ER 201579-PR: Demonstrating a Biogeophysics Strategy for Minimally Invasive Post Remediation Performance Assessment

Environmental Restoration Projects

October 2020

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**REPORT DOCUMENTATION PAGE**

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<th>1. REPORT DATE (DD-MM-YYYY)</th>
<th>31-10-2020</th>
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<tr>
<td>2. REPORT TYPE</td>
<td>ESTCP Final Report</td>
</tr>
<tr>
<td>3. DATES COVERED (From - To)</td>
<td>8/17/2015 – 10/20/2020</td>
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<td>4. TITLE AND SUBTITLE</td>
<td>Demonstrating a Biogeophysics Strategy for Minimally Invasive Post Remediation Performance Assessment</td>
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<td>5a. CONTRACT NUMBER</td>
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<td>5c. PROGRAM ELEMENT NUMBER</td>
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<td>5d. PROJECT NUMBER</td>
<td>ER-201579</td>
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<td>5e. TASK NUMBER</td>
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<tr>
<td>5f. WORK UNIT NUMBER</td>
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<td>6. AUTHOR(S)</td>
<td>Timothy Johnson, Frederick Day-Lewis, Lee Slater, Pauline Kessouri, Steve Hammett, Dimitrios Ntarlagiannis</td>
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<td>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</td>
<td>Pacific Northwest National Laboratory 902 Battelle Blvd Richland, WA 99354 USA</td>
</tr>
<tr>
<td>8. PERFORMING ORGANIZATION REPORT NUMBER</td>
<td>ER-201579</td>
</tr>
<tr>
<td>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</td>
<td>Environmental Security Technology Certification Program 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605</td>
</tr>
<tr>
<td>10. SPONSOR/MONITOR'S ACRONYM(S)</td>
<td>ESTCP</td>
</tr>
<tr>
<td>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</td>
<td>ER-2015792</td>
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<tr>
<td>12. DISTRIBUTION / AVAILABILITY STATEMENT</td>
<td>Distribution A: Approved for public release; distribution is unlimited.</td>
</tr>
<tr>
<td>13. SUPPLEMENTARY NOTES</td>
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<tr>
<td>14. ABSTRACT</td>
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<td>15. SUBJECT TERMS</td>
<td>biophysics, minimally invasive, bioremediation, VOC, geophysical footprint</td>
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<tr>
<td>16. SECURITY CLASSIFICATION OF:</td>
<td>17. LIMITATION OF ABSTRACT</td>
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<tr>
<td>a. REPORT UNCLASS</td>
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Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. Z39.18
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1.0 INTRODUCTION

1.1 BACKGROUND

The former Brandywine MD Defense Reutilization and Marketing Office (DRMO) is an 8-acre site that was used from 1943 to 1987 as a storage area for waste and excess government material generated by several U.S. Navy and U.S. Air Force (USAF) installations. Releases of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regulated hazardous substances during operating years resulted in widespread soil and groundwater volatile organic compound (VOC) contamination that subsequently migrated off-site to residential areas neighboring the DRMO. The DRMO was placed on the National Priorities List in 1999. In 2006, an Interim Record of Decision was adopted that involved bioaugmentation with dechlorinating bacteria and addition of carbon substrate to reduce time to reach remediation goals. Carbon substrate injections with pH adjustments and bioaugmentation were performed from February 2008 through July 2008 to promote anaerobic biodegradation and reductive dechlorination of halogenated solvents in groundwater.

ESTCP Project ER-200717 ‘Optimized Enhanced Bioremediation Through 4D Geophysical Monitoring and Autonomous Data Collection, Processing and Analysis’, was conducted at the Brandywine DRMO during and after bioaugmentation from 2008 to 2011 (Major et al., 2014). The primary objective of the project was to validate and demonstrate the use of autonomous time-lapse electrical resistivity tomography (ERT) as an effective amendment emplacement monitoring tool. Time-lapse three-dimensional (3D) imaging data sets were collected before and after amendment emplacement for approximately 2.5 years, resulting in a comprehensive ‘four-dimensional (4D)’ data set.

Figure 1. 3D time-lapse ERT images from the ESTCP ER-200717 project showing bioamendment emplacement and movement, seen as increased bulk electrical conductivity (first column), followed by later increase in bulk conductivity arising from microbe-induced precipitation of iron sulfides (e.g., FeS) (second column). These time-lapse images demonstrate the sensitivity of electrical imaging to long-term biogeochemical alterations from bioremediation.
set consisting of nearly 800 images. Spatially dense geochemical data sets consisting of major ions, organic acids, pH, and fluid specific conductance were also collected three times during the monitoring period, with two additional data sets consisting of fluid specific conductance and pH. These data sets (1) established the chemical signature of the amendment, and (2) demonstrated the capability of ERT to effectively monitor in 3D the geophysical signature of the emplacement and migration of carbon substrate and pH buffer after injection. During the first year, amendment was shown to slowly sink down to a lower confining unit and spread due to groundwater flow. As described by Johnson et al. (2015) the second and subsequent years revealed a large increase in subsurface conductivity within the treatment zone due to enhanced microbial activity (Figure 1). We postulated this increase to be the result of microbially-induced iron sulfide precipitation, although biogeochemical research indicates that the same effect could have been caused by the formation of biofilms along pore-grain interfaces (Slater et al., 2009). These findings demonstrated the sensitivity of time-lapse ERT imaging to critical bioremediation processes at the field scale and underscore the opportunity to monitor the long-term performance and impacts of bioremediated sites using remote and non-invasive electrical geophysical imaging methods. In the current project, ESTCP 201579-PR, we returned to the DRMO site to demonstrate and evaluate this approach for long term site monitoring, particularly to assess the long-term impacts of bioremediation on the subsurface.

1.2 OBJECTIVES OF THE DEMONSTRATION

There were three primary objectives of the field demonstration.

1. Identify the long-term geophysical footprint of active bioremediation at a VOC contaminated site. By so doing, assess of the long-term spatial extent of the altered zone using surface-based geophysical imaging techniques.

2. Determine the significance of the geophysical footprint with respect to solid phase mineral transformations and/or biofilms induced by the treatment process. This would enable geophysical alterations within the treatment zone to be interpreted in terms of biogeochemical impacts, which can then be mapped in space and time using geophysical imaging with limited sampling.

3. Demonstrate the use of 1 and 2 above to map gradients in the geophysical footprints of biostimulation along a transect crossing the boundary of the treatment area at an active remediation site and interpret those gradients in terms of long-term biogeochemical impacts.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Electrical geophysical imaging is a method of remotely estimating the distribution of subsurface electrical properties by 1) measuring the response of the subsurface to a low-frequency current transmission, and 2) recovering the distribution of electrical properties that gave rise to the response. In a typical electrical geophysical survey, four-electrode measurements are used. Two
of these serve as current electrodes, and two of these as potential (or measurement) electrodes (Figure 2). These electrodes are typically made of metal (predominantly stainless steel, even though graphite electrodes are also used). A voltage (typically 10-200 V) is applied to the current electrodes, resulting in an induced potential distribution within the subsurface, which is measured across the potential electrodes. Many such measurements are strategically collected over an array of 10’s to 100’s of electrodes to generate a full survey. Each data set comprising a survey is then analyzed via tomographic inversion to produce an estimate (or image) of subsurface conductive and capacitive properties. Repeating this process in a continuous sequence constitutes time-lapse imaging, whereby changes in electrical properties are interpreted in terms of some subsurface process of interest. For instance, changes in bulk electrical conductivity were used to study three-dimensional bio-amendment transport and subsequent bio-mineralization in the precursor to this project (Johnson et al., 2010a, 2015; Figure 1).

![Figure 2. Schematic diagram of a low frequency electrical resistivity tomography measurement. Current is injected between electrodes A and B, and the resulting potential is measured across electrodes M and N.](image)

Application of time-lapse electrical geophysics to assess and monitor in-situ remediation (either natural or biostimulated) is an emerging field with research driven by the need for information on the distributions of injected biostimulants and subsequent biogeochemical activity. Numerous studies have documented that there are unique geophysical signatures associated with microbial degradation of hydrocarbon contamination in the subsurface (Atekwana and Slater, 2009; Atekwana and Atekwana, 2010). These signatures result from the long-term accumulation of degradation end products that cause a different geophysical response within active zones relative to uncontaminated or untreated regions of the subsurface. Specific geophysical signatures during degradation have been shown to result from [1] production of organic acids and associated mineral dissolution (Atekwana et al., 2004; Atekwana and Slater, 2009, Johnson et al., 2014), [2] biofilm accumulation (Ntarlagiannis and Ferguson, 2008; Slater et al., 2009) and [3] precipitation of new solid phases, particularly iron oxides and iron sulfides (Williams et al., 2005, Slater, et al., 2007). Slater et al. (2009) showed how electrical geophysical signatures of biomineralization could be
interpreted in terms of breakthrough behavior associated with microbial activity. At the DRMO, Johnson et al., (2014) demonstrated the capability to monitor biogeochemical impacts (either iron sulfide precipitation or biofilm formation) beginning nearly one year after and continuing to at least three years after bio-augmentation injections. The goal of this project was to return to the DRMO, approximately 8 years after amendment injections, and assess the utility of static electrical geophysical imaging to study the long-term impacts of bioremediation, as stated by the objectives in section 1.2.

