EXECUTIVE SUMMARY

Investigating the Sensitivity of Emerging Geophysical Technologies to Immobile Porosity and Isolated DNAPL and Dissolved/Sorbed VOC Mass in Fractured Media

SERDP Project ER-2421

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TABLE OF CONTENTS

Page

1.0 INTRODUCTION 1
2.0 OBJECTIVES 2
3.0 TECHNICAL APPROACH 2
4.0 RESULTS AND DISCUSSION 3
5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS 6

LIST OF FIGURES

Page

Figure ES1. Project Overview Showing Central Tasks of the Work Performed. 3
Figure ES2. Example NMR Permeability Prediction Equations and Associated Coefficients 4
Figure ES3. Predicted TVOC from Borehole Geophysical Logs vs. True TVOC from Rock Cores 5
Figure ES4. Electrical Tracer Experiment Apparatus 6
Figure ES5. Hysteresis Loops for (a) HC-MP24S-P-006-1V, (b) HC-MP24S-P-007-2H, and (c) SS-C3-P-019. 7

ACRONYMS AND ABBREVIATIONS

CR	Complex resistivity
DFN	Discrete Fracture Network
DoD	Department of Defense
DNAPL	Dense non-aqueous phase liquid
HCC	Hydrite Chemical Co.
NAPL	Non-aqueous phase liquid
NAWC	Naval Air Warfare Center
NMR	Nuclear Magnetic Resonance
SSFL	Santa Susanna Field Laboratory
TVOC	Total volatile organic compound
VOC	Volatile organic compound

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1.0 INTRODUCTION

Dense non-aqueous phase liquid (DNAPL) and dissolved/sorbed phase volatile organic compound (VOC) contamination of fractured rock remains a long-term, persistent Department of Defense (DoD) problem. At most 'aged' sites where DNAPL releases occurred decades ago, contaminant mass now resides in the much lower permeability matrix blocks between fractures (immobile porosity). Fluid samples taken from wells primarily represent the mobile porosity produced by the fracture networks and therefore often fail to accurately quantify contaminant mass. For chlorinated solvents, contaminant storage can occur by several mechanisms, including: (1) non-aqueous phase liquid (NAPL) accumulation in or on low-permeability layers or dead-end fractures, resulting in a long-term source for dissolved contamination; (2) sorption of dissolved contaminants on surfaces of grains or fractures; (3) diffusion of aqueous phase contaminants into low-permeability matrix blocks between fractures or in and from dead-end fractures. There is increasing recognition that the third mechanism, storage of dissolved contamination in low-permeability zones, is of principal importance.

Nearly all sedimentary rocks have substantial effective matrix porosity (2-20%), allowing large amounts of contaminant mass storage due to diffusion into the matrix. Sorption enhances the storage capacity in the early decades of contamination, and out of the matrix in later decades or centuries. Although it is typical that nearly all groundwater flow occurs in the fracture network, at 'aged' contaminated sites most contaminant mass now resides in the much lower permeability matrix blocks between fractures. However, this mass can diffuse from the rock matrix back into the more permeable fractures, resulting in long term contaminant persistence even if source zones are depleted or remediated. Conventional approaches for investigating fractured rock are inadequate because they are biased toward answering questions most relevant to present-day groundwater quantity and water supply quality; hence, the rock matrix is ignored and most of the fractures with active flow and transport go unrecognized. For lack of rock core contaminant data, conventional studies commonly fail to characterize mass distribution in fractured porous rock. The performance of remediation is therefore critically dependent on development of methodologies that can quantify pore geometric properties controlling storage of contaminant mass in the rock matrix and also sense/monitor long-term changes in that mass. Furthermore, reducing the costs associated with such quantification is critically dependent on the development of approaches more efficient and less invasive than extensive coring and detailed rock core sampling for assessing the pore geometric properties and contaminant mass local to fractures.

This project explored relationships between two emerging geophysical technologies, complex resistivity (CR) and nuclear magnetic resonance (NMR) and the pore geometric properties (pore size distribution and permeability) controlling transport of contaminant mass. Secondly, it investigated relationships between the distribution of contaminant mass in the rock matrix and measurements acquired from a broad suite of geophysical logs under the assumption of a common control of the pore geometric properties of the rock mass. Thirdly, it explored an innovative electrical geophysical approach to identifying signatures of mass transfer between relatively mobile and immobile pore domains from coupled electrical geophysical and fluid electrical conductivity measurements during injection of a conductive tracer.

