

FINAL REPORT
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Complex Electrical Resistivity
for Monitoring DNAPL Contamination

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Executive Summary

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 using the complex resistivity method which indicate that organic solvents, notably toluene, PCE, and TCE, residing in clay-bearing soils have distinctive electrical signatures. These results have suggested to many researchers the basis of an ideal new measurement technique for geophysical characterization of DNAPL pollution. Encouraged by these results we proposed to bring the field measurement of complex resistivity as a means of pollution characterization from the conceptual stage to practice. We planned to document the detectability of clay-organic solvent 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.

As with any new research endeavor we note the extreme importance of trying to reproduce the work of previous researchers to ensure that any effects observed are due to the physical phenomena occurring in the specimen and not due to the particular experimental apparatus or method used. To this end, we 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. The capabilities and reliability of this technique were documented. Using various standards we performed measurement accuracy,

repeatability, and noise immunity tests of this system and we were able to reproduce some key complex resistivity effects quoted in the literature.

We attempted numerous times to reproduce the seminal results of Olhoeft and Sadowski on the complex resistivity response of toluene-contaminated clay-rich samples. While we observe similar responses to theirs for plain clays with brine, the addition of toluene does not produce the effects they claimed. We can only produce effects of similar magnitude if we intentionally introduce a large artificial dielectric heterogeneity in the specimen.

We have also performed laboratory studies to test the sensitivity of the complex resistivity method to toluene and methanol contamination in sands, clays, and rocks. Additionally, we performed 4-wire IP 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.

This work indicates, at best, a low sensitivity of the complex electrical resistivity method to organic contamination in rocks and soils. This reduces the short-term prospects of using complex resistivity as an effective technique to directly detect organic contamination. However, as noise suppression techniques improve and further understanding of electrical responses in Earth materials is achieved, the potential of the complex resistivity technique should improve. In contrast, we find that certain electrically polarizing materials, some clays for example, have responses large enough compared to sandy and silty soils to be reliably imaged through a detailed field IP survey. Thus, quantifying soil heterogeneity (which may relate to DNAPL distribution and transport) is an immediate potential application of this technique.

1 Research Objectives

1.1 Introduction

The U.S. Department of Energy faces enormous environmental remediation and waste management problems resulting from decades of cold-war nuclear weapons development and production. More than 10,000 individual hazardous waste sites have been identified and need attention. The volume, extent, broad distribution, and complexity of the contaminated soils and groundwater resulting from past DOE activities pose formidable technical challenges. The costs associated with remediation of many of DOE's largest plumes of contaminated groundwater and sediments have not been determined, but estimates range from tens to hundreds of billions of dollars [*U.S. Department of Energy*, 1995].

Organic solvents, particularly chlorinated hydrocarbons such as perchloroethylene (PCE) and trichloroethene (TCE), make up an inordinately large fraction of DOE's soil and groundwater contamination [*Riley et al.*, 1992]. Indeed, much of the cleanup effort will focus specifically on chlorinated organics because they are important components of Dense Non-aqueous Phase Liquids (DNAPL), which are hard to locate and remove. Fuel hydrocarbons, many components of which are examples of Light Non-aqueous Phase Liquids (LNAPL), comprise another serious pollution problem at DOE sites. There is a need for external or non-invasive sensing techniques to locate these organic compounds in the subsurface and to track their spread and their breakdown or removal by natural or engineered means.

1.2 A Potential New Method of Characterization

In the past few decades, there have been some new findings on the electrical response of contaminated soil/water systems which suggest a new remote geophysical method to identify and delineate plumes of organic contaminants including the common components of DNAPL's and LNAPL's. This pioneering work has been performed primarily by G. Olhoeft and coworkers (specific references follow), wherein they have noticed that distinct signatures of certain pollutants can be identified when the electrical resistivity of a laboratory specimen is measured over a range of excitation frequencies. This type of measurement is referred to in this report as 'complex resistivity.'

The nature of the complex resistivity is controlled by various charge transfer and electrochemical mechanisms acting among the minerals, water, and pollutants present in the sample. When the imposed electrical disturbance coincides with the rate of certain chemical charge transfer mechanisms, the measured electrical response will be affected. Therefore, the resistivity measured as a function of excitation frequency contains a direct indication of certain active chemical processes. Of particular interest here is the dependence of complex resistivity on chemical reactions between clay minerals and many organic chemicals commonly involved in soil pollution. In recent years, G. Olhoeft and others have observed empirically that the complex resistivity measurement contains some distinct frequency-dependent features which depend on the pollutant type. In some cases a physical mechanism has been proposed for these effects. For example, *Olhoeft and King* [1991] surmised that a prominent complex resistivity effect observed when toluene was present along with montmorillonite was due to a polymerization process between the solvent and clay. Many other

organic pollutants also show complex resistivity effects, including PCE and TCE [e.g., *Olhoeft and Jones, 1996*].

At the time this project began, despite these promising revelations, complex resistivity had not become a viable field geophysical technique for the characterization of contaminated rocks or soils. There have been several formidable obstacles to overcome. The complex resistivity effects as documented in the literature were limited almost exclusively to laboratory studies with typically only limited examples of each case. Therefore, the repeatability and robustness of the measurements were not clear. With few exceptions, parameter studies were not reported describing the effects of changes in soil or rock type or varying water chemistry or fluid saturation levels. Questions arose as to the ability of a field measurement to discern the effects quoted in the preliminary work in the presence of natural and cultural noise levels.

1.3 Background and Survey of Previous Studies

1.3.1 Complex Resistivity

Electrical resistivity is measured by imposing an electric current I and measuring the resulting electric potential or voltage V . The excitation signal can be constant in time (known as direct current or DC) or alternating in time (known as alternating current or AC). During a DC measurement, the resistance R is defined by Ohm's law as the ratio of the voltage to the current, i.e. $R = V/I$. A parameter known as the *resistivity* is a material property derived from the measured resistance by applying a sample geometry correction. For an AC measurement, the capacitance properties of the medium manifest themselves in addition to the pure resistance. In this case Ohm's law has been generalized to allow for the resulting frequency-dependent effects, and the ratio of the voltage to the current, $Z = V/I$, is known as the impedance rather than the resistance. However, the term resistivity is often used for both DC and AC measurements.

During an AC electrical resistivity measurement of soil or rock we find that at any given frequency of excitation the measured voltage incurs a phase lag in time relative to the excitation current (Figure 1). To describe this effect, the output voltage can be expressed as the vector sum of both *in-phase* (*real*) and *out-of-phase* (*quadrature* or *imaginary*) components. Therefore, the electrical impedance Z of the medium can be expressed as a complex number where both the magnitude and phase lag of the voltage relative to the input current depend on the specific electrical properties of the sample. This is the origin of the term *complex resistivity*.

We often find that the resistivity and the amount of phase lag in the measured voltage signal is a function of the excitation frequency. In fact, in gross terms, the measured resistivity of rocks and soils is found to decrease as the excitation frequency is increased from zero. Under these conditions the soil acts as a capacitor, in that it inhibits the passage of direct currents, but passes alternating currents with increased efficiency at the higher frequencies. Under closer inspection, however, one often finds that there are many smaller-scale frequency-dependent effects in the resistivity.

Measurements of the variation of resistivity with frequency have been performed for many years in exploration geophysics (particularly in the exploration for low-grade ore deposits such as disseminated sulfides) and are widely known under the name *induced polarization* or *IP*. Descriptions of IP including the many underlying mechanisms and examples of its applications are given in several places [e.g., *Marshall and Madden, 1959; Bodmer et al., 1968; Wong, 1979; Klein et al., 1984;*

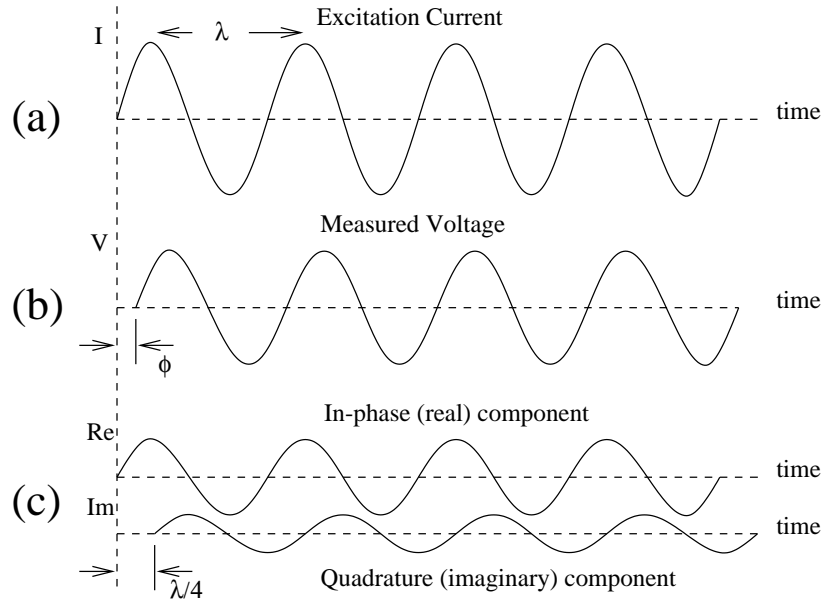


Figure 1: Complex resistivity definitions. (a) A sinusoidal electric current I of period λ is imposed on a medium and (b) the resulting voltage V is measured. The measured voltage is characterized by a phase lag in time ϕ relative to the excitation current. (c) The voltage signal is expressed as the vector sum of both in-phase (real, R_e) and quadrature (imaginary, I_m) components. The magnitude of the measured voltage is $|V| = \sqrt{R_e^2 + I_m^2}$ and the phase angle is $\phi = 2\pi/\lambda \cdot \arctan(I_m/R_e)$. The in-phase component is aligned in time with the excitation current signal and the quadrature component lags behind by a quarter of a wavelength. The ratio of the voltage V to the current I comprise the complex electrical impedance of the medium, where both its magnitude Z and the phase lag ϕ depend on the specific electrical properties of the sample.