2.2 RELATIONSHIPS BETWEEN ELECTRICAL, PHYSICAL, AND CHEMICAL PROPERTIES

To aid in interpretation of the data, in this section we review the relationships between low-frequency electrical properties and corresponding physical and chemical properties of unconsolidated earth materials. The measured complex electrical conductivity $\sigma^*$ is given as,

$$\sigma^* = \sigma' + i*\sigma'' = |\sigma| * (\cos(\varphi) + i * \sin(\varphi)) = (\cos(\varphi) - i * \sin(\varphi))/|\rho|,$$

where: $\sigma'$ and $\sigma''$ are the real and imaginary part of the complex conductivity; $|\sigma|$ and $|\rho|$ are the amplitude of the electrical conductivity in S/m and the electrical resistivity in $\Omega$-m respectively; $\varphi$ is the phase shift of the electrical conductivity.

Subsurface complex conductivity is interrogated using field induced polarization (IP) measurements. In the low frequency range (e.g. less than 100 Hz), where IP measurements are made, the complex conductivity can be modeled as arising from two distinct mechanisms: (i) electrolytic conduction ($\sigma_{el}$) occurring in the interconnected pore space, and (ii) surface conduction and polarization associated with bound charges at the interface of the interconnected pore surface, in the electrical double layer (EDL), represented by a complex surface conductivity $\sigma^*_{surf}$. Assuming a parallel addition of these mechanisms (e.g. Lesmes & Frye, 2001; Vinegar & Waxman, 1984):

$$\sigma^* = \sigma_{el} + \sigma^*_{surf} = (\sigma_{el} + \sigma'_{surf}) + i*\sigma''_{surf}$$

where $\sigma'_{surf}$ and $\sigma''_{surf}$ are the real and imaginary parts of the surface electrical conductivity respectively.

The IP method directly measures the amplitude and phase of the electrical conductivity $\sigma^*$ or electrical resistivity $\rho^*$, allowing for the measured real conductivity $\sigma'$ and imaginary conductivity $\sigma''$ to be determined. As shown by equation 2, $\sigma''$ is exclusively attributed to the surface polarization $\sigma''_{surf}$. A direct linear relationship between $\sigma''_{surf}$ and $\sigma'_{surf}$, and thus between $\sigma''$ and $\sigma'_{surf}$, was first proposed by (Börner et al., 1996) and experimentally verified with a large database by Weller et al. (2013):

$$\sigma'' = \sigma''_{surf} \approx 0.042 * \sigma'_{surf}$$

(3)
Equation (3) offers the opportunity to separate the electrolytic conduction and surface conduction contributions to the total conductivity. Archie (1942) demonstrated that $\sigma_{el}$ can be related to the properties of the saturated interconnected pore space and the pore filling fluid conductivity $\sigma_w$:

$$\sigma_{el} = \sigma_w \cdot \phi_{int}^m$$  \hspace{1cm} (4)

where $\phi_{int}$ is the interconnected porosity and $m$ is a cementation factor related to the tortuosity of the pore space. This petrophysical relation can be used to determine information on porosity and tortuosity of the formation. In contrast, the surface conductivity is controlled by the surface area of the samples as well as the electrochemical properties (ionic mobility, surface charge density) of the EDL (Revil & Glover, 1997, 1998).

### 2.3 TECHNOLOGY DEVELOPMENT

As described in the Introduction, this work is a follow on project to ESTCP Project ER-200717 ‘Optimized Enhanced Bioremediation Through 4D Geophysical Monitoring and Autonomous Data Collection, Processing and Analysis’ (Major et al., 2014), whereby cross-hole ERT was successfully demonstrated to image the distribution of injected bio-amendment and subsequent effects of enhanced bioactivity over a three year period. Readers are encouraged to refer to the ER200717 final report a detailed review of that technology.

### 2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The primary alternative technology to electrical geophysical imaging with sparse sampling, is dense, direct sampling and analysis of groundwater chemistry. The primary advantages of the technology include:

1) the ability to provide volumetric (2D and 3D) information concerning geophysical properties that are related to biogeochemical states and/or processes at relatively high resolution. Alternative technologies rely on direct measurements in soil and groundwater, which are expensive to collect and analyze.

2) subsurface electrical properties are remotely estimated, meaning that direct sampling is not required. Consequently, geophysical imaging provides the opportunity to non-invasively assess all regions of the treatment zone, thereby significantly reducing uncertainty concerning remediation performance and impact.

3) subsurface electrical properties are typically highly sensitive to the biogeochemical properties and processes of interest in bioremediation applications (Atekwana et al., 2004; Atekwana and Slater, 2009).

4) long-term monitoring applications can be completely automated from data collection through data processing and presentation.

Disadvantages of geophysical imaging include:

1) Non-uniqueness. Biogeochemical properties and processes must be inferred from corresponding electrical properties or changes therein, respectively. The relationship between biogeochemical and electrical properties can be complex and uncertain. Consequently, direct sampling is typically necessary to accurately interpret geophysical images, albeit at significantly reduced density in comparison to the alternative direct-sample only approach. This limitation is particularly pertinent for static imaging (i.e. this...
project) because the effects of native conditions must be disentangled from the effects of bioremediation to make useful interpretations. It is less pertinent for time-lapse imaging (i.e. Project ER-200717) where the effects of native conditions are removed, leaving only the effects caused by bioremediation operations.

2) Limited depth resolution. Imaging resolution decreases with distance from electrodes, often rendering surface-based images of little use for deep imaging targets. Such targets generally require borehole electrode installations, which increase deployment costs.

3) Sensitivity. Electrical properties of the subsurface are influenced by multiple factors. Although this provides the opportunity to study numerous processes, it can also confound interpretation of static images in particular, and time-lapse images to a lesser degree. This issue can be resolved in part through limited direct sampling efforts to correlate geophysical responses to subsurface conditions.

4) Background data. As demonstrated herein, the capability to conduct time-lapse imaging from baseline, pretreatment conditions is critical for optimal interpretation of geophysical images in terms of bio-amendment and subsequent microbial induced subsurface alterations. This in turn requires permanent ERT arrays, or arrays that can be repeatedly deployed in the same location from pre-treatment through the project cycle. Without time-lapse imaging, whereby baseline, static effects are removed from the geophysical response, image interpretations are more prone to be confounded by the influence of pre-existing geochemical, geological, biological, and hydrological conditions.
### 3.0 PERFORMANCE OBJECTIVES

Table 1 shows the primary performance objectives of the project followed by a description of each objective, whether the objective was achieved and why or why not.

**Table 1. Performance Objectives**

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<td><strong>Qualitative Performance Objectives</strong></td>
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</tbody>
</table>
| Determine the long-term 3D extent of the biogeochemically altered zone | - Pre-treatment imaging data  
- Current imaging data collected inside and outside of the treatment zone. | - Conclusively identify/image treatment-induced alterations in electrical geophysical properties. The chi-squared value between pre-post treatment measurements, and between within and without treatment zone measurements will exceed 2 for a successful demonstration. | Achieved   |
| **Quantitative Performance Objectives** |                   |                                                                                  |             |
- Core-scale geophysical and biogeochemical measurements on cores from inside and outside of the treatment zone. | - Conclusively identify (MCC >= 0.7) the geophysical signatures of treatment-induced biogeochemical conditions. | Partially Achieved |
| Map biogeochemically induced changes in electrical properties to specific mineral alterations, pore fluid chemistry changes and/or biofilm presence at the field scale | - Pre-treatment and current imaging data.  
- Soil and groundwater samples | - Predict specific geochemical conditions from electrical geochemical images with MCC >= 0.6 | Not Achieved |

The performance objectives stated in Table 1 are cumulative, meaning that a given performance objective cannot be achieved if any of the preceding objectives are not achieved.

#### 3.1 PERFORMANCE OBJECTIVE #1:
**Identify the long-term 3D spatial extent of the biogeochemically altered zone**

Geophysical based investigation of the biogeochemically altered zone requires biogeochemical alterations to produce a recognizable geophysical signature. Those signatures may be identifiable
in space and/or time. In contrast to project ER-200717, it was not possible to investigate changes over time relative to background conditions because 1) the geophysical monitoring system was decommissioned at the conclusion of that project, and 2) it was not possible to reproduce the imaging array used for that project, which is requisite for time lapse imaging. Instead we investigated treatment-induced variations in geophysical properties in space by imaging both inside and outside of the treatment zone, and by collecting continuous images across the known treatment zone boundary. We were also able to visually compare field images with those collected prior to treatment. As shown in Section 6, these images show clear alterations in electrical properties between the treated and untreated zone that we attribute to biogeochemical alterations. Given estimated noise levels at the site, the imaging data were fitted to a normalized chi-squared value of 2 (i.e. underfit at the estimated noise level), yet the electrical alterations across the treatment zone boundary are evident. We therefore consider this performance criteria successful.

3.2 PERFORMANCE OBJECTIVE #2: Determine the significance of the geophysical footprint with respect to treatment induced biogeochemical transformations

Successful demonstration of performance objective #2 required the development of conclusive relationships between bioremediation-induced subsurface biogeochemical alterations and corresponding alterations in geophysical properties. Field scale images and laboratory investigations both showed clear amendment induced biogeochemical impacts. However, we were unable to establish clear relationships between biogeochemical alterations and geophysical alterations to a degree that enable successful demonstration of objective 3. As noted in section 3.1 we were unable to deploy geophysical instrumentation in a manner (i.e. equivalent to ER-200717) that enabled the remediation-induced geophysical alterations to be separated from the pre-treatment geophysical properties. We therefore consider this objective to be only partially demonstrated. More detailed discussions are provided in Sections 6 and 8.

