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FINAL REPORT

Bench-Scale Assessment of NMR and Complex Resistivity (CR) Screening Technologies for Rapid Assessment of PFAS in Soils and Sediments

Lee Slater
Kristina Keating
Rutgers University Newark

Charles Schaefer
CDM Smith

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Lee Slater, Samuel Falzone, Charles Schaefer & Kristina Keating

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Environmental Sciences,
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101 Warren St, Newark,
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14. ABSTRACT
The significant sorption of PFASs onto soils opens the door to the possibility that two existing geophysical technologies, nuclear magnetic resonance (NMR) and complex resistivity (CR), might show some measurable response to high PFAS concentrations in AFFF source zones. This exploratory project investigated the hypothesis that, "sorption of PFAS compounds onto soil-fluid interfaces will result in a detectable CR and/or NMR response". Specific objectives of the project focused on evaluating the potential for using these technologies as rapid screening tools for evaluation of PFASs in soils and sediments. The study conclusively showed that the low-field NMR geophysical method does not have adequate sensitivity to detect PFAS in soils. In contrast, laboratory measurements provided evidence that sorption of PFAS contaminants onto artificial and natural soils may result in a detectable CR signature. CR signals on artificial soils saturated with synthetic PFAS-contaminated groundwater captured the temporal evolution of a polarization attributed to PFAS sorption.

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PFAS, AFFF, sorption, geophysics, nuclear magnetic resonance, complex resistivity

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ACRONYM LIST

AFFF	Aqueous Film Forming Foam
BET	Brunauer–Emmett–Teller
CC	Complex conductivity
CR	Complex resistivity
CVOC	Chlorinated volatile organic compound
EDL	Electrical double layer
ERSON	Environmental Remediation Statement of Need (SON)
JBMDL	Joint Base McGuire-Dix-Lakehurst
MICP	Mercury Injection Capillary Pressure
MS	Magnetic susceptibility
NAPL	Non-aqueous phase liquid
NMR	Nuclear Magnetic Resonance
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFSA	Perfluorosulfonic acid
PFCA	Perfluorinated carboxylic acid
RF	Radio frequency
RPM	Remediation project manager
SC	Fluid specific conductance

KEYWORDS

PFAS, geophysics, sorption, nuclear magnetic resonance (NMR), complex resistivity (CR)

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4 EXECUTIVE SUMMARY

4.1 Introduction

The nature and distribution of PFASs in AFFF-impacted source areas remains poorly understood. AFFF-impacted soils and sediments are relatively enriched over groundwater in the anionic long-chain PFSAs and PFCAs as indicated by measurements of individual PFASs (Anderson et al., 2016) and by the total oxidizable precursor (TOP) assay (Houtz et al., 2013). Sorption is expected to play an important role in determining the fate and transport of PFASs with cationic and zwitterionic PFASs more strongly associated with soil phases and serving as a long-term source via slow desorption and/or transformation. Recent studies have shown that increases in dissolved organic matter and ionic strength impact sorption of PFASs to solids (Carmosini and Lee, 2008; Tang *et al.*, 2010; Jeon *et al.*, 2011; Wang et al., 2012), and that redox conditions can impact the sorption of PFOS (Ololade et al., 2016)). The significant sorption of PFASs onto soils opens the door to the possibility that two existing geophysical technologies, nuclear magnetic resonance (NMR) and complex resistivity CR, might show some measurable response to high PFAS concentrations in AFFF source zones. As geophysical screening tools, CR and NMR methods are unique in that they are sensitive to the interfacial properties of soils. Both measurements are sensitive to the total pore volume normalized surface area (S_{por}); this sensitivity has been exploited to good effect for permeability prediction from both methods (Coates et al., 1999; Revil and Florsch, 2010). However, it is the potential sensitivity of both methods to the electrochemical properties of the mineral-fluid interface that motivated this project. These technologies respond to changes in the interfacial chemistry/mineralogy properties of the surface of soil particles.

This project responded to Statement of Need (SON) ERSON-19-C2 “explored the hypothesis that, “development of environmental sampling methods for per- and polyfluoroalkyl substances (PFASs) in the subsurface”. The primary hypothesis of the work was that sorption of PFAS compounds onto soil-fluid interfaces will result in a detectable CR and/or NMR response”. A positive evaluation of this hypothesis would benefit DoD as both CR and NMR could be implemented from a borehole or surface measurement for rapid screening to assess PFAS distribution, identify/delineate sources, and facilitate evaluation of remedial performance. Such a technology would promote management and treatment strategies based on field-scale geophysical datasets. A negative evaluation of this hypothesis would also be valuable as it would dissuade DoD from investing funds into premature field-scale projects proposing to use geophysical technologies to assist with PFAS characterization. There is a tendency for geophysical practitioners to oversell their tools/technologies to remedial project managers (RPMs) having limited understanding of the capabilities/limitations of the methods. This is particularly prevalent when a new class of contaminants is identified and in need of detection.

4.2 Objectives

The overarching objective of this project was to perform the bench-top experiments needed to evaluate the potential for using two existing borehole-deployable geophysical technologies, complex resistivity (CR) and nuclear magnetic resonance (NMR), as rapid screening tools for evaluation of PFASs in soils and sediments. Sorption is expected to play an important role in determining the fate and transport of PFASs. PFOA and PFOS, the most studied PFASs, are anions at typical environmental pH values, but still exhibit strong interactions with solid-phase organic carbon (Enviro Wiki, 2021). It is reasonable to assume that cationic and zwitterionic PFASs will be more strongly associated with soil phases. The tantalizing possibility that CR and NMR measurements may be sensitive to PFASs in source zones results from the potential for PFAS sorption onto soil surfaces to sufficiently modify the interfacial chemistry/mineralogy parameters that control these geophysical responses.

Specific objectives of the original project scope were:
(1) acquire bench top CR and NMR measurements on three types of synthetic samples [sand/organic soils, sand/clays, sand/iron oxides] contaminated with PFAS and/or AFFF solutions at source zone concentrations
(2) acquire bench top CR and NMR measurements on natural soils from AFFF source zone locations allowing a comparison of signal from contaminated versus uncontaminated soils.

During the project, an opportunity arose to extend the scope of work and perform some small-scale, field measurements at Joint Base Dix Mcguire Lakehurst (JBMDL), located in Burlington and Ocean Counties of New Jersey, the site of the AFFF source zone where samples were acquired. A third objective was therefore added:
(3) acquire initial field-scale measurements at an AFFF source zone location to evaluate whether CR signatures of PFAS sorption observed in the laboratory experiments could be captured with field instrumentation.

A limited scope project was originally proposed given the relatively high technical risk of a negative result (i.e., that the geophysical technologies would not be sufficiently sensitive to real world PFAS concentrations (or in the complex mixtures associated with AFFF sources) to provide diagnostic, measurable signatures. This project was designed to acquire key data needed to demonstrate proof of concept at minimal cost/investment, negating any futile expenditure on field-scale application of existing geophysical technologies for screening of PFAS contaminated sites.

4.3 Technical Approach

Two geophysical technologies, CR and NMR, currently deployable either from a borehole or, in the case of CR, from the surface for investigating shallow soils (~ top 50 cm) were used in this study. The CR method is unique in applied geophysics in that it has strong sensitivity to both the geometry of the pore space (like NMR) and the electrochemistry of the mineral-fluid interface. This method also provides information on the distribution of the pore sizes within a rock. Research on the CR method is also increasingly demonstrating its potential to detect and monitor geochemical and biogeochemical processes that alter both the physical and chemical properties of the mineral-fluid interface. Recent work indicates that CR measurements hold strong promise for detecting sorption processes. Such studies have already demonstrated that sorption of ionic compounds sufficiently modifies the electrical properties of a porous material to be detectable with laboratory CR measurements.

The low field NMR method has emerged as a geophysical technology unique in geophysics in that it is foremost directly sensitive to the presence of hydrogen associated with water or hydrocarbons. NMR measurements can be collected in the field, using a borehole tool or a surface-based instrument (beyond the scope of this project), or in the laboratory. The NMR method is foremost used to detect variations in the porosity and pore size distribution of soils and rocks, from which estimates of permeability can be obtained. The possibility of sensing PFAS sorption using NMR relates to the surface relaxivity, which accounts for the control of the chemical properties of the pore surface on NMR measurements. Some studies have shown that sorption of contaminants such as hydrocarbons can have a mediating effect on surface relaxation. This phenomenon has been attributed to the ability of a surface coating of contaminant to block proton/paramagnetic coupling, therefore reducing surface relaxivity.

The technical approach involved two phases. In the first phase, CR and NMR measurements were acquired on artificial soils and natural soils acquired from the AFFF source zone at Joint JBMDL. The artificial soil experiments involved measurements on sand/organic material, sand/clay material and pure sand mixtures contaminated to evaluate the sensitivity of CR and NMR measurements to sorption of PFAS constituents in a commercial AFFF solution. Initial measurements on natural soils focused on samples acquired from impacted and uncontaminated locations around the source zone at JBMDL. These soils were saturated with a synthetic groundwater based on that previously determined at JBMDL as part of ongoing SERDP Project ER18-1204.

The second phase of the technical approach focused solely on CR data acquisition. In this phase, three natural soil samples from JBMDL were monitored for one month during continuous flushing of the samples with the synthetic groundwater to promote desorption of PFAS compounds from the contaminated soil. In a related effort, the CR response of PFAS contaminated soils from JBMDL before and after methanol treatment to remove strongly sorbed PFAS constituents was investigated. The second phase also exploited a unique opportunity to perform a series of preliminary field-scale CR measurements within the vicinity of the source zone at JBMDL. This included an initial round of spot measurements close to versus far from the AFFF source zone, followed by a more detailed transect spanning the expected extent of the source zone.

4.4 Results and Discussion

The study conclusively showed that the low-field NMR geophysical method (not NMR relaxometry) does <u>not</u> have adequate sensitivity to detect PFAS in soils through hypothesized blocking of proton/paramagnetic coupling by sorbed constituents on mineral surfaces. No detectable signals were observed in the laboratory, so the technology was not pursued in the subsequent preliminary field-scale investigations.

Laboratory measurements provided evidence that sorption of PFAS contaminants onto artificial and natural soils may result in a detectable CR signature. This is consistent with the known sensitivity of the CR method to the electrical double layer chemistry, specifically the effects of sorption and desorption on the surface charge density and surface ionic mobility. Comparisons of CR signals on artificial soils saturated with synthetic PFAS-contaminated groundwater constructed from a 500-fold dilution of AFFF versus the same contaminated groundwater without the addition of AFFF captured the temporal evolution of a polarization enhancement in the AFFF contaminated soil that we attribute to PFAS sorption. In contrast, experiments on the same artificial soils found no significant difference in the temporal CR response for samples saturated with PFAS contaminated groundwater acquired near an AFFF-impacted source area at Ellsworth Air Force Base versus samples saturated with a synthetic groundwater matching the major ion chemistry and specific conductance. This might be expected as PFAS constituents in contaminated groundwater likely exclude those strongly sorbing zwitterionic and cationic compounds that are present in diluted AFFF formulations.

Laboratory measurements on natural soils acquired from the JBMDL site did not conclusively establish a link between soil PFAS concentrations and CR signal. Elevated CR signals were recorded for two out of three samples showing PFAS contamination (concentrations between 72-1336 ppb) relative to four samples taken away from the source zone (concentrations less than 6 ppb). However, the sample with the highest concentration did not show a significant elevation in CR relative to the samples acquired away from the source zone.

Mixed results were obtained for the experiments aimed at examining the CR signals before and after removal of sorbed PFAS from natural soils. No significant change in CR was recorded during the one month of flushing of contaminated JBDML soils with synthetic groundwater. Although a negative result, the lack of a CR response in this experiment may be consistent with a growing body of literature suggesting that it is very challenging to remove PFAS constituents sorbed to soil particles via flushing. CR measurements before and after the methanol treatment aimed to remove PFAS did result in a significant reduction of polarizability following the treatment. This decrease in polarizability is consistent with the removal of sorbed ionic constituents that control the magnitude of the CR response and supported by PFAS concentrations for the pre-wash and washed samples.

Field-scale CR measurements on the transect crossing the source zone at JBMDL revealed a region of distinctly elevated polarizability consistent with a localized region of high soil PFAS contamination as confirmed by soil sampling and PFAS analysis. Consistent with the laboratory results, this region of high polarizability is not associated with an elevated real conductivity and is therefore unlikely to result from changes in soil texture. In contrast, another zone of high polarizability identified along the survey line is associated with a corresponding increase in the real conductivity. This response is likely the result of a change in soil texture. The phase measurement of the CR response appears to be more directly diagnostic of soil polarizability resulting from PFAS sorption and insensitive to change in polarizability resulting from changing variations in soil texture at this JBMDL site. Further soil sampling and PFAS analysis is needed to verify the statistical significance of the relationship between the CR signal and soil PFAS concentrations in these field datasets.

4.5 Implications for Future Research and Benefits

Any further geophysical investigations of contaminated soils from PFAS source zones should focus on the CR method only. This project conclusively showed that the low-field NMR response to the presence of sorbed PFAS constituents was either negligible, or too ambiguous, to warrant further investment in this technology. The low-field NMR method is a promising technology for characterization of water content, porosity and permeability in soils and rocks, but it is not a candidate technology for characterization of PFAS contaminants in soils.

This project identified the CR signal to the presence of sorbed PFAS contaminants by examining (a) synthetic soils contaminated with a 500-fold dilution of commercially available AFFF solution, and (b) natural soils from the vicinity of a known PFAS source zone. Experiments on the natural soils included, (1) a laboratory comparison of soils from confirmed PFAS contamination locations versus uncontaminated locations, (2) a two-month flushing experiment done to try and remove sorbed PFAS, (3) a comparison between soils prior to and after a methanol wash designed to promote removal of sorbed PFAS, and (4) an in situ transect of field CR measurements crossing the JBMDL source zone.

Additional field-scale CR measurements at multiple sites are needed to fully understand the potential for using this geophysical technology as a PFAS source zone screening method. Field-scale deployment of CR was not within the original scope of the SEED project. However, preliminary field observations were acquired at the JBMDL site given that an opportunity arose with little additional cost. The measurements at JBMDL confirmed the quality of the field CR measurements and provided initial evidence that a field-scale CR signature of PFAS-contamination in soils might exist. The maximum PFAS concentration recorded in the sampled soils from JBMDL was 1336 ppb. Although high, this is substantially less than concentrations recorded at some other well-characterized PFAS source zone sites (e.g., Ellsworth Air Force Base), providing the motivation for the proposal that seeded this project. It would be valuable to learn whether a significant correlation between CR response and PFAS concentration is revealed as these higher PFAS concentrations are encountered.

The objective of the follow-on work would therefore be to further evaluate the sensitivity of field-scale CR to PFAS contaminated soils by acquiring measurements over multiple source zones, supported by acquisition of a large enough population of soil samples, with subsequent analysis of PFAS analytes to make a statistically significant assessment of field-scale CR sensitivity to PFAS contamination. At JBMDL, additional acquisition and analysis of soil samples along the initial 2D transect of CR measurements, with samples separated by depth, would statistically verify whether the identified region of high polarizability is indeed attributable to elevated PFAS contamination. The benefits of this work would include a robust assessment of what information on PFAS contamination is realistically extractable from field-scale SIP measurements of shallow contaminated soils from measurements made at the surface.

If further field work merits additional investment in the technology, future laboratory work might focus on determining the sensitivity limits of CR to PFAS contamination in soils. CR will only serve as a technology for screening PFAS source zones and the information will be inherently semi-quantitative at best. It will never be possible to link CR signals to specific concentrations of PFAS constituents. Given that CR signals are expected to be foremost controlled by the cationic and zwitterionic PFASs, some empirical calibration of CR signal against concentrations of these strongly sorbing PFAS constituents might be possible. In this respect, the simplest follow-on experiment would involve measurements on a range of AFFF dilutions at concentrations lower than the 500-fold dilution tested in this study. To enhance field relevance, these experiments would be conducted on natural soils representing PFAS source zones rather than the artificial (sand-organic sediment, sand-clay) mixtures investigated in this study. Soils could be obtained from multiple PFAS source zone locations where concentrations are documented at levels similar to those explored in this study. The major benefit of this additional research would be an understanding of the minimum PFAS concentrations in soils that might be detected with the CR technology.