Ward, 1990; Keary and Brooks, 1991]. In this report, we use the terms IP and complex resistivity interchangeably.

As mentioned, several mechanisms are responsible for the frequency dependent complex resistivity. Olhoeft [1985] has cataloged the various low-frequency electrochemical and electrode effects. One such mechanism, known as *membrane polarization* or *electrolytic polarization* is particularly important to this proposal because of its sensitivity to reactions among clay minerals and organic contaminants [e.g., Ward, 1990; Keary and Brooks, 1991].

The passage of electric current through a rock or soil is accomplished mainly by motion of ions in the pore fluid under the imposed electric field. The surfaces of rock-forming minerals characteristically have an unbalanced electric charge (often negative). Ions in the pore fluid are attracted to the exposed mineral grain surfaces to balance this excess surface charge. The presence of these ions produces a highly viscous low-mobility layer in the fluid immediately adjacent to the pore.

Both fluid flow and electrical conductivity in porous materials are controlled by the distribution of open connected pathways within the pore structure. Porosity in rocks and soils is often envisioned as a complex network of large *pores* and narrow *throats*. The net fluid permeability and the electrical conductivity is controlled to a large extent by the constrictions in the pore structure, i.e.

the throats [e.g., *Koplik*, 1984].

In the throats, where the pore walls are close together, the ionic surface layer can become an impediment to the motion of other ions acting under the influence of an electric field. DC and low-frequency AC electrical resistivity measurements require long-distance motion of ions, whereas higher-frequency AC measurements only force the ions to move back and forth a small amount. The distance over which the charges move is a decreasing function of the excitation frequency. The observed decrease in resistivity with excitation frequency results from the inability of ions to move freely through the electrical obstruction formed by the double layer inside the small pores. In narrow throats, the thick double layer will be comprised largely of, say, cations which can move through the throat under modest force, but this region of positive charge will at the same time repel anions and impede their motion [e.g. *Ward*, 1990; *Keary and Brooks*, 1991]. In this sense the throat acts as an ion-selective membrane, thus the terminology *membrane polarization*.

Membrane polarization will have a pronounced effect in the presence of clays, presumably because of both the small throats and the strong tendency of clays to form an associated double layer as compared to many minerals. However, membrane polarization tends to be less prevalent when the pore fluid has high salinity. Likewise, any chemical property (such as pH) or chemical reaction (affected by an electric field) which can change the properties or thickness of the double layer will likely affect the complex resistivity.

1.3.2 Resistivity and Clay-Organic Solvent Interactions

At high excitation frequencies, the electrical properties are thought to be controlled by physical interactions [*Olhoeft*, 1985]. A sample composed of a mixture of two materials with different (frequency-independent) electrical properties will have frequency-dependent electrical properties from the Maxwell-Wagner effect. This effect arises at the interfaces and discontinuities between the two components, where charges pile up and diffuse away slowly during electric field changes. The finite diffusion time of electric charge results in a frequency dependence.

At low frequencies (< 1000 Hz), however, the frequency-dependent effects are dominated by water-rock chemical reactions [*Olhoeft*, 1985]. The occurrence of these effects at low frequencies is of practical significance, since most geophysical field instruments for ground conductivity operate at these low frequencies due to the larger depth of penetration from the earth's surface. G. Olhoeft and colleagues [e.g., *Olhoeft*, 1985, 1986; *Olhoeft and King*, 1991] have cataloged many of these effects and show that oxidation-reduction reactions, ion-exchange reactions, and clay-organic solvent interaction can be distinguished from one another and from the properties of chemically inert rocks. However, in many cases the exact electrochemical mechanisms responsible for the signals are unknown. An essential element in our research proposal was based on the notion extended by Olhoeft that organic pollutants tend to interact chemically with clay minerals or at least shield them from the rest of the pore fluid, resulting in marked effects on the complex resistivity.

Olhoeft and King [1991] give an illustrative example of the ability of complex resistivity to identify and track the extent of pollution by organic compounds. Figure 2, modified from *Olhoeft and King* [1991] shows complex resistivity measurements of uncontaminated soil as compared to the same soil contaminated with various organic compounds, including petrochemical wastes and oil-field brines. The samples come from two separate wells at the waste disposal facility in

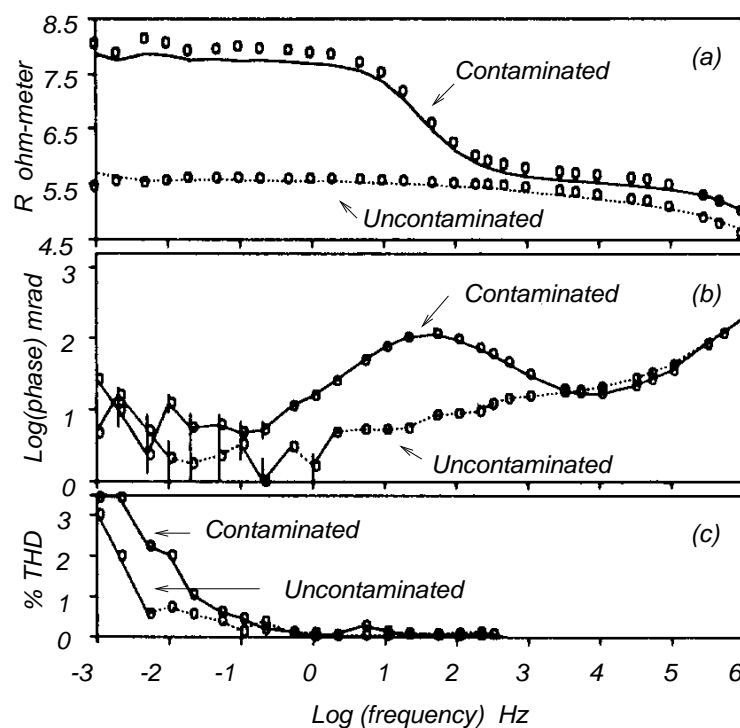


Figure 2: Complex resistivity laboratory measurements for core samples the waste disposal facility in Willow Springs, Calcasieu Parrish, Louisiana (modified from Figure 1 of *Olhoeft and King* [1991]). Shown are measurements, from two separate wells, of uncontaminated soil as compared to the same soil contaminated with various organic compounds, including petrochemical wastes and oil-field brines. (a) Magnitude of the resistivity as a function of excitation frequency. The magnitude of the Hilbert distortion is 2.35% for the contaminated sample and 1.23% for the uncontaminated sample. (b) Phase angle of the complex resistivity as a function of frequency. The magnitude of the Hilbert distortion is 0.77 milliradians for the contaminated sample and 0.14 milliradians for the uncontaminated sample. (c) Total harmonic distortion as a function of frequency. Note the large anomaly in phase angle for the contaminated sample centered around a frequency of 200 Hz, indicating a strongly chemically-reacting mixture.

Willow Springs, Calcasieu Parrish, Louisiana. The uncontaminated sample shows relatively little frequency dependence in both magnitude and phase and relatively small total harmonic distortion (THD) and Hilbert nonlinearity (HD) (terms borrowed from the fields of audio amplifier design and the analysis of vibrations), presumably indicating limited chemical activity resulting in frequency dependence. The contaminated sample shows large frequency dependence, THD, and HD. There is a large anomaly in phase angle for the contaminated sample centered around a frequency of 200 Hz, indicating a strongly chemically-reacting mixture. Later laboratory measurements, where contaminants were added to samples with clays, along with supporting clay surface chemistry literature suggested to Olhoeft that this anomaly was due to the polymerization of toluene to bibenzyl in the Lewis Acid environment on the surface of montmorillonite.

1.4 Promises and Problems

The apparent success of the complex resistivity method at identifying organic pollutants in the lab as shown in Figure 2 is quite impressive, and leads us naturally to search for further understanding and new applications for environmental remediation. However, the state of knowledge of this phenomenon is not yet sufficient to allow reliable application to field problems.

