# INVESTIGATING GEOPHYSICAL SIGNATURES OF LONG TERM BIODEGRADATION AT THE OIL SPILL SITE IN BEMIDJI, MINNESOTA

by

ASHLEY LAURA SAMUEL

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#### ABSTRACT OF THE DISSERTATION

## Investigating Geophysical Signatures of Long Term Biodegradation at the Oil Spill Site in Bemidji, Minnesota

#### By ASHLEY LAURA SAMUEL

**Dissertation Director:** 

Dr. Lee Slater

Biogeophysics is a sub-discipline of geophysics that examines how microbial interactions with geologic materials affect the geophysical signatures within the subsurface. Biogeophysical measurements were performed at the National Crude Oil Spill Fate and Natural Attenuation Research Site in Bemidji, Minnesota where biodegradation of hydrocarbon contaminants is occurring. Geophysical measurements were acquired to ascertain whether changes in the pore fluid conductivity and/or the production of secondary iron minerals such as magnetite affect geophysical signatures at this site. The effects of hydrology, geology, oil levels and temperature on geophysical signatures within both an uncontaminated zone and a biodegraded contaminated zone were investigated.

Resistivity, time domain induced polarization and frequency domain induced polarization measurements were acquired from a contaminated location and an uncontaminated location at the site. Results of this study suggests that the changes in the pore fluid conductivity primarily control the geophysical signatures when compared to the effects of the formation of magnetite within the smear zone in the contaminated zone. Hydrology, oil levels and temperature do not appear to explain the geophysical signatures from the contaminated location, although natural water table variations can explain the resistivity variations at the uncontaminated location. This study demonstrates that geophysical methods can be used to assist in the monitoring of the long term changes in geophysical signatures due to natural attenuation processes associated with biodegradation of a crude oil spill.

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#### 1. INTRODUCTION

Biogeophysics is being used at Bemidji, MN as a method of monitoring long term natural attenuation. Natural attenuation is defined as the natural processes, such as biodegradation of contaminants, that remediate the soils and groundwater at a contaminated site. The aim of this study is to determine the factors that influence geophysical signatures consistent with natural attenuation at the oil spill site in Bemidji, MN. The factors that come under scrutiny include: grain size distribution, hydrology, pore fluid conductivity, magnetite content, magnetic susceptibility, oil levels and ground water temperatures. Field investigations together with laboratory experiments will aim to determine which of these factors contribute substantially to the overall changes in geophysical signatures.

Grain size distribution will be analyzed and compared via a statistical analysis between the uncontaminated zone and the contaminated zones at Bemidji, MN. This is to rule out major differences in basic grain size distribution and geology between the uncontaminated and contaminated regions. Next, the hydrology will be explored by comparing the precipitation data and water level data at the site. The specific conductance, or the pore fluid conductivity will be studied by analyzing field data and setting up a series of laboratory experiments which will determine how substantially it contributes to the geophysical signatures. In this same set of laboratory experiments, magnetite will be added to the uncontaminated sediment samples in amounts double the maximum concentration naturally occurring in the field, in order to isolate the SIP response to just the magnetite itself. Magnetic susceptibility will be investigated in order to gauge the presence of iron minerals in both the field and laboratory settings. Finally, oil levels and temperature variations will be studied to determine whether they contribute to changes in geophysical signatures.

#### **Biogeophysics**

Over time the microbes at Bemidji, MN are breaking down the hydrocarbons and developing various byproducts via a process called biodegradation. Geophysical signatures within a contaminant plume where biodegradation has taken place are associated with lower resistivities when compared with areas without contamination (Atekwana, et al., 2009). Through the biodegradation process, microbes are consuming the crude oil and are producing biomass, metabolic byproduct and microbial remediated processes which in turn can increase the electrolytic conductivities of the pore fluid (Atekwana, et al., 2009).

By utilizing geophysical field and laboratory methods, we aim to examine the resistivity, time domain induced polarization and frequency domain induced polarization response from both a contaminated and an uncontaminated location in Bemidji, Minnesota. This should demonstrate that geophysical methods can be used to monitor the long term changes in geophysical signatures.

