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. 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 phase (or time) lag 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, have been seldom successful.

Based on this promising previous work we have 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 report summarizes work after 1.5 years of a 3-year project. Progress over the last year for the two institutions is as follows:

- **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. To date we have independently designed and built a laboratory system (sample holder, electrodes, electronics, and data analysis software) for the measurement of the complex electrical resistivity properties of soil contaminated with organic solvents. 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 a 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 microstructure. The electrodes are 14k gold discs and wire (standard jewelry materials), and we have compared these
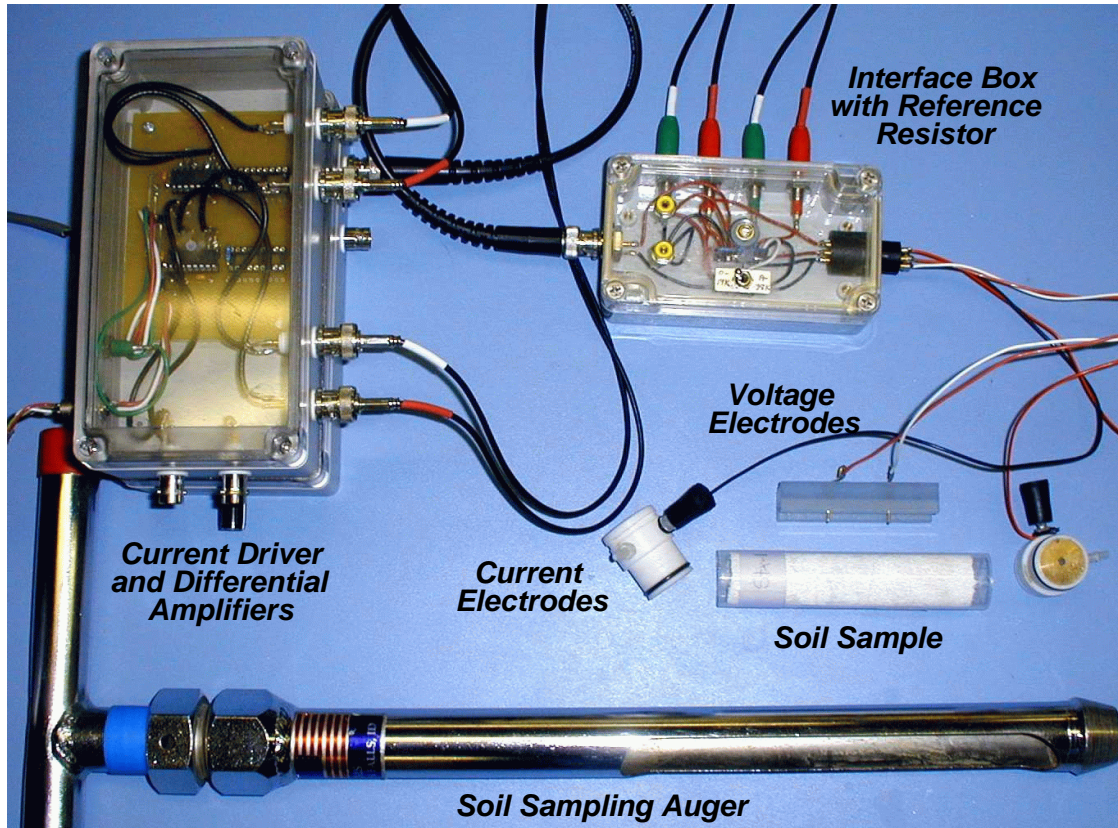
Figure 1: Bench-top soil resisitivity apparatus.

to Ag-AgCl (dry), Cu-CuSO4 (wet), and Pt wire with good results. This sample holder is simple, robust, cheap, and the gold electrodes perform well.

Using resistor and brine standards we have been performing 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.

For eventual testing and cataloging of natural variability, we have taken random samples from the South Burlington Vermont landfill cap, clayey soil near Sandia National Laboratories, New Mexico, clayey soil from the town of Los Alamos, New Mexico, and Columbia River river bank mud from Hanford, Washington.

For eventual field use, we are designing and constructing a portable battery-powered function generator and oscilloscope box with a single serial port interface based on a "bitscope" and "protopod" (www.bitscope.com). Once the electronics bread-boarding and serial port programming is finished and this system works with a Linux computer, we will explore the possibility of using a Palm Pilot as the acquisition/control computer.

Our immediate task now is 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.

- **Boston College** We have developed a unified model for the electrical impedance response of rocks and soils. We have used this model to successfully predict the hydraulic conductivity and capillary pressure curves for a suite of eight sandstone samples. Estimation of these hydraulic parameters is essential in order to predict the flow and transport of DNAPLs in the subsurface. We have also tested this model using broad-band 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. This model is formulated in terms of the physiochemical properties of the porous medium and it will be used to interpret the DNAPL experiments on rock and soil samples, which we are currently conducting.

Planned Activities

- **Remainder of FY 2001:** Laboratory parameter studies on idealized systems. Perform complex resistivity laboratory studies of baseline soil samples and samples contaminated by various organic solvents.

- **FY 2002:** Continue parameter studies and prepare a journal article containing the results of attempts and failures to reproduce work by previous workers. Work will continue toward understanding the electrical response of NAPL contaminated soils with the aim of assessing the feasibility of field measurements.

Information Access

- Lesmes, D. P., and Frye, F. K., 2001, The influence of pore fluid chemistry on the complex conductivity and induced polarization responses of Berea sandstone, *J. Geophys. Res.*, 106, 4079-4090.

- Lesmes, D. P., and Morgan, F. D., 2001, Dielectric spectroscopy of sedimentary rocks, *J. Geophys. Res.*, in press.

- Slater, L., and Lesmes, D. P., 2001, IP Interpretation in environmental investigations, *Geophysics*, in press.

- Slater, L., and Lesmes, D. P., Electrical-hydraulic relationships observed for unconsolidated sediments, *Water Resour. Res.*, submitted.