On one hand, Olhoeft has found distinctive complex resistivity ‘signatures’ in the laboratory for many organic pollutants in clay-bearing samples. However, *Börner et al.* [1993] performed similar experiments involving a different range of organic pollutants. They found that while the presence of contaminants could be detected, the effects were much more subtle. A range of contaminants in a single clay-rich sample mixture tended to result in only simple level shifts or slope changes in the real and imaginary parts of the resistivity.

There have been a few attempts to apply complex resistivity to discern contaminants in the field. *Olhoeft and King* [1991] were able to use the general observation of frequency-dependent conductivity to find an organic plume in the field which could not be detected through conventional interpretation of field data. They measured the ground conductivity at two different frequencies (10 and 0.01 Hz) on the Earth’s surface at a contaminated site and produced a spatial contour map of the difference in phase of these two measurements. A distinct plume was apparent in this map, which was assumed to be due to toluene contamination based on lab experiments in similar materials. This plume did not appear in a standard electrical conductivity survey.

Encouraged by this result *Daily and Ramirez* [1996] [also see *Ramirez et al.*, 1996] tried to produce images of pollution location by combining electrical resistance tomography and complex resistivity. By differencing the tomograms taken at only two fixed frequencies (1 Hz and 64 Hz), they had only limited success at producing meaningful images of a controlled release of PCE. While there were detectable signals, they were barely observable above the measurement uncertainty.

Vanhala et al. [1992], *Vanhala and Soininen* [1995], and *Vanhala* [1997] measured the complex resistivity in both the laboratory and field in an attempt to map oil contamination. They found measurable differences between contaminated and uncontaminated experiments in both the lab and field. However, laboratory and field results on the same materials were similar in only a qualitative sense. There was a profound time dependence of the signals in polluted samples, whereas measurements in uncontaminated samples were stable. They went so far as to suggest that time dependence alone could be an indicator of pollution.

These promises and problems lead us to propose further work on this effect. We proposed to obtain better descriptions of the complex resistivity signatures due to various contaminants and develop guidelines for recognizing them and to provide an evaluation of the robustness of these effects in light of other soil, rock, and groundwater variables. We felt that the magnitude of these effects relative to the typical noise in field environments must be known and appropriate measures must be taken to enhance the signal strength and lower the uncertainty during interpretation.

2 Methods and Results

2.1 Technical Objectives

Using these promising initial studies as a starting point, we proposed to: (1) document the detectability of clay-organic solvent interactions with geophysical measurements in the laboratory, (2) develop further understanding of the underlying physical and chemical mechanisms, and then (3) apply these observations to develop field techniques to monitor the remediation of organic pollutants. To accomplish these goals, we proposed the following tasks for the research project:

- Perform focused laboratory studies to identify complex resistivity signatures of the 2 or 3 most important components of DNAPL's.
- In the context of this method, evaluate the signal and noise levels in the field.
- Identify distinguishing characteristics of complex resistivity contaminant signatures and develop algorithms to identify them.
- Perform parameter studies of complex resistivity signature changes among natural rocks, soils, fluid chemistry, and saturation levels.
- Evaluate the ability of standard electrical geophysics field equipment to measure these effects. If standard equipment is unsuitable, develop prototype frequency-sweeping portable equipment with modern phase lock-in electronics to give field measurements the noise immunity required to reliably discern the low-level signals.
- Develop a broad-band pulse method for rapid data acquisition and scoping measurements (similar to a standard time domain IP signal with new interpretation).
- Develop measurement techniques and software for complex resistivity imaging from arrays of surface electrodes.

2.2 New England Research Technical Activities

2.2.1 Reproducing Previous Results

As with any new research endeavor we note the extreme importance of trying to reproduce the work of previous researchers, both as a check on our measurement techniques and as a check on those preceding us (note the illuminating discussion of this topic by Richard Feynman in the 1974 Caltech Commencement Address, published under the name *Cargo Cult Science* [Hutchings, 1997]). We need to ensure that the effects we see are due to the physical phenomena occurring in the specimen and not due to the particular experimental apparatus or method we are using. In this vein we will now describe the evolution of our measurement equipment, techniques, and results in some detail.

Early Qualitative Results At the beginning of this project we had available at our laboratory a system for measuring the complex resistivity of rock samples under high confining and fluid pressures. This system relied upon an industry standard electrical impedance analyzer designed for electrical engineering and electronic component testing purposes. Aside from upgrading the frequency response of the preamplifiers, we felt that primarily what was necessary for this project was to design a sample holder for soils and other granular materials rather than rock core. As a first step, we built a sample holder similar to the design used by G. Olhoeft and colleagues [Olhoeft, 1979a] for their bench-top work on rock core samples under room temperature and pressure conditions. This particular apparatus separates the brine-saturated specimen from both the current and voltage electrodes by a chamber filled with pure liquid brine. This apparatus was only modified from the original design by adding a means to contain the loose granular specimen inside the apparatus. We tested the background behavior of the apparatus by substituting the various electrolyte solutions for the soil sample with good results.

Upon completing the preliminary tests we then prepared the same brine saturated montmorillonite clay soil mixtures described by Olhoeft and Sadowski [Sadowski, 1988], both with and without toluene contamination. Upon measurement of these specimens we found that although we could reproduce the same background signal as they did for uncontaminated clay, the toluene contaminated sample was for all practical purposes indistinguishable from the uncontaminated one with regard to the phase lag. In contrast, Olhoeft and Sadowski found a large phase lag ‘bump’ at low frequencies for the contaminated sample relative to the uncontaminated baseline sample. We noted one serious problem in our experiments, however. As the sample sat in the brine, the clay swelled and the ends of the specimen itself moved closer and closer to the sensing electrodes. Measurements made during this time showed this effect dramatically. Upon further investigation, we found that all clayey soils with or without toluene showed nearly identical effects in this regard. Further variants on this test lead to the conclusion that simply an interface between brine and clay has its own electrical properties and can thus severely affect the phase lag measurement with or without the presence of an organic solvent.

To be fair, we did not use the exact apparatus for soils specified by Olhoeft and Sadowski. Therefore, we then took care to reproduce their soil resistivity apparatus, which differs from the one described earlier in that the electrodes are within the sample itself, forming a sandwich with no liquid brine chambers involved. The electrodes they used were made of fine-mesh platinum screens the same diameter as the cylindrical sample holder and soil specimen. We found through calibration tests that for the voltage sensing electrodes, both platinum screens and a single strand of platinum wire served the purpose equally well. We chose to use single wires since the screens were difficult to clean. Again we prepared the standard mixtures of plain clayey soil and clayey soil contaminated with toluene. Again we were able to reproduce the uncontaminated soil background signal, and yet again the toluene contaminated sample was the same, lacking the strong phase lag anomaly quoted in the literature.

However, we noticed that during preparation and disassembly of the samples, the toluene tended to separate from the clay, easily squeeze out of the sample, and collect on the ends. We speculate that had we used platinum screens within the sample, then free toluene would tend to fill in around the sensing electrodes themselves. Toluene is not a particularly good conductor of electricity, which means that the disc-shaped film of toluene formed at the sensing electrodes is essentially a thin electrically-insulating layer. Since the wire screen sensing electrodes completely cut across

the sample, a leaky capacitor could be formed at the electrode itself, which would have easily produced the measured phase lag. We checked this hypothesis several times over by inserting an oil- or toluene-saturated filter paper near one of the sensing electrodes in plain clay samples, and in glass bead packings with only a few percent clay. The measured phase lag was remarkably similar both in magnitude and at the same frequency to the published results attributed to toluene contamination. A filter paper saturated with brine could not be seen. Again we suggest that an interface between contrasting properties is a key element to the observed phase lag behavior.

Repeatability Studies Given this sorted history, our immediate new task was to take a step back from trying to reproduce Olhoeft's results. We intended through more careful work 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 and to provide the necessary evidence and documentation for refuting some of the previous results we had not been able to reproduce. Our most recent work on repeatability is documented in detail in Jason Sorenson's M.S. Thesis from Boston College [Sorenson, 2003].

We first proceeded to develop a new complex resistivity measurement system and carefully document its capabilities and reliability. This system includes sample holders, electrodes, electronics, and data analysis software. The system has a measurement bandwidth from <0.001 Hz to about 10 kHz, however we have typically used the 0.01–1000 Hz range (see Figure 3).

Photographs and corresponding sketches of the two types of sample holders that were employed in this study are shown in Figure 4. We designed our primary 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. This design is modeled after one used by Vanhala and others [Vanhala *et al.*, 1992; Vanhala and Soininen, 1995; Vanhala, 1997]. Heavy gauge 14k gold (Au) wire functioned as potential electrodes by superficially penetrating the axial surface of the sample through holes in the Teflon tube. Current electrodes are 14k gold discs (22.225 mm in diameter) mounted to Delrin end plugs. We have compared these gold electrodes to Ag-AgCl (dry), Cu-CuSO₄ (wet), and platinum (Pt) wire electrodes with good results. This sample holder is simple, robust, inexpensive, and the gold electrodes perform well. The integrity of the sample is maintained while inserting the electrodes and performing the experiment.