#### **Summary of Research and Significance**

The contaminated area in Bemidji, MN is referred to as The National Crude Oil Spill Fate and Natural Attenuation Research Site, and is a natural laboratory for the investigation of biophysicochemical processes associated with the intrinsic bioremediation of a crude oil spill (Cozzarelli et al., 2001; Eganhouse et al., 1993). The objectives of this study were to demonstrate how field scale geophysical methods such as resistivity and time domain induced polarization can be used to compare differences in geophysical signatures between the uncontaminated and contaminated regions at the oil spill site in Bemidji over time. Geophysical signatures can also serve as proxy sensors of biodegradation processes. The effects of any differences in grain size distribution, hydrology, pore fluid conductivity, magnetite content, magnetic susceptibility, oil levels and ground water temperatures at the field site on acquired geophysical signatures were also considered.

Furthermore, this study aimed to conduct supporting laboratory frequency domain induced polarization experiments on Bemidji sediment samples taken from the uncontaminated region and mixed with magnetite to explore the effects of the addition of magnetite and pore fluid conductivity on geophysical signatures. Goethite and siderite were not considered because they do not emit as strong a magnetic susceptibility signal as magnetite. Additionally, laboratory magnetic susceptibility measurements and soil porosity measurements were obtained in order to determine the major contributing factors to changes in geophysical signatures.

This research study involved geophysical signatures from the oil spill site in Bemidji, MN which were then analyzed at the field scale and in a laboratory setting concurrently. The geophysical signatures between the field contaminated zone were compared to the uncontaminated zone, and the effects of grain size distribution (soil texture) and water table levels were explored. Laboratory SIP (Spectral Induced Polarization) experiments were performed in order to examine the effects of pore fluid conductivity and the addition of magnetite.

#### **Biodegradation at Bemidji**

Biodegradation which is defined as the breakdown and consumption of contaminants by microbes, is the main process at Bemidji site (Figure 1). During biodegradation, "microbial organisms transform or alter, through metabolic or enzymatic action, the structure of chemicals introduced into the environment" (Atekwana et al., 2009). Natural attenuation is defined as the reliance on natural processes such as biodegradation to gradually reduce the contamination in the soil or groundwater. At this site, it has been found that iron-reducing bacteria such as Geobacter bemidjiensis sp. and Geobacter psychrophilus sp. occur in contaminated aquifers and are specifically responsible for the biodegradation process in Bemidji, MN (Nevin et al., 2005). When microbes are present in the subsurface, they utilize the organic carbon from the crude oil and other nutrients found in the soil as well as the existing mineral substrate to form biomass, metabolic byproducts and microbial-mediated processes such as biomineralization. The interaction of microbes with organic carbon and mineral substrate can also produce metabolic byproducts such as organic acids, biogenic gases, biosurfactants and solvents. The crude oil carbon source can then be used by the microbes to reduce Fe(III) to Fe(II) (Lovely et al., 1989). The combination of hydrocarbon biodegradation and iron reduction can result in the formation of minerals such as magnetite and siderite (Lovely et al., 1987).



Figure 1: Biodegradation Processes and Effects on Geophysical Signatures flowchart version taken from *Atekwana and Atekwana, et. al, 2009* (adapted from Davis, 2009).

#### Linking Geophysical Signatures to Biodegradation

Geophysical properties such as electrical conductivity and resistivity can change dramatically when biodegradation occurs. When an oil spill first occurs, the resistivity of the crude oil contamination is very high, above 2.0 X 10<sup>9</sup> Ohm-m (Potter, 2007). This means it has an extremely low conductivity, approximately 4.46 X 10-<sup>10</sup> S/m. Over time as biodegradation occurs the electrical conductivity increases and the resistivity decreases substantially.

Previous studies have shown that the production of biomass during biodegradation changes the substrate so that the porosity, permeability and hydraulic conductivity decrease (e.g., Taylor et al., 1990; Cunningham et al., 1991; Vandevivere and Baveye, 1992; Baveye et al., 1998; Seifert and Engesgaard, 2007; Brovelli et al., 2009). This creates preferential flow pathways and changes the surface area, roughness and pore throat geometry of the subsurface (e.g., Seifert, 2005; Brovelli et al., 2009). The formation of metabolic byproducts can lead to physical and chemical changes such as changes in pore fluid chemistry, enhanced mineral dissolution, increased porosity, permeability and pore pressure and changes in wettability (e.g., Abdel Aal et al., 2004; Atekwana et al., 2004a, 2004b, 2004c, Atekwana et al., 2009).

Natural attenuation occurs when biodegradation and natural hydraulic processes are allowed to happen naturally and without human intervention. Biogeophysics provides an alternative method for monitoring natural attenuation by studying changes in geophysical signatures. The most important mechanisms relevant to this study are the well-established biogeophysical signatures related to changes in electrolytic conductivity due to solid and aqueous phase processes accompanying biodegradation (Atekwana, et. al, 2009). The combination of redox reactions and biomineralization occurring simultaneously during biodegradation leads to reduced species, redox gradients and enhanced mineral precipitation. All of these processes including: production of biomass, generation of metabolic byproducts and microbial-mediated processes can potentially lead to changes in geophysical properties such as electrolytic and interfacial conductivities (Atekwana, et. al, 2009).