There is growing evidence that PFAS constituents sorb to the air-water interface in addition to the mineral-water interface. In fact, PFAS contamination levels have been found to be higher in unsaturated soils than saturated soils, with evidence of flushing out of PFAS contaminants following destruction of air-water interfaces during infiltration or rainfall events. Previous laboratory studies indicate that CR is sensitive to both the air-water interface and the mineral-water interface. Therefore, CR measurements on PFAS contaminated, unsaturated soils versus uncontaminated soils at the same level of contamination might be worth pursuing in the future. These measurements could be performed on natural soils from the vicinity of a PFAS source zone. Benefits of this work would include some understanding of the potential application of CR for monitoring PFAS dynamics in unsaturated soils, as well as advances in general understanding of PFASs in the unsaturated zone.

5 Abstract

Introduction and Objectives:

The significant sorption of PFASs onto soils opens the door to the possibility that two existing geophysical technologies, nuclear magnetic resonance (NMR) and complex resistivity (CR), might show some measurable response to high PFAS concentrations in AFFF source zones. This exploratory project investigated the hypothesis that, "sorption of PFAS compounds onto soil-fluid interfaces will result in a detectable CR and/or NMR response". Specific objectives of the project focused on evaluating the potential for using these technologies as rapid screening tools for evaluation of PFASs in soils and sediments.

Technical Approach:

In the first phase, CR and NMR measurements were acquired on (1) artificial soils and, (2) natural soils, collected from the PFAS source zone at Joint Base McGuire Dix Lakehurst (JBMDL), NJ. The artificial soil experiments involved measurements on sand/organic material, sand/clay material and pure sand mixtures contaminated to evaluate the sensitivity of CR and NMR measurements to sorption of PFAS constituents in a commercial AFFF solution. Initial measurements on natural soils focused on samples acquired from impacted, suspected impacted and assumed uncontaminated locations around the source zone at JBMDL. These soils were saturated with a synthetic groundwater based on the composition of groundwater obtained from JBMDL.

In the second phase, three natural soil samples from JBMDL were monitored for one month during continuous flushing of the samples with the synthetic groundwater to promote desorption of PFAS compounds from the contaminated soil. In a related effort, the CR response of PFAS contaminated soils from JBMDL before and after methanol treatment to remove strongly sorbed PFAS constituents was investigated. The second phase also exploited a unique opportunity to perform a series of preliminary field-scale CR measurements on a transect crossing the source zone at JBMDL.

Results and Discussion:

The study conclusively showed that the low-field NMR geophysical method does not have adequate sensitivity to detect PFAS in soils. No detectable signals were observed in the laboratory, so the technology was not pursued in the subsequent preliminary field-scale investigations. In contrast, laboratory measurements provided evidence that sorption of PFAS contaminants onto artificial and natural soils may result in a detectable CR signature. CR signals on artificial soils saturated with synthetic PFAS-contaminated groundwater captured the temporal evolution of a polarization attributed to PFAS sorption. However, laboratory measurements on natural soils acquired from JBMDL did not conclusively establish a link between soil PFAS concentrations and CR signal. Although no detectable CR response was recorded from flushing a natural PFAS-contaminated soil to promote desorption over a 1-month period, a significant decrease in imaginary conductivity was recorded following a methanol wash procedure to promote PFAS desorption. Field-scale CR measurements at JBMDL revealed an intriguing complex conductivity pattern, with imaginary conductivity increasing towards the expected source of the contamination.

Implications for Future Research and Benefits:

Any further geophysical investigations of contaminated soils from PFAS source zones should focus on the CR method only. Future experiments should determine, to the extent possible, the sensitivity limits of CR to PFAS contamination. Additional experiments on natural soils and/or field-scale measurements could be performed at other well-characterized PFAS source zone sites where much higher source zone PFAS concentrations are documented. Finally, given the growing evidence that PFAS constituents sorb to the air-water interface in addition to the mineral-water interface, CR measurements on PFAS-contaminated unsaturated soils are warranted.

6 Objective

The overarching objective of this project was to perform the bench-top experiments needed to evaluate the potential for using two existing borehole-deployable geophysical technologies, complex resistivity (CR) and nuclear magnetic resonance (NMR), as rapid screening tools for evaluation of PFASs in soils and sediments. Sorption is expected to play an important role in determining the fate and transport of PFASs. PFOA and PFOS, the most studied PFASs, are anions at typical environmental pH values, but still exhibit strong interactions with solid-phase organic carbon (Enviro Wiki, 2021). It is reasonable to assume that cationic and zwitterionic PFASs will be more strongly associated with soil phases. The tantalizing possibility that CR and NMR measurements may be sensitive to PFASs in source zones results from the potential for PFAS sorption onto soil surfaces to sufficiently modify the interfacial chemistry/mineralogy parameters that control these geophysical responses.

Specific objectives of the original project scope were:
(1) acquire bench top CR and NMR measurements on three types of synthetic samples [sand/organic soils, sand/clays, sand/iron oxides] contaminated with PFAS and/or AFFF solutions at source zone concentrations
(2) acquire bench top CR and NMR measurements on natural soils from AFFF source zone locations allowing a comparison of signal from contaminated versus uncontaminated soils.

During the project, an opportunity arose to perform some small-scale, field measurements at the site of the AFFF source zone where samples were acquired. A third objective was therefore added:
(3) acquire initial field-scale measurements at an AFFF source zone location to evaluate whether CR signatures of PFAS sorption observed in the laboratory experiments could be reliably measured with field instrumentation

A limited scope project was originally proposed given the relatively high technical risk of a negative result, i.e., that the geophysical technologies would not be sufficiently sensitive to real world PFAS concentrations (or in the complex mixtures associated with AFFF sources) to provide diagnostic, measurable signatures. This project was designed to acquire key data needed to demonstrate proof of concept at minimal cost/investment, negating any futile expenditure on field-scale application of existing geophysical technologies for screening of PFAS contaminated sites.

7 Background

The nature and distribution of PFASs in AFFF-impacted source areas remains poorly understood. AFFF-impacted soils and sediments are relatively enriched over groundwater in the anionic long-chain PFSAs and PFCAs as indicated by measurements of individual PFASs (Anderson et al., 2016) and by the total oxidizable precursor (TOP) assay (Houtz et al., 2013). Sorption is expected to play an important role in determining the fate and transport of PFASs with cationic and zwitterionic PFASs more strongly associated with soil phases and serving as a long-term source via slow desorption and/or transformation. Recent studies have shown that increases in dissolved organic matter and ionic strength impact sorption of PFASs to solids (Carmosini and Lee, 2008; Tang *et al.*, 2010; Jeon *et al.*, 2011; Wang et al., 2012), and that redox conditions can impact the sorption of PFOS (Ololade et al., 2016)). The significant sorption of PFASs onto soils opens the door to the possibility that two existing geophysical technologies, NMR and CR, might show some measurable response to high PFAS concentrations in AFFF source zones. As geophysical screening tools, CR and NMR methods are unique in that they are sensitive to the interfacial properties of soils. Both measurements are sensitive to the total pore volume normalized surface area (S_{por}); this sensitivity has been exploited to good effect for permeability prediction from both methods (Coates et al., 1999; Revil and Florsch, 2010). However, it is the potential sensitivity of both methods to the electrochemical properties of the mineral-fluid interface that motivated this work. As described below, these technologies respond to changes in the interfacial chemistry/mineralogy properties of the surface of soil particles.

A positive evaluation of this hypothesis would benefit the DoD as both CR and NMR could be implemented from a borehole or surface measurement for rapid screening to assess PFAS distribution, identify/delineate sources, and facilitate evaluation of remedial performance. Such a technology would promote management and treatment strategies based on field-scale geophysical datasets. A negative evaluation of this hypothesis would also be valuable as it would dissuade DoD from investing funds into premature field-scale projects proposing to use geophysical technologies to assist with PFAS characterization. There is a tendency for geophysical practitioners to oversell their tools/technologies to remedial project managers (RPMs) having limited understanding of the capabilities/limitations of the methods. This is particularly prevalent when a new class of contaminants is identified and in need of detection.

7.1 Geophysical technologies

As geophysical screening tools, CR and NMR methods are unique in that they are sensitive to the interfacial properties of soils. Both measurements are sensitive to the total pore volume normalized surface area (S_{por}); this sensitivity has been exploited to good effect for permeability prediction from both methods (Coates et al., 1999; Revil and Florsch, 2010). However, it is the potential sensitivity of both methods to the electrochemical properties of the mineral-fluid interface that motivated this exploratory project.

7.1.1 Complex resistivity (CR)

The CR method is unique in applied geophysics in that it has strong sensitivity to both the geometry of the pore space (like NMR) and the electrochemistry of the mineral-fluid interface (e.g. Knight et al., 2010). This method also provides information on the distribution of the pore sizes within a rock (e.g. Scott & Barker, 2003; Tong et al., 2006). Research on the CR method is also increasingly demonstrating its potential to detect and monitor geochemical and biogeochemical processes that alter both the physical and chemical properties of the mineral-fluid interface (Atekwana and Slater, 2009).

7.1.1.1 Basic principles of CR

The CR measurement records the combination of conduction and polarization properties of the subsurface. Conduction pathways determine how easily a rock conducts an electric current; the stored-charge response at low frequencies (below 1 kHz) is determined by diffusive polarization mechanisms associated with ions in the electrical double layer (EDL) forming at the mineral-fluid interface. Laboratory measurements are usually collected in the frequency domain (Figure 1) where an alternating low frequency current is injected and the change in voltage at a pair of receiving electrode(s) is measured along with the current phase lag φ. These CR measurements are frequency (f) dependent.

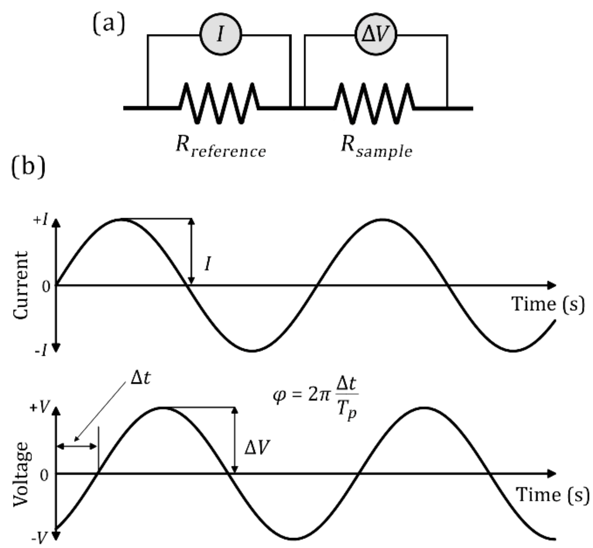

Figure 1: Complex resistivity measurements in the frequency domain, where the voltage magnitude and phase lag are recorded relative to the current waveform. From Binley and Slater (2020)

The complex conductivity σ^* is commonly described by the real σ' and imaginary σ'' conductivity components, which represent the conduction and polarization processes, respectively. The (frequency dependent) polarization strength represented by σ'' depends on S_{por} and the specific polarizability (c_p) (Weller *et al.*, 2010),

$$\sigma'' = c_p S_{por}, \qquad (1)$$

where c_p accounts for how the interfacial polarization is controlled by the electric double layer (EDL) chemistry.

CR measurements can be collected across a range of frequencies and a dominant relaxation time τ $(\tau = 1/(2\pi f))$ can be defined, which corresponds to a characteristic frequency at which the polarization is strongest. This relaxation time is related to a dominant relaxation length-scale of the polarization, such as the pore or grain diameter (d), via a diffusion coefficient (D_+) that is controlled by the EDL chemistry (Schwarz, 1962; Revil *et al.*, 2015),

$$\tau = \frac{d^2}{2D_+}. \qquad (2)$$

D_+ is related to the effective ionic mobility β_+^s , temperature T, the Boltzmann's constant k_b and the charge of counterions in the Stern layer q_+ by the Nernst-Einstein relationship $D_+ = k_b T \beta_+^s / |q_+|$. The form of equation 2 has been repeatedly used to relate polarization spectra to a dominant grain or pore size in porous media (Binley et al., 2005; Scott & Barker, 2003; Zisser et al., 2010). Commonly, short relaxation times τ correspond to small pores and large relaxation times correspond to large pores (Figure 2).

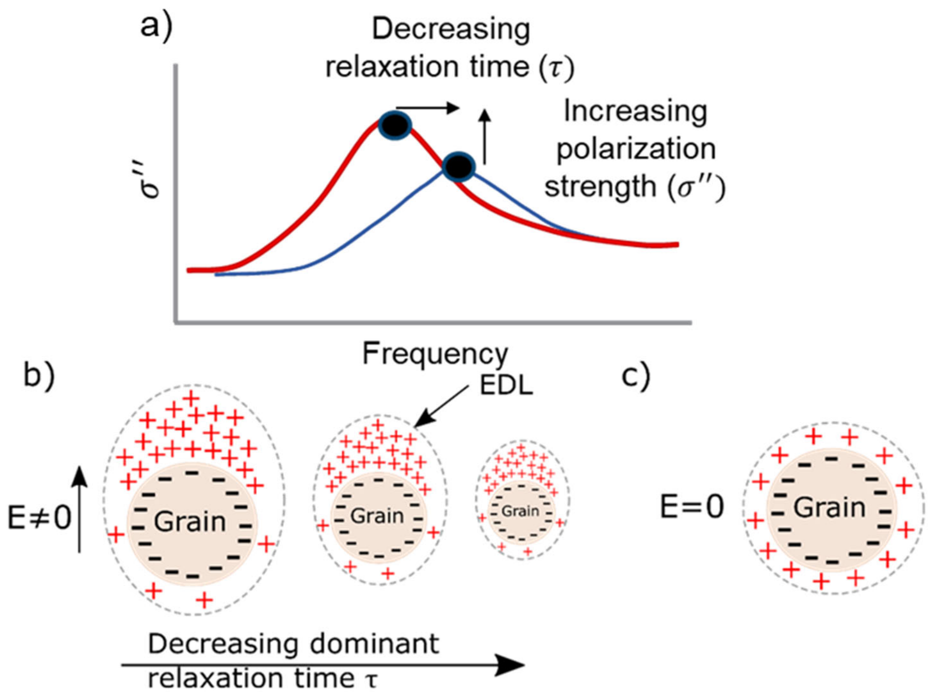

Figure 2: (a) Changes in polarization strength (σ'') and dominant relaxation time (τ) in CR spectra; (b) Conceptual representation of the relationship between grain size τ following application of an electric field (**E**).

Strong correlations exist between geometric length scales which control mass transfer and hydrogeological properties and CR measurements. The pore volume normalized specific surface area S_{por} has been strongly correlated with σ" in numerous studies. (e.g. Kruschwitz et al., 2016; Weller et al., 2010) . In addition, a strong correlation between τ and the pore radius (e.g. Revil et al., 2014) has been demonstrated.

