustness of the effects of organic solvent contamination on the complex resistivity properties of soils. Therefore, we first had to develop a measurement technique and carefully document its capabilities and reliability. We have independently designed and built a laboratory system, including a sample holder, electrodes, electronics, and data analysis software, for the measurement of the complex electrical resistivity properties of soil contaminated with organic solvents (Figure 1). This new system has a measurement bandwidth from <0.001Hz to about 10kHz. We typically use the 0.01-1000 Hz range.

  We have designed our sample holder system from thin-walled Teflon tubing which fits directly into an agricultural soil sampling auger, allowing natural samples to be collected and their electrical properties measured with minimal disturbance to the soil micro-structure.

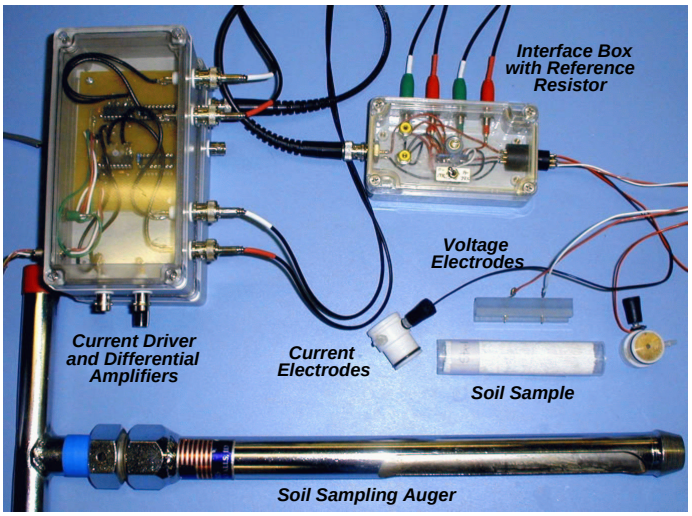

Figure 1: Bench-top soil resistivity apparatus.

The electrodes are 14k gold disks and wire (standard jewelry materials), and we have compared these to Ag-AgCl (dry), Cu-CuSO4 (wet), and Pt wire electrodes with good results. This sample holder is simple, robust, inexpensive, and the gold electrodes perform well. Additionally for comparison we have built a sample holder following Olhoeft's design, in which the sample is divided into 3 parts separated by through-going platinum screen voltage electrodes and with platinum screen current electrodes on the ends.

Using resistor and brine standards we have performed measurement accuracy, repeatability, and noise immunity tests of this system. At the present time we can resolve, with confidence, complex resistivity phase angle changes of about a milliradian over the entire frequency range. We find that under typical conditions in the laboratory the noise floor for this type of measurement is at the 1–2 milliradian level, requiring phase signals or anomalies to be larger than this to hold much significance in interpretations.

Our immediate task has been to reproduce some key complex resistivity effects quoted in the literature, such as membrane polarization due to clays and phase lag effects due to disseminated sulfides – both of which have been observed by a variety of other researchers and have physical models explaining them. Membrane polarization is an electrical effect resulting from clay particles partially blocking pore throats which gives rise to a phase lag similar to that discussed above. Other researchers have suggested that NAPL contamination interferes with the membrane polarization process. The purpose of our attempts to reproduce these key previous results is to lay a solid foundation documenting the performance of our measurement system, leading to a clear understanding of the true effects of organic solvent contamination. These more fundamental studies are important in looking for geophysical indicators of NAPL contamination.

With our equipment, we have successfully reproduced the well-known published results of Klein and Sill [1982] for the amplitude and phase response of glass-bead packs with specified volume fractions and grain diameters of iron pyrite. We have also reproduced exactly their experimental results for the phase and amplitude response of brine-saturated glass beads

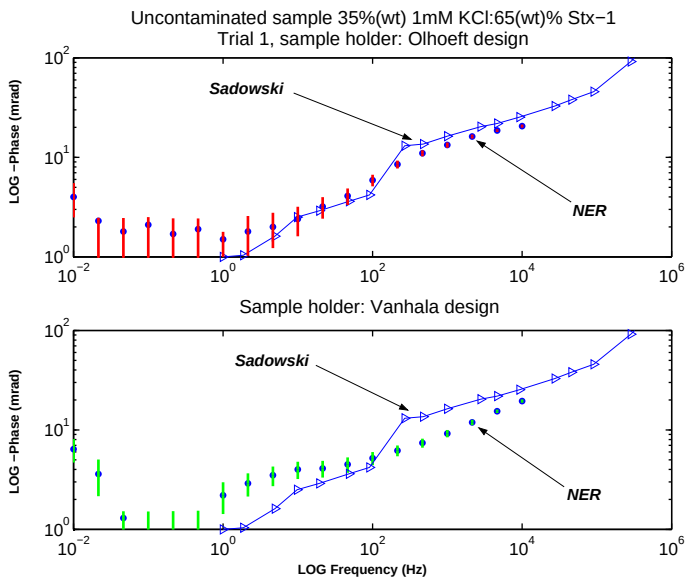

Figure 2: Comparison of results for uncontaminated sample of Stx-1 Ca-Montmorillonite Clay with KCl Brine.

mixed with calcium montmorillonite clay. We feel, therefore, that our equipment is working properly and that our methods are suitable for study of the effects of organic solvents on soil properties.