3.3 PERFORMANCE OBJECTIVE #3: Map biogeochemical impacts based on geophysical footprints

Objective 3 was the culminating objective for this project and required successful completion of objectives 1 and 2. Specifically, the relationships between geophysical properties and biogeochemical alterations identified in objective 2 were to be applied to the altered zone identified in objective 1 to produce a 3D map of specific mineral alterations in objective 3. Because we were unable to conclusively identify relationships between static electrical properties and corresponding biogeochemical alterations, performance objective 3 was not achieved.
4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

Given the nature of this project as a follow-on to ESTCP project ER-200717 the demonstration site was pre-determined. The Brandywine Defense Reutilization Marketing Office (DRMO) location, history, geology, and contaminant distribution are described in the final report for ER-200717 and summarized below.

The Brandywine DRMO (EPA 2006, Figure 3) is an inactive U.S. Department of Defense (DOD) facility that occupies approximately eight acres of land. The U.S. Navy operated the site as a storage yard and marketing office from an unknown date until 1955, when it was transferred to the U.S. Air Force. In 1973, the Defense Supply Agency (DSA) assumed control of the site, and the Defense Property Disposal Organization (DPDO) received a permit from Andrews Air Force Base (AFB) to use the property. The Brandywine DRMO site is located in southern Prince George's County, Maryland, about 8 miles south-southeast of the AFB. The site lies within the Potomac River Basin. A remedial investigation was completed in 2005 (URS 2005), and thus the site is well characterized.

From approximately 1953 until 1988, the DRMO site was used principally as a storage area for surplus electrical equipment, other materials, and for storage of hazardous wastes. The site accepted materials, including hazardous wastes, from several installations, including Andrews AFB, Bolling AFB, the Washington Naval Yard, the Navy Research Laboratory, the Naval Surface Warfare Center (NSWC)-Indian Head Ordnance Station, and White Oak Laboratory (now known as NSWC-White Oak). Drums of waste solvents, capacitors and transformers containing polychlorinated biphenyls (PCBs) were stored at the DRMO. Records indicate there were two burn pits used for disposal and burn of waste and several above and below ground tanks. The Air Force (AF) removed the burn pits and tanks in 1989. This site was proposed to the National Priorities List of the most serious uncontrolled or abandoned hazardous waste sites requiring long-term cleanup action on July 28, 1999. The site was formally added to the list May 10, 1999, making it eligible for federal cleanup funds (EPA 2006).
4.2 SITE GEOLOGY/HYDROGEOLOGY

Shallow subsurface materials at the Brandywine DRMO consist of silt, silty-sand, and sand. Two formations are identified on the site: the Brandywine formation (about 0-30 feet) and the Calvert formation (directly below the Brandywine formation), which is a fined-grained unit that behaves as an aquitard. Contamination is shallow, extending to about 30 ft below ground surface (bgs) in the Brandywine Formation. The target zone for remediation was bounded below by the Calvert Formation. The water table is at about 5ft bgs. Groundwater flow is toward the northwest (URS 2005), with a measured groundwater velocity of about 50 ft/year.

4.3 CONTAMINANT DISTRIBUTION

The extent of groundwater contamination at the Brandywine site prior to remediation efforts is discussed in depth in the Brandywine Remedial Investigation (RI) report (URS 2005). The material presented in this section is verbatim from section 2.5.3 the ROD (EPA 2006). “Based on historical evidence and the groundwater and soil data presented and discussed in the Brandywine RI, the releases of CERCLA-regulated hazardous substances at the Brandywine DRMO resulted in three distinct plumes of dissolved chlorinated solvents in the groundwater. The area of highest contaminant concentrations occurs west and northwest of the DRMO yard. The release or releases responsible for generating this plume most likely occurred near the northwest corner of the DRMO yard. A smaller, disconnected plume is located within the DRMO yard. There also is a smaller plume located to the northeast of the DRMO yard. The spill...
or spills responsible for groundwater contamination within the DRMO yard were events separate from the spills responsible for groundwater contamination northwest of the yard; the plumes are spatially disconnected. The plume within the DRMO yard is smaller and has lower concentrations of contaminants as is the smaller plume to the northeast. The most significant groundwater contaminants at the site, as defined by areal extent and concentrations above the maximum contaminant levels (MCLs) for federal drinking water standards, are trichloroethene (TCE), tetrachloroethene (PCE), and cis-1,2-dichloroethene (DCE). The maximum concentrations of TCE and PCE measured at the site are 224.2 milligrams per liter (mg/L) and 0.349 mg/L, respectively. The MCL for TCE and PCE is 0.005 mg/L. The maximum cis-1, 2-DCE concentration measured at the site was 13.4 mg/L. The MCL for cis-1, 2-DCE is 0.070 mg/L. The results of the site investigations indicate that the VOCs in groundwater at the Brandywine site are present both as dissolved contaminants and as droplets or pools of dense nonaqueous phase liquid (DNAPL) that contain primarily TCE. A Focused Feasibility Study (FFS) was undertaken in 2005 to evaluate remedial action alternatives that would address contamination associated with groundwater at the Brandywine site (URS 2006). The FFS concluded that the Contaminants of Potential Concern (COPCs) in groundwater at the site are TCE, PCE, cis-1, 2-DCE, vinyl chloride, naphthalene, 2- methyl-naphthalene, iron, and manganese. The TCE and PCE were likely released into the groundwater due to site activities.”
Figure 4. Ground-water elevations and contaminant distribution prior to remediation efforts in the vicinity of the Andrews AFB DRMO, Brandywine, MD. The field study described here focused on an area within the plume in the DRMO area.
5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The experimental design used to evaluate the performance objectives was divided into five 1-week field campaigns and a laboratory-based effort for analysis of soil and water samples. Early field campaigns included borehole installations of geophysical and water sampling infrastructure, soil core collection, and preliminary geophysical data collection. Later field campaigns involved comprehensive geophysical data acquisition and groundwater sample collection. The laboratory campaign began after the first field campaign, and involved a detailed investigation of biological, geochemical, and geophysical properties of soil cores collected inside and outside of the treatment zone. The analysis of geophysical datasets included a comparison against pre-amendment geophysical datasets from ER-200717 and against geochemical datasets acquired as part of this demonstration.

5.2 BASELINE CHARACTERIZATION

Baseline geophysics

Pre-treatment geophysical imaging and supporting geochemical data collected under ER-200717 established the biogeochemical and geochemical conditions prior to treatment within the contaminated zone of the aquifer. Figure 5 presents a baseline image of the 3D electrical conductivity structure of the site prior to the treatment centered on the amendment injection. Information on data acquisition and processing needed to generate the image shown in Figure 5 can be found in ER-200717. The 3D resistivity image captures the bulk electrical conductivity structure of the site at the injection location. The coarse-grained aquifer (the Brandywine Formation, section 4.2) is resolved as a low electrical conductivity formation with evidence of significant heterogeneity within the formation. The underlying, relatively fine-grained confining unit (the Calvert Formation, section 4.2) resolved as a high electrical conductivity unit. This high electrical conductivity (being up to two orders of magnitude higher than in the aquifer) is a consequence of the finer-grained sediments increasing surface conduction (see Section 2.2). Note that in ER200717 crosshole imaging extended approximately 2 m below the Brandywine/Calvert formation contacts. In this project the crosshole imaging terminated at approximately 10 m below ground surface and did not extend beneath the contact.
Figure 5. Pre-treatment 3D ERT image from the Brandywine site collected in 2009 under ER-200717

A reconnaissance electromagnetic (EM) survey was performed in 2016 to determine the larger scale patterns of electrical resistivity at the site and to evaluate whether the plot locations selected for the ERT surveys in this post remediation demonstration are representative of overall site conditions (from an electrical geophysics standpoint) and are devoid of any unknown infrastructure. Figure 6 shows the plan view of apparent resistivity (an approximation of the true resistivity) for an estimated depth of 3.2 m determined from a Dualem 421 EM survey superimposed on a map of the site, including the extent of amendment injections and the general groundwater flow direction. The locations of the boreholes and surface ERT lines forming the focus of this demonstration are shown, along with pre-existing boreholes with water chemistry monitoring data (described in the next section). The EM survey shows that the plot scale infrastructure used in this demonstration is located in a region devoid of any interference from unknown infrastructure. The localized very low resistivity values in the north of the EM survey area likely result from local metallic infrastructure.
Baseline geochemistry

Geochemical datasets acquired from 2007-2015 are reported in (USACE, 2016). Figure 7 shows concentrations of different chlorinated solvents over time measured on water samples extracted from different wells in the treated and in the untreated areas (see Figure 3). The expected degradation pathway (PCE → TCE → cis-1,2-DCE → VC → Ethene) is well reproduced in the groundwater data from inside (red) and at the edge of the treatment zone (yellow). The uncontaminated and untreated zone is shown in green for comparison. The baseline geochemistry data support the effectiveness and long-term footprint of the amendment injection on the aquifer chemistry.
Figure 7. Concentration of different chlorinated solvents from 2007 to 2015, measured on water samples extracted from different wells in the treated and in the untreated areas: PCE = polychloroethylene; TCE = trichloroethylene, Cis-1,2-DCE = cis-1,2-dichloroethene; VC = vinyl chloride. See Figure 3 for well locations. Timing of 1st and 2nd injections shown. Data from USACE (2016).