2.0 OBJECTIVES

The primary objectives of this research were to [1] determine the sensitivity of two emerging borehole geophysical technologies (NMR and CR) to key pore geometric properties (primarily pore size distribution and permeability) controlling contaminant transport, [2] investigate the potential sensitivity of geophysical logging methods (both emerging and established) to contaminant mass (as DNAPL and/or aqueous phase) isolated within the immobile porosity of fractured rock and inaccessible to aqueous sampling techniques, and [3] develop an electrical tracer test strategy for estimating the mass transfer coefficient and the mobile to immobile porosity ratio controlling back-diffusion of contaminant mass. A secondary objective was to obtain better information at high spatial resolution on the distribution of contaminant mass within the immobile porosity of a fractured rock relative to primary fractures governing flow/transport. Sub-objectives included [1] determining quantitative relationships between NMR/CR parameters and pore size distribution, and surface area and permeability of the rock matrix and assessing variations with site geology; [2] applying recently developed analytical and numerical models to estimate representative mass transfer rate coefficients from joint measurements of CR and fluid specific conductance.

3.0 TECHNICAL APPROACH

The technical approach involved an integration of field, laboratory, and numerical methods (Figure ES1). Field activities included acquisition of core samples, sampling of contaminant mass, and borehole logging using a variety of geophysical and hydrophysical techniques. Laboratory activities included contaminant mass analysis distribution on core samples, quantification of rock properties, CR/NMR measurements, and electrical tracer tests for estimating mass transfer coefficients. Rock properties measurements included pore size distributions from mercury porosimetry, specific surface area from gas adsorption, and permeability from a combination of Darcy flow tests and pulse decay analysis (the latter for low permeability mudstones). The numerical methods focused on pore network modeling of electrical current flow and solute transport. Specific aspects of the technical approach included [1] fine-scale delineation of contaminant mass around fractures using a discrete fractured network (DFN) strategy, [2] fine-scale delineation of porosity, permeability, and pore size distribution from core samples acquired as part of the DFN, [3] laboratory and borehole NMR and CR logging, and [4] development of first-of-a-kind laboratory instrumentation whereby tracer experiments coupled to pore-network models are used to quantitatively link geophysical responses to contaminant mass transfer parameters. Laboratory measurements on cores and borehole logging data were acquired at three sites of DoD relevance: [1] the Naval Air Warfare Center (NAWC), West Trenton, NJ, [2] Santa Susana Field Laboratory (SSFL) in Southern California, and [3] Hydrite Chemical Company (HCC) in Wisconsin. The Santa Susana site is composed of sandstone with minor interbeds of shale and siltstone and occasional conglomerate of similar mineralogy. The sedimentary rocks at the Hydrite site are more heterogeneous, including sandstones and dolomite with variable grain size. The NAWC site is characterized by alternating sequences of grey mudstones ranging from massive to thinly laminated, along with occasional thin black organic rich 'fissile' layers. Measurements at three contrasting sites permitted assessment of geophysical technology performance across a range of sedimentary rock geological settings.