7.1.1.2 Relationship between CR and sorption processes

Recent work indicates that CR measurements hold strong promise for detecting sorption processes. A number of recent studies have already demonstrated that sorption of ionic compounds sufficiently modifies the electrical properties of a porous material to be detectable with laboratory CR measurements. Zhang *et al.* (2012) showed experimental results and developed a conceptual model for the increase in CR response in silica gel as a result of hydroxide ion adsorption. (Vaudelet *et al.*, 2011a) demonstrated the sensitivity of CR to the sorption of Na, Zn and Pb onto silica sands and showed how the CR response depends on the affinities of these cations with the silica mineral surface. (Vaudelet *et al.*, 2011b) demonstrated the sensitivity of the CR response to ion exchange between sodium and copper on the surface of silica grains. Schwartz and Furman (2012) found that adsorption of crystal violet (a polar organic pollutant) decreased the CR response because of the decrease in inorganic ion site densities with adsorbed crystal violet. More recently, Hao *et al.* (2015) reported a strong CR response to the sorption of sodium cations on the mineral surface. They used a radioactive ^{22}Na tracer to independently track Na^+ accumulation onto silica gel. Important to this proposal, Hao et al. (2015) found a very strong (R^2 =0.99) relationship between ^{22}Na and σ'' measured with CR. They even demonstrated a methodology to estimate the number of surface sorption sites from the CR response. The striking correspondence between the ^{22}Na tracer and the CR parameters makes a compelling argument for conducting the proposed research. In a follow up study, Hao *et al.* (2016) compared CR estimates of deprotonation and subsequent sorption of Na^+ ions against estimates from geochemical modeling of potentiometric acid titration data. They observed small differences in the estimated surface site density from the two methods. Despite the fact that the experiments by Zhang *et al.* (2012) and Hao *et al.* (2015) considered much simpler systems than we anticipate for PFAS-impacted soils, the results of this study clearly support further research into the possible potential of CR for detecting sorption processes in porous media.

7.1.2 Nuclear magnetic resonance (NMR)

In this project we focus on low field NMR spin relaxometry measurements that can currently be acquired relatively inexpensively with existing logging tools. Others are exploring the use of NMR spectroscopy which can potentially be tuned to directly sense specific contaminants (*Longstaffe and Konzuk*, 2015). Although NMR spectroscopy has great potential for contaminant assessment, it is currently not possible to log a borehole at a PFAS contaminated site using a spectroscopic NMR measurement.

7.1.2.1 Basic principles of NMR

The low field NMR method has emerged as a geophysical technology unique in geophysics in that it is foremost directly sensitive to the presence of hydrogen associated with water or hydrocarbons. NMR measurements can be collected in the field, using a borehole tool or a surface-based instrument (beyond the scope of this project), or in the laboratory.

NMR measurements are commonly utilized in the evaluation of petroleum reservoirs to determine porosity, to estimate the distribution of pore sizes and permeability, and to distinguish mobile fluid content from clay or capillary bound fluid content, (e.g. Allen et al., 2000; Kleinberg et al., 1992). NMR measurements have more recently been used to determine water content and estimate hydraulic conductivity in shallow aquifers (Knight et al., 2016). Recent advances in NMR data collection strategies have encouraged exploration of the sensitivity of NMR measurements to different fluid types (i.e., hydrocarbons from water as reported by Song, 2010).

The NMR relaxation phenomenon results from the fact that all nuclei with an odd number of protons or neutrons possess a nuclear spin angular momentum. In a static magnetic field, the nuclear spins of a fraction of the protons will align with the static field resulting in a total magnetization that is proportional to the number of protons in the sample. In the NMR experiment an oscillating radio frequency (RF) pulse tuned to perturb hydrogen spins, is applied to the sample for a short time (Figure 3a), The frequency of the RF pulse is called the Larmor frequency, f_0, and is related to the strength of the static magnetic field, B_0, and the gyromagnetic ratio of hydrogen. The application of a series of RF pulses causes the nuclear spins to diverge from their equilibrium position; the return to equilibrium results in a measurable change in the bulk nuclear magnetization over time, *t*. For NMR measurements collected in the laboratory f0 ranges from 0.25 MHz to 900 MHz and is typically 2 MHz for rock core analyzers used for geophysical studies. For NMR borehole measurements f_0 ranges from 0.25 MHz to 2 MHz depending on instrument type and configuration. For a water-saturated geological material, the measurable signal, $I_{xy}(t)$, exhibits multi-exponential decay (e.g., Timur, 1969),

$$I_{xy}(t) = I_0 \sum_i f_i e^{-t/T_{2i}} \qquad (3)$$

where the sum is taken over the pore environments in the measured volume. I_0, the initial signal magnitude, is proportional to the total number of hydrogen atoms (i.e., the water content) in the measured volume and can be used to estimate the porosity in a saturated sample and the water content in a partially saturated sample. F_i is the proportion of the measured signal that relaxes with a time of T_{2i}. The value of f_i is typically plotted versus T_{2i} to yield a distribution of NMR relaxation times (T_2-distributions).

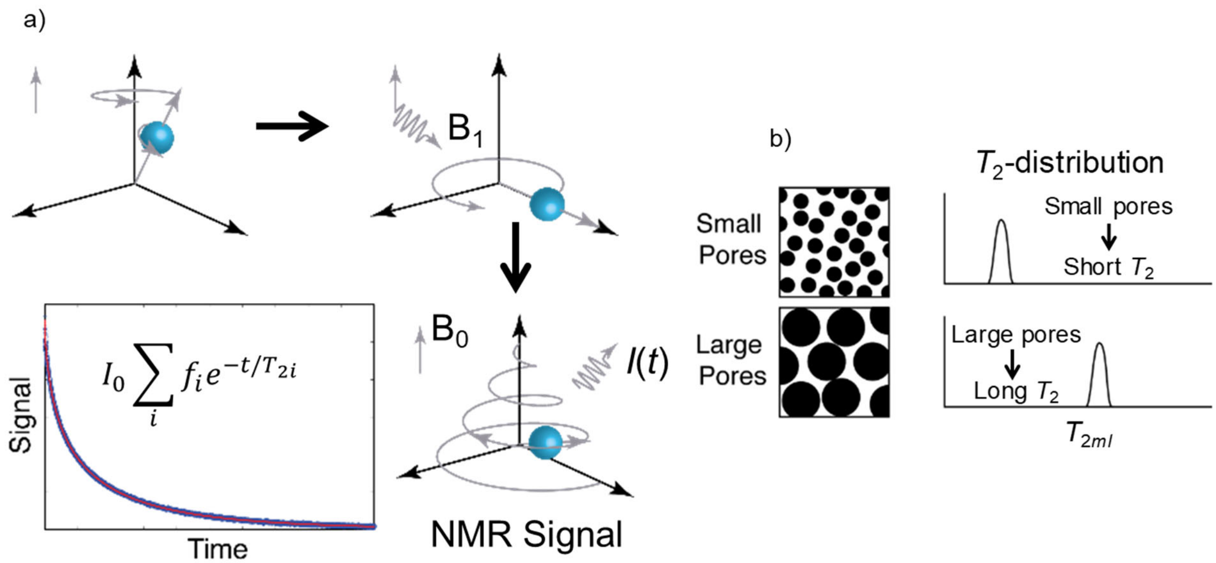

Figure 3: Basic principles of low-field nuclear magnetic resonance (NMR): (a) Initial signal intensity directly proportional to water content; (b) Signal relaxation is related to pore size distribution. Immobile and mobile porosity/water content can be discriminated.

The value of T_{2i} is related to the physical and chemical properties of the pore. In a fully saturated pore, the inverse of T_{2i} is commonly assumed to be proportional to the radius of the ith pore r_i,

$$\frac{1}{T_{2i}} = \frac{\rho_{2i}}{r_i}, \quad (4)$$

where the constant of proportionality, ρ_{2i}, is called the surface relaxivity and is related to the paramagnetic content (e.g., unpaired electrons in iron(III)) on the surface of the pore (Foley et al., 1996; Keating & Knight, 2007). This equation allows the T_2-distribution to represent the distribution of pore sizes in the measured volume (Figure 3b). The T_2-distribution can be used to determine the fraction of capillary bound fluid and the fraction of free fluid within a sample.

The NMR relaxation time is often expressed with a single time, the mean log relaxation time, T_{2ML} (i.e., the weighted mean of the T_2 distribution). If the surface relaxivity, ρ_2, is uniform throughout the pore-space, T_{2ML} can be used to determine the characteristic pore radius, i.e., S_{por}, of the measured volume,

$$\frac{1}{T_{2ML}} = \rho_2 S_{por}. \quad (5)$$

This equation assumes that there are no heterogeneities in the static magnetic field and that relaxation occurs in the "fast diffusion" regime where protons can move from the bulk fluid to the surface of a pore within the time scale of the measurement. Fast diffusion is valid as long as $\rho_2 r/D$ <<1 where D is the self-diffusion coefficient of water ($2.5x10^{-9}$ m^2/s for free water at 30°C) and r represents the average length traveled by a proton to reach the nearest surface (e.g., Keating & Knight, 2010). Since the assumption of fast diffusion has been found to hold in most geologic materials (Kleinberg, 2001), this relationship allows k to be estimated from NMR measurements via a Kozeny-Carman model (Kleinberg & Jackson, 2001; Yaramanci et al., 1999).

7.1.2.2 Relationship between NMR and sorption processes

The relationship between sorption and NMR-derived ρ_2 is not as direct or intuitive as is the case for CR-derived c_p. Surface chemistry/minerology characteristics primarily determine ρ_2 (Kleinberg and Horsfield, 1990), which describes the extent of the coupling between diffusing energized protons (i.e., hydrogen nuclei in water) and surficial paramagnetic sites (e.g., Fe^{3+} bearing minerals). The magnetic properties of sorbed substances are likely to be important, as the sorption of a paramagnetic substance would increase proton/paramagnetic coupling by increasing ρ_2 (Kleinberg and Horsfield, 1990). In some cases, the sorption of contaminants such as hydrocarbons can have a mediating effect on surface relaxation. This phenomenon has been attributed to the ability of a surface coating of contaminant to block proton/paramagnetic coupling, therefore reducing ρ_2 (Bryar and others, 2008).

7.1.3 Implications for detection of PFAS in soils using CR and NMR

Equations (1-5) show that the CR and NMR measurements both depend both on the pore geometry and the interfacial chemistry/mineralogy. In established applications of the methods for characterizing porous media (e.g., permeability estimation) the interpretation focuses on the linkages between the geophysical measurements and the geometric properties (S_{por}, d), assuming that the terms controlled by the interfacial chemistry/mineralogy are invariant. CR and NMR measurements might be sensitive to PFASs in source zones if PFAS sorption onto soil surfaces sufficiently modifies the interfacial chemistry/mineralogy parameters (ρ_2, c_p, D_+) to result in a detectable geophysical response (T_{2S}^{-1}, σ'' and τ).

A conceptual illustration of the hypothesized responses in CR (a-b) and NMR (c-e) measurements due to PFAS contamination is presented in Figure 4. Under normal conditions (a), the CR response is conceptualized by a redistribution of cations around the particle grain within the EDL as a result of an applied electric field ($\boldsymbol{E_0}$). In the presence of PFAS contamination (b), cationic and zwitterionic PFASs sorb to the surface, enhancing this charge redistribution and presumably leading to an increased polarization response.

Regarding NMR signals shown in Figure 4, under normal conditions (c) energized diffusing protons couple with paramagnetic sites on the pore surface, inducing relaxation and resulting in a relaxation time distribution that is sensitive to the pore size distribution and ρ_2. Two possible responses of NMR measurements to PFAS contamination are hypothesized – (d) Enhanced Relaxation, in which surface sorbed PFASs enhance relaxation by increasing ρ_2, shifting the relaxation time distribution to shorter relaxation times, and (e) Diminished Relaxation, in which sorbed PFASs diminish relaxation by creating hydrophobic surface conditions, resulting in less coupling between energized diffusing protons and paramagnetic surface sites, shifting the relaxation time distribution to longer relaxation times. Furthermore, more complex NMR spin relaxometry measurement methods developed for hydrocarbon exploration have the potential to discriminate contaminants directly (e.g., *Fay and Knight*, 2016) as discussed below. Such possibilities provide the motivation for this Limited Scope project.

As PFASs can occur as anionic, cationic, and zwitterionic ions, individual PFAS compounds may affect the response of CR and NMR differently. Since CR is believed to be most sensitive to sorbed ions, it would likely be most sensitive to cationic PFAS compounds. With NMR, however, any association with the surface could produce a mitigating effect on the influence of surficial paramagnetic sites on energized protons. In this case, NMR may be sensitive to anionic, cationic, and zwitterionic ions. Because these measurements may sense different PFAS contaminants, there may be a benefit in combining CR and NMR surveys to gain additional insight about a site, such as the nature of the original contaminant, the degradation state, and any other characteristic that could be evidenced by differences in the ratio of anionic, cationic, and zwitterionic PFAS compounds.

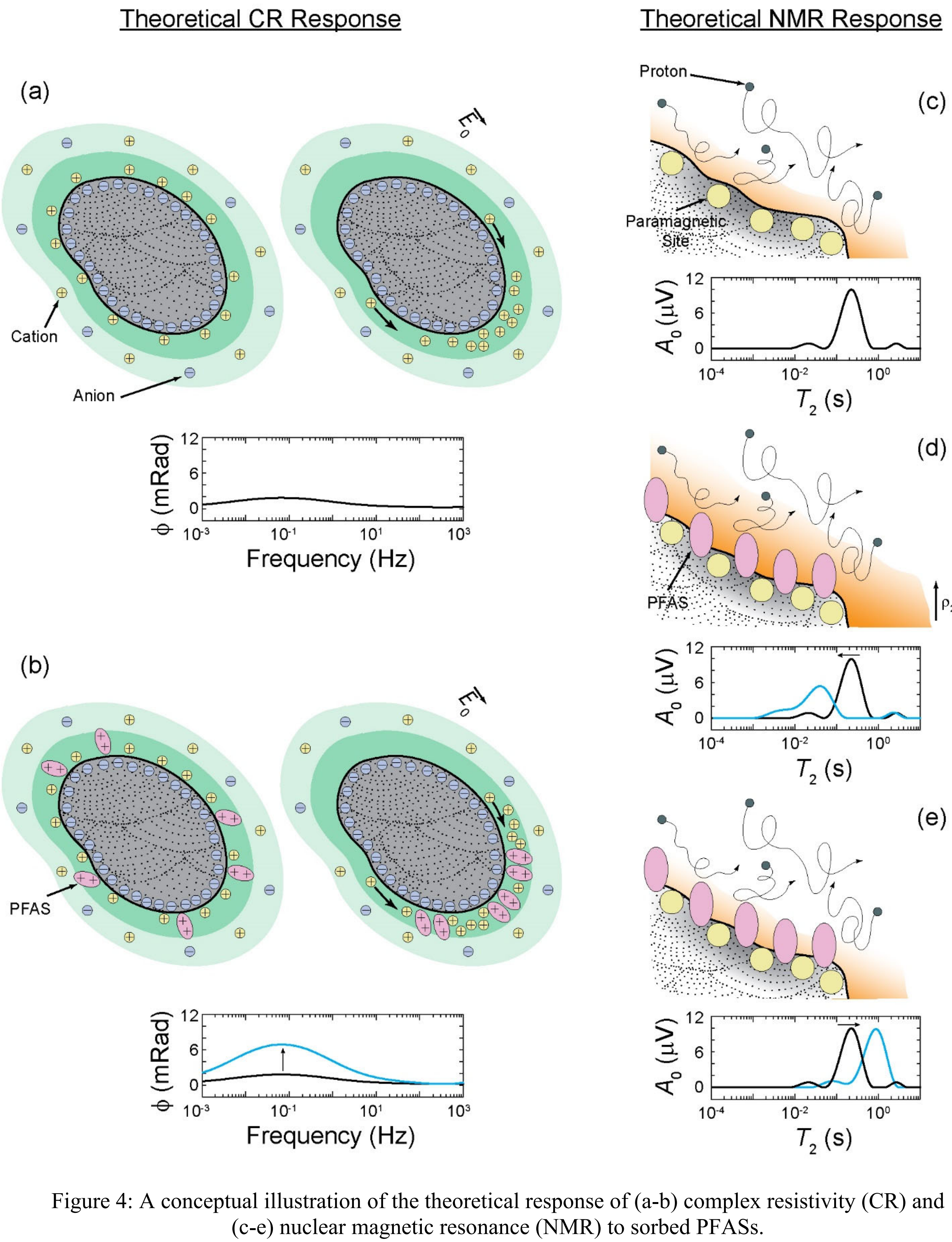

Figure 4: A conceptual illustration of the theoretical response of (a-b) complex resistivity (CR) and (c-e) nuclear magnetic resonance (NMR) to sorbed PFASs.