Figure 8 shows concentrations of major water quality parameters over the same time range. The treated zone (red and yellow data points) is characterized by persistently low Eh, high fluid conductivity ($\sigma_w$) and high pH relative to the untreated zone, five years after the treatment. Despite the high $\sigma_w$ values in the treated zone, a progressive decrease in $\sigma_w$ over time is apparent in this zone. Once again, available baseline datasets provide evidence of a long-term footprint of the amendment injection on the aquifer chemistry.
Figure 8. Concentration of different water quality parameters from 2007 to 2015, measured on water samples extracted from different wells in the treated and in the untreated areas: (a) dissolved oxygen (DO); (b) redox potential (Eh); (c) fluid conductivity ($\sigma_w$); (d) pH. See Figure 3 for well locations. Timing of 1st and 2nd injections shown. Data from USACE (2016).

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

Not applicable to this project

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The field layout is summarized in Figure 9. It included three primary components: (1) 2D surface-based ERT lines, (2) wellbores for joint cross-hole ERT and multi-level groundwater sampler (MLS) deployments, and (3) wellbores for soil cores/geophysical logging. The treatment zone boundary is also shown in Figure 9. Comprehensive borehole and surface based geophysical data sets were collected to establish the electrical geophysical properties under native, uncontaminated conditions. Cross-borehole tomographic imaging data sets were collected between three pairs of ERT/MLS located within the treated zone, and included the following locations: 1) straddling an amendment injection site (E3-E4) 2) within the treated zone boundary but offset from (west of) injection points (E1-E2), and 3) in the untreated zone north of the treatment zone boundary (E5-E6) shown in Figure 9.
Figure 9. Site layout showing test design components. The test components straddle the treatment zone boundary (red dashed line) and includes treated and untreated zones. Blue lines: surface ERT lines. Black circles: borehole ERT lines (E1-E6). White circles: wellbores for continuous soil cores and geophysical logging (W1-W4). Opaque map defines limits of ER0717 survey.

5.5 2D-Surface ERT Arrays

Two 72 m long north-south trending 2D surface ERT lines were deployed as shown in Figure 10 (blue lines) to image the 2D distribution of electrical properties beneath each line. The lines were arranged to provide information inside and outside of the treatment zone, and to coincide with imaging data previously collected under project ER_200717. Each line consisted of 72 stainless steel rods, approximately 25 cm long and 1.5 cm in diameter, driven approximately 20 cm into the surface, with a 1 m spacing between electrodes. Electrodes were connected by cabling at their exposed ends and routed to the data collection instrumentation. These installations were temporary and removed between field tests and at the completion of data collection.
5.6 Borehole ERT/MLS Arrays

A total of eight ERT borehole arrays were constructed, six deployed within the treatment zone and two outside of the treatment zone as shown in Figure 11. Each array consisted of a series of 24 stainless steel electrodes and sampling tubes fastened to a rigid fiberglass spine (tent poles). The array was deployed vertically inside of a narrow diameter direct-push borehole and backfilled to completion. The 24 electrodes were spaced 40 cm apart and spanned the depth range 1.25 - 10.45 m below surface. Three fluid sampling tubes were deployed at each borehole, terminated at depths of 3.2 m, 6.2 m and 9.2 m, within the saturated zone (Figure 12). The borehole electrodes were used to collect cross-hole 2D and 3D geophysical imaging data. The sampling ports on these arrays were the primary means of collecting depth-discrete groundwater samples for geochemical analysis inside and outside of the treatment zone. Figure 12b shows installation of the combined ERT/multilevel sampling (MLS) array in a borehole. Figure 12c shows a close up of one of the multilevel samplers on an array.
Figure 11. Construction of inexpensive cross-borehole ERT arrays (a) installation locations on site layout (b) photograph of ERT arrays under construction in the laboratory.
Figure 12. Photographs showing (a) installation of multilevel sampler (MLS) on ERT array in the field; (b) installation of combined ERT/MLS array; (c) close up of MLS on an ERT array.

5.7 Soil Cores and Geophysical Logging Wellbores

Figure 13 shows the locations of four wellbores (W1-W4) used for collection of continuous soil cores. Two continuous soil cores were acquired within the treated zone to the south of the treatment zone boundary and two were acquired in the untreated zone to the north of the treatment zone boundary (Figure 13). The cores were used for direct laboratory measurement of electrical geophysical properties with depth, inside and outside of the treatment zone. They were also used to investigate the solid phase products inside and outside of the treatment zone. Wellbores W1-W4 were also used to acquire 1D geophysical logging profiles, along with an additional well B1 (DP19) further from the injection (Figure 3). The following geophysical logs were run: magnetic susceptibility (MS), electrical conductivity from an electromagnetic induction (EM) tool and natural gamma.

Magnetic susceptibility measures the ease with which a soil or a rock can be magnetized when a magnetic field is applied. It is foremost related to the concentration of ferrimagnetic grains present in the formation. When the volume concentration of ferrimagnetic minerals is less than a few percent, assuming that the magnetic grain shapes are roughly spherical and the dominant magnetic mineral is magnetite \([\text{Fe}^{2+}\text{(Fe}^{3+})_2\text{O}_4]\) (which can be expected in most natural samples), the volume
fraction of magnetite \( f \) can be estimated from the volume susceptibility \( \kappa \) (in SI) directly, (e.g. Currie & Bornhold, 1983; Mooney & Bleifuss, 1953; Thomson & Oldfield, 1986))

\[ f \approx 3 \times \kappa \]

Magnetic susceptibility measurements were acquired with the QL40-HM tool from Mount Sopris. This tool uses a frequency of 2kHz and a coil spacing of 25 cm, where 70\% of the signal is from an approximately 10 cm radius from the well. The measurement range is from \( 10^{-5} \) to 0.5 SI.

The natural gamma ray logging tool measures radioactivity levels occurring naturally in a formation. Some minerals, particularly clay minerals, fix the radioisotopes that are primarily responsible for natural gamma radiations (potassium, uranium and thorium). The gamma ray index \( I_{GR} \), is defined by,

\[ I_{GR} = \frac{GR_{log} - GR_{min}}{GR_{max} - GR_{min}}, \]

where \( GR_{log} \) is the gamma ray reading at the depth of interest, \( GR_{min} \) and \( GR_{max} \) are respectively the minimum and maximum gamma ray readings recorded across the site. The Mount Sopris instrument states a measurement range from 0 to 100,000 CPS and a resolution of 0.1

Approximately 75\% of the gamma-ray signal comes from within 30 cm of the borehole wall, which can be taken as the investigation depth of the gamma-ray tool.

The MS logs were run to investigate for evidence of possible iron mineral bi-products associated with microbial activity, and to also assess variations in iron minerals between treated and untreated zones. The EM logs were run to provide high resolution 1D vertical profiles of electrical conductivity structure for comparison against the lower resolution 2D surface and 3D cross-borehole ERT surveys. The natural gamma ray logs were run to assess lithological variations associated with variations in clay mineral concentration. Both soil core and wellbore datasets were considered critical for relating field-scale electrical images to long-term biogeochemical impacts.

Each soil core underwent comprehensive laboratory analysis to establish native, uncontaminated and untreated conditions outside of the treatment zone. These analyses are described Section 5.6. Borehole geophysical logs were reduced and interpreted according to standard USGS procedures and archived to enable follow-on research according to USGS.
Figure 13. Location of four wellbores (W1-W4) used for continuous coring and 1D geophysical well logging. Example cores extracted from each location shown.

### 5.8 FIELD TESTING

Field testing was performed during five separate weeks in an effort to map the geophysical footprint of biodegradation. Geophysical datasets were acquired at locations extending from within the treatment area to outside the treatment area and crossing through the experimental plot used in ER-200717 (Figure 9). Table 5.1 summarizes the timing of the major field activities. The initial field campaign (05/02-05/07/16) focused on drilling, coring/soil sampling and well completion, including installation of electrode arrays for 2D cross-borehole imaging. Although 2D surveys were not performed during this week, 1D resistivity and IP profiles were recorded using individual arrays in each of the eight ERT boreholes. The main 2D surface ERT and 2D cross-borehole ERT datasets were acquired during the second week of field measurements (05/18-05/22/16). During this week, groundwater samples were collected from each of the 24 sampling ports (8 MLS wells with 3 sampling depths per well) to establish the pore water chemistry and spatial variations therein. Another round of 1D resistivity and IP profiles was acquired using the individual arrays installed in eight boreholes. Fieldwork conducted during the third week of the campaign (06/01-06/05/15) focused on borehole geophysical logging (electromagnetic (EM) derived electrical conductivity, magnetic susceptibility (MS) and natural gamma), along with one more round of 1D resistivity and IP profiles acquired using individual arrays. A fourth week of data acquisition (06/12-06/16/16) included another round of 2D surface ERT and 1D resistivity/IP data acquisition. A final set of field measurements conducted 11/08-11/12/16 focused on larger scale surface-based reconnaissance electromagnetic (EM) mapping to assess the large scale electrical structure of the...
site beyond the range of the plot-scale remediation study (Figure 6), with the caveat that the EM surface-based EM data are only sensitive to approximately the upper 3.5 m of the subsurface. This integrated dataset was used to establish the distribution of electrical geophysical properties within the test site spanning from the treated to untreated regions. Wells were abandoned at the end of the performance period according to Maryland regulations.

