

STUDENT SPRING INTERNSHIP TECHNICAL REPORT

**Spectral Induced Polarization (SIP)
Measurements on Sediment Columns**

**DOE-FIU SCIENCE & TECHNOLOGY
WORKFORCE DEVELOPMENT PROGRAM**

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ABSTRACT

DOE Fellow and graduate student (Master of Science), Alejandro Garcia, spent ten (10) weeks during the spring of 2016 at the Pacific Northwest National Laboratory where he worked with a team under Dr. Brady Lee's mentorship to initiate a research task on the influence of microbial activity on the spectral induced polarization response within Hanford sediment.

The focus of the internship research was to learn how to conduct spectral induced polarization (SIP) measurements on sediment columns saturated with synthetic groundwater and inoculated with microbes, as well as how to create an enrichment of microbes adapted to an environment high in autunite (a calcium uranyl phosphate mineral).

Spectral induced polarization is a geophysical technique that shows promise due to its ability to quantitatively measure charge storage at grain surfaces; this same charge storage is believed to occur around biofilms as well. Geophysical methods allow scientists to forgo the drilling of expensive boreholes during some studies of the subsurface while continuously and autonomously gathering information over a wide area over a long period of time. The use of SIP to track the activity of microbes used for environmental remediation at Hanford is being investigated.

Delays in the acquisition of column components as well as electrical equipment prevented the completion of the column construction at PNNL during the internship. The materials required to construct the experimental columns and to pack them with sediment will be shipped to FIU from PNNL once available. The columns will then be constructed at FIU with the assistance of staff from PNNL and the initial experiments will begin.

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1. INTRODUCTION

Significant uranium contamination at the U.S. Department of Energy Hanford Site exists within the vadose zone (up to 76 m) in the form of mobile carbonate phases (rutherfordine, liebigite) and silicate phases (uranophane, Na-boltwoodite). Remediation of this zone requires *in situ* sequestration of mobile uranyl-carbonate species (Szecsody et al., 2012).

The first goal of this research is to investigate the influence and corresponding electrical geophysical response of microbial activity on vadose zone uranium sequestration. The second goal of this work is to analyze the ability of geophysical electrical methods, particularly spectral induced polarization (SIP) and electrical resistance tomography (ERT), to detect subsurface microbial activity in a porous medium. Remote geophysical sensing of the subsurface allows scientists to forgo the drilling of expensive boreholes and rely instead on easily and cheaply deployed surface arrays in order to study processes occurring deep in the subsurface. Geophysical methods also allow the continuous collection of data autonomously, which can be remotely accessed and analyzed.

Initial experiments will utilize 1-D laboratory columns.

Background

Overview of 200 Area Subsurface

The underlying bedrock beneath Hanford is the Columbia River Basalt Group; it is composed of hundreds of individual tholeiitic basalt flows that formed during the Miocene (23.03 – 5.3 Ma). Above that lies the Ringold formation which is composed of fluvial sediments approximately 125 m thick and is divided into three principal stratigraphic units: unit A (fluvial gravels), the lower mud unit, and unit E (fluvial gravels). The main aquifer under the 200 West Area is located mostly within unit E; the lower mud unit forms a low hydraulic conductivity base to this aquifer and confines the groundwater stored in unit A. Between the Ringold formation and the Hanford formation lies the Cold Creek unit (formerly the Plio-Pleistocene unit) which has a thickness up to 13.1 meters and is divided into two subunits: the upper CCUz (abundance of silt) and lower CCUc (abundance of pedogenic calcium-carbonate cement). Above the Plio-Pleistocene unit lies the Hanford formation which is composed of Pleistocene (2.58 – 0.0117 Ma) age deposits from cataclysmic floods during the Ice Age. The main constituents of the Hanford formation are three distinct facies: a gravel dominated facie, a sand dominated facie, and a silt dominated facie (Serne et al., 2002; Xie et al., 2003).

The water within the principal unconfined aquifer under Hanford flows from recharge zones in the west towards the NE, E, and SE and eventually discharges into the Columbia River. Estimates of discharge from the Hanford aquifer into the river range from 1.1 to 2.5 m³/s, which is considered to be relatively low. The hydraulic gradient of the water table is gentler under the 200 East Area compared to the 200 West Area due to the effects of a higher subsurface hydraulic conductivity. This is on account of the fact that the top of the aquifer in the 200 East Area lies within the Hanford formation which is more permeable than the Ringold formation (Hartman et al., 2007).