Additionally, for comparison purposes, we built a sample holder following Olhoeft and colleagues' design [Olhoeft, 1979a, b, 1985; Sadowski, 1988; Jones, 1997], in which the sample is divided into 3 parts, each encased in Teflon cylinders, separated by through-going platinum screen voltage electrodes (22.31 mm in diameter) and with platinum screen current electrodes on the ends (Figure 4).

Both the Vanhala and Olhoeft style sample holders have a potential electrode spacing of 25.4 mm as well as end caps/plugs equipped with ports and tapered nozzles that allow fluid to be injected into the sample chamber.

Using resistor and brine standards we performed measurement accuracy, repeatability, and noise immunity tests of this system. We found that we could resolve, with confidence, complex resistivity phase angle changes of about a milliradian over the entire frequency range. Under typical conditions in the laboratory the noise floor for this type of measurement is at the 1–2 milliradian

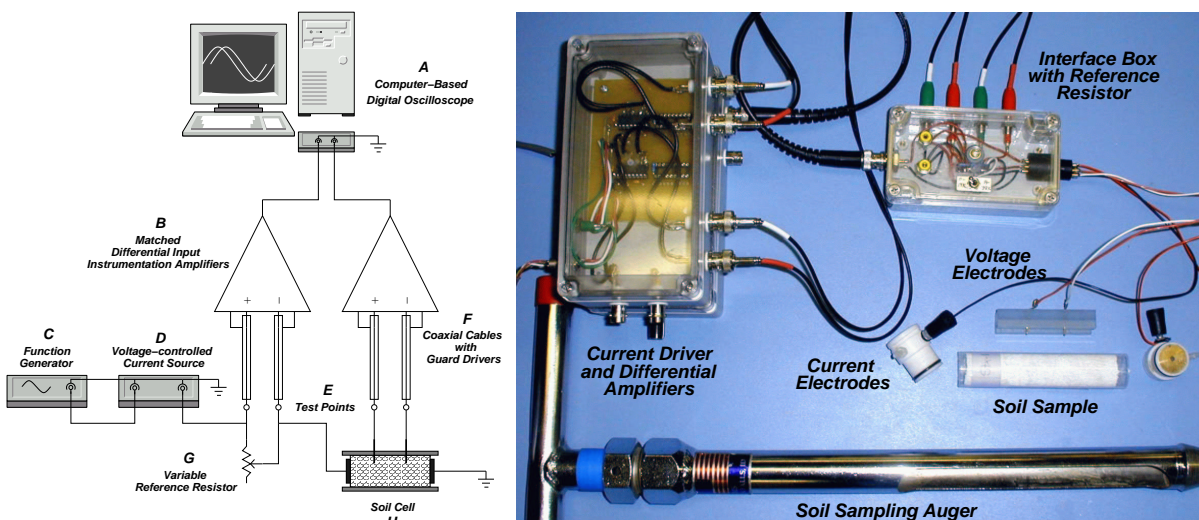


Figure 3: The laboratory apparatus which includes a sample holder, electrodes, electronics, and data analysis software. **Left:** Under computer control, a function generator provides a sinusoidal voltage to a voltage-controlled current source. The resulting sinusoidal current is fed through a reference resistor and the sample wired in series. The voltage drops across the reference resistor and the sample are monitored by the computer and used to compute the complex resistivity of the sample. **Right:** Photograph of measurement system. A thin-walled Teflon sample holder 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.

level, requiring phase signals or anomalies to be larger than this to hold much significance in interpretations (see Figure 5 for results of an error study on this type of measurement).

Our first task was 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 DNAPL 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 DNAPL contamination.

With our equipment, we were able to reproduce successfully 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 (Figure 6). We have also reproduced key features of their experimental results for the phase and amplitude response of brine-saturated glass beads mixed with calcium montmorillonite clay (Figure 7). 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 then attempted numerous times to repro-

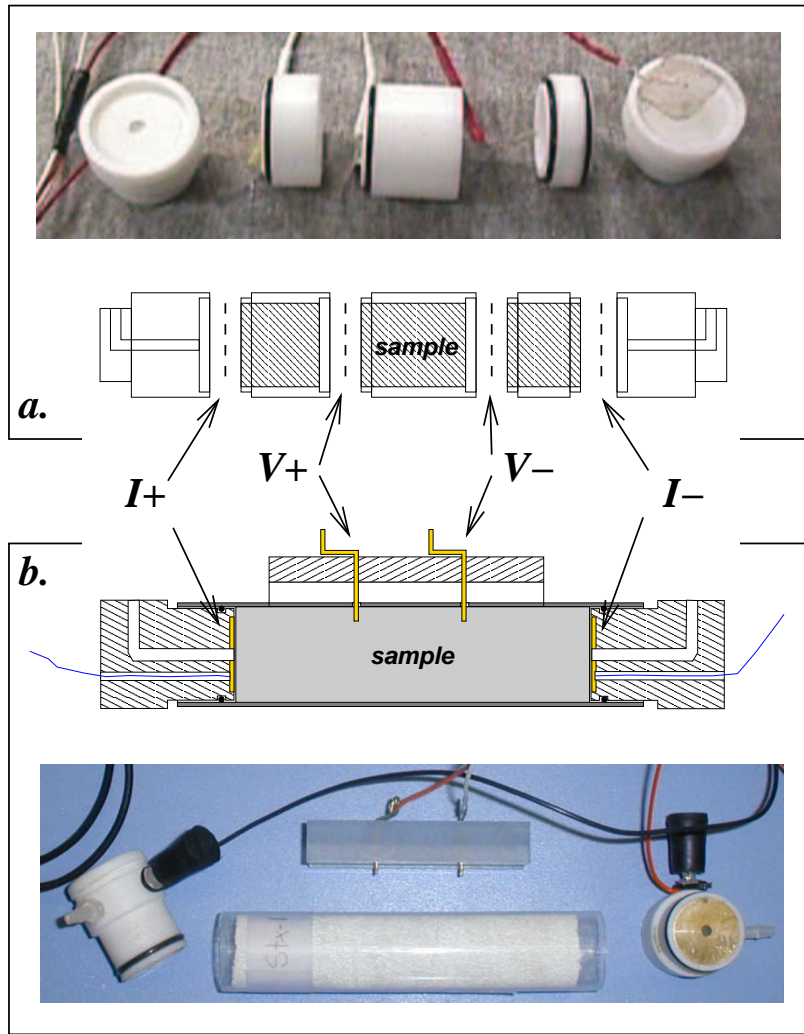


Figure 4: Soil sample holders used for this study. **a.** Olhoeft style sample holder, wherein the sample is divided into three parts each separated by through-going platinum screen electrodes completely separating and covering the sample sections. **b.** Vanhalla style sample holder, where the sample is intact in a single tube. The voltage electrodes are heavy-gage gold wire which only penetrate the outer skin of the sample.

duce the results of Olhoeft and Sadowski [Sadowski, 1988] on the complex resistivity response of toluene-contaminated clay-rich samples. While we observed similar responses to theirs for plain clays with brine (Figure 8), the addition of toluene did not produce the effects they claimed (Figure 9). We could only produce effects of similar magnitude if we intentionally introduced a large artificial dielectric heterogeneity in the specimen (Figure 10).

2.2.2 Sensitivity Analyses

As mentioned, we failed to reproduce the results of Olhoeft and Sadowski for high concentrations (20% by weight toluene) in pure montmorillonite clay. We also performed laboratory studies to

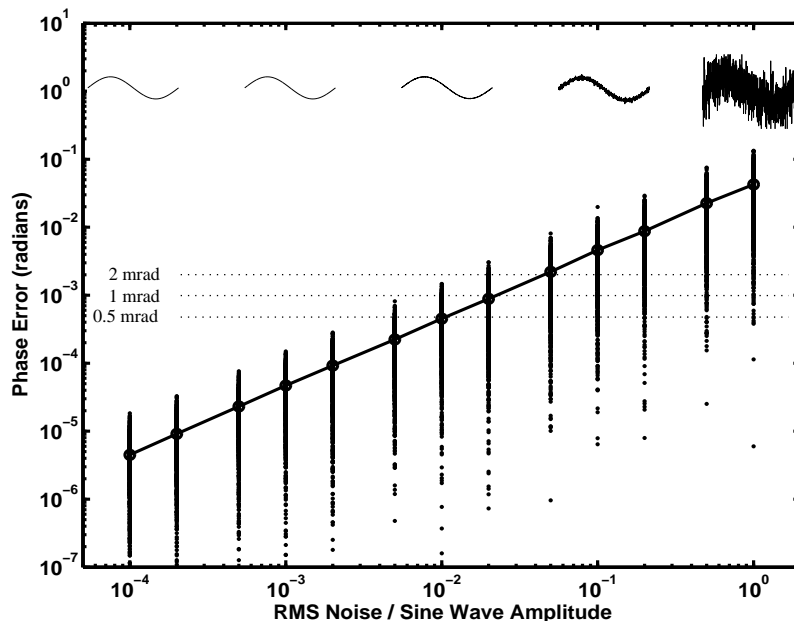


Figure 5: Results of a parameter study to determine the noise sensitivity of the data analysis methods. We find that under typical conditions in the laboratory the noise floor for this type of measurement is at the 1–2 milliradian level, requiring phase signals or anomalies to be larger than this to hold much significance in interpretations.

test the sensitivity of the complex resistivity method to toluene and methanol contamination in sands, clays, and rocks at low contaminant levels more typical of polluted groundwater (100 parts per million (ppm) and smaller). This work is documented in detail in Jason Sorenson’s M.S. Thesis from Boston College [Sorenson, 2003].