Using both sample holder and electrode designs, we have attempted numerous times to reproduce the results of Olhoeft and Sadowski [Sadowski, 1988] on the complex resistivity response of toluene-contaminated clay-rich samples. While we observe similar responses to theirs for plain clays with brine (Figure 2), the addition of toluene does not produce the effects they claimed (Figure 3). We can only produce effects of similar magnitude if we intentionally introduce a large artificial dielectric heterogeneity in the specimen (Figure 4). We are presently documenting our findings for eventual publication.

We have also performed further laboratory studies to test the sensitivity of the complex resistivity method to toluene and methanol contamination in sands, clays, and rocks, and we have performed standard 4-wire IP "field" inversion measurements in a two-dimensional laboratory "ant farm" to test the ability of this technique to image materials with both conductivity and dielectric heterogeneities.

- **Boston College**

  In previous work we developed a physiochemical model for the electrical impedance response of rocks and soils [Lesmes and Morgan, 2001]. We have tested this model using broadband electrical impedance experiments (10^{-3} Hz to 10^{6} Hz) on Berea sandstone made as a function of the pore solution composition, concentration, and pH [Lesmes and Frye, 2001]. We have used this model to successfully predict the hydraulic conductivity and capillary pressure curves for a suite of eight sandstone samples [Baker 2002; Lesmes 2003; Slater and Lesmes, 2002; Lesmes, 2003; Lesmes and Friedman, 2003]. Estimation of these hydraulic parameters is essential in order to predict the flow and transport of DNAPLs in the

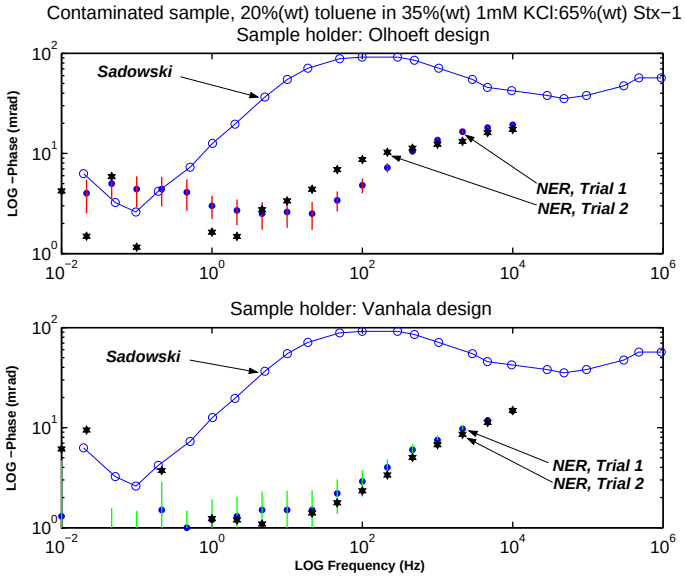

Figure 3: Comparison of results for toluene-contaminated sample of Stx-1 Ca-Montmorillonite Clay with KCl Brine.

subsurface. This model is now being used to interpret the DNAPL experiments that we have conducted on rock and soil samples.

We have also developed a simplified version of the model which is more practical for interpreting IP (Induced Polarization) field surveys. In the *Geophysics* paper by Slater and Lesmes [2002] we use this model to interpret field IP data collected along the coast. This paper shows how changes in the subsurface resistivity (at the freshwater-saltwater interface) can affect the apparent IP response. We argue that field IP parameters (chargeability, percent-frequency-effect, and phase) should be divided by the apparent resistivity to obtain normalized IP parameters, which are much more sensitive to the lithology (e.g. clay content) and surface chemistry (e.g. surface contaminants). We believe that the normalized IP parameters will be much more sensitive indicators of DNAPL contamination than the field (un-normalized) IP parameters. We are currently testing this hypothesis using the data from the DNAPL experiments that we have conducted in the laboratory.