#### **Previous Geophysical Applications to Monitoring Biodegradation**

Prior studies have used field scale geophysical techniques including resistivity and conductivity (Allen, et al., 2007) and magnetic susceptibility (Atekwana, et. al, 2014) to monitor biodegradation at hydrocarbon contaminated sites. Allen, et. al. (2007) showed that the presence of, "microbial populations, including the various hydrocarbon-degrading, syntrophic, sulfate-reducing, and dissimilatory-ironreducing populations, was a contributing factor to the elevated conductivity measurements."

Magnetic susceptibility has been proven to play an important role in identifying zones where microbial-mediated iron reduction is occurring. Within the uncontaminated zone, the area where the water table is fluctuating is known as the water table fluctuation zone. However, in the contaminated region, this area is known as the smear zone because the contaminant is smeared within the fluctuating water table. Atekwana, et al., 2014 observed that magnetic susceptibility values are highest within the smear zone and are also coincident with high concentrations of dissolved Fe(II) and organic carbon content, suggesting that the smear zone is most biologically active.

Laboratory studies have also been performed on sediment samples taken from the research site in Bemidji, Minnesota utilizing frequency domain induced polarization and magnetic susceptibility; specifically, the study performed by Mewafy, et al. (2013) to show the effect of the presence of an amount of magnetite equivalent to that naturally occurring at Bemidji, MN on geophysical signatures. They performed laboratory experiments using magnetite in a matrix of pure sand and saturated the columns using an NaCl solution with conductivity similar to the actual uncontaminated Bemidji conductivity. Their goal was to observe the effect of adding magnetite due to biodegradation on geophysical signatures. They observed a clear increase in the imaginary conductivity response with increasing magnetite content. Their experiment differs from this study in that we used double the amount of the maximum concentration of magnetite found at Bemidji in our column experiments in order to isolate and magnify the effect of the magnetite on the SIP signatures.

Mewafy, et al, (2013) also used actual contaminated Bemidji cores and uncontaminated cores and saturated them with NaCl solution with pore fluid conductivity similar to the actual contaminated Bemidji pore fluid conductivity and uncontaminated pore fluid conductivity, respectively. Samples from the contaminated region were found to have higher conductivity values than those from the uncontaminated region (Mewafy, et. al, 2013).

In addition, Abdel Aal, et. al, (2014) used an agar gel with conductivity similar to the conductivity of the uncontaminated zone at Bemidji for three different iron minerals to study the effect of mineralization on geophysical signatures. Their results indicated that the quadrature conductivity magnitude increased with decreasing grain size diameter of magnetite and pyrite with a progressive shift of the characteristic relaxation peak toward higher frequencies. The quadrature conductivity response of a mixture of different grain sizes of iron minerals was shown to be additive, whereas magnetic susceptibility measurements were insensitive to the variation in grain size diameters (1-0.075mm) (Abdel Aal et. al, 2014). For our study we only used a magnetite grain size of 106mm and studied the

phase response, quadrature conductivity (or imaginary conductivity), real conductivity, resistivity and magnetic susceptibility of the samples.

#### 2. BACKGROUND AND THEORY

#### **Electrical Resistivity**

Electrical Resistivity is a low frequency direct current (DC) geophysical technique for imaging sub-surface structures from electrical resistivity measurements made via electrodes arranged horizontally at the surface, or by electrodes arranged vertically in a borehole configuration. A commonly used electrode measurement configuration due to its higher signal to noise ratio is the Wenner array.

For a Wenner configuration current is injected across two current electrodes A and B, and the potential is measured between two potential electrodes M and N. For a Wenner configuration the order of electrodes is A, M, N and B. Ohm's Law allows the resistance, R, to be calculated by dividing the voltage, V, by the current, I (Equations 1).

$$\mathbf{V} = \mathbf{I}\mathbf{R} \tag{1}$$

The calculated resistances can then be used to approximate the apparent resistivity,  $\rho_a$ , (Equation 2) which is the equivalent resistivity assuming 3D current flow through a homogeneous half space (surface of the) earth:

$$\frac{\Delta V}{I} = R = \frac{\rho_a}{2\pi} \left[ \frac{1}{AM} - \frac{1}{MB} - \frac{1}{AN} + \frac{1}{NB} \right]$$
(2)

Inverse methods are used to determine a model of the subsurface resistivity structure by minimizing the differences between field observations of apparent resistivity and the apparent resistivities determined from a numerical forward model solution for a particular resistivity model.