8 Materials and Methods

Laboratory measurements were performed to explore the sensitivity of the CR and NMR measurements to sorbed PFAS concentrations in soils. In addition, field measurements were conducted to gain initial insights into the possible sensitivity of CR to variations in soil PFAS concentrations in situ across a source zone. The experimental approach is described in this section.

8.1 Laboratory experiments

The sensitivity of CR and NMR to PFAS sorption was examined using (1) synthetic soils spiked with AFFF to represent high concentrations observed in PFAS source zone soils, and (2) natural soils with known PFAS contamination. Natural soils were obtained from an AFFF source zone at Joint Base McGuire-Dix-Lakehurst (JBMDL), described further in Section 8.1.3. All experiments were performed with triplicate soil columns for uncertainty assessment, which, for the synthetic soils, foremost relates to relatively subtle differences in the geophysical signals resulting from differences in the packing of soils. In the case of the natural soils, the differences foremost relate to inherent heterogeneity in the subsurface. Additional experiments using the CR method only were performed on (1) synthetic soils saturated with PFAS-contaminated water from Edwards Air Force Base, and (2) natural soils treated in two ways in an attempt to desorb PFAS constituents from soils. NMR measurements were not made in either of these cases, as the earlier experiments had shown that NMR was an unlikely technology for investigating PFAS contamination in soils.

8.1.1 Synthetic soil samples

A synthetic (uncontaminated) groundwater solution was prepared based on chemical analysis of the groundwater present at the JBMDL site. Columns containing the synthetic soil saturated with (uncontaminated) synthetic groundwater and columns containing the synthetic soil saturated with the synthetic groundwater spiked with a 500-fold dilution of commercially available AFFF solution were prepared in triplicate. This dilution was used to produce characteristic concentrations of PFAS, such as 7.5 mg/L total perfluoroalkyl acids (PFAAs), as confirmed in previous studies from contaminated sites (Backe and others, 2013).

Synthetic soil samples were wet packed into custom-designed sample holders (Figure 5a) by mixing soil in a basin with the saturating fluid and then tamping the slurry into the columns in 2 cm long segments. All synthetic soil samples were prepared in triplicate. CR and NMR measurements of the columns packed with synthetic soils were periodically collected over one month to allow time for full chemical equilibrium between the groundwater and the soil particle surface to be reached. The periodic measurements were intended to capture any evolution of the geophysical signatures as the saturating solution chemistry comes into equilibrium with the surface.

CR data were acquired with a portable lab and field instrument, the PSIP, manufactured by Ontash & Ermac Inc. (NJ, USA) (Figure 5b). Measurements of the impedance magnitude and phase shift were acquired from 0.01 Hz to 20 kHz using a four-electrode configuration.

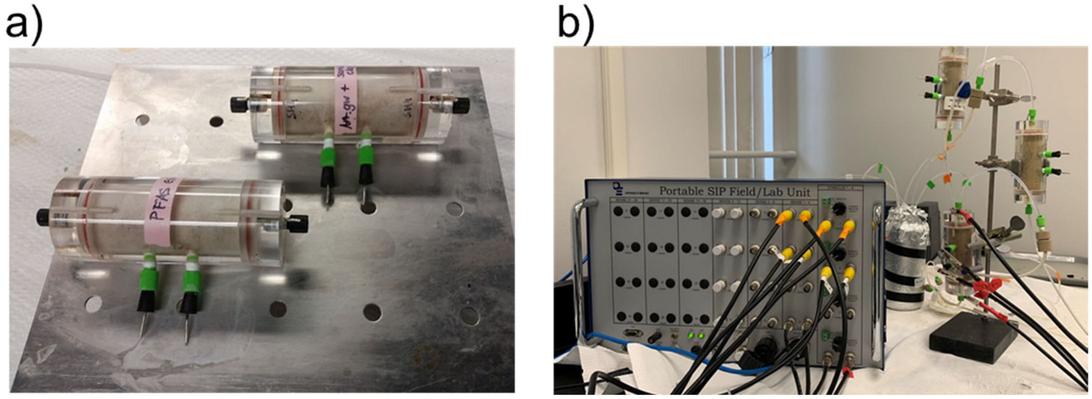

Figure 5: (a) Examples of samples packed into custom-built sample holders for CR and NMR measurements. The potential electrodes shown on the sides of the sample were used for the CR measurements and subsequently removed for the NMR measurements; (b) The PSIP instrument used for CR measurements (columns under test shown in the background).

8.1.1.1 Sand-organic mixtures (CR and NMR)

Experiment 1: Sand-organic mixtures using synthetic JBMDL groundwater

This synthetic soil was composed of sand mixed with peat (10% concentration by volume). Peat was used as an analog for organic material in a natural soil, which increases soil surface area and has a high cation exchange capacity. Organic soil content is commonly considered a key factor determining the extent of PFAS sorption occurring in natural soils. The sand and peat in the synthetic soils were mixed prior measurements to following the preparation procedure described in Section 8.1.1.

Experiment 2: Sand-organic mixtures saturated with PFAS contaminated groundwater from a field site

Given the encouraging results obtained in the first round of experiments, new peat samples were prepared in the same manner as described in Section 8.1.1 except that PFAS contaminated groundwater acquired by CDM Smith from Ellsworth Air Force Base was used in place of the AFFF-contaminated synthetic groundwater. PFAS concentrations in this groundwater are summarized in Table 1.

Table 1: PFAS concentrations (in ng/L) measured in groundwater acquired from Ellsworth Air Force Base.

PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFPeS	PFHxS	PFOS	4:2 FtS	6:2 FtS	8:2 FtS
3522	10181	17795	2752	10305	3076	2603	13397	6082	448	7407	100

for the contaminated sample. The control was prepared using a synthetic groundwater constructed from a major ion analysis of this contaminated groundwater sample (Appendix A). The composition of this synthetic groundwater is also given in Appendix A.

8.1.1.2 Pure sands

Pure sand samples were constructed to serve as a sample control as the surface area and sorption of ions on sand is generally too small to be reliably detected with the CR technique. A pure Wedron sand (a round-grain silica sand, with excellent purity) was used and prepared following the procedure described in Section 8.1.1.

8.1.2 Natural soils

Natural soils were collected from JBMDL, located in Burlington and Ocean Counties of New Jersey. Spanning an area of more than 40,000 acres, JBMDL is the Department of Defense's (DoD's) only tri-service base and is an amalgamation of the United States (US) Air Force's McGuire Air Force Base, the US Army's Fort Dix, and the US Navy's Naval Air Engineering Station Lakehurst. The site selected for this field demonstration is located on the Lakehurst side of JBMDL, in a fenced-in, grassy area near the hazardous waste storage area (Building 691) within the historic Fire Training Area #1 (PFC Area 16). AFFF was reportedly tested in this area and, apparently, the ground surface would foam in the area during rainfall events. No actual firefighting activities have been documented[1]. Figure 6 is an aerial photograph of the hazardous waste storage area (Building 691) at JBNMDL showing seven soil sampling locations and the field CR survey line, which intercepts the fire training area but extends beyond it. Three samples (labeled I1-I3) were from a confirmed source zone, and four samples were from a location far from the source zone and thought to be devoid of substantial AFFF impacts (labeled C1-C4). All samples were collected from the same soil horizon at a depth of 0.3 m, and have similar textural characteristics as determined with laser diffraction particle size analysis, with mean grain diameters between 10.6 and 20.8 μm. Table 2 summarizes PFAS concentrations recorded in shallow groundwater samples obtained within the site source area.

[1] (Final Site Inspections Report of Fire Fighting Foam Usage at Joint Base McGuire-Dix-Lakehurst, Burlington and Ocean Counties, New Jersey, U.S. Army Corps of Engineers, January 2019).

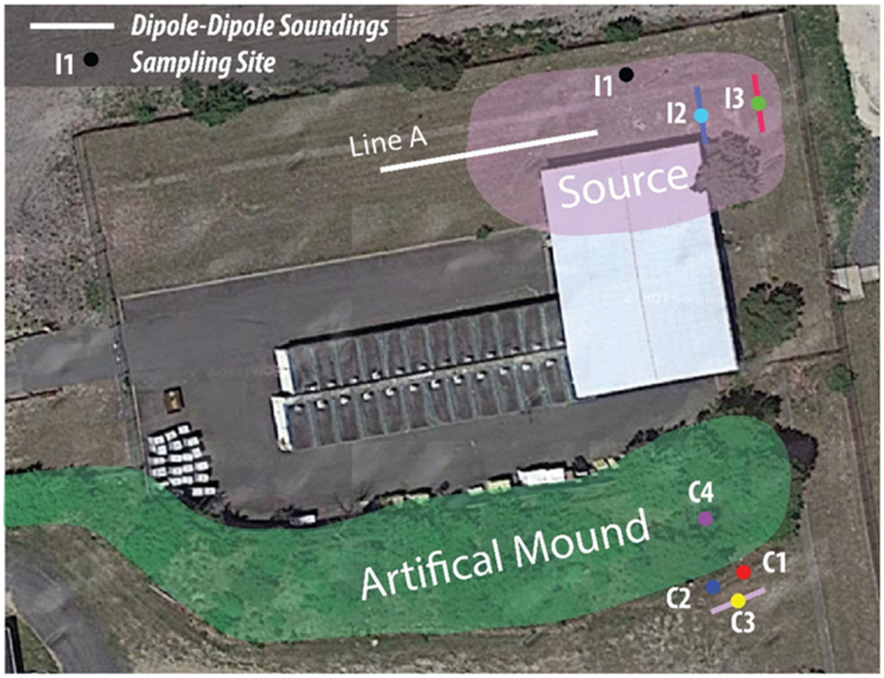

Figure 6: Aerial photograph of Building 691 at JBMDL, showing locations of soil sampling and field CR data acquisition. One sample (I1) was acquired from a location with previously known PFAS contamination, and two samples (I2-I3) were acquired from presumably PFAS-impacted locations. Samples C1-C4 were controls acquired from presumably clean locations. Field CR measurements include three spot locations (I2, I3 and C3) and one sounding line (Line A) where measurements were made at 1 m intervals. The historic fire training area where PFAS contamination is expected to be most extensive is shown.

Table 2: Summary of PFAS concentrations recorded in groundwater samples from the JBMDL site.

PFAS:	conc. (mg/L)	PFAS:	conc. (mg/L)
6:2 FtS :	9.3	PFPeA:	1
PFBS:	15	PFHxA:	35
PFHxS :	36	PFHpA:	4.5
PFHpS :	0.37	PFOA:	22
PFOS:	1.9	PFNA:	0.039
PFBA:	5.7		

Soils were transported to Rutgers University Newark, homogenized, and subsequently split for geophysical measurements and analysis of PFAS constituents and concentrations. Laser particle size analysis was performed to assess whether any significant differences in soil texture exist between the sampling sites as CR and NMR measurements are sensitive to soil texture. Results indicate that textural differences between the sampling locations are generally small.

PFAS analysis was performed by SGS AXYS Analytical Services via LC-MS/MS compliant with US DoD QSM 5.3 Table B-15. Figure 7 summarizes total PFAS concentrations in these seven soils. Samples I1-I3, from the suspected source zone, have total PFAS concentrations between 72 and 1336 ppb. In contrast, the samples from the presumed control location (C1-C4) have PFAS concentrations between 1.4-5.8 ppb. The PFAS source zone concentrations in these samples from JBMDL are an order of magnitude or more lower than the source zone concentrations recorded at Ellsworth Air Force Base (McGuire *et al.*, 2014) that motivated the proposal leading to this project.

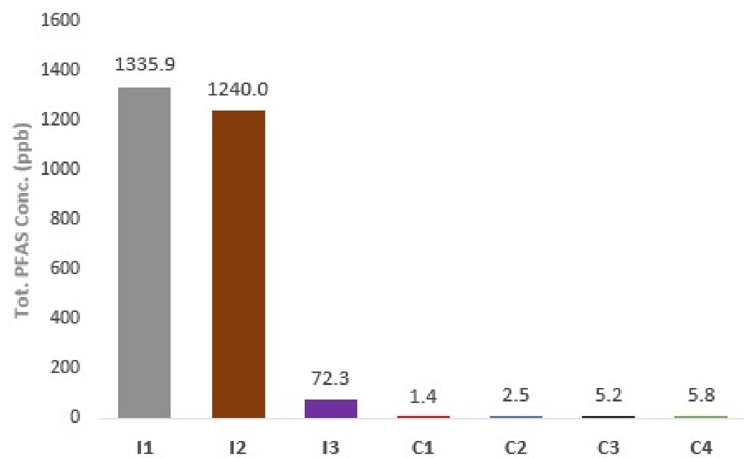

Figure 7: Total PFAS concentrations in soils (in ppb) measured on the seven soil samples acquired at JBMDL (see Figure 6 for soil locations).

8.1.2.1 Soil samples saturated with synthetic groundwater (CR and NMR)

Columns of the natural soils were prepared in triplicate and wet packed in the same way as the synthetic soils. The saturating fluid used for these samples was the same PFAS-free synthetic groundwater used for the synthetic soils. All PFAS present in the soils was therefore exclusively the result of AFFF impacts at the site. CR and NMR measurements were collected immediately after preparation to minimize the effects of PFAS desorption. Unlike the synthetic soils, CR and NMR measurements were not repeated over time.

8.1.2.2 Flushed contaminated samples to promote desorption (CR only)

This experiment was performed in an effort to determine whether a CR signal of PFAS desorption was detectable as a result of extensive flushing of the pore fluid with a synthetic groundwater devoid of PFAS constituents. Sample I1 was selected as it was obtained from a location at JBMDL that was expected to be most heavily impacted by PFAS contaminants. Triplicate columns were created for this experiment. The synthetic groundwater for the JBMDL site was used in this experiment. All three columns were fed from the same container of synthetic groundwater and continuously flushed over a period of 68 days at a rate of approximately 42 pore volumes per week per column using a multichannel peristaltic pump. The samples were kept in an environmental chamber at a constant temperature of 21°C for the duration of the experiment. Figure 8 shows the experimental setup, with the three replicate columns in the background removed from the chamber for clarity.

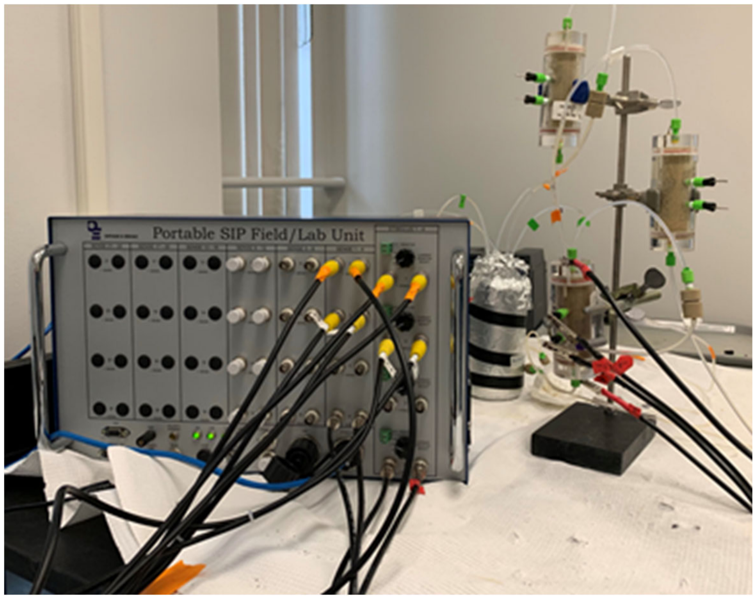

Figure 8: Portable Spectral Induced Polarization (PSIP) for data collection in the foreground, with the triplicate preparations of Sample I1 (a site of known PFAS contamination) shown in the background. Note that the samples were kept in an environmental chamber for the duration of the experiment (the setup shown here is for the photograph only).