Subsurface contamination is split between the River Corridor (wastes derived from the operation of the reactors, mainly strontium-90 and hexavalent chromium) and the Central Plateau (plutonium extraction activities, more varied waste streams). While most subsurface contamination at the 100 Area is strontium-90 and hexavalent chromium, there is a large plume of nitrate and a smaller plume of trichloroethene under the 100-F Area. In addition, all of the areas have nitrate concentrations greater than the maximum contaminant level (MCL) of 45 mg/L. Contamination within the Central Plateau includes carbon tetrachloride, nitrate, tritium, iodine-129, technetium-99, hexavalent chromium, and uranium. Downward migration of contaminants into the vadose zone and the groundwater was facilitated by the intentional and accidental addition of water from wastewater ditches and cribs, water pipe leaks, and meteoric water. Contamination within the vadose zone continues to supply the underlying groundwater with contaminants. Figure 1 shows a map of the major contaminant plumes under the 200 East and 200 West Areas (DOE/RL-2015-07, 2015).

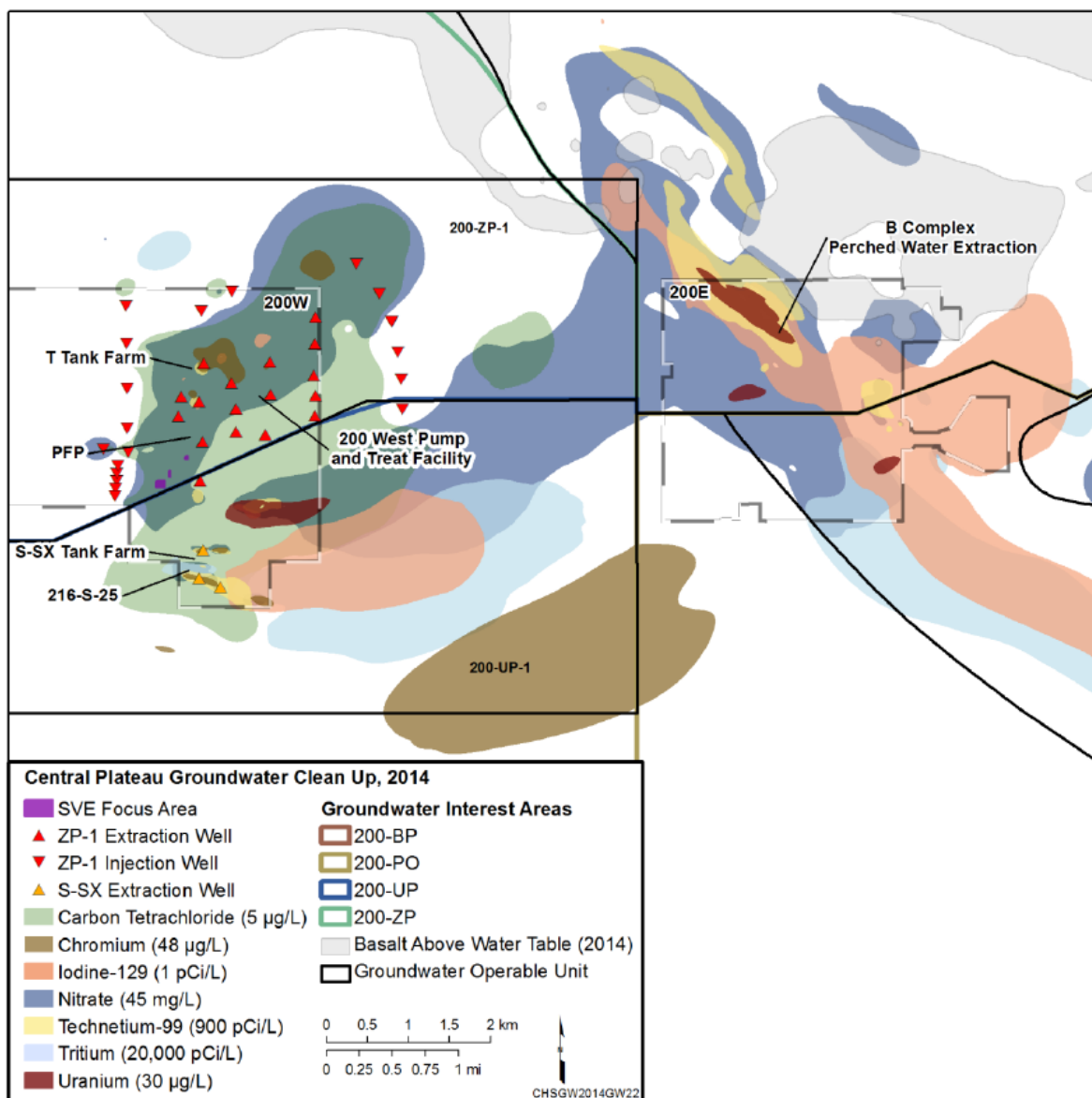


Figure 1. Contaminant plumes under the Hanford 200 Area (DOE/RL-2015-07, 2015).

SIP Method

Electrical geophysical methods allow geophysicists to understand subsurface properties by measuring the voltage response to an electric current. Similar to standard direct current (DC) resistivity methods, most induced polarization (IP) methods employ four electrodes in galvanic contact with the sediment. Two of the electrodes are current electrodes, which act as source and sink for an electric current; the other two electrodes are potential electrodes, which measure a voltage response. Spectral induced polarization (SIP) is a type of IP method that measures a phase-shifted voltage at various injection frequencies. An impedance, in terms of magnitude and phase angle, is then obtained and used as a measure of charge transport and storage (Binley and Kemna, 2005).

The SIP method allows geophysicists to quantitatively study charge storage and transport in porous media through the electrical complex conductivity. SIP has been used in the past to locate metallic ore bodies as well as subsurface zones rich in clay; however, recent work has focused on its applications in studying contaminant fate and transport. The injected current used for SIP measurements normally has a frequency below 1 kHz. The electrical complex conductivity (σ^*), the inverse of the complex resistivity ($\rho^*(\omega)$), is a function of ω (the angular frequency of the applied current). This can then be expressed in terms of σ' (the real part which represents charge transport) and σ'' (the imaginary part that represents charge storage). In the following equation defining the complex conductivity: $i = \sqrt{-1}$ (Hao et al., 2015)