#### **Time Domain and Frequency Domain Induced Polarization**

The measured time domain induced polarization (TDIP) response indicates the ability of a ground material to polarize at its interfaces. Lithology and fluid conductivity determine the induced polarization (IP) response of rocks and soils within the subsurface. IP measurements are sensitive to the low-frequency capacitive properties of rocks and soils, which are controlled by diffusion polarization mechanisms operating at the grain-fluid interface. Induced polarization additionally measures the degree of electrical charge stored in the electrical double layer, forming at mineral-fluid interfaces in porous media (Mwakanyamale, et. al, 2012). IP interpretation typically is in terms of the conventional field IP parameters: chargeability and phase angle. These parameters are dependent upon both surface polarization mechanisms and bulk (volumetric) conduction mechanisms (Slater and Lesmes, 2002).

TDIP is achieved by injecting a material with current and then switching off the current in order to measure the voltage decay curve over a certain time window (Figure 2b):



Figure 2a: Phase shift represented as the angular difference between the voltage and current waveforms (CNX, 1999).



Figure 2b: TDIP concept diagram showing the area of the measured voltage wave form under the curve from times 1 and 2 (CNX, 1999).

The integration of the area under the voltage decay curve within a specified time

window is defined as the chargeability, M (Equation 3):

$$M = \frac{1}{\Delta t} * \frac{1}{Vp} \int_{t1}^{t2} Vr \, dt , \qquad (3)$$

where  $V_r$  is the residual voltage defined between times  $t_1$  and  $t_2$  after the current is shut off, and  $V_p$  is the voltage measured during current application. Normalized chargeability,  $M_n$ , is the chargeability divided by the apparent resistivity, and increases with increasing conductivity:

$$Mn = \frac{M}{\rho a}$$
(4)

The normalized chargeability quantifies the magnitude of surface polarization (Slater and Lesmes, 2002). The angle which represents the degree to which the voltage waveform lags behind the current waveform is known as the phase shift ( $\phi$ ) (Figure 2a).

Phase angles have been found to be empirically related through laboratory experiments to the chargeabilities by multiplying the chargeability by a factor of 1.3 to obtain the phase (Mwakanyamale, et. al, 2012). The phase angle and conductivity magnitude can also be used to calculate both the real ( $\sigma$ ') and imaginary ( $\sigma$ '') parts of complex conductivity (Equations 5 & 6).

The frequency domain induced polarization effect or the spectral induced polarization (SIP) effect is similar to the TDIP effect however it measures the resistances over a spectrum of frequencies as opposed to time. SIP measures the resistances, phase angles and frequency spectrum which can then be used to determine the resistivities along with the real and imaginary conductivities, in the same manner as in TDIP.

SIP can be converted to TDIP, via the Fourier Transform. The Fourier transform decomposes a function of time (a signal) into the frequencies that make it up, and therefore allows TDIP to be converted to SIP (Huang, 1993).

### **Complex Conductivity Measurements**

The complex conductivity is given by:

$$\sigma^* = |\sigma| \exp(i\phi) = \sigma' + i\sigma'', \qquad (5)$$

$$|\sigma| = ((\sigma')^2 + (\sigma'')^2)^{1/2} .$$
 (6)

where  $\sigma^*$  is the complex conductivity, composed of a real component,  $\sigma'$ , and an imaginary component,  $\sigma''$ , i is equivalent to  $\sqrt{-1}$ ,  $|\sigma|$  is the magnitude and  $\phi$  is the phase lag (Mooney, 2013). The magnitude of the complex conductivity is given by Equation 6, where  $\sigma'$  is much greater than  $\sigma''$ , and therefore the magnitude of the complex conductivity essentially reflects the real component of the conductivity. The imaginary part  $\sigma''$  is mostly related to the counter-ion content at the grain and fracture boundaries. The imaginary part (and phase) increases with higher fracture density and with smaller fractures and pores, due to the increase in the overall mineral surface area. If air voids are present, real and imaginary conductivities decrease substantially. However, in fluid filled pores, the real part increases significantly while the imaginary part decreases significantly with increasing water content (Mooney, 2013). The phase,  $\phi$  can be determined from:

$$\sigma' = |\sigma| * \cos(\phi) \tag{7}$$

$$\sigma'' = |\sigma| * \sin(\phi) \tag{8}$$

The imaginary part of the conductivity,  $\sigma$ ", is related to the phase,  $\phi$  by Equations 7 & 8, where the phase lag is the angle which represents the degree to which the voltage waveform lags behind the current waveform and is also known as the phase shift ( $\phi$ ) (Figure 2a).