8.1.2.3 Methanol-treated samples to promote desorption (CR only)

This experiment was performed in response to the inconclusive results of the aqueous flushing experiment described in Section 8.1.2.2. The methanol wash procedure promotes the removal of sorbed PFAS contaminants that could not be removed by extensive flushing of the soil samples with uncontaminated water. Two soil samples from JBMDL (Figure 6) were selected for this investigation: [1] a source zone location (adjacent to the test cell being evaluated as part of SERDP Project ER18-1204), and [2] an uncontaminated location as a control for comparison. Batch soil washing was performed by shaking (95 RPM) 900 g of soil with 2.3 L of methanol in a 100 L glass container for 3 days. After the initial 3 days of shaking, the supernatant methanol was removed, replaced with 2.3 L of fresh methanol, and shaken for an additional 2 days; this methanol replacement and shaking was repeated one additional time, bringing the total soil washing time to 7 days. After the final methanol washing phase, the supernatant methanol was removed and the remaining bulk methanol was evaporated from the soil by drying in a fume hood overnight. Duplicate sub samples of the unwashed and washed soils were sent to an external lab (Onsite Environmental Inc.) for total organic carbon (TOC) analysis using the EPA 9060A method.

8.1.3 *Field Experiments*

All field-scale CR measurements were made using a standard four-electrode resistivity array, the basic approach being shown in Figure 9. Two electrodes are used to inject an electric current (I) and the resulting electric field gradient (ΔV) is recorded between a second pair of electrodes. Knowing the locations of the electrodes, the complex resistivity (ρ^*) can be determined.

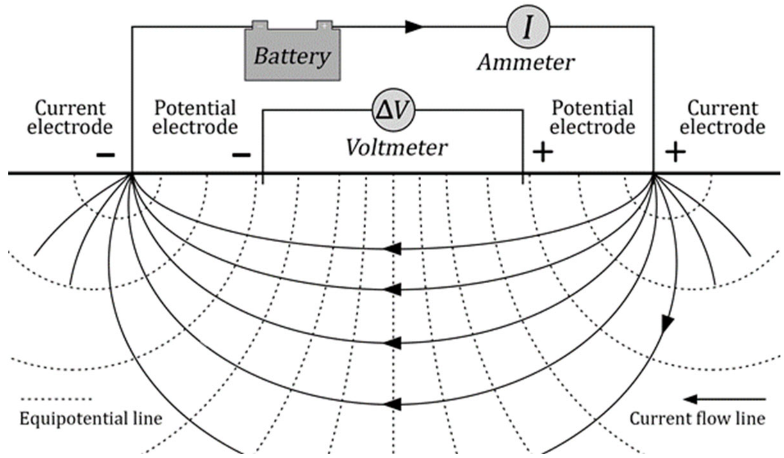

Figure 9: Basic principle of a four-electrode, field-scale CR measurement (from Binley and Slater, 2020).

8.1.3.1 <u>Preliminary field measurements (CR only)</u>

Exploratory field CR measurements were performed within the vicinity of JBMDL during November 2020 Figure 6. PFAS concentrations recorded on grab samples previously acquired and analyzed by CDM Smith were used to decide on four locations. One CR measurement was performed at a known PFAS-contaminated location, two CR measurements were acquired at suspected PFAS-impacted locations, and one was acquired at a presumably uncontaminated location. Nine small diameter stainless steel rods were used to provide point sources of current injection (electrodes 1 and 2) and to sample the resulting electric field generated in the subsurface at different depths (electrodes 3-9). The electrodes were separated by 0.2 m to ensure sensitivity to the upper approximately 0.6 m (approximately 2 ft) of soil and to be consistent with soil sampling. Pairs of potential electrodes further from the current electrodes sensed great depths. Figure 10 shows the typical deployment of the electrode array in the field.

Figure 10: Typical layout of CR field measurements showing electrodes for current injection and voltage recording spaced 0.2 m apart

8.1.3.2 Transect across the source zone (CR only)

Following encouraging results from the preliminary field measurements, permission was acquired from JBMDL to conduct a more extensive set of CR measurements on a transect crossing the suspected source zone (Figure 6). Measurements were acquired on a 60 m line at 3 m intervals. The electrode geometry used for the preliminary measurements (8.1.3.1) was again used here except that the electrodes were spaced 0.3 m apart so that investigation depths were again consistent with soil sampling.

9 Results and Discussion

This section describes the results of the laboratory experiments to determine the possible sensitivity of the CR and NMR methods to the presence of high source zone PFAS concentrations in soils. The laboratory experiments that formed the bulk of the project work are first described. Field results arising from the opportunity to access the JBMDL source zone site are then described. With respect to the interpretation of the CR data, the presence of sorbed PFAS constituents at the concentrations used in this study could possibly influence the polarization (i.e., σ'') as previously hypothesized, but these constituents should not significantly influence the conduction (i.e., σ') occurring in the sample. The σ' signals are also reported in all experiments to provide a check on whether σ'' variations could result from variations in soil structure/texture rather than from the presence of PFAS. Coincidental changes in σ'' and σ' would indicate a likely change in the soil structure/texture rather than an electrochemical effect from sorption that should only be detectable in the polarization (σ'') response.

9.1 Laboratory experiments

Laboratory results of CR and NMR measurements are presented for triplicate measurements in all cases. In most figures, the average of the triplicate samples is presented along with the error bars, representing the standard deviations of the triplicate measurements. In the NMR datasets, all three sample responses are shown to illustrate the consistency in the shapes of the NMR response between triplicates.

9.1.1 Synthetic soil samples

Results of experiments on synthetic soil samples contaminated with (a) a dilute AFFF solution, and (b) a natural groundwater from Edwards Air Force Base are presented in this section.

9.1.1.1 Sand-organic mixtures

Experiment 1: Sand-organic mixtures using synthetic JBMDL groundwater

The CR result on columns packed with the synthetic sand-organic soil are shown for the 12-day period following preparation in Figure 11. The colors represent a different time after preparation and the error bars show the standard deviation of the measurements on triplicate samples. The samples saturated with AFFF contaminated synthetic groundwater (Figure 11b), show different spectral characteristics than the columns saturated with clean synthetic groundwater (Figure 11a). Interestingly, a strong polarization peak (around ~20 Hz) is evident in the AFFF contaminated soils that is muted in the soils saturated with the synthetic groundwater. Error analysis indicates that the variance between triplicate columns is low (the exception being the uncontaminated sample on Day 12), with the measurements repeatable enough to observe a significant increase in σ'' over the experiment run time in both columns. Changes in σ'' in the uncontaminated columns highlight the fact that the effects of sorption can be expected (and observed) in both soils given that ion exchange will occur for the ions in the synthetic groundwater. However, the total polarization is significantly enhanced in the soils containing the AFFF contaminated groundwater. Changes in the real conductivity (σ') likely represent an increase in ionic concentration of the pore-fluid with time due to desorption of weakly sorbing (non-PFAS) ionic constituents. Relative changes in σ' are considerably smaller than relative changes in σ''.

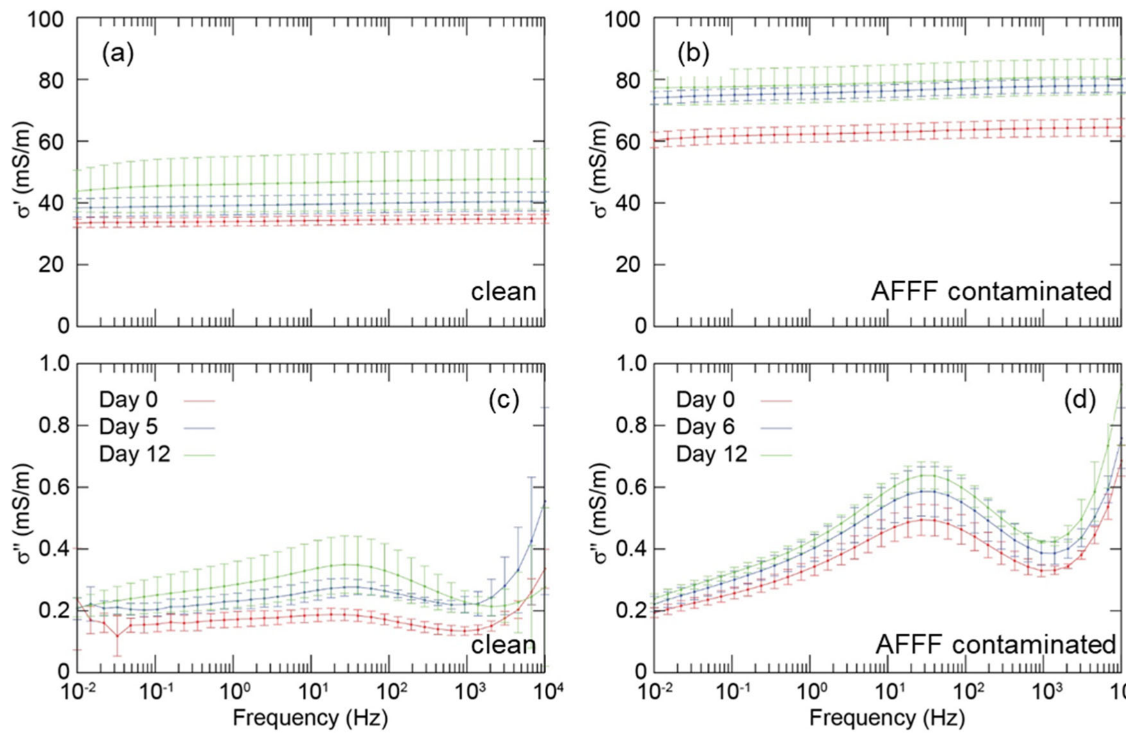

Figure 11: CR measurements (real conductivity (a, b) and imaginary conductivity (c, d)) collected on three AFFF contaminated peat/sand columns (10% peat by volume) (b) show a polarization enhancement relative to uncontaminated peat/sand columns (a) over the course of 12 days. The σ'' is greater for the contaminated soils and the peak in the polarization is more accentuated.

NMR T_2 distributions collected on these same columns (Figure 12) were similar over the first 10 days following sample preparation, showing little evidence of sensitivity to the presence of AFFF in the saturating fluid. The dashed vertical lines represent the mean-log relaxation T_2, or the geometric mean of the distributions. Uncontaminated columns were corrupted after Day 12 measurements, preventing comparison with the NMR response on contaminated columns at later times. The mean-log relaxation T_2 appears to shift slightly from shorter to longer T_2 between Day 10 and Day 24 for the contaminated columns (Figure 12b).

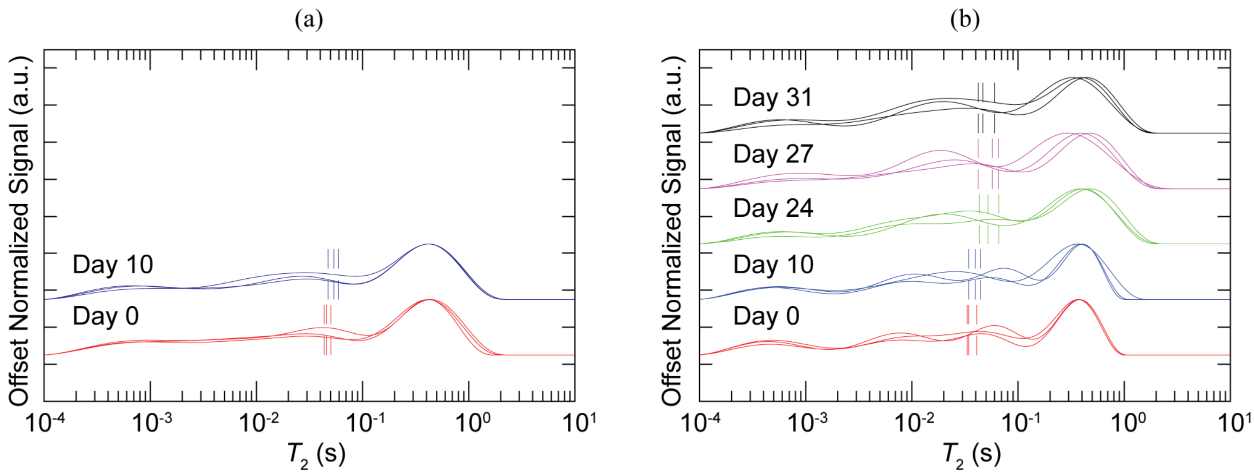

Figure 12: NMR T2 distributions measured on a synthetic soil composed of sand and peat (i.e., 10% peat by volume). Data in (a) were acquired on columns saturated with uncontaminated synthetic groundwater (based on JBMDL groundwater), while data in (b) were acquired on columns saturated with a 500-fold solution of AFFF contaminated synthetic groundwater. The mean-log relaxation times (T_{2ML}) (dashed lines) calculated from each distribution are also shown. Distributions are offset along the y-axis for comparison.

Experiment 2: Sand-organic mixtures using Edwards Air Force Base contaminated groundwater and control

Figure 13 compares the changes in polarization (σ'') and conduction (σ') over a one-month time period for the sand-organic mixtures saturated with PFAS-contaminated groundwater from Ellsworth AFB versus those saturated with a synthetic groundwater. Unlike in the case of contamination with the pure AFFF, the polarization enhancement observed in samples saturated with PFAS-contaminated groundwater is similar to that observed for the samples saturated with the synthetic groundwater. This might be expected as PFAS constituents in contaminated groundwater likely exclude those strongly sorbing zwitterionic and cationic compounds that are present in diluted AFFF formulations. Interestingly, σ' changes in the samples saturated with the PFAS-contaminated groundwater are less than the changes observed in the sample saturated with synthetic groundwater.

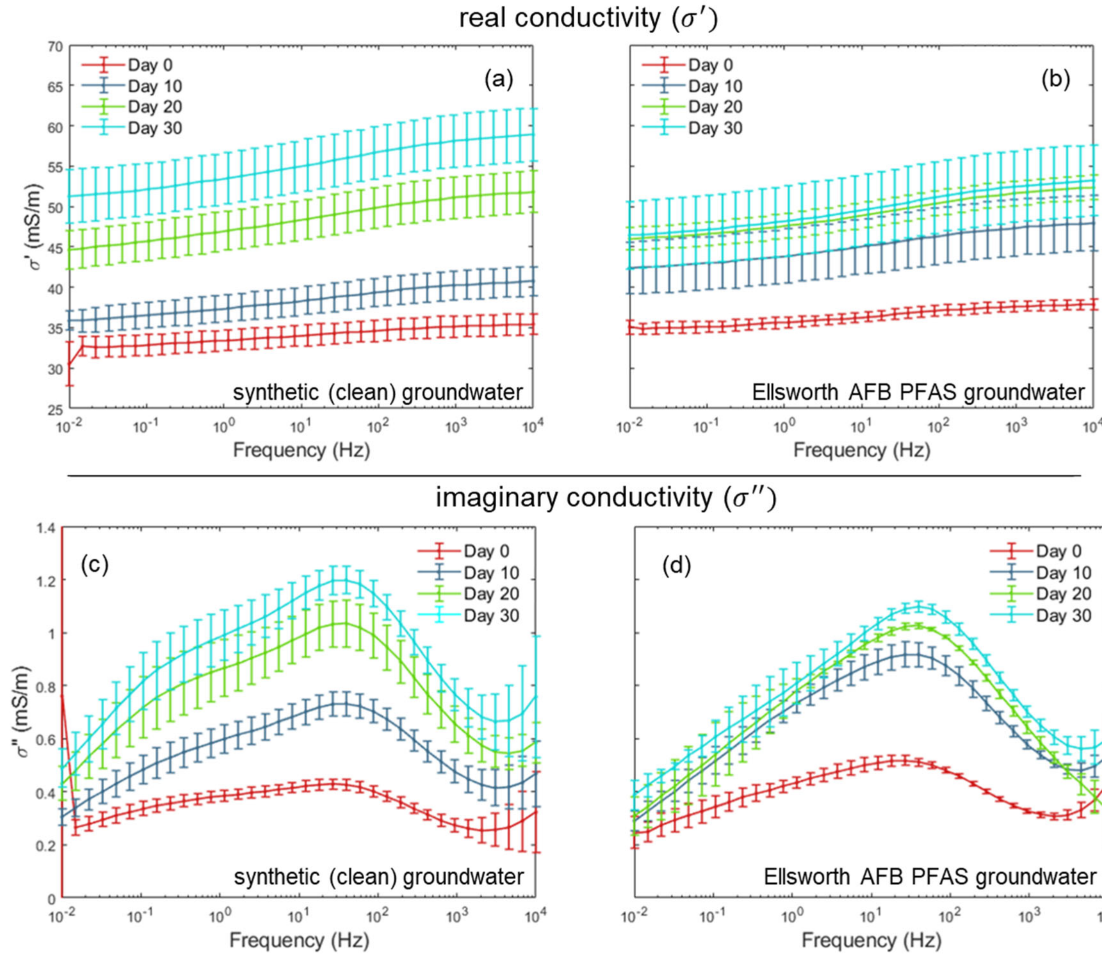

Figure 13: CR measurements (real conductivity (a, b) and imaginary conductivity (c, d)) collected on triplicate peat/sand columns (10% peat by volume) over the course of 1 month comparing the response for PFAS-contaminated water from Ellsworth Air Force Base (b, d) versus a synthetic groundwater (a, c).