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) \quad (1)$$

The impedance can be obtained by measuring the difference between two voltage electrodes and is defined as:

$$Z^*(\omega) = \frac{U}{I} = |Z^*(\omega)|e^{i\varphi(\omega)} \quad (2)$$

Where $Z^*(\omega)$ is the impedance, U is the voltage difference between the measuring electrodes (in V), I is the injected current (in A), ω is the angular frequency (in rad S⁻¹), and φ is the phase angle (in rad). The impedance can be related to the complex resistivity using a geometric factor K (in m) as:

$$\rho^*(\omega) = KZ^*(\omega) \quad (3)$$

This geometric factor is based on the position of the electrodes, the size and shape of the samples, and boundary conditions on the grain surfaces. The complex conductivity is then just the inverse of the complex resistivity:

$$\sigma^*(\omega) = \frac{1}{\rho^*(\omega)} \quad (4)$$

The conductivity magnitude can be expressed in terms of the real and imaginary components:

$$|\sigma| = \sqrt{(\sigma')^2 + (\sigma'')^2} \quad (5)$$

The phase angle can be described in terms of the components of the complex conductivity and an approximation can be made when the phase magnitude is less than 100 mrad. The phase angle is based on the ratio between the polarization and conduction (Okay et al., 2014):

$$\varphi(\omega) = \tan^{-1} \left[\frac{\sigma''(\omega)}{\sigma'(\omega)} \right] \cong \frac{\sigma''(\omega)}{\sigma'(\omega)} \quad (6)$$

There are two proposed mechanisms governing the low frequency polarization response, both relying on a structure known as the electrical double layer (EDL) at the solid-fluid interface. The EDL is formed when an electrolyte solution comes into contact with a charged surface; counterions from the solution are then attracted to the surface, forming two parallel charge layers of opposite polarity. Modern interpretation of the EDL actually designates three layers: the solid phase, the Stern layer, and the diffuse layer. The first theory asserts that at pore constrictions, where a pore becomes drastically thinner, the EDL comes together to form an ion selective membrane that would cause the charge to build up at those locations. The second theory argues that charge builds up when excess ions move at differing speeds in the Stern layer tangential to the solid surface (Scott, 2006).

Scott (2006) conducted SIP measurements on sandstone samples saturated with an agar gel solution in order to prevent the motion of the bulk fluid during current injection. The results show that the quadrature conductivity is mainly unaffected by the use of an agar gel solution. This indicates that polarization is mainly controlled by grain surfaces rather than an ion selective membrane since ionic motion was constrained.