The phase captures the influence of the imaginary part and depends both on electromigration (conduction) properties (through  $\sigma$  ') and charge storage (through  $\sigma$  ") (Mooney, 2013). The phase angle can be used to calculate both the real ( $\sigma$ ') and imaginary ( $\sigma$ ") parts of the complex conductivity.

#### **Petrophysical Properties and Archie's Law**

Geophysical signatures are related to the physical properties of the geologic material. Archie's Law is an empirical quantitative relationship between porosity, electrical conductivity, and brine saturation of rocks (Archie, 1942). In the case where there is only electrolytic conduction, or conduction through the pore fluid, the relationships between the physical properties of the geologic material and the geophysical signatures are given by the following equation (Equation 9):

$$F = \frac{\frac{L}{C}}{\varphi_{int}} = \frac{\tau}{\varphi_{int}},$$
(9)

where the formation factor, F, is a geophysical property which can be expressed as the ratio of the tortuosity,  $\tau$  to the interconnected porosity,  $\phi_{int}$  (Equation 9). Tortuosity is a measure of how tortuous or how much the path through the interconnected pore spaces deviates from the direct linear distance between two points within a certain geologic material. The tortuosity is the ratio between the total length of the tortuous path, L and the direct linear distance, C between any two points (Equation 9). The interconnected porosity or the effective porosity,  $\phi_{int}$ , represents the porosity of a rock or sediment available to contribute to fluid flow through the rock or sediment. The interconnected porosity can be calculated by subtracting the clay bound water (CBW) or the volume of water that remains bound to the surfaces of certain hydrophilic mineral grains and therefore does not contribute to fluid flow, from the total porosity (Equation 10).

$$\varphi_{\rm int} = \varphi - CBW \tag{10}$$

The total porosity,  $\varphi$ , is expressed as the ratio of the total volume of voids (volume of air and volume of water) over the total volume of solids and voids (Equation 11).

$$\varphi = \frac{V_a + V_w}{V_t} = \frac{V_v}{V_t} \tag{11}$$

Alternatively, the formation factor can also be written as the ratio between  $\rho_{earth}$  and  $\rho_w$ , where  $\rho_{earth}$  is the overall resistivity of the geologic material (which is simply the inverse of the electrical conductivity of the geologic material or  $1/\sigma_{earth}$ ) and  $\rho_w$  is the resistivity of the pore fluid or the brine resistivity (Equation 12).

$$F = \frac{\rho_{earth}}{\rho_{w}} = \frac{\sigma_{w}}{\sigma_{earth}}$$

(12)

Electrical resistivity,  $\rho$  is an intrinsic property that quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electric charge. The general term for

the resistivity,  $\rho$ , is equal to the reciprocal of the general term for the electrical conductivity,  $\sigma$ , which is a measure of the ability of a material to conduct electrical current. Furthermore, the conductivity of the fluid within the soil or rock dominates  $\sigma$ '(electrolytic conductivity) if the geologic material is saturated and has reasonable porosity. Therefore, conductivity increases with increasing porosity and water content (Archie, 1942). Due to the inverse relationship between the electrical resistivity and the electrical conductivity, the apparent formation factor can also be rewritten as the ratio of  $\sigma_w$  to the  $\sigma_{earth}$ , where  $\sigma_w$  is the pore fluid conductivity, also known as the brine conductivity or salinity, and  $\sigma_{earth}$  is the overall conductivity of the geologic material (Equation 12).

In rocks with conductive minerals, there is a more complex dependence of the formation factor on  $\rho_w$ , temperature and the type of ions in solution. In these instances, the formation factor is referred to as the apparent formation factor. The apparent formation factor has been shown to be independent of the  $\rho_w$ , (or  $1/\sigma_w$ ) only for a certain class of petrophysically simple rocks (Schlumberger Oil Field Glossary, 2016). Therefore, the apparent formation factor is solely a function of pore geometry and describes how much more resistive the porous rock is relative to the fluid filling pores.