Table 5.1: Summary of Field Campaign Schedule Performed Over Five Weeks in 2016

<table>
<thead>
<tr>
<th>2016</th>
<th>05/02-05/07</th>
<th>05/18-05/22</th>
<th>06/01-06/05</th>
<th>06/12-06/16</th>
<th>11/08-11/12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well installation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil sampling</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1D resistivity and IP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2D surface ERT</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3D cross-hole ERT</td>
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<tr>
<td>Water sampling</td>
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<td></td>
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<tr>
<td>Borehole geophysical logging</td>
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<td></td>
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<tr>
<td>Large scale EM mapping</td>
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</tbody>
</table>

5.9 SAMPLING METHODS

Soil Core Samples

Undisturbed soil cores were collected from wellbores W1-W4 during the first field campaign. Cores were sectioned, logged by depth, and placed in anaerobic (N2-filled) portable glove bags immediately after collection. Samples were shipped to Rutgers University Newark and handled under anaerobic conditions to the extent possible. Detailed analysis of soil cores focused on ~8 samples per borehole.

Laboratory geophysical measurements were made on selected cores (chosen based on the field results) to help identify relationships between geophysical properties (primarily electrical conductivity and MS), mineral composition, and fluid chemistry. Low-frequency electrical geophysical properties (complex electrical conductivity over the frequency range 0.001-1000 Hz) and magnetic susceptibility were measured on soil samples using high-precision laboratory equipment. Complex resistivity, an extension of a regular resistivity measurement, provides additional critical information to permit assessment of whether the conductivity enhancement is due to changes in surface mineralogy as opposed to changes in pore fluid chemistry.

Solid phase ferrozine analysis was performed on selected cores (again chosen based on the field results) to assess the potential iron minerals that may be present, including iron oxides and iron sulfides. Iron oxides and iron sulfides are often associated with biodegradation and are known to generate anomalous geophysical signatures (Slater et al., 2007; Williams et al., 2009). Iron content was determined using the hydroxylamine extraction method, modified to distinguish between ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron, (Chao & Zhou, 1983; Lovley & Phillips, 1987). Fe^{2+} was
measured by HCl extraction (0.5 M) and total Fe was measured on a similar sample, treated with 6.25 N hydroxylamine and then acidified. Fe$^{3+}$ was calculated by subtracting Fe$^{2+}$ from total Fe. Additionally, the samples used for Fe$^{2+}$ estimation were treated with 6.25 N hydroxylamine and acidified again in order to directly measure Fe$^{2+}$. Sulfides were determined through acid volatile analysis utilizing the gas diffusion method (Cline, 1969). Additional solid phase analysis included x-ray diffractionometry (XRD) to identify mineralogy, and environmental scanning electron microscopy (E-SEM) to investigate for evidence of biofilms and/or biomineralization within the treated zone.

**Groundwater Samples**

Groundwater samples were collected from inside and outside of the treatment zone, using all eight ERT/MLS wells and compared to baseline datasets (Section 5.2). Groundwater samples were collected manually using established methods from three different depths: 3.2, 6.2 and 9.2 m. Tubing was first purged and produced water collected and disposed of appropriately, per the environmental and health safety plan for the site. Prior to collecting water samples, field parameters, including Fluid electrolyte conductivity, pH, temperature, dissolved oxygen (DO), and redox potential (Eh) were acquired using a YSI multi-parameter meter. In addition, to better assess the in-situ conditions of the highly redox-sensitive species, field analyses for total iron, ferrous iron (Fe$^{2+}$) and hydrogen sulfide (HS$^{-}$) concentrations were conducted using HACH field kits immediately upon sample retrieval.

Water samples from each of the sampling ports were stored on ice, shipped to the lab and analyzed for major anions and cations. The laboratory measured analytes, completed within 72 hours of sampling, are summarized in Table 5.1. They include major cations and anions replicating the sampling performed under ER_200717. Laboratory analyses were performed using New Jersey Department of Environmental Protection (NJ-DEP) certified facilities at the Meadowlands Environmental Research Institute (MERI), part of Rutgers University Newark at the time of the work.

**Table 5.2: Summary of the measured analytes, including total number of samples analyzed**

<table>
<thead>
<tr>
<th>Analyte(s)</th>
<th># samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anions</strong></td>
<td>33</td>
</tr>
<tr>
<td>[Fluoride, Chloride, Nitrate/Nitrite, Bromide, Phosphate, Sulfate]</td>
<td></td>
</tr>
<tr>
<td><strong>Cations</strong></td>
<td>31</td>
</tr>
<tr>
<td>[Sodium, Ammonia, Potassium, Calcium, Magnesium]</td>
<td></td>
</tr>
<tr>
<td><strong>Iron</strong></td>
<td>28</td>
</tr>
<tr>
<td><strong>Chemical oxygen demand (COD)</strong></td>
<td>28</td>
</tr>
</tbody>
</table>

**Calibration of Analytical Equipment**
All handheld instrumentation and sensors were tested and calibrated at the beginning and end of the measurement period using either reference solutions or known standards. Laboratory analytes were measured at the MERI laboratory, a NJ-DEP certified analytical laboratory subject to rigorous calibration checks to maintain its certification.

**Quality Assurance Sampling**
The NJ-DEP certified MERI laboratory performs rigorous quality assurance sampling in order to maintain its state certification.

**Decontamination Procedures**
The primary residuals produced under this effort were the purge volumes associated with the groundwater sampling. Volumes of fluid purged during groundwater sampling were discharged to a holding tank and removed from the site and disposed of appropriately. Drilling fluids and by-products of drilling were containerized by the contract driller. All equipment and machinery were decontaminated in accordance with the Brandywine Environmental Health and Safety Plan. The USGS handled disposal of produced fluids and solids from this project.

**Sample Documentation**
All data acquired at the site were stored in an online shared database with backup to local hard drives at Rutgers University Newark.

### 5.10 SAMPLING RESULTS

**Borehole Geophysical Logging**

Figure 14 compares the borehole geophysical logging datasets at the four locations (W1-W4 Figure 13) and also shows logs for borehole (B1, DP19) located about 100 m from the treatment site for comparison (Figure 3). Figure 14 also highlights the lower contaminated aquifer that underwent treatment (Figure 1). The EM-derived electrical conductivity shows generally higher values in the treated aquifer and below relative to the upper aquifer. The exception is borehole B1 (far from the treatment) where electrical conductivity is relatively uniform except below 8.5 m. The gamma ray profiles are very similar for W1-W4 and similar to B1 except between 2- 4 m depth, where B1 shows an anomalously high gamma ray count.
Figure 14. Borehole geophysical logging profiles: (a) EM-derived electrical conductivity; (b) gamma ray count; (c) magnetic susceptibility (MS). Treated zone (W1), edge of treated zone (W2), edge of untreated zone (W3) and untreated zone (W4). B1 far from treatment zone shown for comparison.

Finer-grained sediments, including clay minerals, are present below 8 m depth. The increase in EM measured conductivity is most likely due to an increase in surface conduction associated with the presence of clay minerals at these depths. The increase in the gamma ray count below 8.5 m depth is consistent with the presence of clay minerals.

The magnetic susceptibility is higher in the treated zones (W2 near to the treated/untreated boundary; W1 – further from treated/untreated boundary;) relative to the untreated zone (W3 – near to treated zone boundary; W4 – further from treated zone boundary) within the experiment plot; Borehole B1, far from the treatment zone, shows the lowest MS signal. At the treated zone (W1) the MS signal in the upper aquifer is notably higher than elsewhere. Focusing on the contaminated/treated aquifer below 5.5 m depth the MS is significantly higher in the treated zone relative to the untreated zone.

Groundwater samples

Figure 15 shows water chemistry parameters that inform the general geochemical conditions in the aquifer in 2016, approximately 8 years after the amendment injection. In all water chemistry
analyses shown in this section, samples were obtained from three depths (3.2, 6.2 and 9.2m) and averaged for 2 boreholes each (E1 and E2 for the treated area, E3 and E4 for injection well area at the edge of the treated zone and E5 and E6 for the untreated area). The treated zone is generally characterized by higher fluid conductivity (the exception being the value at 6.2 m), lower Eh (the exception being the value at 9.2 m) and higher chemical oxygen demand relative to the untreated zone of the aquifer.

Figure 15. Water chemical measurements informing the general geochemical conditions within the aquifer in 2016: (a) fluid electrical conductivity, (b) pH, (c) redox potential (Eh), (d) Chemical Oxygen Demand (COD) and e) chloride Cl⁻ concentration. Samples are from three depths (3.2, 6.2 and 9.2m), with average for 2 boreholes shown (E1 and E2 for the treated area, E3 and E4 for injection well area and E5 and E6 for the untreated area).
Figure 16 summarizes key indicators of reduction state from the analysis of the water samples extracted from wells at the site. Distinct differences between the treated zone and the untreated zone exist, with a number of the analytes indicating the persistence of reducing conditions in the treated zone nine years after the amendment injection. Relative to the untreated zone, treated zone locations show lower DO at depth, high Fe$^{2+}$, low Fe$^{3+}$, Fe$^{2+}$/Fe$^{3+}$ ratios, low NO$_2^-$ (except at 9 m), low SO$_4^{2-}$ and high HS$^-$ concentrations.