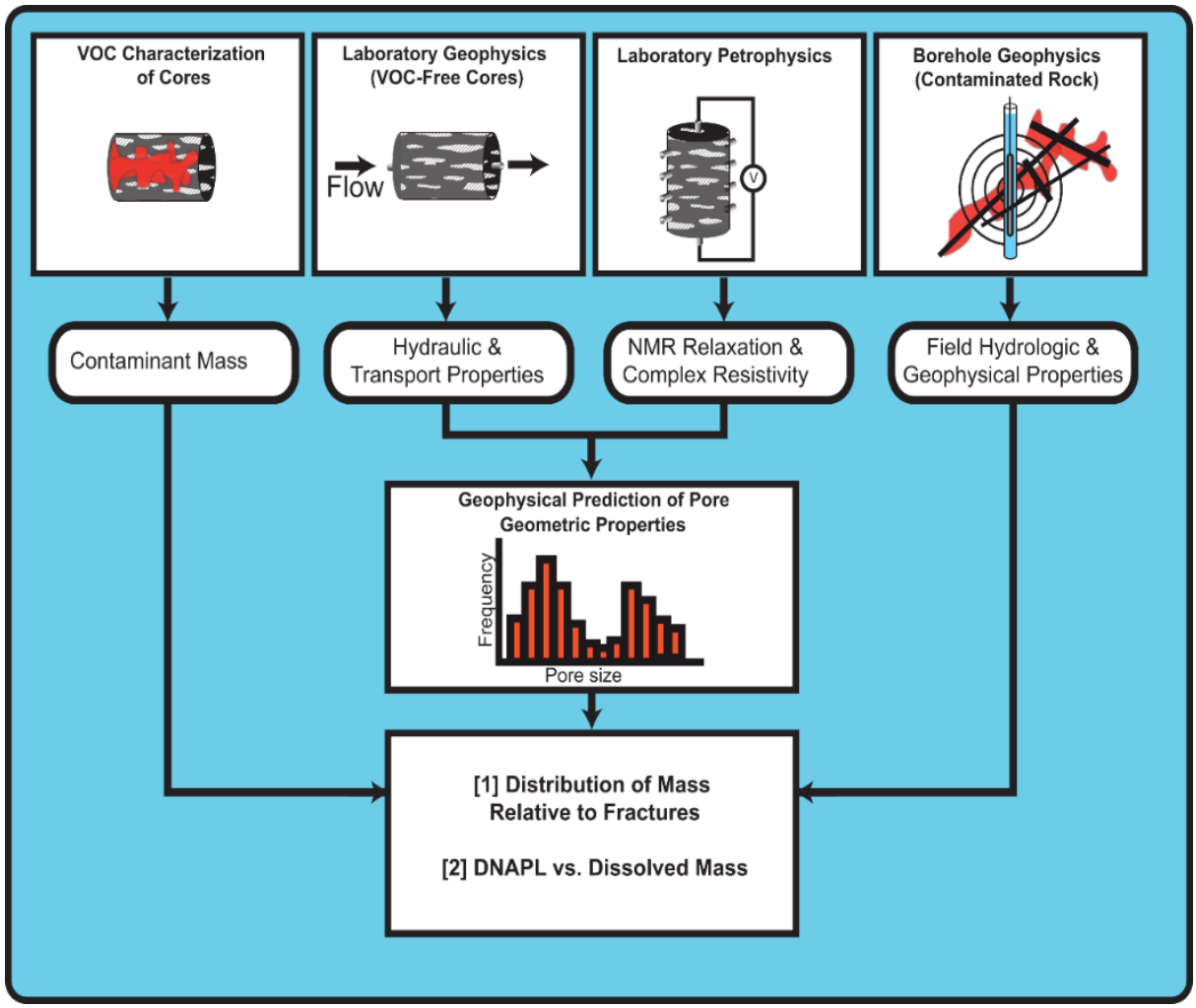

Figure ES1. Project Overview Showing Central Tasks of the Work Performed.

4.0 RESULTS AND DISCUSSION

A number of key findings regarding the role of, NMR, CR, and geophysical technologies in general in support of remediation of contaminated sites resulted from this project. The exhaustive laboratory analysis of 75 cores from the three sites demonstrated that quantitative assessment of pore size and permeability is possible using NMR and CR. Both NMR- and CR-derived relaxation times were shown to be correlated with characteristic pore sizes derived from mercury porosimetry and surface area from gas adsorption. These correlations were strong for the sandstone-dominated cores from the SSFL and Hydrite sites. However, the mudstone cores from the NAWC site did not align well with the relationships obtained for the other two sites. One exception was the relationship between the NMR relaxation time and the pore volume normalized specific surface area (S_{por}), where a single strong relationship exists for all three sites. The NMR method contained sufficient sensitivity to the pore size distribution to allow estimation of the ratio of the immobile to mobile porosity of samples. Both CR and NMR measurements provide a link to permeability through the definition of geophysical length scales that can be used in place of established geometric length scales in models of permeability prediction. An example for NMR measurements is shown in Figure ES2.

Comparison of geophysical predictions of permeability using recently proposed models with direct Darcy-test measures of permeability showed that both NMR and CR contain sufficient information on the pore geometry to permit order-of-magnitude estimates of permeability entirely from geophysical measurements. The joint use of NMR and CR data did not significantly improve permeability prediction relative to using the information extracted from a single measurement alone. However, none of the relationships were universal, highlighting the caution needed when applying such relationships outside of the lithology used for the calibration. Field-scale NMR logging highlighted the potential to extract information on variations in these pore geometric properties in situ along a borehole, albeit with lower resolution. CR measurements from an existing commercially available borehole logging tool did not have the sensitivity needed to reliably detect these variations in pore geometry in situ.