Berea Sandstone and varved clay from Putney, VT served as natural samples. Berea Sandstone cores were cut from a single block originating from northern Ohio. Cores of varved clay deposited in Glacial Lake Hitchcock [Van Diver, 1987] were collected directly into the resistivity sample holder using a manual soil auger. Source Clay Repository SWy-2, a Na-rich montmorillonite clay from Crook County, WY, and U.S. Silica 250 μm diameter ground silica sand, and glass beads functioned as the artificially packed samples.

Uncontaminated natural samples were saturated in background electrolyte (0.01 Molar (M) NaCl brine) under a vacuum before testing. Packed samples were placed in glass jars and background electrolyte was added and mixed with a stainless steel spatula. All brine-saturated samples were stored in glass jars at room temperature until ready for use.

Toluene and methanol were chosen as the two organic species for the sensitivity analysis. Contaminated brine solutions were mixed to a desired concentration by pipetting and the concentrations were checked by two independent laboratories: Alpha Analytical Laboratories in Westborough, MA and Severn-Trent Laboratories in Billerica, MA. Finally, these dilute contaminated solutions were used to saturate the samples.

Natural samples needed to be artificially contaminated by injection. Fifty pore volumes of con-

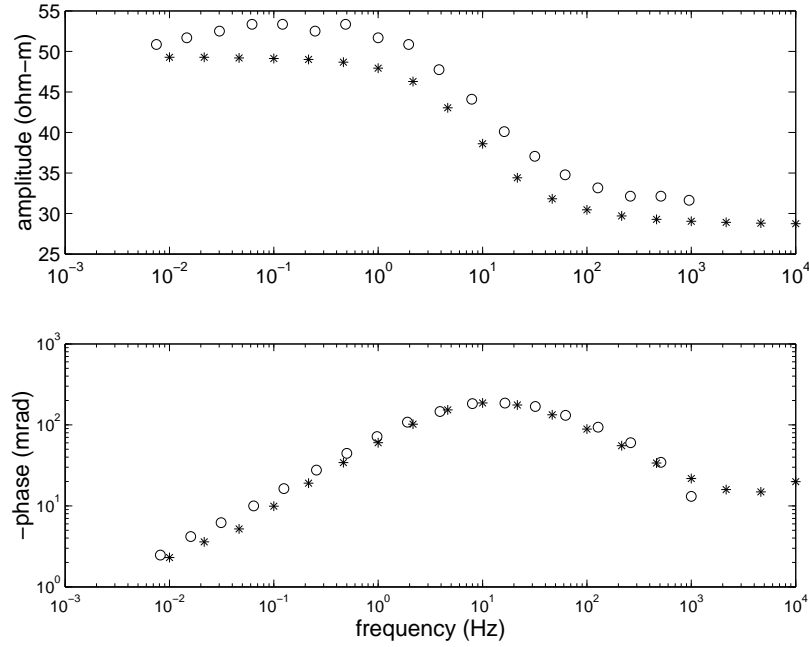


Figure 6: Reproduction of the results of *Klein and Sill* [1982] for the response of glass-bead packs with a 10% iron pyrite (2–4 mm diameter) by volume disseminated in glass beads (100–170 mesh) saturated with 0.001 Molar NaCl. In the plots, ‘open circles’ are results of Klein and Sill and ‘stars’ are our results. The agreement is excellent.

taminated brine were injected into the Berea sandstone plugs via the sample holder end cap ports. The clays are much less permeable than the sandstone making injection of contaminated brine through the end caps impossible. Therefore, approximately twenty pore volumes of contaminated brine were injected directly into the varved clays via a hypodermic needle. Packed samples were contaminated artificially by directly adding contaminated solutions to dry samples in glass jars. The samples were mixed with a stainless steel spatula. The contaminated samples were stored in glass jars until tested.

Several sets of measurements were made on both the artificially-contaminated samples and their respective background samples saturated with uncontaminated electrolyte. The first set was made one week after saturating the samples and the second set was measured one month later. A third set was made another week later on end-member concentrations only (i.e. 100 ppm and 1 ppt for methanol, and 20 ppm and 0.2 ppt for toluene).

The primary goal of this study was to explore the sensitivity of complex resistivity to varying concentrations of toluene and methanol. Results from each of the trials presented were repeatable; however some variability exists between measurements. Sources of variability include sample holder integrity, poor sorption interaction, and volatilization of organics. When obvious discrepancies arose and experimental error was suspected, the source of the problem was found and the experiment was then repeated.

Silica sand and Berea sandstone samples contaminated with toluene and methanol have resistivities greater than their respective background resistivities by factors of approximately 1.5 and 1.2. Contaminated Na-montmorillonite resistivities are greater than the background by as much

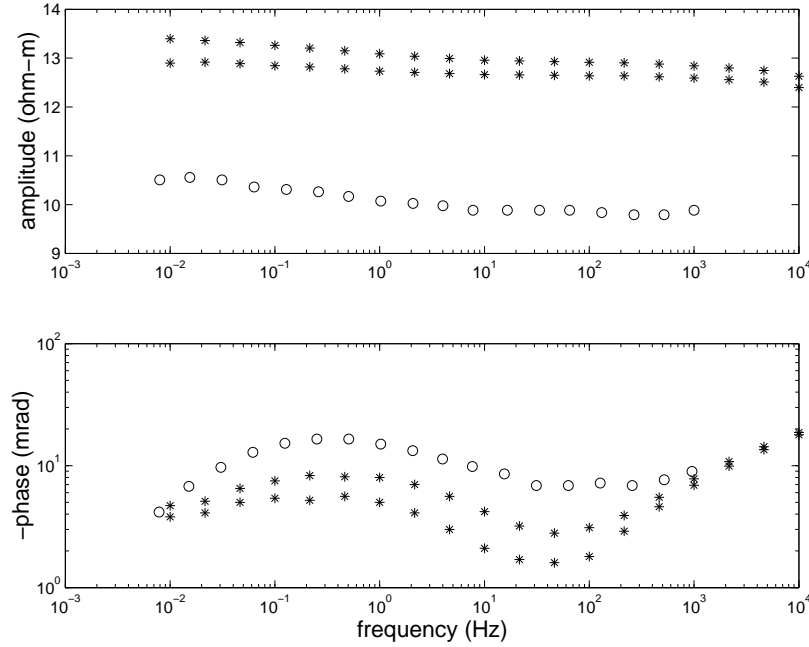


Figure 7: Reproduction of the results of *Klein and Sill* [1982] for the response of glass-bead packs with a 3% Ca-montmorillonite clay saturated with 0.01 Molar NaCl. In the plots, ‘open circles’ are results of Klein and Sill and ‘stars’ are our results. For two subsequent trials, we find a phase anomaly at the same frequency, but lower in amplitude, compared to their work. This level of disagreement is reasonable considering the sensitivity to differences in sample preparation techniques [see Sorenson’s Thesis, 2003].

as 10 times, while the varved clay and glass bead contaminated samples are nearly identical to their respective background samples. For both contaminants, the phase changes compared to the uncontaminated specimens are relatively small (factor of 2 or less). The Na-montmorillonite and varved clay showed larger phase effects than the sand and sandstone.