In Archie's Law, the interconnected porosity is raised to a cementation exponent, m, which models the degree of connectivity of the pores and is thus related to tortuosity and how much 'cementation' has occurred in the pores. If the pore network were to be modelled as a set of parallel capillary tubes, a cross-sectional area average of the rock's resistivity would yield porosity dependence equivalent to a cementation exponent of 1 (Glover, 2012). However, the tortuosity if the rock increases the cementation exponent to a number higher than 1 and less than 5 (Glover, 2012). This relates the cementation exponent to the permeability of the rock, or the ability of a geologic material to allow liquids to pass through it. Increasing permeability decreases the cementation exponent.

Saturation,  $S_w$ , is the ratio of the volume of water,  $V_w$  to the volume of voids,  $V_v$  (Equation 13).

$$S_{w} = \frac{V_{w}}{V_{a} + V_{w}} = \frac{V_{w}}{V_{v}}$$
(13)

When the  $S_w$  is raised to a saturation exponent, n, it can be expressed as the ratio  $\rho_{earth}$  to the  $\rho_{sat}$ , where  $\rho_{sat}$  is the resistivity of the geologic material when it is fully saturated (Equation 14). Similarly, the  $S_w^n$  can also be expressed as the ratio of the  $\sigma_{earth}$  to the  $\sigma_{sat}$ , where  $\sigma_{sat}$  is the conductivity of the geologic material when fully saturated (Equation 14) (Archie, 1942).

$$S_w^n = \frac{\rho_{earth}}{\rho_{sat}} = \frac{\sigma_{earth}}{\sigma_{sat}}$$

(14)

The saturation exponent, n, models the dependency on the presence of nonconductive fluid (such as hydrocarbons) in the pore-space, and is related to the wettability of the rock, or the tendency of one fluid to spread on, or adhere to, a solid surface in the presence of other immiscible fluids (Glover, 2012). The higher the wettability of geologic materials, even for low water saturation values, the more likely that a continuous film along the pore walls is maintained, making the geologic material conductive along the surface of its constituent minerals (Abdallah, 2007).

Assuming only electrolytic conduction, all of these aforementioned physical properties of geologic materials, including the interconnected porosity and saturation, are empirically related to their geophysical signatures such as the electrical conductivity of the pore fluid and the overall conductivity of the geologic material through Archie's Law (Equation 15). Archie's law, which applies when it relates the bulk conductivity to the conductivity of a pore fluid.

$$\sigma_{\text{earth}} = \frac{1}{\rho_{\text{earth}}} = \frac{\sigma_{\text{w}}}{F} = (\sigma_{\text{w}})(\phi_{\text{int}}^{\text{m}})(S_{\text{w}}^{\text{n}})$$
(15)

However, there are other conduction paths available to electrical current including conduction along the surfaces of mineral grains and through the mineral grain itself. Archie's Law can be modified to include surface conduction (Equation 16) in the following equation:

$$\sigma_{\text{earth}} = \frac{1}{\rho_{\text{earth}}} = \frac{\sigma_{\text{w}}}{F} + \sigma_{\text{surf}} , \qquad (16)$$

where  $\sigma_{surf}$  is electrical conductivity along the surface of the mineral grains. Surface conduction along mineral grains is due to the existence of the electrical double layer (EDL) which acts as a conduit for electrical current. The EDL is a distribution of charges that is on the surface of the mineral grain as a result of the fluid. It consists of a structure of negatively charged mineral grain adjacent to a mixture of positive and negative charges that develop in response to the negatively charged mineral grain. The EDL contains three parallel layers of charge surrounding the mineral grain. The first layer, also known as the Stern Layer, is associated with the fluid itself comprised of negative ions adsorbed onto the object due to chemical interactions. The second layer is composed of positive and negative ions attracted to the surface charge via the coulomb force, electrically screening the first layer. This third layer, also known as the diffuse layer, is loosely associated with the mineral grain because it is made of free ions that move in the fluid under the influence of electrical attraction and thermal motion rather than being firmly anchored (Bard, 1980). As temperature increases, the electrical conductivity through the EDL also increases.

#### **Magnetic Susceptibility**

Magnetic susceptibility is the ability of a material to become magnetized, and indicates whether a material is attracted into or repelled out of a magnetic field. Quantitative measures of the magnetic susceptibility also provide insights into the structure of materials, such as bonding and energy levels.