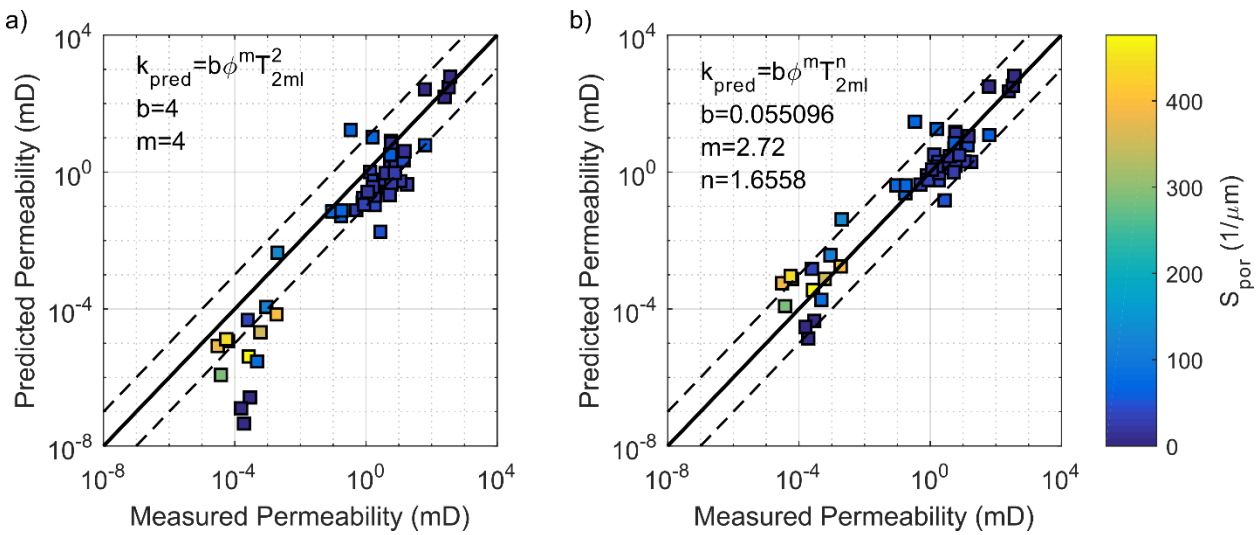

Figure ES2. Example NMR Permeability Prediction Equations and Associated Coefficients a) Coefficients Established as Representative of Sandstones, and b) Calibrated Coefficients for Entire SERDP Dataset.

Statistical analysis of the NMR and CR logging signatures against contaminant mass distributions recorded in six boreholes from the three sites did not show a conclusive dependence of NMR or CR parameters on contaminant mass. Assessment of the sensitivity of the NMR and CR measurements to contaminant mass relied on comparison of the NMR and CR borehole logging data against total volatile organic compound (TVOC) measurements from cores. The contaminant mass analysis involved an extraction procedure performed in the field; it was not possible to reliably preserve contaminants in core in situ to allow for precision laboratory NMR and CR measurements on contaminated core. The logging data had the advantage that measurements were acquired on the in-situ contaminants/rock matrix adjacent to the borehole wall. The effectiveness of the multivariate linear regression approach to the prediction of contaminant mass from geophysical logging data was shown to depend on the dataset used for the calibration. Results suggest that predictive models built with multivariate linear regression will be more likely to predict variations in contaminant mass distributions within a single borehole (Figure ES3) rather than between boreholes or across sites of varying lithology. However, the existing borehole logging tools do not provide the precision data obtainable with the laboratory instrumentation.

Therefore, the results of the contaminant mass sensitivity analysis relate to the information content extractable from currently available logging tools; these results do not represent the information ultimately obtainable from these emerging geophysical technologies as the logging tools improve.