In summary, the results on synthetic soils show promise for the use of CR as a tool for investigating AFFF source zones. The results highlight that the CR method will only be sensitive to strongly sorbing cationic and zwitterionic PFAS constituents in soils and at the relatively high concentrations found only in AFFF source zones. In contrast, NMR results do not show promise in this use of this technology for characterization of AFFF source zones.

9.1.1.2 Pure sands

The CR response for the pure Wedron sand is shown in Figure 14. As expected for this control, no significant enhancement of the polarization is recorded in the presence of AFFF. The sensitivity of CR is insufficient to detect any effect of sorption onto a silica surface at the concentrations tested. The significance of the slightly higher polarization recorded on Day 0 in the presence of AFFF is uncertain given the relatively large errors bars from the triplicate measurements. This elevated CR response disappears with time, being contrary to what would be expected if PFAS sorption was significantly impacting the CR signal.

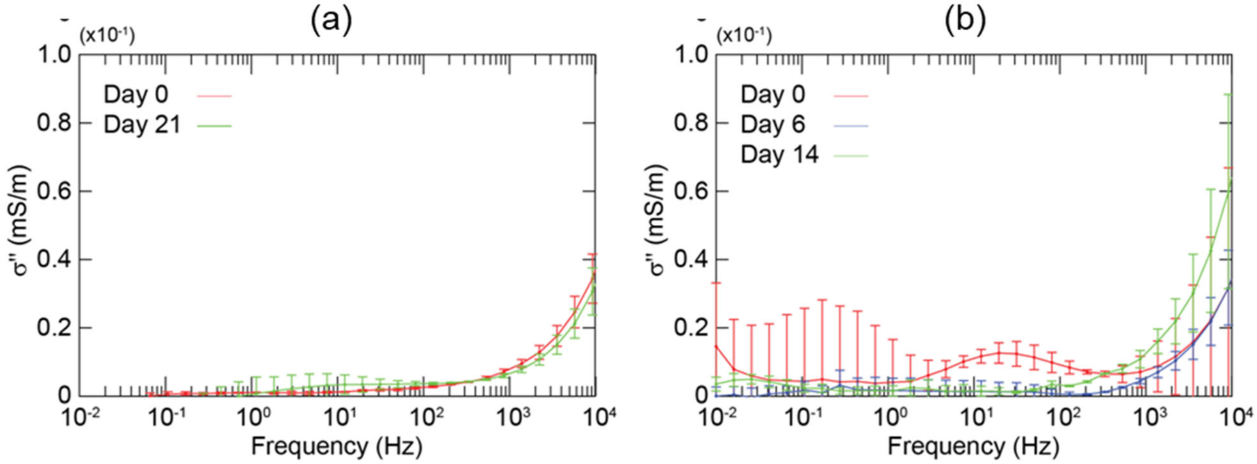

Figure 14: CR response (σ'' only for brevity) for the pure Wedron sand sample contaminated with AFFF (b) versus uncontaminated (a). No significant polarization of the sand-fluid interface is recorded as expected of this control.

9.1.2 Natural soils

9.1.2.1 Soil samples saturated with synthetic groundwater

Figure 15 summarizes the results obtained for the seven natural soil samples acquired from JBMDL. Results above 1000 Hz are ignored in this analysis as instrumentation errors at these frequencies can result in imaginary conductivity variations that mask the soil sample response. Impacted soils I2 and I3 show an imaginary conductivity response that is consistently and significantly (based on the error bars) elevated over control samples C1-C3 for the entire frequency range up to 1000 Hz. However, sample I1 (with the highest total PFAS concentrations as shown in Figure 7) does not show an elevated σ'' response, except above 100 Hz where field measurements are challenging. Relatively high error bars are recorded for σ'' in sample I2.

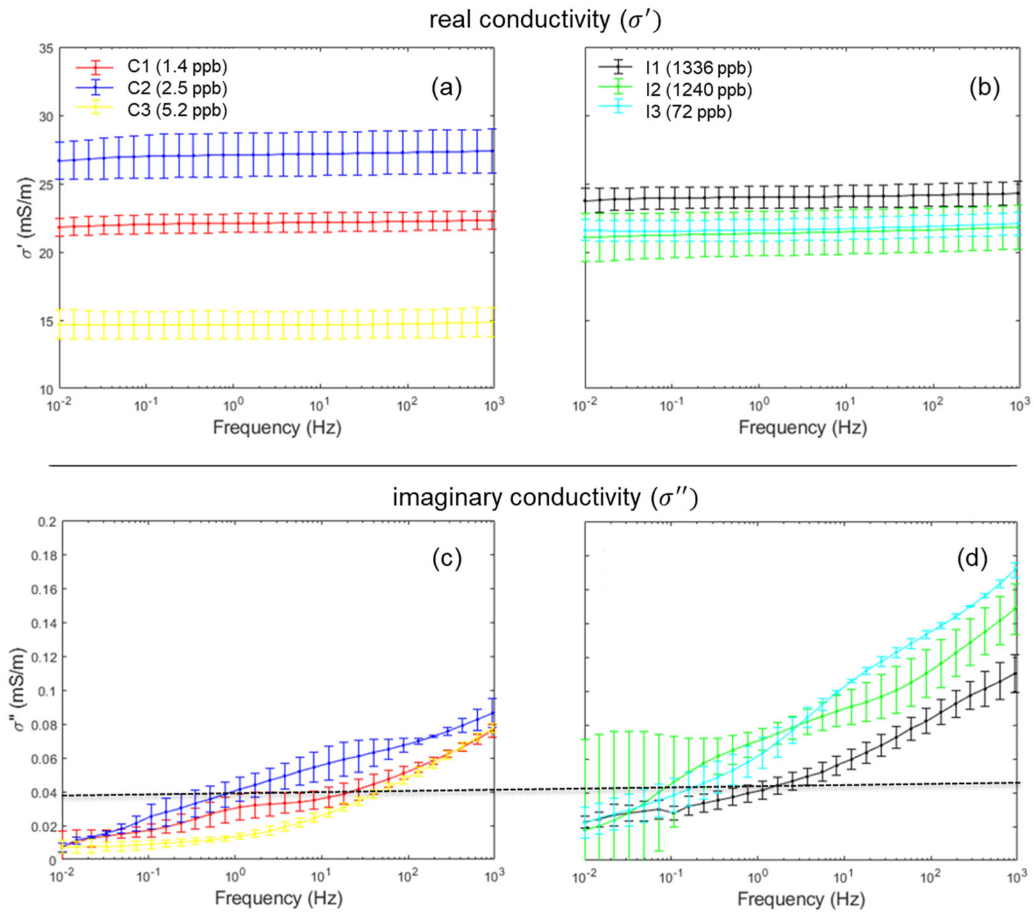

Figure 15: CR measurements (real conductivity (a, b) and imaginary conductivity (c, d)) collected on soils taken from JBMDL: (a and c) locations minimally impacted by PFAS contamination; (b and d) locations impacted by PFAS contamination. See Figure 6 for sample locations. PFAS concentrations are defined in the legend.

The T_2 distributions from the NMR measurements show only subtle variations between soil samples I1, C2 and C3 (Figure 16). These minor differences are most apparent in the spectral peaks at the longer relaxation times (i.e., $10^{-2} \leq T_2 \leq 10^0$ s). However, given that the impacted sample I1, with a total PFAS concentration of 1336 ppb, has an NMR spectrum very similar to samples C2 and C3, any sensitivity of the NMR response to soil PFAS concentrations is unsupported by these measurements. Sample C4 (Figure 6) is included to demonstrate the strong effect of soil texture on the NMR response. This sample was taken from an artificial mound composed of distinctly different soils. The strong change in the NMR response is most evident between $10^{-2} \leq T_2 \leq 10^0$ s.

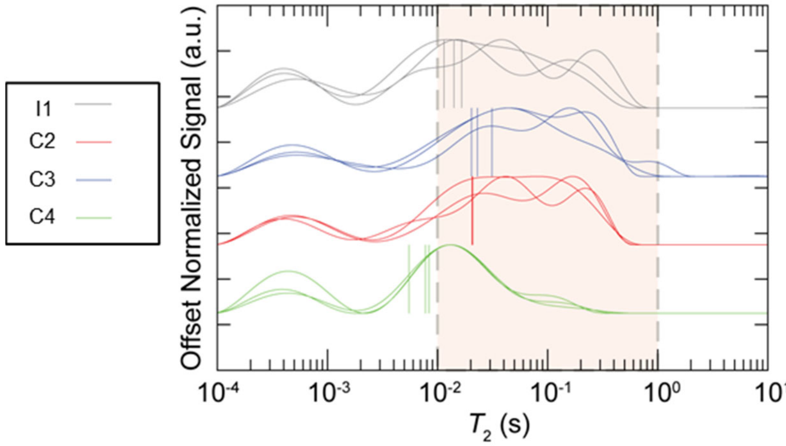

Figure 16: NMR data collected from soils sampled from JBMDL showing a comparison of PFAS impacted sample I1 and samples C2-C4 away from the source zone. Dashed lines are the mean-log T_2 values associated with each T_2 distribution. Shaded areas represent the range of T_2 values over which there is evidence of a potential PFAS associated response.

9.1.2.2 <u>Water-flushed contaminated samples to promote desorption</u>

Results of the 67-day experiment that involved the flushing of PFAS-impacted samples (sample I1) are shown in Figure 17. The average values and the error bars are shown at three different frequencies. No trend in the σ'' values is apparent over the 67 days. Instead, σ'' fluctuates between 0.15 and 0.3 mS/m and shows no evidence for the expected pattern of decreasing σ'' with time as was hypothesized based on sorbed (charged) PFAS constituents being removed from the surface. A notable (approximately 10%) increase in σ' with time is observed. The cause of this increase is unclear. As the pore fluid specific conductance and temperature were well-controlled, the most plausible explanation is change in the pore geometry of the loosely packed sediments as a result of the extensive flushing, e.g., possible removal of fines from pores. Assuming that σ'' measurements have sufficient sensitivity to PFAS sorption/desorption, this result would be consistent with a growing body of literature suggesting that it is very challenging to remove PFAS constituents sorbed to soil particles via flushing (Schaefer *et al.*, 2022). However, the result could equally represent the limited sensitivity of these measurements to desorption of a small mass of PFAS.

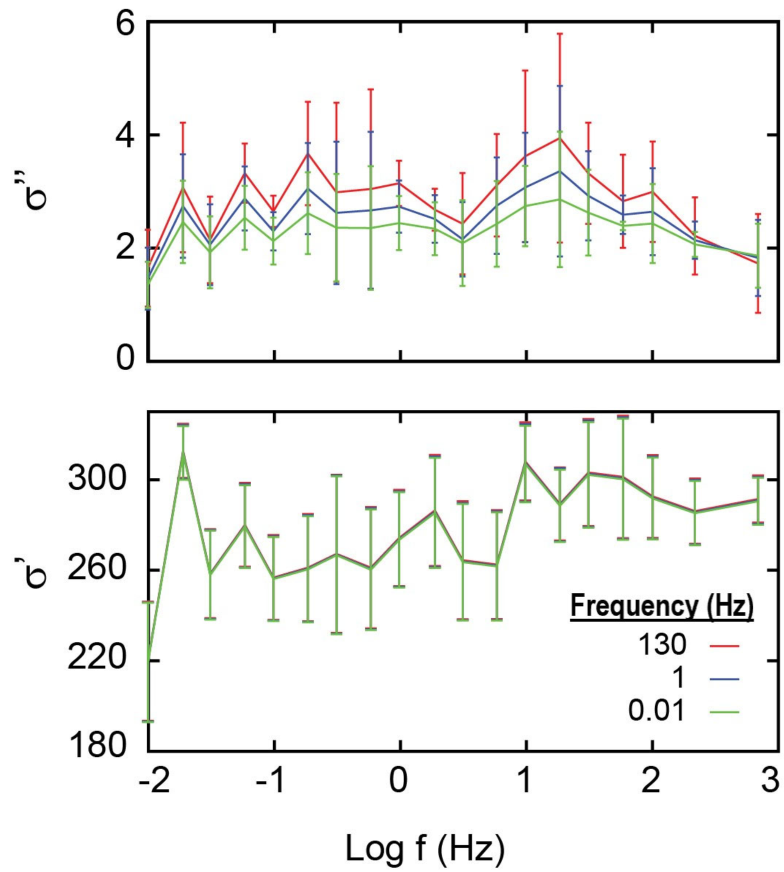

Figure 17: Summary of imaginary conductivity (σ'', top) and real conductivity (σ', bottom) variations over a 67-day experiment designed to promote PFAS desorption from contaminated soil I1. The graph shows the average values and error bars for the triplicate samples at three different frequencies (in Hz). Units are mS/m in both cases.

9.1.2.3 Methanol-washed versus unwashed natural soils

The CR measurements on the unwashed soil and methanol-washed PFAS-contaminated soil are presented in Figure 18. Lab analysis showed that the PFAS concentration in this soil sample was reduced from 860 ppb to 494 ppb as a result of the methanol wash. The methanol washed soil exhibits a statistically significant (i.e., greater than the size of the error bars) decrease in σ'' across the entire frequency range. In contrast, σ' shows no statistically significant difference between the washed and unwashed samples. This result is consistent with a CR response to removal of sorbed PFAS constituents, i.e., a reduction in interfacial polarization but no variation in the texture/structure of the soil. This result is further evidence of the sensitivity of CR to sorbed PFAS constituents. TOC analysis on the washed versus unwashed samples showed that the methanol wash procedure significantly reduced the TOC of the soil. TOC (% carbon of soil) for the unwashed soil was 0.95 (0.79) whereas TOC for the washed soil was 0.5 (0.3 for the duplicate). Organic constituents of a soil matrix have a relatively high surface area and cation exchange capacity that may significantly influence CR signals. However, the effect of the methanol wash procedure on the imaginary conductivity of uncontaminated sample C4 (Figure

19) is insignificant relative to that observed for I3 (Figure 18), suggesting that TOC removal is not the reason for the difference observed for the PFAS contaminated soil in Figure 18. The substantially greater change in the CR response for the contaminated sample is encouraging and consistent with the measured PFAS concentrations.