The principle of operation of the probe (Operating manual, Bartington Instruments) is based on the magnetic state of a specimen, which is generally described by the following equation:

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$$

where B is the flux density of the specimen in Tesla,  $\mu_0$  is the permeability of free space equal to a constant ( $4\pi \times 10^{-7}$ ), H is the applied field strength in AT/m and M is the magnetization of the specimen in Tesla. Dividing through by H, we get:

$$\mu_r = \mu_0 + \mu_0 k$$

(18)

where  $\mu_r$  is the relative permeability of the specimen (dimensionless) and  $\kappa$  is the magnetic susceptibility of the specimen (dimensionless). Rearranging, we get:

(19) 
$$\mu_0 k = \mu_r - \mu_0$$

Magnetite is an iron rich mineral with chemical formula Fe<sub>3</sub>O<sub>4</sub>, and it is ferrimagnetic. Ferrimagnetic mineral precipitates such as magnetite will have a much higher magnetic susceptibility (MS) signal than other minerals which are not magnetic. Magnetite is important because its presence signifies the precipitation of iron minerals due to biodegradation. Therefore, MS measurements are a useful technique for determining the presence of ferrimagnetic minerals.

## 3. SITE DESCRIPTION

**Site History** 

In August 1979, a high pressure crude oil pipeline burst just northwest of the town of Bemidji, Minnesota, spilling 1,700,000 L of crude oil onto the ground surface, contaminating the underlying shallow outwash aquifer (Figure 4). The contaminated region covered an area of 6500 m<sup>2</sup>. Cleanup efforts were made in 1980, after which about 24% (or 400,000 L) of the crude oil remained infiltrated throughout the subsurface in the unsaturated zone and around the water table (USGS Fact Sheet 084-98, 1998). This crude oil spill continues to be a source of contaminants to a shallow outwash aquifer. The oil is moving as a separate fluid phase, as dissolved petroleum constituents in ground water, and as vapors in the unsaturated zone.

The contaminated area in Bemidji, MN is referred to as The National Crude Oil Spill Fate and Natural Attenuation Research Site, and is a natural laboratory for the investigation of biophysicochemical processes associated with the intrinsic bioremediation of a crude oil spill. The smear zone, the area located below and above the water table, was found to have predominantly residual and free phase hydrocarbon. The biodegradation of the toxic chemicals leaching from the crude oil by microbial populations within the smear zone is our target area of interest (Cozzarelli et al., 2001; Eganhouse et al., 1993).

USGS scientists studying the site found that toxic chemicals leaching from the crude oil were rapidly degraded by natural microbial populations. Significantly, it was shown that the plume of contaminated ground water stopped enlarging after a few years as rates of microbial degradation came into balance with rates of contaminant leaching. This was the first and best-documented example of intrinsic bioremediation in which naturally occurring microbial processes remediates contaminated ground water without human intervention (Chapelle, U.S.G.S., Fact Sheet FS-054-95)

The contaminated area in Bemidji, MN offers a unique opportunity to study the geophysical signatures of a mature oil spill. The spill history at the site has been well characterized and monitored by the USGS for the last 37 years.

#### Magnetite at Bemidji

Magnetite is an important mineral precipitate at Bemidji because it indicates a certain level of biodegradation occurring within the smear zone. Magnetite is a black, metallic mineral that can be formed or precipitated either through abiotic mineralization or biotic mineralization. Abiotic mineralization, or inorganic mineralization, refers to a process where an inorganic substance precipitates in an inorganic matrix without the aid of biological organisms (Dupraz, 2009). Chemical conditions necessary for abiotic magnetite mineral formation develop via environmental processes, such as evaporation or degassing. Furthermore, the substrate for mineral deposition is abiotic (i.e. contains no organic compounds). Abiotic magnetite is a mineral which is formed as part of a variety of igneous rocks, pegmatites, contact metamorphic rocks and hydrothermal veins. In our modern Earth, magnetite seldom forms in sedimentary environments. During the Early Proterozoic Eon (2.5 to 1.6 billion years ago), however, large deposits of magnetite precipitated directly from seawater, as it was a time when the world's oceans and atmosphere had not yet become as oxygen-rich as they are now (University of Minnesota Geology Department Website, 2016). Bemidji is located in the area that

is in the slightly Northwestern part of Minnesota (Figure 3) (Google Maps, 2016). The iron ranges of Minnesota and Wisconsin once held enormous amounts of magnetite and hematite, along with lesser amounts of other iron ores, such as goethite and siderite. Although hematite forms the bulk of the iron ore in Minnesota and Wisconsin iron ranges, enough magnetite occurs in the deposits that many of them were originally discovered and mapped by their impact on compass readings.