Chloromethanes like methanol have a greater affinity for air than water due to a high vapor pressure and low solubility, suggesting minimal reaction between a rock or soil particle, as well as a low residence time in water. *Moore and Ramamourthy* [1984] collected results from previous chloromethane sorption experiments that show only about 20% of chloromethane sorbed onto dry bentonite and powdered limestone, while samples with high organic detritus content had a higher sorptive capacity of 40%. Toluene is a monocyclic aromatic compound that has approximately half the solubility as methanol. Toluene has a stronger affinity for organic materials in rocks and soils compared to methanol. However, the sorptive capacity of toluene is greater than methanol, and the toluene dilutions were approximately an order of magnitude smaller than the methanol. Nevertheless, differences observed in the complex resistivity responses between toluene- and methanol-contaminated samples were small. Comparing organically-contaminated and background-electrolyte sample resistivity shows changes that are similar in shape and magnitude for both organic species despite differences in species and concentration. Phase changes are generally small, and in addition, the most significant phase changes generally occur at frequencies smaller than 100 Hz. Toluene and methanol responses in similar materials do not appear to be

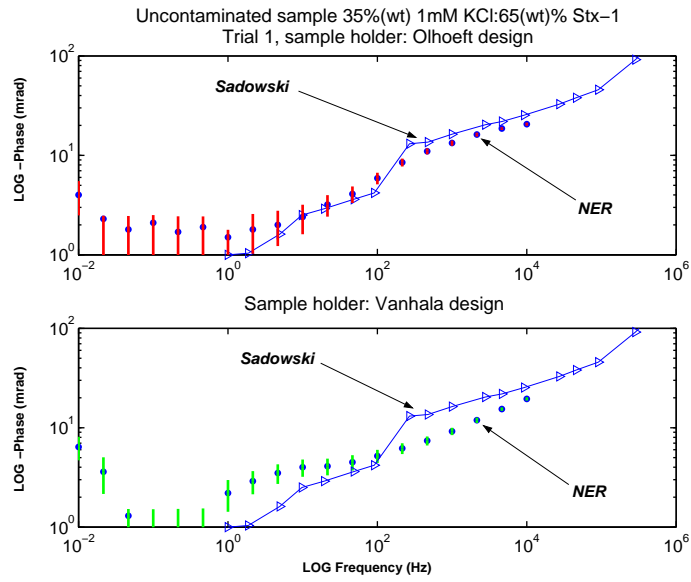


Figure 8: Comparison of results of *Sadowski* [1988] for an uncontaminated sample of Stx-1 Ca-montmorillonite Clay with KCl Brine. Agreement is excellent with both sample holder designs.

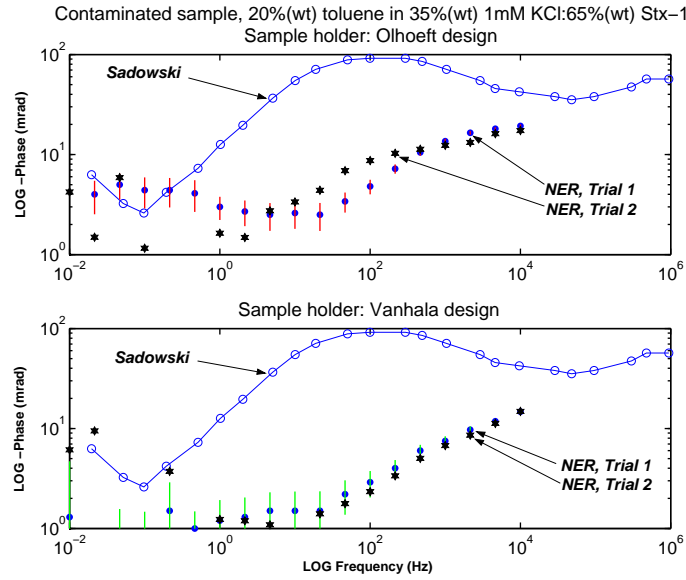


Figure 9: Comparison of the results of *Sadowski* [1988] for toluene-contaminated sample of Stx-1 Ca-montmorillonite Clay with KCl Brine. Under repeated trials we did not see the large phase anomaly with either sample holder design.

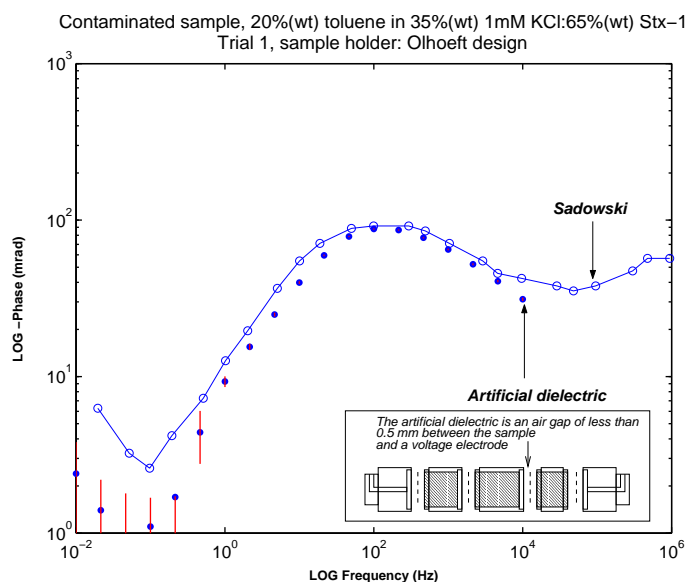


Figure 10: Comparison of results for toluene-contaminated sample of Stx-1 Ca-montmorillonite Clay with KCl Brine using the Olhoeft sample holder and electrode design, with the introduction of an artificial dielectric in the sample (simply an sub-millimeter air gap at one of the voltage electrodes). Note that before the dielectric was introduced, the plot was similar to Figure 9.

easily differentiated.

In the field, noise from coupling, cultural, and grounding effects has a wide range and can be very large: between 1–2% under ideal conditions, and up to 100% in some situations. Noise suppression capability of a typical field IP/resistivity meter is most efficient at frequencies greater than 20 Hz [AGI, 2003]. EPA drinking water standards list the MCLG for toluene as 1 mg/L and the MCL for toluene as 1 g/L. Five United States cities have toluene concentrations between 0.1 and 19 g/L in potable water samples [EPA, 2003]. Typical concentrations at contaminated sites where organics are the dominant pollutant are on the order of milligrams per liter and range from 10 to 100 ppm.

Given the low magnitude of the resistivity and phase anomalies relative to background samples as seen in our experiments, the factors listed above reduce the short-term prospects of using complex resistivity as an effective technique to remotely detect organic contamination, certainly at concentration levels less than 100 ppm (our maximum concentration tested). However, as noise suppression techniques improve and further understanding of electrical responses in Earth materials is achieved, the potential of the complex resistivity technique should improve.

2.2.3 Bench-Scale Complex Resistivity Imaging

Our sensitivity studies show, in some cases, small level shifts in the phase corresponding to contamination similar to that described by Börner *et al.* [1993]. Also, we note that clays absorb contaminants differently than sandy materials, and that clayey soils may each have a distinct complex resistivity signature (Figure 11). Therefore, we decided to perform standard 4-wire IP ‘field’ inversion measurements in a two-dimensional laboratory ‘ant farm’ (Figure 12) to test the ability of

complex resistivity (or IP) to image materials with both conductivity and dielectric heterogeneities.

A series of experiments were run to test the feasibility of using surface profiles measured across a range of frequencies to study the frequency dependent complex resistivity properties of subsurface features (Figure 13). Subsurface images were calculated from surface complex resistivity measurements using *RES2DINV*, a commercially available inversion software package published by Geotomo Software Inc., Malaysia. The frequency range was chosen to match used by *Klein and Sill* [1982] in their study of artificial sand-clay mixtures. They made direct measurements of their samples using methods similar to our repeatability studies, while the electrical properties shown here are calculated remotely from resistivity measurements along the surface of our 2-D specimen.

Each profile is calculated from a dipole-dipole electrode array that was moved across the sample surface at three different depth settings. At each frequency, a total of 24 surface resistivities were measured. The resistivity inversion software then turns these 24 surface measurements into 36 subsurface blocks, each with its own complex resistivity properties. The plots shown here (Figure 13) are interpolations between those blocks.

During background experiments, the testing apparatus was filled with sand that was not packed or manipulated, in order to prevent sorting by grain size. The variations in the resistivity magnitude and phase seen in images resulting from these experiments are assumed to be artifacts of the experimental apparatus, procedure, and of the mathematical model used for analysis. Whatever the source, the variations were systematic, appearing the same in every background experiment. Therefore, in later experiments, only deviations from this baseline are considered to be of significance.

Experiments were performed where the sample holder was filled with pure sand containing a single, approximately 40 mm diameter, heterogeneity. Following exactly our repeatability studies described earlier, in one case the heterogeneity was sand with 10% iron pyrite grains. Another experiment contained a heterogeneity composed of a mixture of sand and 3% Ca-montmorillonite clay. As seen in Figure 13, the heterogeneity was physically located inside the magenta circle. For the clay experiment, the inverted image around the montmorillonite heterogeneity shows a phase bump centered around 5 Hz, with a peak of 10–15 milliradians, matching Klein and Sill's experiment for 3% Ca-montmorillonite. The results were just as good for the pyrite experiment. Other studies further varied the clay content of the heterogeneity. We found cases where the heterogeneities would show up clearly in the phase images, even though their resistivity contrast with the background material was low enough to render them nearly invisible in the amplitude image.