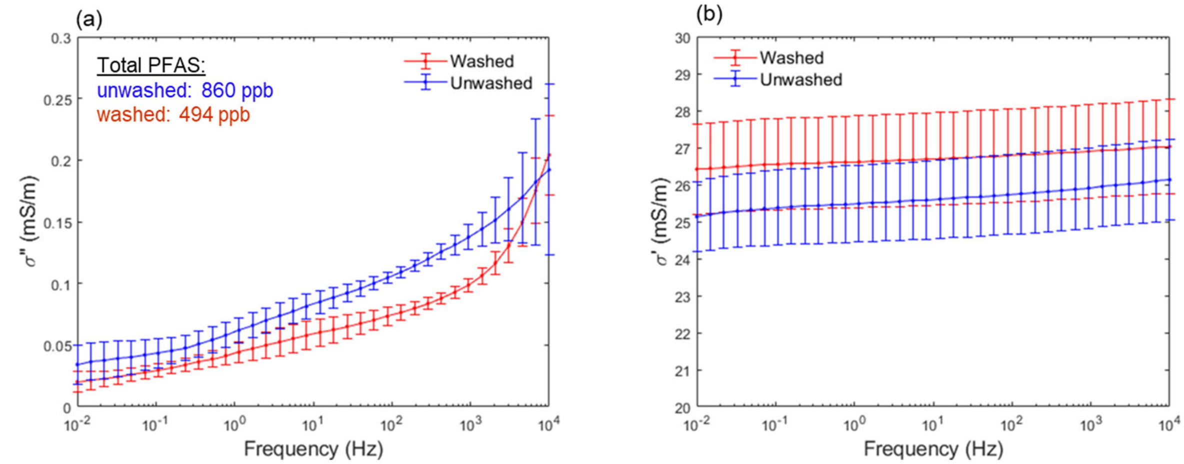

Figure 18: Comparison of methanol-washed versus unwashed PFAS-contaminated sample from JBMDL: (a) imaginary conductivity (σ''); (b) real conductivity (σ'). Solid lines are averages of triplicate columns prepared in an identical manner with error bars shown.

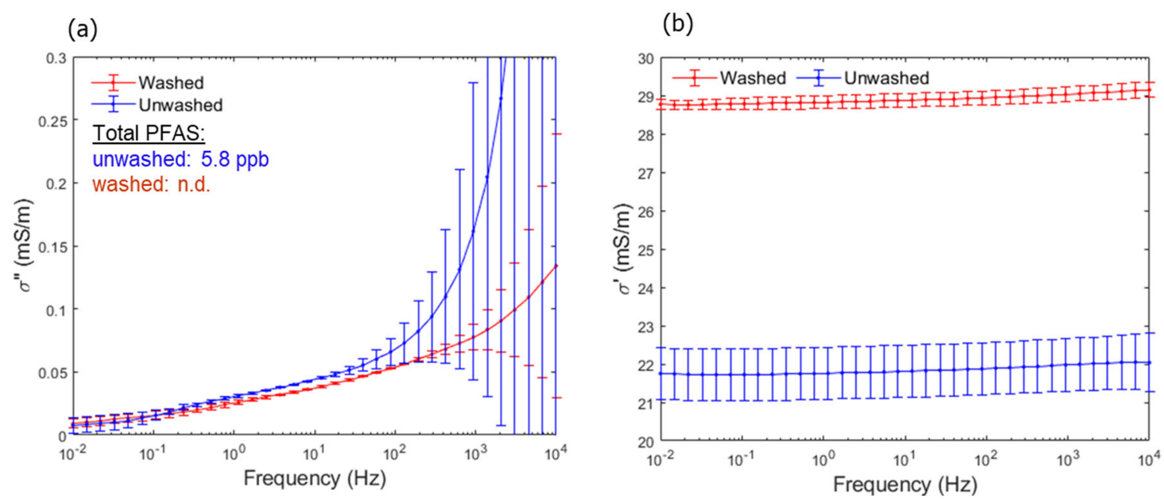

Figure 19: Comparison of methanol-washed versus unwashed uncontaminated sample C4 from JBMDL: (a) imaginary conductivity (σ''); (b) real conductivity (σ'). Solid lines are averages of triplicate columns prepared in an identical manner with error bars shown.

9.2 Field Experiments

Field experiments at JBMDL were conducted in two phases. The first set of exploratory measurements compared field observations at two source zone locations (I2 and I3) versus "uncontaminated location" C3 to the south. A follow up set of more extensive field observations recorded CR measurements at approximately 1 m separation on a transect across the source zone (shown in Figure 6).

9.2.1.1 Preliminary field measurements

Imaginary conductivity spectra for the preliminary field measurements are shown in Figure 20. The spectra acquired are largely consistent with those obtained in the laboratory, confirming the possibility of acquired CR measurements in situ at shallow depths over source zones. Sample I2 is significantly more polarizable than sample C3, whereas sample I3 is much more comparable in terms of polarizability than Sample C3. Interestingly this is consistent with the variation in PFAS concentrations observed for these sample locations (Figure 7), with Sample C3 having a comparable PFAS concentration to sample I3. However, as this observation is only based on three test measurement locations, the primary significance of these preliminary field measurements is that CR measurements comparable to the laboratory can be acquired in situ for shallow source zone soils.

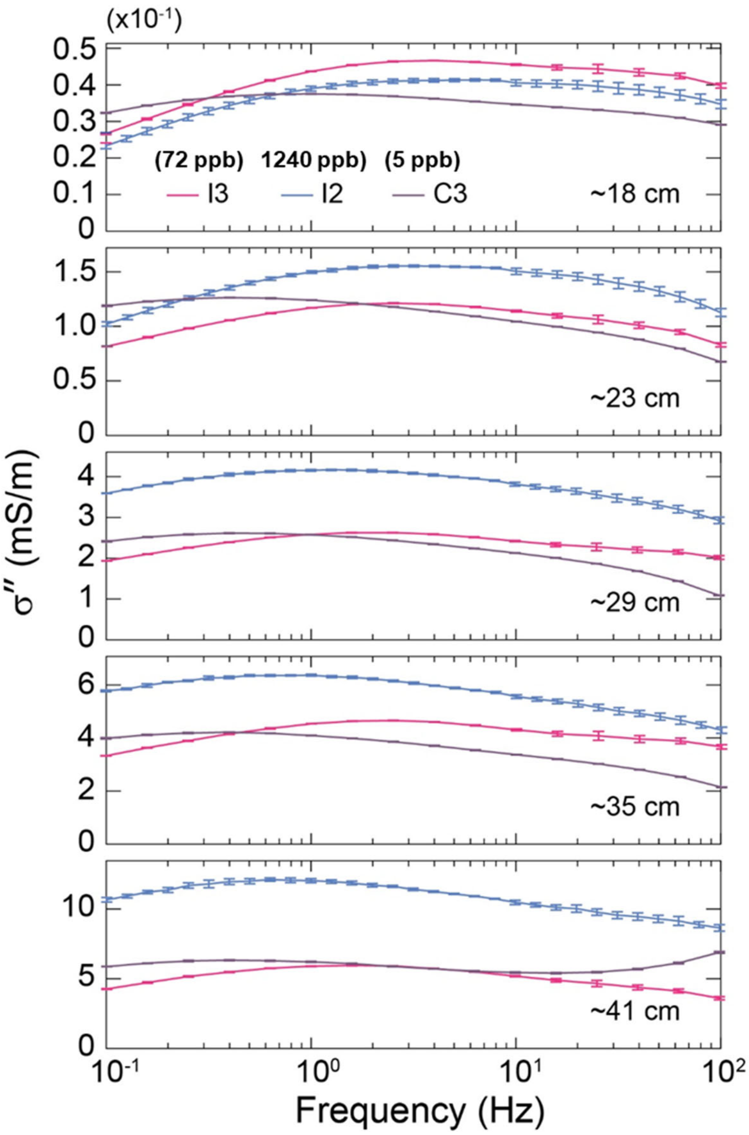

Figure 20: Comparisons of dipole-dipole geophysical measurements acquired at impacted sites I2 and I3, and uncontaminated site C3 (see Figure 6). Below 18 cm, I2 exhibits significantly elevated polarization over C3 and I1, consistent with the lab CR measurements and the PFAS analysis (Figure 7). Note that the lab measurements were done on soils extracted from approximately 15 cm depth and that field measurement selectively targeted the upper ~50 cm (deeper measurements are possible).

9.2.1.2 Transect across the source zone

Figure 21 shows the transect of imaginary conductivity (σ'') and real conductivity crossing the source zone at JBMDL depicted in Figure 6. Two regions of elevated polarizability are captured in the line. The biggest increase in polarizability occurs between 20 and 45 m along the line. However, there is also a coincidental, similar in relative change, increase in the real (σ') conductivity at this location. As PFAS sorption/desorption would not significantly influence the real conductivity, this response is indicative of a significant change in soil texture/structure. A second region of enhanced polarizability occurs between -15 to 0 m on the line, being closest to the dumpster formerly located at this site. This region of elevated σ'' does not have a σ' footprint and is the first field-scale evidence that CR might be a viable technology for delineation of PFAS hot spots in source zones.

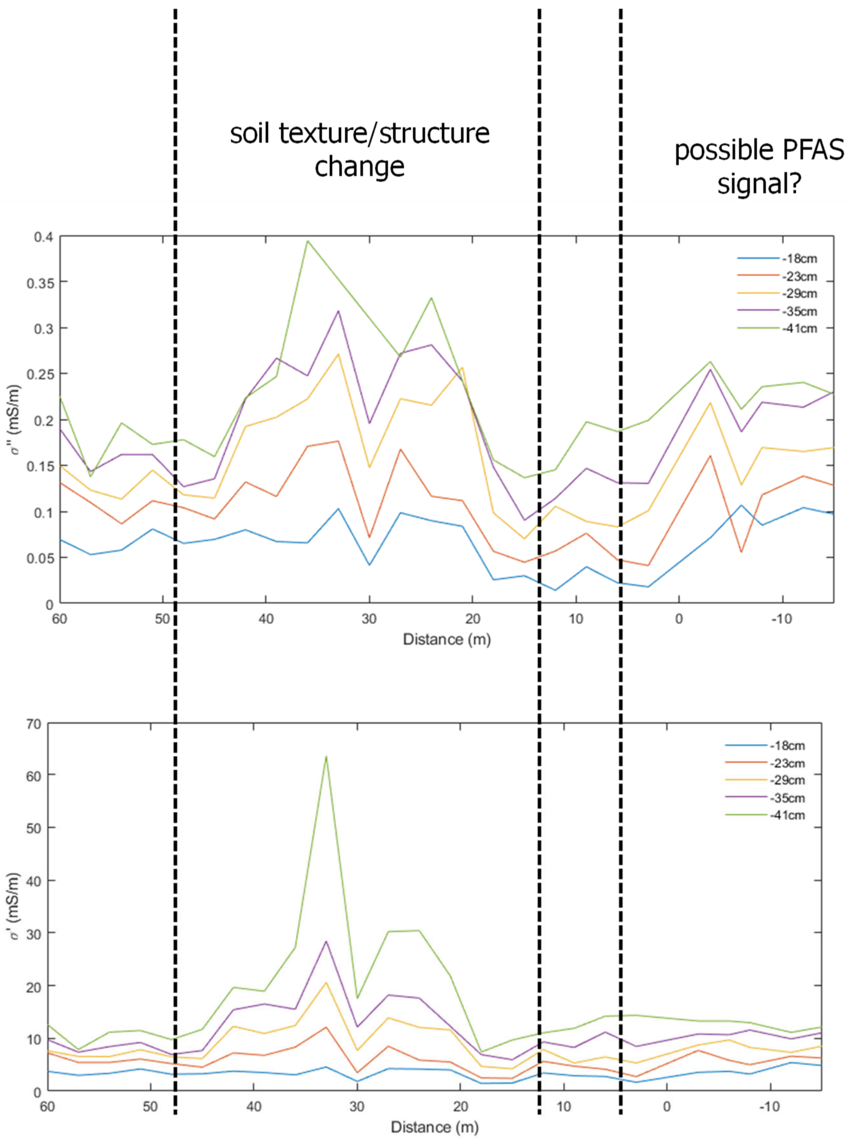

Figure 21: (a) Imaginary conductivity (σ'') and (b) real conductivity (σ') along the transect crossing the assumed source zone at JBMDL shown in Figure 6.

Additional soil sampling and PFAS analysis made possible by funding provided by the Environmental Protection Agency allowed an initial assessment of the hypothesis that the CR signal between -15 m and 5 m on the transect is associated with high soil PFAS concentrations. Although soil sampling is sparse, (11 points total on the transect) anomalously high PFAS concentrations were indeed found to coincide with the anomalous CR signal identified in on the transect (Figure 22). Interestingly, the phase measurement, being approximately the ratio of polarization to conduction ($\phi \approx \sigma''/\sigma'$) may be a better indicator of the contamination in the presence of significant soil variations, as can be expected at most sites. Given the limited number of samples and the difference in measurement scale between the PFAS soil sample and the field-CR measurement, the correlation is considered promising but not statistically significant at this stage. Further measurements are needed to establish statistical significance.

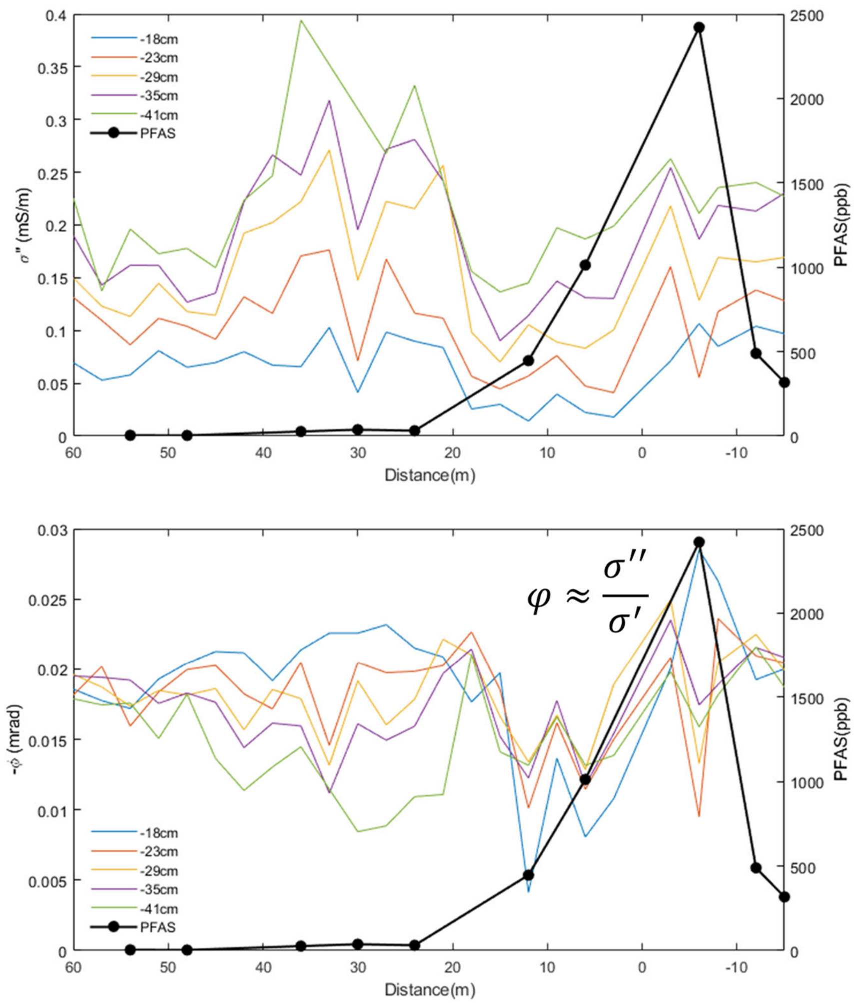

Figure 22: Comparison of CR signals along the field transect at JBMDL versus PFAS concentrations measured for 11 soil samples acquired at discrete points along the profile: (a) imaginary conductivity (σ''); (b) phase (ϕ). PFAS analysis was funded by EPA Interagency Agreement (IA) (DW-014-92497401) with USGS and USGS-Rutgers cooperative agreement.