Figure 16. Water chemical analysis inferring the reduction state of the formation from least reducing to most reducing indicators: a) Dissolved Oxygen (DO); b) Nitrate NO$_3^-$ and nitrite NO$_2^-$; c) Ferric (Fe$^{3+}$) and ferrous (Fe$^{2+}$) iron concentrations and Fe$^{2+}$/Fe$^{3+}$ ratio; d) Sulfate (SO$_4^{2-}$) and hydrogen sulfide (HS$^-$) concentrations. Samples are from three depths (3.2, 6.2 and 9.2m), with average for 2 boreholes shown (E1 and E2 for the treated area, E3 and E4 for injection well area and E5 and E6 for the untreated area).
Figure 17 compares (a) the Fe$^{2+}$/Fe$^{3+}$ ratio profiles with (b) the continuous borehole geophysics-measured MS profiles for the treated zone (far from injection), at the edge of the treated zone (near the injection) and in the untreated zone. Low MS values and high Fe$^{2+}$/Fe$^{3+}$ ratios (relative to the untreated zone) in the lower part of the aquifer (around 6 m) of the treated area are consistent with more reducing conditions that promote the transformation of Fe$^{3+}$ to Fe$^{2+}$. High MS but slightly higher Fe$^{2+}$/Fe$^{3+}$ ratios in the upper part of the aquifer (around 3 m) in the treated zone may reflect moderately reducing conditions where iron reduction is still occurring. In contrast, the untreated area has both a low MS and low Fe$^{2+}$/Fe$^{3+}$ ratio consistent with more oxidizing conditions.

Figure 17. Comparison of (a) ferrous/ferric (Fe$^{2+}$/Fe$^{3+}$) iron ratio measured in depth-discrete groundwater samples against (b) continuous borehole geophysics-measured magnetic susceptibility (MS). In (a) samples are from three depths (3.2, 6.2 and 9.2m), with average for 2 boreholes shown (E1 and E2 for the treated area, E3 and E4 for injection well area and E5 and E6 for the untreated area).

In summary, the analysis of groundwater samples from the site indicates the persistent footprint of the contamination and treatment within the treated portion of the aquifer nine years after the active remediation. The analysis of the iron chemistry is generally consistent with the borehole MS profiles in terms of likely distribution of iron minerals.

Soil Core Analysis
Comparison of results on cores obtained from the four cross sections were used in an effort to help identify evidence for treatment-driven biogeochemical and geophysical gradients and correlations between them. Efforts focused on understanding the significance of differences in MS between treated and untreated zones captured in borehole MS logging datasets.

Results of the solid phase ferrozine analysis provide insights into the distribution of MS recorded in the borehole logs. Figure 18 shows MS profiles contrasted with solid phase \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) concentrations determined from the discrete soil samples at different depths. The \( \text{Fe}^{3+} \) profiles show some consistency with the MS logging profiles with higher MS correlating with higher \( \text{Fe}^{3+} \), likely indicating the contribution of MS responses from different Fe-oxides containing \( \text{Fe}^{3+} \) (likely primarily magnetite). In the untreated part of the aquifer (above 5 m) the MS signal is high and \( \text{Fe}^{3+} \) dominates the total iron concentration. However, below 5 m MS is low and \( \text{Fe}^{2+} \) dominates the total iron in the treated zone (although \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) concentrations are almost equal at this depth close to the edge of the treated zone and in the untreated zone). The \( \text{Fe}^{2+} \) concentrations also show some correlation with the MS profile for the treated zone (E1-E2) with higher values above 5 m relative to between 5-9 m depth. In contrast, \( \text{Fe}^{2+} \) concentrations are relatively uniform with depth near the edge of the treated zone and in the untreated zone. These results highlight how MS provides insights into the biogeochemical conditions associated with iron mineralogy in the aquifer.

**Figure 18. Comparison of MS profiles with \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) concentrations determined from the ferrozine analysis**
Figure 5.19 shows example SEM images of samples from within the treated zone, at the edge of the treated zone and outside of the treated zone focused on the high MS recorded with borehole logging in the treated zone at a depth of 4 m. Although morphological differences between treated and untreated zones are apparent in the images, no evidence for the presence of biofilms was observed. It is likely that the sample preservation procedures were inadequate for detecting the presence of biofilms.

Figure 19. SEM images of samples from within the treated zone (red), at the edge of the treated zone (yellow) and outside of the treated zone (green) focused on the high MS recorded with borehole logging in the treated zone

Figure 20 compares the XRD spectra for a series of samples from the treated zone (E1E2) with increasing depth, passing through the zone of high MS (Figure 14). The XRD patterns are almost identical for all samples, suggesting that either the concentration of iron oxides causing the high MS at E1E2 was too low to be detected or, more likely, some mineral transformations occurred during preservation, storage and laboratory analysis prior to XRD analysis.
Figure 20. Results of XRD analysis from the treated area (E₁E₂) showing negligible change in the XRD spectra with depth passing through the zone of high MS recorded in the borehole logging dataset (Figure 14).
6.0 PERFORMANCE ASSESSMENT

6.1 2D Surface ERT Lines

Tomographic ERT data were analyzed for noise characteristics and filtered to remove erroneous measurements. The ERT and IP data were inverted using the open source, finite element, E4D code (https://e4d.pnnl.gov; Johnson et al., 2010, Johnson et al., 2015), which has been qualified as safety software under NQA1-B software quality control standards.

Figure 21 shows the 2D imaging result beneath the surface ERT lines. These lines cross the treatment zone boundary (shown by the red line) to provide a spatial comparison between the treated and the untreated zone. There is a demarcation in electrical conductivity across the treatment zone boundary with higher conductivity exhibited in the treatment zone, particularly between the ground surface and approximately 8 m depth, which is the approximate depth to the lower confining unit (Calver Fm). This is consistent with time-lapse difference images collected for two years post injection under ER200717 (Figure 1), which showed increases in conductivity due to the presence of amendment and a secondary increase due to microbial activity (either iron sulfide precipitation or biofilm production) approximately 1 year after injection. Lines 1 and 2 both show increases in conductivity near the amendment injection points (i.e. point 0.0 on the x-axis and 0-6 m on the depth axis). Line 2 shows a similar increase in conductivity between -15 to -10 m along the x-axis, suggesting possible proximity to another injection point (injection points were spaced ~8 m apart within the treated zone).

Figure 21. 2D surface ERT imaging results beneath lines 1 and 2. View are present from the +x direction facing the -x direction. Results show higher overall conductivity in the treated zone.
6.2 Cross-hole ERT Imaging

The cross-hole ERT and IP imaging results are shown in Figure 11. The 2D imaging panel between wells E1-E2 lies within the treatment but was not centered on an injection point. The 3D imaging panel including wells E3-E4 is within the treatment zone, near the treatment boundary, and centered around and injection location. The 2D panel between E5-E6 is outside of the treatment zone. Conductivity near the injection point is clearly elevated compared to both the E1-E2 and E5-E6 panels, particularly above approximately 4m depth. The conductivity differences between panels E1-E2 and E5-E6 are less conclusive regarding treatment impacts. For example, the E5-E6 panel displays elevated conductivity from 5-8m depth in comparison to the E1-E2 panel. This could be caused by northward migration of injected amendments along the lower confining unit (~8 m depth) or could be the unimpacted, native condition. Without pre-treatment images, it is not possible to distinguish the origin. Specifically, interpretations concerning the long terms effects of the treatment are largely confounded by native heterogeneity. This comparison highlights one of the primary conclusions and lessons learned from this work. Baseline, pre-treatment images are necessary to enable the effects of native heterogeneity to be subtracted from post-treatment images through time-lapse difference imaging, thereby isolating the changes in electrical properties caused by the treatment alone. This approach was used for ER-201717 which provided the motivation for this work.

Figure 22. Bulk conductivity (upper panels) and phase (lower panels) images of the regions between imaging panels. Panel E1-E2 is located within the treatment zone but was not centered on an injection point. Panel E3-E4 is located near the treatment zone boundary and is centered around an injection point. Panel E5-E6 is outside of the treatment zone boundary.

Figure 22 also shows the phase shift images (see section 2.2) in each panel, which can be considered a measure of the capacitive properties of the subsurface. The phase shift images show
clear differences between the treated and untreated zones, with elevated phase shifts occurring in the treated zone, particularly near the injection point (panel E3-E4).

Figure 23. 2D cross-hole images superimposed on 2D surface-based images show the relative value of each type of imaging. View is from +x direction facing toward -x direction. White lines on cross-hole show interpreted location of the lower confining unit (Calvert Fm). Red line marks the treatment zone boundary.

To compare the relative merits of each type of imaging (2D surface vs. crosshole) Figure 23 shows the 2D crosshole images superimposed on the corresponding 2D surface image (line 2). The 2D lines interrogate a larger area of the subsurface but at lower resolution in terms of both spatial variable and the magnitude of conductivity variations. The cross-hole images provide higher resolution but lower spatial coverage. Each approach has distinct advantages. For example the 2D cross-hole images clearly delineate the Calvert formation contact and the impacts of treatment near the injection points, both of which are more subtle in the 2D surface images. The 2D surface images provide a more holistic view and reveal the overall increase in conductivity within the treated zone above ~8m that is more difficult to extract from the 2D crosshole images.

6.3 1D electrical profiles

In order to simplify the interpretation of the ERT results against 1D vertical profiles of aqueous chemistry from groundwater samples and borehole geophysical logs, 1D profiles of the electrical electrolytic component of the conductivity ($\sigma_{el}$) and surface component of the surface conductivity ($\sigma_{surf}$) were obtained by averaging the conductivity and phase values in the 2D cross-borehole images over a 2 m horizontal interval.
Insight into the electrical structure of the site is obtained by plotting the calculated electrolytic conductivity ($\sigma_{el}$) and surface conductivity ($\sigma_{surf}$) components of the total conductivity using Equations 1-4 in section 2.2 for locations in the treated zone (profile E1-E2, near the edge of the treated zone and centered over an injection point (profile E2-E3) and in the untreated zone (profile E4-E5). The electrolytic conductivity (Figure 24a) is higher in the upper part of the aquifer for the treated zone relative to the untreated zone. However, in the lower part of the aquifer, $\sigma_{el}$ is actually lower for the treated zone relative to the untreated zone. Figure 24b shows that the surface conductivity is higher throughout the aquifer (at least to 7 m depth) in the treated zone relative to the untreated zone.