Skold et al. (2011) argues that there may exist a proton hopping mechanism at silica surfaces which may also contribute to polarization. This charge movement would be based on a Grotthuss cooperation mechanism where the charge moves along a surface through the breaking and reforming of hydrogen covalent bonds.

SIP Responses to Inorganic Factors

The specific surface area (S_p) is the ratio between the pore surface area and the pore volume. Generally, as grain size increases, specific surface area decreases due to the decreasing ratio between surface area and pore volume. There exists a positive correlation between the specific surface area and the imaginary conductivity (Lesmes and Friedman, 2005).

Sediment clay content has been shown to have a positive correlation with both the in-phase and quadrature conductivities. Clays contribute greatly to the cation exchange capacity (CEC) of sediment, which is a measure of a sediments ability to absorb cations that in turn leads to higher quadrature conductivity. For kaolinite rich sediments, the quadrature conductivity increases in response to higher salinities; on the other hand, smectite rich sediments display a quadrature conductivity that is mostly independent of salinity (Okay et al., 2014).

Sediment grains generally have a negatively charged surface; however, if pH reaches the point of zero charge (PZC), the net surface charge becomes neutral, leading to reduced sorption of cationic groups. Reductions in pH below the PZC can lead to a positive surface charge as H^+ attaches to all

negative sites on the grain surface. Low pH can reduce the effects of surface conductivity and polarization (Lesmes and Frye, 2001).

SIP Responses to Subsurface Biofilm Formation

Bacteria in the subsurface are seldom found as solitary mobile organisms; rather, most microorganisms form interconnected immobile colonies known as biofilms. These biofilms are supported by extracellular polymers, which the individual cells excrete. These polymers serve to strengthen attachment to a solid surface as well as to provide structural integrity to the biofilm. Biofilm formation can produce various changes in the physical and electrical properties of a porous medium. These changes include: clogging of pores (changes to porosity, permeability, and hydraulic conductivity), changes to overall shear strength and elastic moduli of media, production of proteinaceous extracellular appendages that facilitate electron transport and increase bulk electrical conductivity, alterations to pore fluid electrolyte concentrations, dissolution of minerals leading to increased surface roughness, and precipitation of magnetosomes (Atekwana and Slater, 2009).

Modern research towards the direct detection of bacteria in subsurface porous media has placed a significant focus on the SIP method. Most bacteria have higher concentrations of anionic groups, which lead to a negatively charged cell wall. This in turn, when in the presence of an electrolyte solution, causes the formation of an EDL by counterions. Due to this effect, the bacterial surface can store charge when in the presence of a time-oscillating electric field in a fashion similar to charged mineral grains. Only bacteria that are alive contribute to the SIP response (Atekwana and Slater, 2009).

Experiments using artificial biofilm consisting of alginate mixed with microbial cells in a silica bead packed column have shown significant low frequency (0.1 – 1 Hz) SIP responses to biofilm formation. By using artificial biofilm and silica gel beads with a very smooth surface area, this study isolated the SIP response to the actual presence of biofilm rather than grain roughness or changes in the chemical makeup of pore fluid (Ntarlagiannis and Ferguson, 2008).

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the spring of 2016, a DOE Fellow intern, Alejandro Garcia, spent 10 weeks doing an internship at Pacific Northwest National Laboratory under the supervision and guidance of Dr. Brady Lee. The intern's project was initiated on February 8, 2016, and continued through April 15, 2016 with the objective of learning how to conduct SIP column experiments using columns packed with Hanford sediment and saturated with synthetic groundwater.

3. RESEARCH DESCRIPTION

Research work at PNNL during the spring 2016 internship included observation of existing SIP column experiments being conducted as well as preparation for the construction of six SIP columns at FIU during summer 2016.

During the internship, Alejandro Garcia learned the procedures used at PNNL for the performing of column experiments. This included learning to collect effluent samples, to collect pore water samples from the sides of the column, and to take spectral induced polarization measurements. The student also practiced constructing a column and filling it with sediment in anticipation of building columns for further experimentation at FIU.

The body of each column will be composed of a clear polyvinyl chloride (PVC) tube with holes drilled on the side corresponding to four potential electrodes and three sampling and injection ports. Each tube will be sealed on both ends except for an opening for a tube through which water can flow. The ends of the column will also contain coiled Ag/AgCl current electrodes which will create a homogenous 1D current flow through the length of the column.