10 Technology Transfer

The project team participated in one technology transfer activity organized by co-PI Schaefer at the JBMDL source zone site on September 9, 2021 (Figure 23). This activity was foremost a site tour of the field test cell that was put into service as a part of SERDP Project E18-1204: *Insights into the Long-Term Mass Discharge & Transformation of AFFF in the Unsaturated Zone* (PI, Schaefer). Schaefer extended the tour to provide an opportunity for the project team to provide a high-level overview of the activities on this project. PI Slater and graduate student Ethan Siegenthaler demonstrated the setup of spectral induced polarization measurements in the field and discussed the scientific basis for possible screening of PFAS-contaminated soils using this non-invasive electrical method. Multiple attendees emphasized the need for rapid screening methods for source zone characterization. However, the team was careful to emphasize the exploratory nature of this project and the need to avoid overselling the capabilities of geophysical measurements for contaminant characterization. The tour was attended by a mix of regulators, remediation professionals, academics, and students.

Figure 23: Technology transfer activities at the JBMDL source zone site: Left: PI Slater discusses SIP signals of possible soil PFAS contamination at the site; Right: participants view the SIP data acquisition system in operation

11 Conclusions and Implications for Future Research

This section summarizes the primary conclusions of the project and recommendations for future research that could be performed to better assess the CR technology for field-scale characterization of PFAS source zones.

11.1 Overall conclusions of proof of concept

This proof-of-concept study explored the potential of the CR and NMR geophysical methods for delineating PFAS-contaminated soils at source zone concentrations. The study showed that the low-field NMR geophysical method (not NMR relaxometry) does not have adequate sensitivity to detect PFAS in soils through hypothesized blocking of proton/paramagnetic coupling by sorbed constituents on mineral surfaces. Despite the negative result with the NMR method, this proof-of-concept study went beyond the initial scope of work by taking the CR measurements from the laboratory setting and into a field setting at a site with a PFAS source zone.

Laboratory and field CR measurements reveal that sorption of PFAS contaminants onto artificial and natural soils may result in a detectable CR signature. This is consistent with the known sensitivity of the CR method to the electrical double layer chemistry, specifically the surface charge density and surface ionic mobility. Comparisons of CR signals on artificial soils saturated with synthetic PFAS-contaminated groundwater constructed from a 500-fold dilution of AFFF versus the same contaminated groundwater without the addition of AFFF captured the temporal evolution of a polarization enhancement in the AFFF contaminated soil that we attribute to PFAS sorption. Experiments on the same artificial soils found no significant difference in the temporal CR response for samples saturated with PFAS contaminated groundwater from a source zone versus samples saturated with an equivalent synthetic groundwater. This perhaps is to be expected as the PFAS constituents in groundwater are unlikely to be those that strongly sorb to soil. In contrast the diluted pure AFFF is expected to contain cationic and zwitterionic constituents that strongly sorb to soil surfaces.

Laboratory experiments on PFAS contaminated soils taken from the vicinity of the source zone at JBMDL showed no conclusive evidence of an elevated CR response relative to soils from the locality away from the source zone and characterized by low PFAS concentrations (control samples). The most heavily PFAS contaminated soil (sample I1) from the source zone showed the least polarization enhancement over the control samples, although two other samples with high PFAS concentrations (I2 and I3) did show a polarization response substantially elevated over the control samples. One possible reason for the inconclusive findings from the measurements acquired on samples from JBMDL is the relatively low maximum soil PFAS concentrations (~1300 ppb) at this site relative to much higher concentrations reported at other source zones, e.g. ~70,000 ppb at Ellsworth AFB (McGuire *et al.*, 2014) that motivated the proposal written to fund this research.

Experiments designed to detect the removal of sorbed PFAS contaminants from soils via continuous flushing of a PFAS-impacted JBMDL soil with a synthetic groundwater for a 30-day period did not result in any significant change in the soil polarization. This is actually consistent with a growing body of literature showing that it is very challenging to remove PFAS constituents sorbed to soil particles via flushing, although it could simply reflect the limited sensitivity of CR to such a desorption process. In a second experiment, a methanol wash procedure known to promote the desorption of FPAS constituents from soil surfaces did result in a significant (beyond the error bars of the triplicate measurements) decrease in the CR signal relative to the unwashed soil, providing another line of evidence for the sensitivity of CR to PFAS sorption to soils. In this experiment, no significant change in conduction was observed, supporting the case that imaginary conductivity decrease resulted from removal of sorbed PFAS constituents and its effect on electrical double layer polarization.

Preliminary field-scale measurements focused on non-invasive sensing of the electrical properties of the top 50 cm of soil at JBMDL indicate that the CR signal to PFAS sorption at source zone concentrations is measurable beyond the laboratory using commercially available geophysical instrumentation. The CR signal to sorbed PFAS constituents is stronger than variations in the CR signals that arise from soil heterogeneity at this site. A CR transect crossing the JBMDL source zone provides evidence of a CR signal due to the presence of elevated sorbed PFAS soil concentrations, although additional soil sampling and laboratory PFAS analysis is needed to statistically verify this finding.

11.2 Potential next steps and objectives of follow-on research

Further geophysical investigations of contaminated soils from PFAS source zones should focus on the CR method only. This project conclusively showed that the low-field NMR response to the presence of sorbed PFAS constituents was either negligible, or too ambiguous, to warrant further investment in this technology. Although the low-field NMR method is a promising technology for characterization of water content, porosity and permeability in soils and rocks, it is not a candidate technology for characterization of PFAS contaminants in soils. The following areas of research could further advance understanding of the potential of the CR method as a PFAS source zone characterization and monitoring technology. We start with a proposal for additional field trials of the technology as a direct continuation of the work performed under this exploratory project. Additional areas of future research are also proposed if the additional field trials produce positive results supporting further investment.

11.2.1 Additional field testing of the CR technology at PFAS source zones

Additional field-scale CR measurements are needed to better understand the potential for using this geophysical technology as a PFAS source zone screening method. Field-scale deployment of CR was not within the original scope of the SEED project. However, preliminary field observations were acquired at the JBMDL site given that an opportunity arose with little additional cost. The measurements at JBMDL confirmed the quality of the field CR measurements and provided strong evidence that a field-scale CR signature of PFAS-contaminated soils exists. Immediate follow-on work could focus on a further soil sampling along the CR transect (Figure 21)with subsequent soil PFAS analysis to statistically validate the anomalous CR signature attributed to elevated soil PFAS concentrations. Follow-on field work should also seek to further evaluate the sensitivity of field-scale CR to PFAS contaminated soils by acquiring CR measurements and supporting soil sampling along transects over other source zones at sites of relevance to the DoD (Figure 24). The transects across additional sites would expand the field testing to include source zones where PFAS concentrations in soils are higher than recorded at JBMDL and cover a wider range of soil types (e.g., with varying organic matter content). Candidate sites, including Ellsworth Air Force Base and Oceana, would represent source zones being investigated in ongoing SERDP and ESTCP supported research. Similar to what was done at JBMDL, soils would be sampled down to a few feet in depth. PFAS concentrations would be determined as a function of depth to better assess the statistical significance of the correlation with the CR signal. Given that our laboratory results suggest a possibly important role of TOC in the sensitivity of CR to sorbed PFAS concentrations, soils will be analyzed for TOC as a function of depth for comparison against the different depth intervals sensed with the CR measurement. This work would facilitate the acquisition of a large enough population of soil samples to permit a statistically significant analysis of field-scale CR sensitivity to PFAS contamination and the role of the TOC in determining the sensitivity of CR to PFAS sorption to soils. The cost to perform this work is estimated to be between $200k to $300k depending on the field sites selected for data acquisition.

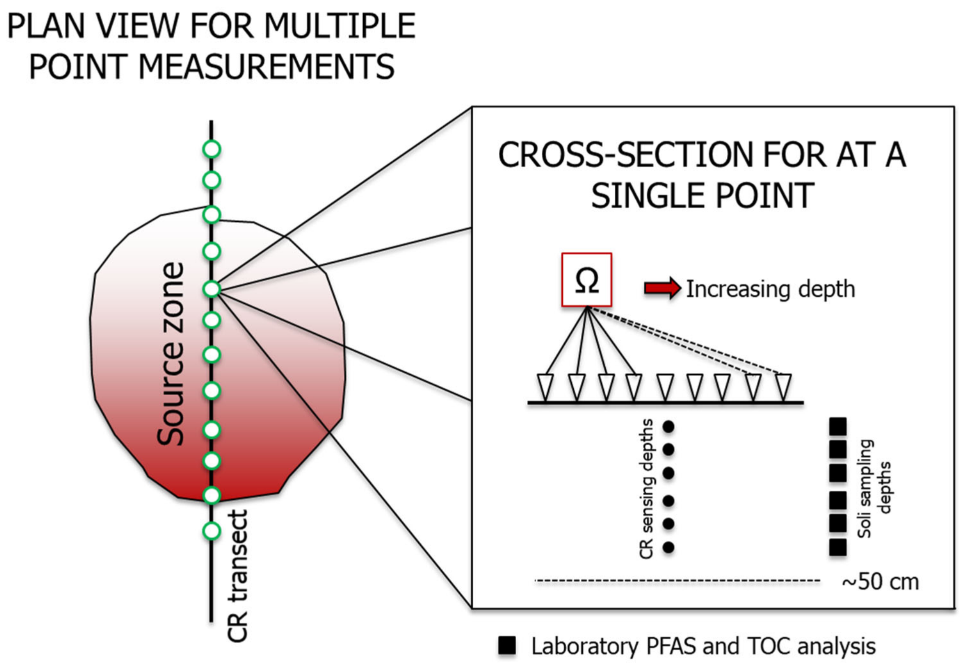

Figure 24: Conceptual diagram for proposed follow-on work over PFAS source zones involving in situ CR sensing of shallow soils followed up with soil sampling for PFAS and TOC analysis.

11.2.2 Future possible experiments (pending a positive outcome from 11.2.1)

Other experiments that could be performed in future projects are detailed below. However, these experiments are only recommended if additional field tests proposed in Section 11.2.1 yield a positive outcome.

<u>Improving understanding of CR to the sensitivity of PFAS concentration</u>

This project identified the CR signal to the presence of sorbed PFAS contaminants by examining (a) synthetic soils contaminated with a 500-fold dilution of commercially available AFFF solution, and (b) soils from the vicinity of a known PFAS source zone, including comparison of soils from confirmed PFAS contamination locations and uncontaminated locations. The scope of the project did not involve any attempt to determine the sensitivity limits of CR to PFAS contamination. This is the logical next step in assessing the utility of the technology for source zone investigations. However, it is important to reemphasize that CR can only serve as a technology for screening PFAS source zones and that the information is inherently semi-quantitative at best. It will never be possible to link CR signals to specific concentrations of PFAS constituents. Given that CR signals are expected to be foremost controlled by the cationic and zwiterrionic, strongly absorbing constituents, some empirical calibration of CR signal against concentrations of these strongly sorbing PFAS constituents should be possible. In this respect, the simplest follow-on experiment would involve measurements on a range of AFFF dilutions at concentrations lower than the 500-fold dilution tested in this study. To enhance field relevance, these experiments would be conducted on natural soils representing PFAS source zones rather than the artificial (sand-organic sediment, sand-clay) mixtures investigated in this study. Soils would be obtained from multiple PFAS source zone locations where concentrations are documented at levels similar to, or higher than, those explored in this study.

<u>Further evaluation of CR signatures following a methanol wash procedure</u>

The CR measurements on PFAS contaminated soils from the JBMDL site revealed a substantial decrease in the polarization of the soils after the methanol wash used to remove sorbed PFAS constituents. Assuming that the CR reduction was due to the removal of PFAS, this would be a very significant finding. However, the methanol wash also appears to have removed organic carbon from the soil, which might also partly explain the reduction in CR. Further experiments are needed to corroborate the results and build confidence in the interpretation. These experiments should include additional uncontaminated soils subject to an identical methanol wash procedure for control.

<u>CR measurements on unsaturated PFAS-contaminated soils</u>

To simplify comparisons between samples, all laboratory (not field) experiments performed in this study were performed on saturated soils. However, there is growing evidence that PFAS constituents sorb to the air-water interface in addition to the mineral-water interface. Previous laboratory studies indicate that CR is sensitive to both the air-water interface and the mineral-water interface (Shefer et al., 2013; Ulrich & Slater, 2004). Therefore, CR measurements on PFAS contaminated unsaturated soils versus uncontaminated soils at the same level of contamination are warranted. These measurements would be performed on natural soils from the vicinity of a PFAS source zone. The objective of this follow-on work would be to determine the sensitivity of CR to PFAS constituents absorbed on air-water interfaces, and to evaluate whether dynamic processes, such as the reduction in PFAS concentrations when air-water interfaces are destroyed, can be observed with CR monitoring.

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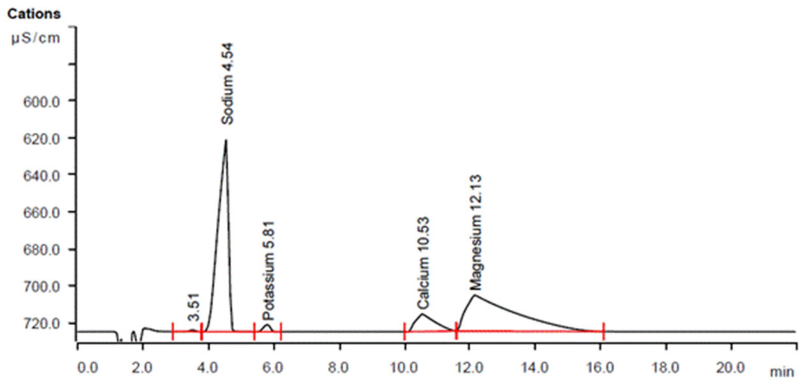
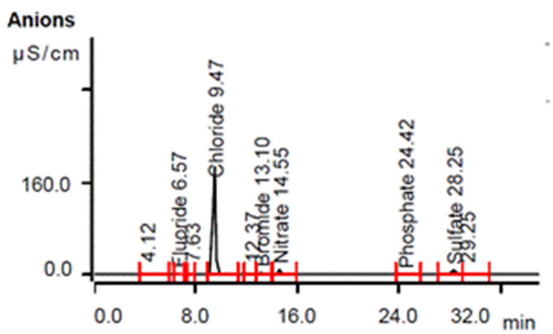
13 Appendix A: Laboratory Datasets



Peak number	Retention time	Area	Height	Concentration	Component name
	min	(µS/cm) x min	µS/cm	ppm	
1	3.510	0.1852	0.848	invalid	
2	4.542	37.5508	103.530	175.463	Sodium
3	5.807	0.9233	3.864	8.186	Potassium
4	10.528	6.3564	9.444	33.768	Calcium
5	12.130	33.3748	19.416	84.906	Magnesium



Retention Time	Concentration	Component name
6.57	0.490	Fluoride
9.47	163.797	Chloride
13.10	4.662	Bromide
14.55	11.210	Nitrate
24.42	0.148	Phosphate
28.25	14.810	Sulfate

Figure A1: Major cations and anions determined for the groundwater sampled from Ellsworth Air Force Base

Table A1: Salt concentrations in synthetic groundwater constructed from major ion analysis of groundwater sampled from Ellsworth Air Force Base

Salt	**Concentration (mg/L)**
NaCl	231.28
NaBr	6.01
$CaCl_2$	93.51
$MgSO_4$	18.56
$NaNO_3$	15.37
K_2SO_4	28.49
NaOH	178.09
$Mg(OH)_2$	203.73