![Figure 24. 1D (a) electrolytic conductivity ($\sigma_{el}$) and (b) surface conductivity ($\sigma_{surf}$) profiles for the treated zone, near the edge of the treated zone and in the untreated zone](image)

As shown in Equation 4 (section 2.2), $\sigma_{el}$ is controlled by porosity and pore fluid conductivity ($\sigma_w$) (Archie, 1942). Assuming that porosity variations between the three locations are similar, a strong correlation between $\sigma_{el}$ and $\sigma_w$ should be expected. Figure 25 compares the (a) fluid specific conductance ($\sigma_w$ at 25°C) measured on discrete groundwater samples against (b) continuous geophysics-measured electrolytic conductivity ($\sigma_{el}$) extracted from the 2D cross-borehole resistivity images for the treated zone (far from injection), the treated zone near the injection and the untreated zone. Figure 25c shows that variation in $\sigma_{el}$ is largely explained by the variation in $\sigma_w$ in all three zones, except at the depth of 9.2 m, being in the fine-grained confining unit (Calvert Fm), where $\sigma_{el}$ is elevated at all locations. The confining layer at this
depth is characterized by finer-grained sediments, with clay minerals. The increase in $\sigma_{el}$ may reflect a higher porosity for this finer grained unit (despite the smaller pore sizes). Alternatively, it is possible that the fine-grained soils might create a dual domain, with significant diffusion of mass between relatively mobile and immobile parts of the pore space. In this case, water samples will only sense the properties of the more mobile pore space whereas $\sigma_{el}$ measured with electrical geophysics senses the average $\sigma_w$ of the fluids in both the more mobile and less mobile domains (Day-Lewis et al., 2017; Singha et al., 2007). The scatter of the points at 9.2 m (Figure 25c) may indicate the presence of higher $\sigma_w$ fluids in the less mobile domain relative to the mobile domain in these fine-grained sediments. Furthermore, the source of the higher $\sigma_w$ may be the high conductivity amendment injected in 2008. This hypothesis is supported by the time-lapse ERT monitoring images collected during ER-200717, which revealed density driven downward migration of the amendment to the lower confining unit.

![Figure 25](image)

Figure 25. Comparison of (a) fluid specific conductance ($\sigma_w$) measured on discrete groundwater samples against (b) 1D electrolytic conductivity ($\sigma_{el}$) profiles (c) linear correlation between $\sigma_{el}$ and $\sigma_w$ observed in the aquifer but not in the fine-grained confining unit (depth of 9.2 m). (Note points within the grey dashed circle are all collected within the fine grained lower confining unit).

Possibly the most interesting observation in the electrical datasets is the substantially higher surface conductivity ($\sigma_{surf}$) throughout the aquifer in the treated zone relative to the untreated zone. The enhancement in $\sigma_{surf}$ is stronger at the location near the injection relative to further into the treated zone. The surface conductivity depends on the amount of surface area in the sediments as well as the electrochemical properties of the electrical double layer (EDL) at the sediment-fluid interface (Revil & Glover, 1998). There is no reason to expect the surface area of the sediments to be consistently greater throughout the entire aquifer in the treated zone relative
to the untreated zone. A growing body of geophysical literature has shown that the surface conductivity is enhanced by sorption and ion exchange processes (Hao et al., 2015; Vaudelet et al., 2011; Zhang et al., 2012). It is quite likely that the biogeochemical alteration of the aquifer resulting from the contaminants and the amendment injection resulted in modification or enhancement of surface sorption and ion exchange processes which have resulted in a distinct increase in $\sigma_{surf}$ throughout the aquifer. The surface conductivity can only be computed from IP measurements. This highlights the potential value of IP for investigating biogeochemical processes at complex contaminated sites.

6.4 PERFORMANCE OBJECTIVE #1:
Identify the long-term 3D spatial extent of the biogeochemically altered zone

The culminating goal of this demonstration is expressed in objective #3 (section 6.6); namely to make useful inferences concerning the spatial extent and nature of long-term biogeochemical impacts of bioremediation using geophysical methods. The first requirement for achieving that goal is to demonstrate that biogeochemically alterations produce corresponding geophysical alterations that are detectable or ‘imageable’ at the field scale (i.e. performance objective #1). In other words, objective #1 is to identify the spatial extent of the altered zone using geophysical methods. To meet objective #1, we used surface-based 2D ERT imaging, cross-hole ERT and IP imaging, and 1D borehole logging of magnetic susceptibility, electrical conductivity, and gamma activity. Of these methods, 2D surface imaging was most useful for locating the larger scale footprint of the altered zone, expressed clearly as an increase in electrical conductivity within the treated zone compared to the untreated zone (Figure 21). Cross-borehole imaging provided more detailed, local scale identification of altered zones in terms of both electrical conductivity and phase shift (Figure 22). Borehole logs, particularly MS, successfully identified anomalous regions along wellbores in treated zones that were in clear contrast with corresponding measurements in untreated zones. We considered this objective to have been successfully demonstrated.

6.5 PERFORMANCE OBJECTIVE #2:
Determine the significance of the geophysical footprint with respect to treatment induced biogeochemical transformations

Performance objective #2 requires successful demonstration of performance objective #1, and is the next requirement for mapping spatial extent and nature of long-term biogeochemical impacts of bioremediation using geophysical methods. Objective #2 is focused on establishing the relationships between remediation-induced geophysical and biogeochemical alterations. If such relationships can be established, they can be used to interpret the imaging results demonstrated in objective #1 in terms of specific biogeochemical alterations and impacts. As outlined in Section 5, we undertook a relatively comprehensive laboratory investigation to address objective #2. That effort identified geochemical contrasts between the untreated and treated zones that clearly originated with the bioremediation injections that occurred in 2008. It also established evidence of the relationships between biogeochemical and geophysical anomalies, include the relationship between magnetic susceptibility and Fe$^{2+}$ and Fe$^{3+}$ ratios, and between precipitated minerals (or biofilms) and surface conductivity. However, those relationships were not conclusive enough to interpret the geophysical data in terms of specific biogeochemical impacts. We therefore
consider this objective only partially achieved. A primary difficulty limiting the success of
objective #2 relates to the ambiguity between pre-existing geophysical conditions and
geophysical alterations caused by bioremediation. There is a solution to this issue that is
discussed in detail in Section 8.

6.6 PERFORMANCE OBJECTIVE #3:
Map biogeochemical impacts based on geophysical footprints

Objective 3 was the culminating objective of the demonstration and required successful
demonstration of both objectives 1 and objectives 2. Because objective 2 was not fully
demonstrated, objective 3 was not achieved.
7.0 COST ASSESSMENT

Cost elements associated with our technology comprise (1) material costs, including the physical components of the ERT/MLS arrays and boreholes; (2) installation costs, including direct-push costs, labor involved in installing the ERT/MLS arrays, and labor involved in setting up the surface arrays; (3) operational costs associated with data collection (borehole logs, ERT, sampling) to support inference of the electrical signature of bioremediation effects; and (4) long-term monitoring costs. We note that the scope of our project did not extend to (4), but rather focused on the link between our geophysical observations and the long-term effects of the remedial amendment; however, our cost analysis considers the costs and potential benefits of using our technology to help verify and map the efficacy of bioremediation. Thus, we consider scenarios for scaling up our demonstration both spatially (i.e., to application across a site) and in time (i.e., for long-term monitoring).

Assigning value/cost to geophysical information is challenging, as the information content of geophysical results includes both qualitative and quantitative aspects. Furthermore, geophysical information is not a substitute for conventional methods, but a complement. Here, we focus on our Objective #1 (*Determine the long-term 3D extent of the biogeochemically altered zone*), for which success was achieved.

The integrated electrical/sampling arrays were designed by our team and fabricated at Rutgers University during the course of our work. Capital costs associated with materials and fabrication were recorded, as detailed below. We base the following cost model and calculations on costs associated with deployment at the Brandywine, MD site. In the calculations that follow, we assume arrays similar in length and design to those used at Brandywine, and we base installation costs on the direct-push contract obtained through USGS’ competitive bidding process.