Current electrodes were constructed by hand at PNNL from a long piece of silver wire; the electrodes, once coiled, were then dipped into bleach and allowed to sit overnight in order to allow the formation of AgCl on the surface. Twelve current electrodes were made in total for the six columns.

Learning from challenges faced by existing experiments at PNNL, the six new columns will have a filter at each end that will prevent sediment from entering the tubing. Each column will also be packed tightly with sediment, leaving no empty space. Columns at PNNL have had air bubbles that could disturb the sediment in the column and cause discontinuous stretches of air along the length of the column. Tighter packing should prevent the sediment from moving if air begins to enter the column.

Potential electrodes, also Ag/AgCl, were prepared similarly to the current electrodes using bleach as a chlorine source. These electrodes, however, were not coiled but rather were inserted into a PVC nipple with a cap that serves as an enclosure. In the future, the PVC nipples will be filled with agar gel which will reduce contact resistance and allow for better potential and phase measurements.

Work also began to create a microbe culture adapted to an environment with high levels of autunite. This was done by having a 100 g sample of Hanford sediment sit within a synthetic groundwater solution with added glucose and autunite. Every one or two weeks, a small amount of the enrichment was transferred to a fresh batch to allow for growth. It is currently unknown what microorganisms are growing in the solution; however, the expectation is that these are native microbes from the sediment adapted to the autunite after consecutive transfers. This enrichment will be sent to FIU during summer 2016 in order to inoculate the SIP columns.

The medium in which the microbes were grown is synthetic groundwater (SGW1). Table 1 shows the stock solutions (titled A, B, and C) used to make SGW1 and the process used to make SGW1 follows.

Table 1. SGW1 Stock Solution Chemical Makeup

SGW1 Stock Solutions	Concentration (g/L)
A	
NaHCO ₃	12.1
KHCO ₃	1.6
B	
MgSO ₄	3.06
CaSO ₄	0.82
C	
Ca(NO ₃) ₂ ×4H ₂ O	5.43
CaCl ₂ ×2H ₂ O	9.56

Procedure to create 1 L SGW1: Pipette 10 mL each of solutions A and C and 20 mL of solution B into 900 mL deionized water, then dilute to 1 L using deionized water. The SGW1 solution that was used also contained a concentration of yeast extract equal to 500 mg/L.

Synthetic groundwater was used rather than natural groundwater to allow for precise control of the chemical constituents of the solution. From a logistics standpoint, it is also easier to use synthetic groundwater which can be made in the lab rather than shipping natural groundwater long distance. The SGW solution will be pumped through the columns using a peristaltic pump at a flow rate of 0.10 L/d. The solution will need to be prepared regularly in order to maintain a constant supply to the columns.

Table 2. SIP Column Contents

Proposed Column Contents	
Column 1	0 mM HCO ₃
Column 2	3 mM HCO ₃
Column 3	0 mM HCO ₃ + Carbon Source
Column 4	3 mM HCO ₃ + Carbon Source
Column 5	0 mM HCO ₃ + Carbon Source + Inoculum
Column 6	3 mM HCO ₃ + Carbon Source + Inoculum

There will be six variations of the solution used, as described in Table 2. These will allow the testing of various factors affecting the SIP response and allow for isolating the effect of the microbes.

4. RESULTS AND ANALYSIS

Delays in the acquisition of column components as well as electrical equipment prevented the completion of the column construction at PNNL during the internship. The materials required to construct the experimental columns and to pack them with sediment will be shipped to FIU from PNNL once available. The columns will then be constructed at FIU with the assistance of staff from PNNL and the initial experiments will begin. Results and analysis for these experiments will be provided in project reports.

5. CONCLUSION

Initial preparations for SIP column experiments were completed at PNNL for continued work at FIU. This involved the construction of electrodes as well as the procurement of materials. A bacterial culture was prepared that is adapted to conditions high in autunite to be used when column experiments begin. The student sent to PNNL was instructed in the skills necessary for conducting SIP column experiments at FIU. Currently, FIU is preparing an area where work involving radioactive materials can be conducted. This area will include space for: a stand to hold the columns upright, a pump, SIP electrical equipment, synthetic groundwater solution, and temporary waste collection. FIU is also pursuing the required approvals to proceed.

6. ACKNOWLEDGMENT

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