David Lesmes is assisting Dr. Roelof Versteeg and two post-docs at the Idaho National Laboratory on their complex resistivity (IP) research project. The aim of this collaboration is to transfer the knowledge learned from this EMSP research project to the on-going complex resistivity research and site-characterization projects at INEEL. David Lesmes will spend July and August working with Dr Versteeg and his research group at INEEL. David Lesmes has also advised Dr Susan Hubbard at Lawrence Berkley Laboratory on the design of a laboratory complex resistivity system to characterize the biodegradation of organic contaminants. Lastly, David Lesmes is working with Lee Slater to model laboratory complex resistivity measurements made on partially saturated sediments. This research should facilitate the interpretation of the complex resistivity measurements made in the unsaturated zone. As many DNAPL contaminants are located in the vadose zone (e.g., Hanford) it will be important to understand the effects of varying water saturation on the IP response in order to properly

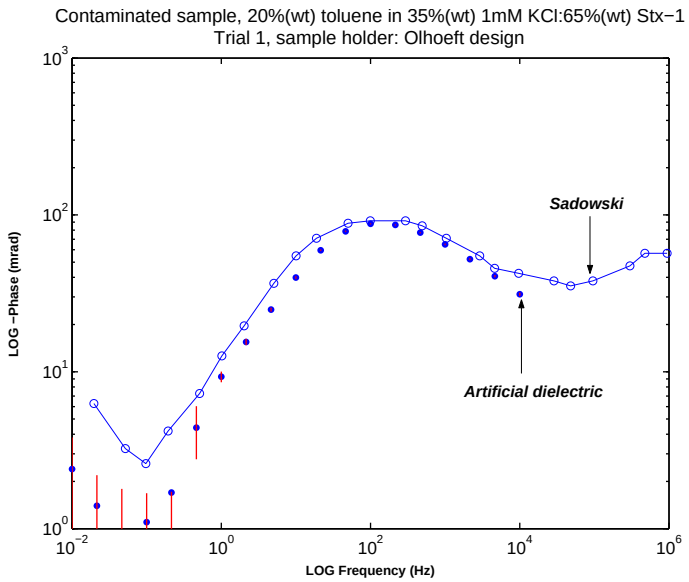

Figure 4: Comparison of results for toluene-contaminated sample of Stx-1 Ca-Montmorillonite Clay with KCl Brine using the Olhoeft sample holder and electrode design, with the introduction of an artificial dielectric in the sample (simply an sub-millimeter air gap at one of the voltage electrodes).

interpret IP surveys conducted in these environments.

Planned Activities

Final Documentation: Preparation of final report and preparation and submission of key papers for peer-reviewed journals. These reports will include documentation of our attempts to reproduce published results for toluene contamination, a catalog the baseline response of natural soil samples, results of studies of the response of heterogeneities in artificial soils, and results of studies of the limits of detectability of organic contaminants above the background response in soils.

Information Access

Papers:

- Brown, S. R., A laboratory study of the complex electrical resistivity response of soils, *in preparation*.
- Lesmes, D. P., and Friedman, S., The relationships between the electrical and hydrological properties of rocks and soils, chapter to be published in the following book: *Hydrogeophysics*, S. Hubbard and Y. Rubin, eds.
- Slater, L., and Lesmes, D. P., Electrical-hydraulic relationships observed for unconsolidated sediments, *Water Resour. Res.*, 38 , 1213, 2002..

- Slater, L., and Lesmes, D. P., IP interpretation in environmental investigations, *Geophysics*, 67, 77-88, 2002.

Presentations:

- Lesmes, D. P., Electrical-impedance spectroscopy of sedimentary rocks: Prediction of hydraulic conductivity and soil water retention curves, invited presentation, AGU-EGS-EUG joint meeting, Nice, France, 2003.
- Lesmes, D. P. Electrical Properties of Rocks and Soils: Prediction of Hydrological and Geochemical Properties, Lecture, NATO Advanced Study Institute Workshop on Hydrogeophysics, Charles University, Czech Republic, July 2002.
- Lesmes, D. P., Electrical-impedance spectroscopy of rocks and soils: Prediction of hydraulic and geochemical parameters, Geological Society of America Annual Meeting, Boston, November 5-8, 2001.
- Slater, L. D., Lesmes, D. P., and Glaser, D., Relationships between electrical, lithological, and hydraulic properties of sediments, AGU Fall Meeting, San Francisco, December 10-14, 2001.

Theses:

- Baker, Hana, *Prediction of Capillary Pressure Curves using Dielectric Spectra*, M.S. Thesis, Boston College, 2002.
- Sorenson, Jason, *Spectral IP Response of Organic Compounds in Synthetic and Natural Aggregates*, M.S. Thesis, Boston College, 2003, in preparation.