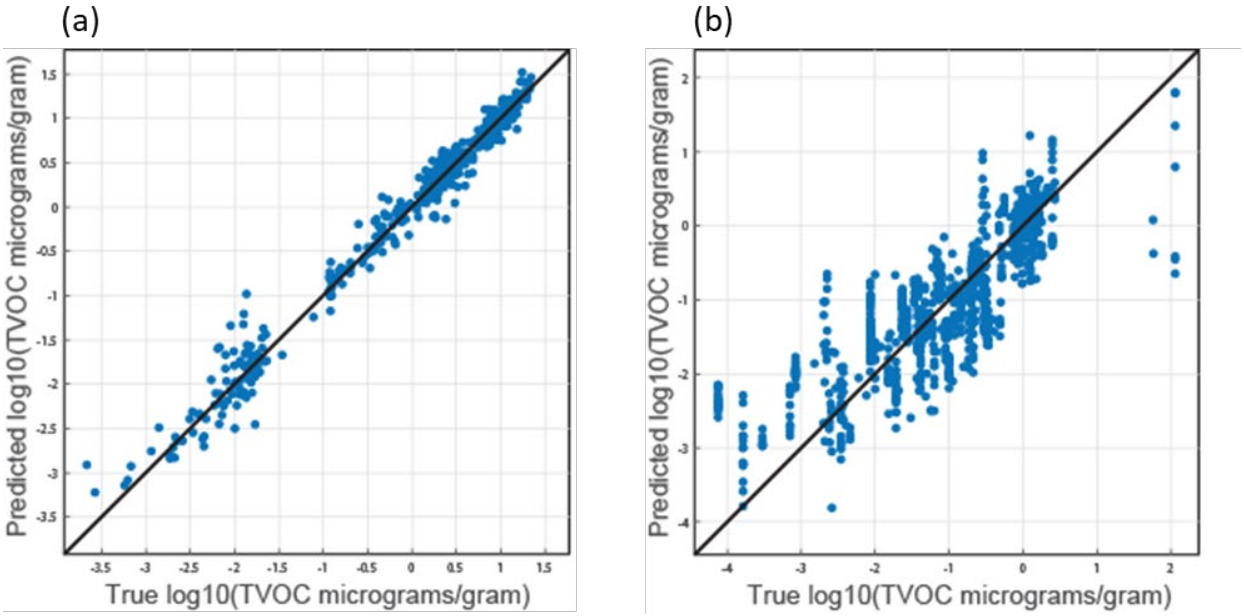

Figure ES3. Predicted TVOC from Borehole Geophysical Logs vs. True TVOC from Rock Cores for Based on Multivariate Linear Regression with Interaction Between Predictors (a) Hydrite M25S; (b) SSFL RD109.

First-of-a-kind electrical tracer experiments combined with pore-network modeling led to estimates of mass transfer coefficients and mobile/immobile porosity ratios from coupled simultaneous measurements of bulk electrical conductivity and fluid conductivity. Instrumentation based around a Hassler sleeve core holder encased in a pressure vessel was developed to perform tracer breakthrough tests on representative cores from the three field sites (Figure ES4). Non-linearity in the relationship between bulk conductivity and fluid conductivity was identified, being diagnostic of a dual domain with mass transfer occurring between domains (Figure ES5). Extension of the approach to include measurements of the real and imaginary (polarization response) parts of the complex conductivity might allow the modeling of mass transfer parameters to be improved by using the imaginary conductivity to account for the effects of surface conduction. The experiments revealed conclusive evidence for mass transfer occurring at a scale within the rock matrix, independent of a fracture network. Immobile/mobile porosity ratios were estimated through the application of a recent analytical model. This process may have significant implications for the fate and transport of contaminant mass, especially given the high surface area of the matrix porosity versus the fracture network.