2.2.4 Summary

Attempts to repeat the phase maxima observations of *Sadowski* [1988] in toluene-contaminated clays were unsuccessful. Introduction of an artificial dielectric between a potential electrode and the sample made it possible to match Olhoeft and Sadowski's phase peaks, and suggests that the phase response may not be a function of the contaminated sample, but secondary to a dielectric barrier at the electrode/sample interface. The ability of this method to detect contaminants at low concentration was explored through sensitivity analyses of toluene- and methanol- contaminated samples. Phase responses were small at frequencies less than 100 Hz; frequencies similar to those used in field applications. Phase responses greater than 100 Hz can begin to be affected by

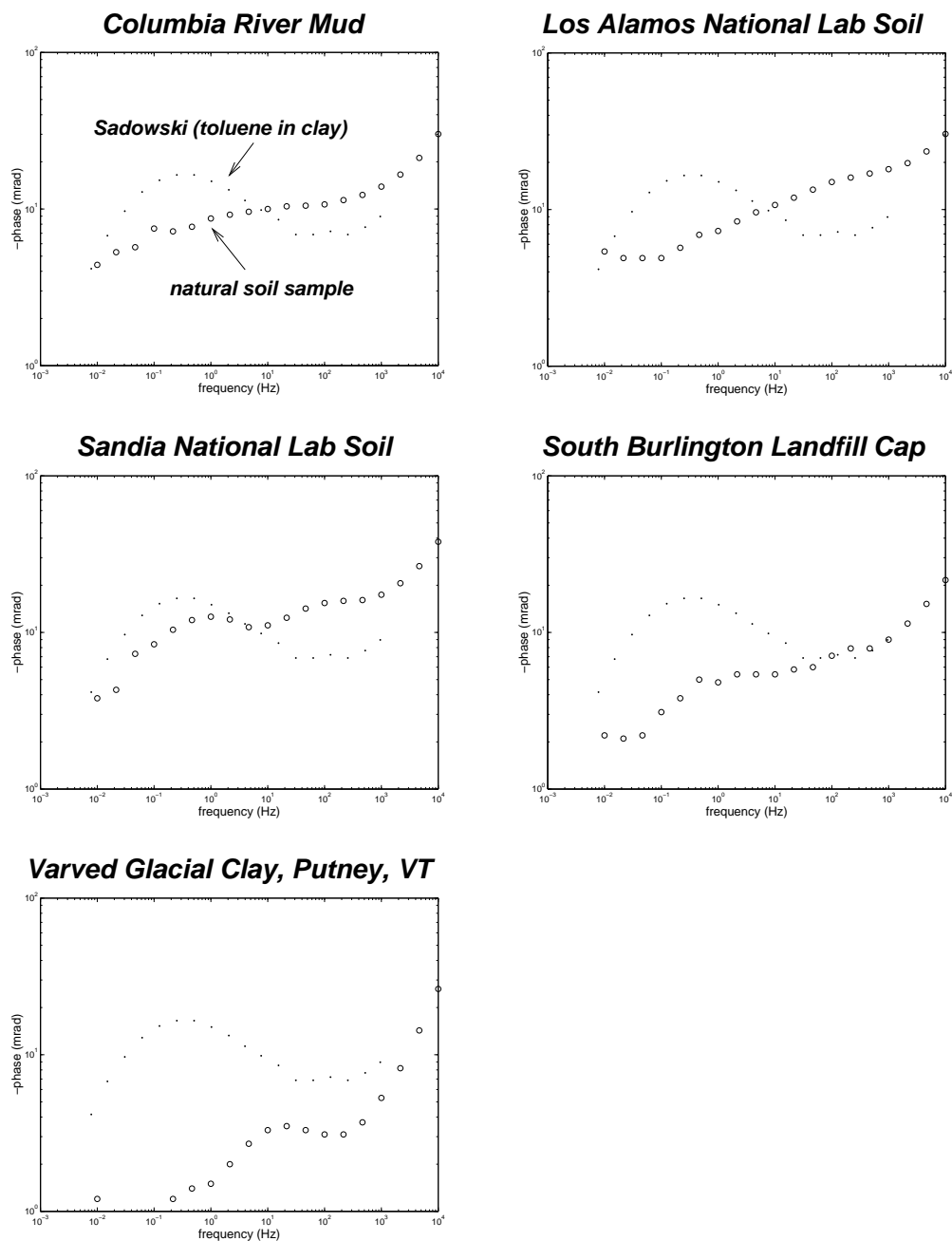


Figure 11: Phase signatures for several uncontaminated clayey soils. The results of *Sadowski* [1988] for a toluene-contaminated montmorillonite are shown for comparison.

capacitive coupling of the electronics and wiring. Toluene phase signatures were very similar to methanol phase signatures despite being lower in concentration by an order of magnitude. Samples that produced the most significant phase responses possessed the greatest surface area for sorptive reactions to occur. Soils and rocks with a clay fraction of approximately 3% by weight, and pure clay samples yielded phase responses that are potentially resolvable in the field.

The largest imaginary conductivity responses appear to be a function of the surface area avail-



Figure 12: Photograph of bench-scale 2-D resistivity apparatus ‘ant farm’. A lexan box approximately 58cm by 28cm by 1.5cm contained a soil sample with known heterogeneities. Standard 4-wire IP dipole-dipole array measurements were made using the laboratory electronics system. After correction of the raw measurements to account for the true 2-D nature of the apparatus, IP imaging was performed using the RES2DINV software.

able for adsorption of contaminants as well. Natural samples possessing clay fractions or organic detritus have the largest sorptive capacity and therefore produced the largest responses in imaginary conductivity. Low-frequency imaginary conductivity shifts occurred in pure clay samples, but the average magnitudes were the same for contaminated and uncontaminated samples. From the laboratory data examined here, complex resistivity surveys in the field ideally require contaminant concentrations on the order of 100 ppm or greater, since at smaller concentrations we did not see clear distinctions from the background samples. Even at 100 ppm, the signals we see are subtle and could be easily confused with noise or electrode effects. Pure product tank experiments only generate complex resistivity responses in the range of 20 to 30%, which would be difficult to discern in an area with a small signal to noise ratio. Noise levels in the field have a wide range, and noise suppression ability is limited at frequencies less than 50 Hz. Contaminated sites are also generally a mixture of many contaminants, and are rarely one species at large concentrations. These considerations make the prospects for definitive detection of a distinct organic species in a contaminant plume by complex resistivity unlikely at this point. Determining the existence of a plume via complex resistivity may nonetheless be possible, and the likelihood is increased if a multidisciplinary approach is used. Integration of ground penetrating radar (GPR), and or seismic refraction methods with complex resistivity would allow remote imagery of both the lithologic variability and imagery of the contaminant itself to be obtained. And as mentioned earlier, improvements in noise suppression and improved understanding of the electrical response in Earth materials can also improve the viability of complex resistivity as an environmental geophysics tool.

We also find that certain electrically polarizing materials, some clays for example, have responses large enough compared to sandy and silty soils to be reliably imaged through a detailed field IP survey. These materials often show up clearly in the phase signals, even though their resis-

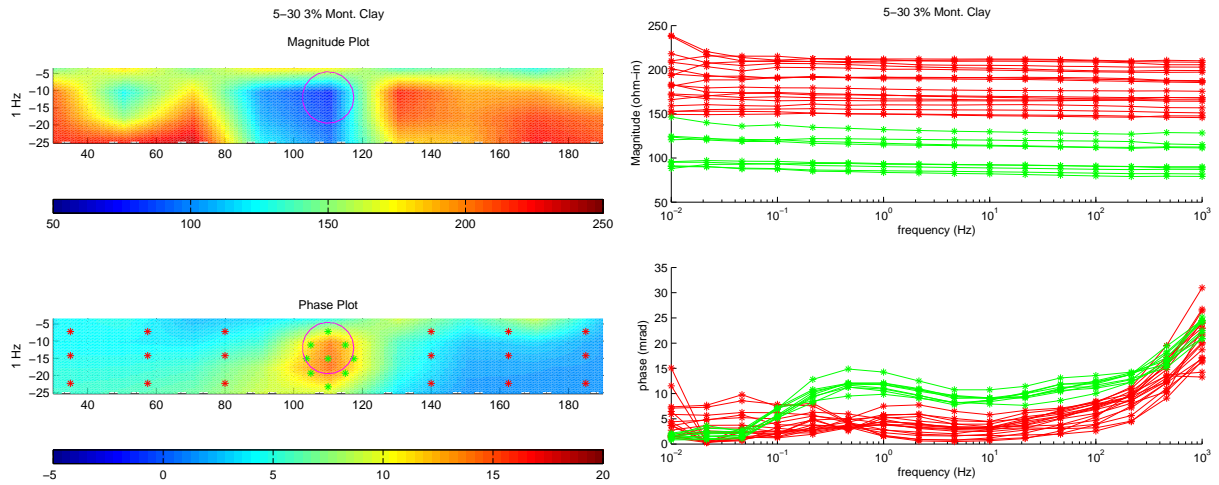


Figure 13: Results of an ‘ant farm’ experiment where the sample was formed by clean homogeneous arkosic sand with a single heterogeneity comprised of a 4cm diameter by 1.5cm thick disk which was a mixture of sand and 3% Ca-montmorillonite clay (prepared in the same way as the Klein and Sill samples of Figure 7). **Left:** Images of the amplitude and phase structure of the sample as output by RES2DINV. The clay-rich sample is physically located inside the magenta circle. Dots in the image represent spatial positions where the complete frequency-phase plot has been extracted and plotted on the right. **Right:** The phase of the inverted image shows a phase bump centered around 5 Hz, with a peak of 10–15 milliradians, matching Klein and Sill’s experiment of 3% Ca-montmorillonite. The magnitude data is not well-enough resolved to determine whether or not there is an inflection point at the same frequency.

tivity contrast with the background material may be low enough to render them invisible to a standard resistivity measurement. Thus, quantifying soil heterogeneity (which may relate to DNAPL distribution and transport) is an immediate potential alternative application of this technique.