7.1 COST MODEL

The cost model presented in Table 7.1 covers the unit cost associated with fabrication of a ERT/MLS array, installation of an array, collection of a surface ERT line, and field and laboratory work to link geophysical and remedial signatures. Again, we emphasize that these costs are based on site conditions, target depths, and the spatial scale of our demonstration. Issues of scale are discussed subsequently through consideration of different deployment scenarios.
Table 7.1. Cost Model for ERT/MLS Installation

<table>
<thead>
<tr>
<th>Cost Element</th>
<th>Data Tracked</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>ERT/MLS fabrication</td>
<td>Materials: Fiberglass rods for ERT/MLS backbone; jacketed copper multi-conductor wire; adhesive-backed stainless steel; HDPE sampling tubing and ports; tape and labels.</td>
<td>Material unit cost of ~$150</td>
</tr>
<tr>
<td></td>
<td>Labor: 4 hours of assembly</td>
<td>Labor costs of 4 x $15/hr = $60</td>
</tr>
<tr>
<td></td>
<td>Total cost on the order of ~$200/each ERT/MLS</td>
<td></td>
</tr>
<tr>
<td>Installation of borehole arrays</td>
<td>Drilling costs based on contract</td>
<td>Drilling contract $13,300 for 4 conventional wells and 8 arrays, with per-array cost of ~$800</td>
</tr>
<tr>
<td></td>
<td>Labor costs for installation of arrays</td>
<td>Labor for 8 ERT/MLS arrays at 2 people for 1 day, ~$800, or ~$100/array</td>
</tr>
<tr>
<td></td>
<td>Total cost on order of ~$900 per installation</td>
<td></td>
</tr>
<tr>
<td>Borehole geophysical logging</td>
<td>Labor and equipment use for just one well, neglecting mob/demob, shipping and travel costs</td>
<td>Labor for suite of logs (MS, EM/gamma) at 1 person for 1/2 day per well, <del>$200 plus equipment use (</del>$200) for Total cost of ~$400/well</td>
</tr>
<tr>
<td>Surface arrays</td>
<td>Labor costs for 2 lines of ~100 m, assuming no capital costs for short-term deployment and neglecting travel costs</td>
<td>Labor for 2 people for 1 day, ~$800 for 2 lines</td>
</tr>
<tr>
<td></td>
<td>Total cost of ~$400 per line</td>
<td></td>
</tr>
<tr>
<td>Linking geophysical signatures to biogeochemical changes (post installation)</td>
<td>Labor to collect water and core data</td>
<td>Water/core sampling: 2 people for 1 day, for ~$800/event</td>
</tr>
<tr>
<td></td>
<td>Labor to conduct ERT inversion</td>
<td>ERT inversion: 1 person for 1 day, for ~$400/event</td>
</tr>
<tr>
<td></td>
<td>Analysis of water and core samples</td>
<td>Analysis costs ~$3000/event</td>
</tr>
<tr>
<td></td>
<td>Labor to identify geophysical signatures in the lab and through analysis of data</td>
<td>Labor and time required to infer geophysical signature of bioremediation: 5 person days at ~$4000</td>
</tr>
<tr>
<td></td>
<td>Total cost of ~$8200/event</td>
<td></td>
</tr>
</tbody>
</table>
7.2 COST DRIVERS

Important cost drivers include (1) drilling costs, which are strongly dependent on site geologic conditions, the depth and lateral extent of remediation targets, and infrastructure; and (2) fabrication costs for the ERT/MLS arrays, which could be manufactured more efficiently and cost effectively using advanced machining and 3D printing technology, e.g., as being used under ESTCP-201732. Commercialization of the technology and integration into direct-push rigs could facilitate widespread application. Applications in fractured-rock environments would, of course, require conventional drilling or coring and use of packers or well liners to isolate fractures for sampling and to prevent cross contamination between fractures; such applications would involve substantial additional costs not considered here.

7.3 COST ANALYSIS

To illustrate the potential cost savings for operational implementation of ERT/MLS arrays, we consider a field-scale application based on the remediation conducted at the study site in Brandywine, MD. We assume a treatment area of 100 x 100 m and deployment of (1) four 100-m long surface ERT lines; (2) one crosshole ERT/MLS line comprising 8 ERT/MLS installations with coring, and (3) borehole logging at one well (Table 7.2). The total cost for 3 monitoring events (one pre-treatment and two post-treatment) totals $48,000. This test design spans the study area with high-resolution (sub-meter to meter) in the vicinity of the MLS/ERT arrays, and lower resolution elsewhere (~several meters along the surface lines). The borehole geophysical logging and surface lines provide additional information to fill gaps in space. In practice, cost savings would be realized for subsequent sampling events, as the geophysical data analysis would likely be streamlined for the second and subsequent events.

For a conventional characterization (Table 7.3), we assume two lines of direct-push sampling points each extending 100 m, for a total cost of $77500. This design provides coverage of the same area as for the geophysical monitoring design, but with only 10-m resolution along the two lines, which is inferior to that provided by the surface ERT along the same lines.

For the example considered here, cost savings on the order of 40% are possible. Greater savings are predicted if (1) more sampling events are considered, i.e., improved temporal resolution is required, or (2) more ERT/MLS and direct-push lines are considered, i.e., improved spatial resolution is required. Although the hydrogeophysical results are more indirect than results from conventional approaches, they are groundtruthed at the locations of the MLS and provide higher-resolution over a larger area. Obviously for the hydrogeophysical approach, there are design tradeoffs between (1) geophysical coverage vs. cost savings, and (2) geophysical resolution vs. cost savings, and (3) the density of direct sampling vs. cost savings; however, similar tradeoffs exist with conventional characterization, with coverage and resolution affecting cost.
<table>
<thead>
<tr>
<th>Cost Element</th>
<th>Description</th>
<th>Costs</th>
</tr>
</thead>
</table>
| ERT/MLS fabrication and installation             | 8 installations, spacing 5 meters apart, over 35 m, used to characterize in high resolution over an area of high gradient identified by surface ERT | Fabrication cost of $200/each x 8 = $1600  
Installation cost of $900/each x 8 = $1800  
Travel/shipping $2000  
**Total: $5400** |
| Borehole geophysical logging                      | Borehole logging (MS/EM/gamma) at one well                                    | Labor for suite of logs (MS, EM/gamma) at $400  
Travel/mob/demob/shipping/processing of $2000  
**Total: $2400** |
| Surface arrays                                   | 2 surface lines each 100-m long                                               | Labor for 2 people for 1 day, ~$800  
Travel/mob/demob/shipping/processing of $2000  
**Total: $2800** |
| Linking geophysical signatures to biogeochemical changes | Installations and collection of data for 3 events (one before treatment and two after)  
Analysis of samples from MLS and cores | Installations $3400 once  
Costs as in **Table #1**, $8200/event x 3  
Travel/mob/demob/shipping/processing of $3000 x 3  
Analytical costs of $3000 x 3  
**Total: $48000** |
8.0 IMPLEMENTATION ISSUES

Project ER-201579 was motivated by project ER-201717, where daily 4D monitoring of amendment delivery and subsequent biogeochemical activity over a 2 year period was successfully demonstrated using autonomous time-lapse electrical resistivity tomography (Johnson et al., 2015). In time-lapse imaging, the baseline pre-treatment geophysical properties are subtracted from the time-lapse images to reveal only what has changed over time, or equivalently what geophysical alterations are caused by the treatment. In ERT-201717, changes in fluid conductivity and organic acids associated with the migration of injected amendments were demonstrated to be highly correlated to changes in bulk electrical conductivity, thereby enabling electrical conductivity to be used as a proxy for monitoring 4D amendment transport. After approximately 1 year, increases in treatment induced increases in conductivity occurred that were apparently caused by bio-induced iron sulfide mineral precipitation (as evidenced by the presence of black particulates in sample water) or biofilm generation. Although the scope and budget of ERT-201717 did not permit a detailed investigation into the origin of the secondary increase in conductivity from pre-treatment conditions, it was clearly caused by bio-activity, pointing to the potential of geophysical imaging for 4D monitoring of both amendment transport and subsequent bio-chemical alteration.

For this project (ER-201579) we were unable to collect geophysical data that permitted the change in geophysical properties to be directly imaged in the same way they were for ER-201717. This is

<table>
<thead>
<tr>
<th>Cost Element</th>
<th>Description</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct push sampling</td>
<td>2 lines of 10 direct-push sampling points, for a total of 20 per event</td>
<td>Drilling costs $18000 <strong>Total: $18000 per event</strong></td>
</tr>
<tr>
<td>Linking geophysical signatures to biogeochemical changes</td>
<td>Collection of data for 3 events (one before treatment and two after)</td>
<td>Drilling costs of $18000 x 3 = $54000 Analytical costs proportional to number of sampling locations, 2.5 x the costs in Table 2# = 2.5 x $9000 = $23500 <strong>Total cost of $77500</strong></td>
</tr>
</tbody>
</table>
because the demobilization and well abandonment procedure used at the conclusion of ER-201717 did not permit re-occupation of the original monitoring/ERT boreholes, and therefore did not permit deployment of electrodes in the same positions as used in ERT-201717. Equivalent electrode positions are required for time-lapse imaging. Consequently, we were not able to subtract pre-treatment geophysical properties from the geophysical images and were not able to produce the changes in geophysical properties caused by the bioremediation process alone. We were required to interpret both the geophysical and geochemical with confounding influence of background, pre-treatment heterogeneity, rather than interpreting changes in geophysical properties with changes in geochemical properties caused exclusively by bioremediation processes. We consider the confounding influence of background heterogeneity (both geochemical and geophysical) to be primary cause of our failure to achieve objectives 2 and 3.

ER-201717 demonstrated the potential of geophysical-based bio-remediation monitoring from near term amendment transport to long-term biogeochemical impacts. However, to enable optimal interpretability, pre-treatment geophysical and geochemical data must be collected to enable bioremediation induced changes in subsurface conditions to be clearly identified. Furthermore, electrical geophysical arrays must be permanently deployed or deployed such that electrode positions can be re-established over time for longer term. These necessities will require site owners and/or remediation operators to plan for and implement geophysical monitoring arrays up front, prior to field remediation operations. As shown in this report, post remediation geophysical assessments can be successful at identifying the long-term spatial footprint of the impacted zone but are at risk of failure when used inform the nature of biogeochemical impacts without baseline data. Fortunately, the same geophysical arrays used for baseline imaging and monitoring amendment placement can be used for long-term autonomous monitoring of biogeochemical impacts if properly designed.
9.0 REFERENCES


# APPENDICES

## Appendix A: Points of Contact

<table>
<thead>
<tr>
<th>POINT OF CONTACT Name</th>
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