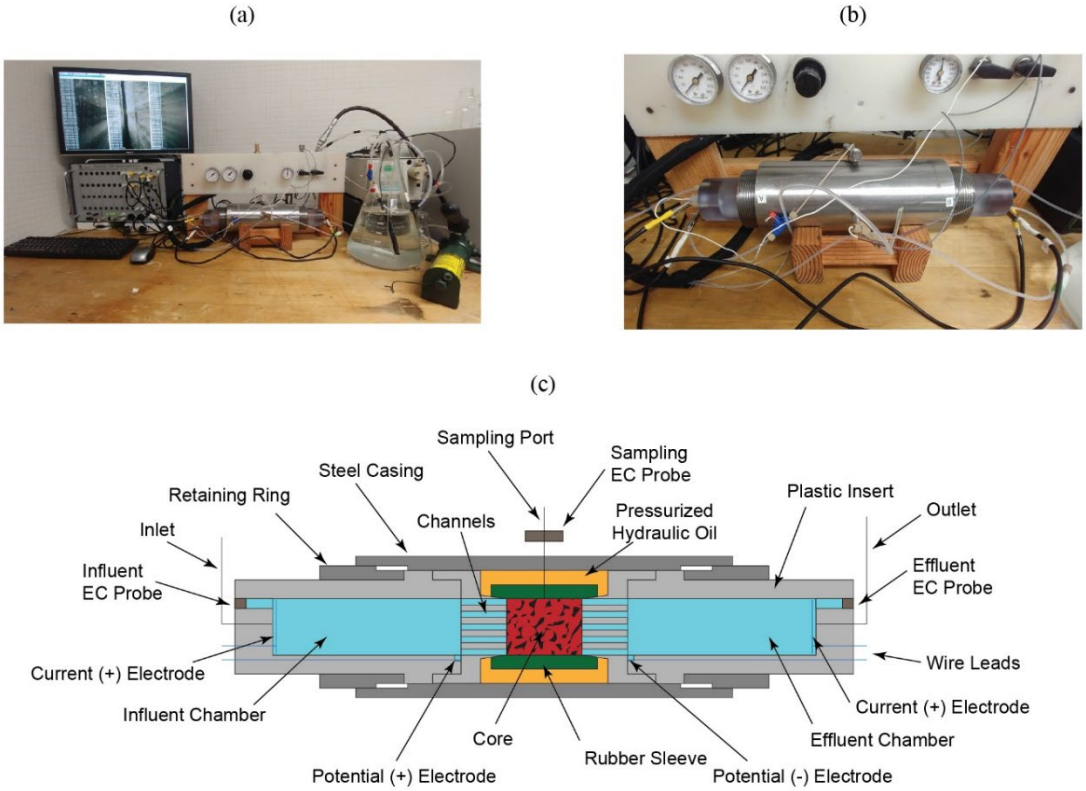

Figure ES4. Electrical Tracer Experiment Apparatus (a), Including the Sample Chamber (b) and Schematic (c) Developed to Investigate the Electrical Signatures of Mass Transfer.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Besides assessing the information content of the emerging NMR and CR geophysical technologies, this project also acquired a wealth of information on the distribution of physical properties, fracture zones, and contaminant distributions at three high-profile chlorinated solvent sites. The DFN approach was modified to incorporate information from NMR and CR measurements. This comprehensive approach coupled coring/analysis with in-well measurements and provided new insights into the distribution of contaminant mass in fractured rock settings at the three study sites, particularly around hydraulically active fracture zones. Distinct contrasts in contaminant mass distributions around fractures between the three sites were observed. Such extension of the DFN will benefit future efforts to develop conceptual site models for complex fractured rock sites.

Establishing robust relationships between geophysical logging datasets and contaminant mass would allow commercially available geophysical technologies to be employed for efficient monitoring of the effectiveness of multiple existing remedial technologies (bioremediation, thermal treatment, monitored natural attenuation, chemical addition) in reducing contaminant mass in the rock matrix, particularly adjacent to hydraulically active fractures. Geophysical logs could be repeatedly run in a borehole at a fraction of the cost of conventional sampling methods that rely on direct quantification of mass from cores. Such geophysical monitoring data would provide early information to help predict the long-term performance of remedial technologies and aid in decision making, e.g. with respect to discontinuation of a technology or implementation of an alternative.

However, further research is needed to better constrain the value of machine learning methods for linking geophysical logging datasets to contaminant mass distributions via a common dependence on the pore geometric properties of the matrix.

One of the most promising outcomes of this work is the possible estimation of mass transfer coefficients and the ratio of mobile to immobile porosity of the rock matrix from a relatively simple tracer test involving simultaneous measurements of bulk fluid conductivity and specific conductance. Although only demonstrated in the laboratory, the measurement could be transferred to an in-borehole test with only a limited amount of technology development. The advantage of this measurement is its inherent scalability. Information on the scaling of mass transfer coefficients from the matrix scale to larger scales that integrate across fracture zones would be possible. Knowledge of the spatial variability in mass transfer coefficients could significantly advance understanding of long-term contaminant fate and the role of back-diffusion at heterogeneous sites.