2.3 Boston College Technical Activities

The work performed at Boston College under the direction of Professors David Lesmes and John Fourkas was supported by a subcontract from New England Research. The purpose of this work was to evaluate previous and develop new theoretical models for complex resistivity response in porous materials. The emphasis of these models was primarily to relate geophysical response to pore geometry, fluid flow, and contaminant transport parameters.

At Boston College, we developed a model for the broadband electrical impedance response of rocks and soils [Lesmes and Morgan, 2001]. We have tested this model using electrical impedance measurements (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 subsurface.

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.

David Lesmes is currently assisting Dr. Roelof Versteeg and the geophysics group at the Idaho National Engineering and Environmental Laboratory (INEEL) on their complex resistivity 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 the INEEL. David Lesmes will work on the complex resistivity project at the INEEL from July through September. The researchers at INEEL were using a sample cell similar to that used by Olhoeft where the current electrodes were in the current path. As we have previously observed, this causes large systematic phase errors. After redesigning the INEEL sample cell to move the potential electrodes out of the current path the systematic phase errors were eliminated and the phase errors were on the order of ± 0.5 milliradians over the frequency range of 1 mHz to 1 kHz. David Lesmes is now working with INEEL scientists to conduct complex resistivity and NMR experiments on sand and clay mixtures containing TCE and PCE. At INEEL they are also using complex resistivity and NMR to characterize the biodegradation of TCE and PCE in synthetic and natural soils.

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 will 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 interpret IP surveys conducted in these environments.

3 Relevance, Impact, and Technology Transfer

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. This project was initiated to help fill DOE's need for characterization and cleanup of sites contaminated with organic compounds.

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. This suggested to many the basis of an ideal new measurement

technique for geophysical characterization of DNAPL pollution. This new non-invasive technique, based on the measurement of complex electrical resistivity, if developed further would significantly reduce costs and lower risks during characterization. However, early attempts at applying this technique had been unsuccessful.

Encouraged by the aforementioned laboratory results, we proposed to perform a fundamental science study to better understand the obstacles in realizing this needs-driven applied technology. For this purpose we intended to document the detectability of clay-organic solvent 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.

As with any new research endeavor we note the extreme importance of trying to reproduce the work of previous researchers, both as a check on our measurement techniques and as a check on those preceding us. We need to ensure that the effects we see are due to the physical phenomena occurring in the specimen and not due to the particular experimental apparatus or method we are using. We began by building appropriate equipment and developing new techniques and then strived to reproduce the key previous results upon which this new technique was based. We 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. Using various standards we performed measurement accuracy, repeatability, and noise immunity tests of this system and we were able to reproduce some key complex resistivity effects quoted in the literature.

We attempted to reproduce the seminal results of Olhoeft and Sadowski [*Sadowski*, 1988] on the complex resistivity response of toluene-contaminated clay-rich samples. Repeated attempts to reproduce these results failed, even though we could show that our equipment and methods worked reliably for other well-documented cases. This work indicates, at best, a low sensitivity of the complex electrical resistivity method to organic contamination in rocks and soils. This reduces the short-term prospects of using complex resistivity as an effective technique to remotely detect organic contamination, certainly at concentration levels less than 100 ppm.

We 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 performed simulated ‘field’ IP inversion measurements in a two-dimensional laboratory specimen to test the ability of this technique to image materials with both conductivity and dielectric heterogeneities.

Documenting the non-reproducibility of some previous work is not a set-back, but is a natural self-correcting feature of the scientific method. In this particular case, application of the scientific method led us to find both potential sources of error in the early work and at the same time has led us to find a potential new application of this principle, which still addresses DOE’s problems. We are fortunate that DOE has a viable scientific program such as EMSP. We believe the results of this project require the redirection of future work on this technique away from finding organic compounds in soils toward the characterization of soil type and heterogeneity. Publication of these results will affect the thinking of all future work in this field.

4 Project Productivity

The project did not accomplish all of the proposed goals. The first task in the research plan, after the development of equipment and techniques, was to study the reproducibility and robustness of the seminal complex resistivity results upon which this project was based. We found that we could not. At this point the project took a turn to verify this controversial result by carefully documenting the equipment and methods for accuracy, repeatability, and noise immunity. We again tried multiple times to reproduce the key result, with no success. The work plan was revised toward carefully documenting this negative outcome for publication. We then began to explore potential reasons for the observations and to determine the sensitivity of the basic measurement method to various contaminant levels and soil types. We were able to show that the method does have a potential important use in characterization of contaminated sites, albeit not the one anticipated at the outset. While this outcome is not what was anticipated the results are no less useful, for this project will have marked effects on directing future work.

During the course of this project, we had a personnel change (a junior scientist returned to graduate school), which resulted in this project being understaffed. We applied for and obtained a 9 month no-cost extension to enable completion of the key technical tasks.

5 Personnel Supported

- **New England Research (NER) Employees:** Gregory N. Boitnott (senior scientist), Stephen R. Brown (PI, senior scientist), Thackery I. Brown (student technician), Emily E. Horrell (scientist), Christopher Knudsen (electrical engineer), William A. Lauten (senior scientist), Jason R. Sorenson (graduate student and scientist).
- **Boston College Employees:** Hana Baker (graduate student), John Fourkas (co-PI, professor), David Lesmes (co-PI, professor).

6 Publications

Papers submitted in support of or in partial support of this project

Baker, H., Prediction of Capillary Pressure Curves from Dielectric Spectra, M.S. Thesis, Boston College, 2002.

Brown, S.R., J.R. Sorenson, and T.I. Brown, A laboratory study of the complex electrical impedance response of soils, in preparation.

Brown, S.R. and E.E. Horrell, Complex electrical impedance imaging of heterogeneities: A bench-scale laboratory study, in preparation.

Lesmes, D. P., and Friedman, S., Relations between the electrical and hydraulic properties of rocks and soils, in Hydrogeophysics, edited by Rubin, Y, and Hubbard S., to be published by Kluwer, 2003.

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

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- Sorenson, J.R., Complex resistivity of Organic Compounds in Natural and Packed Rocks and Soils, M.S. Thesis, Boston College, December, 2003.

7 Interactions

Presentations made in support of or in partial support of this project

- Brown, S.R., Attended yearly EMSP Meetings, Richland, Washington.
- 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.
- Lesmes, D. P., NATO Advanced Study Institute Workshop on Hydrogeophysics, Charles University, Czech Republic, Electrical Properties of Rocks and Soils: Prediction of Hydrological and Geochemical Properties, July 2002.
- Lesmes, D. P., AGU-EGS-EUG joint meeting, Nice, France, Electrical-Impedance Spectroscopy of Sedimentary Rocks: Prediction of Hydraulic Conductivity and Soil Water Retention Curves, April, 2003.
- Lesmes, D. P., Idaho National Engineering and Environmental Laboratory, Complex Resistivity for Environmental Characterization and Monitoring: A Review, July, 2003.
- Lesmes, D. P., August, Idaho National Engineering and Environmental Laboratory, Electrical Impedance Spectroscopy and NMR Spectroscopy of Rocks and Soils, 2003.
- 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.

8 Transitions

Bill Daily and Abe Ramirez, of LLNL and Jim Shinn and Rex Morey of Applied Research Associates (ARA) have used cone penetrometer technology to emplace electrodes to be used for cross-hole electrical impedance tomography. Based on the early work of Olhoeft, they had hoped to use IP imaging to locate contaminants and track movements of contaminant plumes. Our work points out the problems with this endeavour and will affect interpretations of their data.

9 Patents

None

10 Future Work

This work indicates, at best, a low sensitivity of the complex electrical resistivity method to organic contamination in rocks and soils. This reduces the short-term prospects of using complex resistivity as an effective technique to remotely detect organic contamination at concentration levels less than 100 ppm. However, we have only tested a limited set of materials and therefore we can't rule out discernable signatures arising from other combinations of contaminants and soils. Since, complex resistivity laboratory measurements of the type described here are relatively simple to perform, current and new field characterization problems should still be evaluated on a case by case basis to evaluate the potential utility of this method.

We found that certain electrically polarizing materials, some clays for example, have responses large enough compared to sandy and silty soils to be reliably imaged through a detailed field IP survey. Thus, quantifying soil heterogeneity (which may relate to DNAPL distribution and transport) is an immediate potential application of this technique. Therefore, we believe the results of this project require the redirection of future work on the complex resistivity technique for environmental applications away from finding organic compounds in soils toward the characterization of soil type and heterogeneity.

Irregardless of the application, new methods which reduce noise in resistivity and IP measurements will increase the chances of discerning the small effects in field measurements.

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