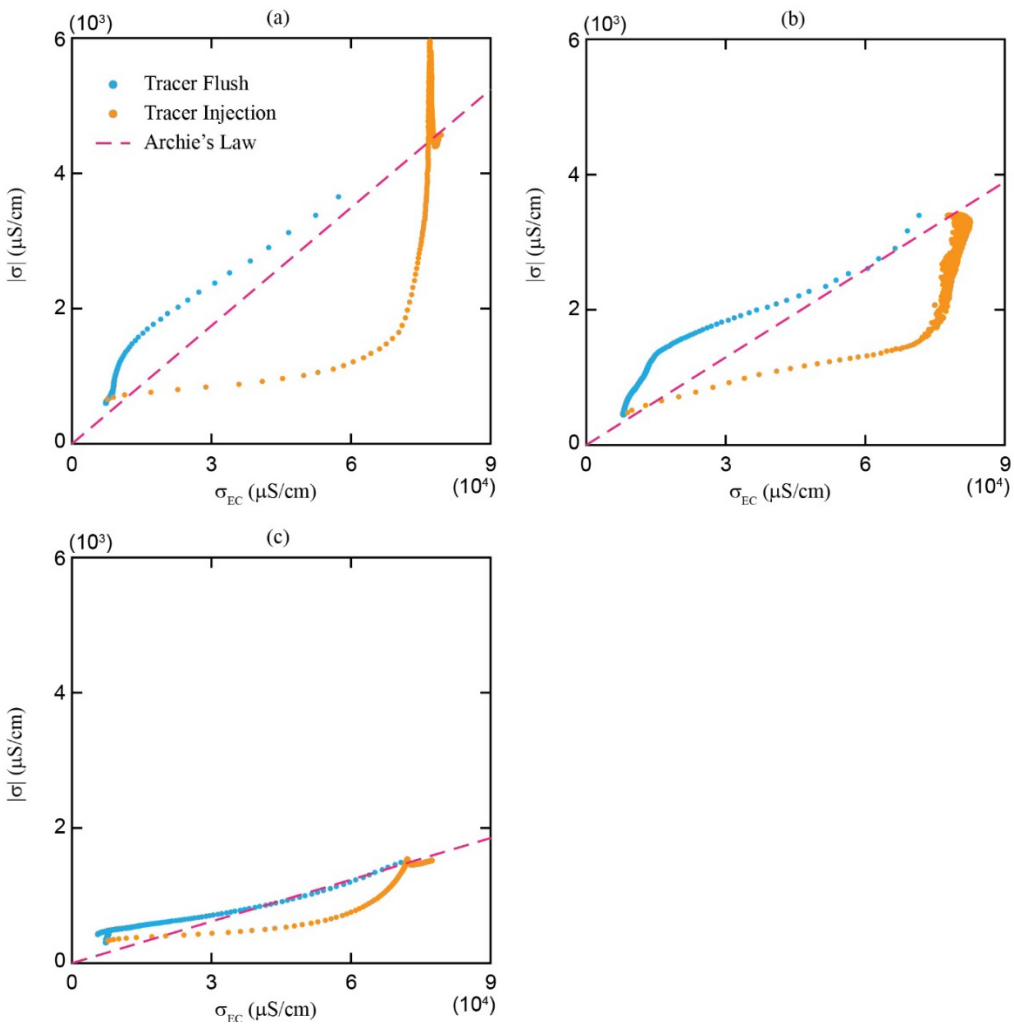

Figure ES5. Hysteresis Loops for (a) HC-MP24S-P-006-1V, (b) HC-MP24S-P-007-2H, and (c) SS-C3-P-019.

The hysteresis loops are diagnostic of a mass transfer between relatively mobile and immobile pore domains. All hysteresis loops are plotted alongside Archie's Law, using the formation factor calculated during the initial phase of the tracer experiment for each sample.

In total, results of this project support the adoption of two emerging geophysical technologies, NMR and CR, for the relatively rapid and cost-effective acquisition of information on the distribution of pore geometric properties controlling contaminant transfer at chlorinated solvent sites. These non-invasive borehole logging technologies provide information that cannot be readily obtained from the existing suite of geophysical logs that are in routine use at contaminated sites. The results of the project do not provide a compelling case for the direct detection of contaminant mass in situ. Future improvements in the sensitivity of borehole logging instrumentation so that they have similar sensitivity to the laboratory measurements may improve opportunities to detect contaminant mass with these measurements. However, results of this project suggest that these techniques should currently primary be focused on improving information on the spatial distribution of critical pore geometric properties controlling flow and transport such as the pore size distribution and permeability. In addition to providing valuable information on the likely distribution of contaminant mass, such high-resolution information could be invaluable for validating a variety of contaminant transport models.