In biotic mineralization, or biomineralization, native microbes are converting the petroleum derivatives into carbon dioxide, methane, and other biodegradation products. During biomineralization, magnetite can be nucleated and grown by biologically inducing chemical reactions. Magnetite can also be precipitated at a specific location within or on the cell of a microorganism, by having Fe(III) convert to Fe(II) which leads to the precipitation of the minerals either by nucleation or growth, which is controlled by ferrous iron concentration and/or pH (Bazylinkski and Frankel, 2003).

#### Site Geology

Geographically, Bemidji, MN is located in the slightly Northwestern part of Minnesota. The area in which the Bemidji oil contaminated site is located, which both include and surround glacial lakebeds, include a variety of geologic rock types. These glacial lakebed areas lie in a vast plain in the bed of Glacial Lake Agassiz, which extends north and northwest from the Big Stone Moraine (or Iron Range), beyond Minnesota's borders into Canada and North Dakota (University of Minnesota Geology Department, 2016 The Big Stone Moraine of Northwestern Minnesota once held enormous amounts of magnetite and hematite, along with lesser amounts of other iron ores, such as goethite and siderite. Although hematite forms the bulk of the iron ore in Minnesota and Wisconsin iron ranges, enough magnetite occurs in the deposits that many of them were originally discovered and mapped by their impact on compass readings. This is an important reason why the long term geophysical monitoring of biodegradation processes at the oil spill site in Bemidji, MN is being researched.



Figure 3: USGS Northwestern Minnesota Topographic Map Screenshot showing Bemidji, MN Geology (USGS, 2016).

#### Site Hydrogeology and Groundwater Temperature Variations

Cumulative precipitation in Bemidji, MN for the two week period prior to each field resistivity survey were obtained from the Minnesota Department of Natural Resources website (MNDNR, 2016). These data show a decrease in total precipitation from July 2013 to August 2015 (Figure 5). Water level data from well 310D in the contaminated region (Figure 4) were obtained from the USGS Minnesota Water Science Center website and are not entirely consistent with the precipitation data (USGS, 2016). While the precipitation data show a definite decrease over time with each consecutive year from 2013 to 2015, the water level data increases slightly from 2013 to 2014 and then decreases from 2014 to 2015. Currently there are no definitive explanations for the inconsistency between these data sets other than the possibility of human error in either collecting or recording these data.



Figure 4: Water level (green line) at the Bemidji, MN Oil Spill Site approximately 2 weeks prior to each field resistivity and IP data measurement (MatLab graph created by Ashley Samuel).


Figure 5: Precipitation data collected from the Bemidji, MN Oil Spill Site approximately 2 weeks prior to each field resistivity and IP data measurement (Excel graph created by Ashley Samuel). resistivity data were collected were recorded by the USGS Minnesota Water Science Center website (USGS, 2016). The groundwater temperatures for July, 2013 start low, and then decrease further during August, 2014, increase during April, 2015 and then decrease to the lowest point during August, 2015. The groundwater temperature variations are small and range from 43 to 44.5 degrees Fahrenheit.

# **Magnetic Susceptibility Field Measurements**

Magnetic susceptibility field surveys were previously conducted in 2011 by Atekwana (2014) along two nearly-perpendicular profiles; one in the direction of the groundwater flow and the other nearly perpendicular to the groundwater flow (Atekwana, 2014). The field magnetic susceptibility data were acquired from cased boreholes within the contaminated (G0906) and uncontaminated regions (925F) using a BSS-02B borehole magnetic susceptibility sonde (Bartington Instruments). The BSS-02B is a borehole probe for measurement of magnetic susceptibility from 10<sup>-5</sup> to 10<sup>-1</sup> centimeter-gram-seconds (cgs) and operates at 1.36 kHz. The magnetic susceptibility probe is characterized by high vertical and horizontal resolution up to 25 mm, with the region of detection being situated 190 mm from the end of the borehole (Atekwana, et. al, 2014). This probe identifies areas of microbial mediated iron reduction, resulting in a high positive response to ferrimagnetic minerals such as magnetite.

For both the field uncontaminated and contaminated zones, the magnetic susceptibilities were mostly 13.0 m<sup>3</sup>/kg throughout the measured subsurface with the exception of the peaks within the fluctuating water table zone or smear zone (Figure 6a). In the uncontaminated zone, a magnetic susceptibility peak of around 13.5 m<sup>3</sup>/kg is observed within the fluctuating water table zone (Figure 6b). However, in the contaminated zone, a magnetic susceptibility peak is observed around 15.6 m<sup>3</sup>/kg within the smear zone.



Figures 6a-b: Magnetic susceptibility field data from Bemidji, MN from contaminated and uncontaminated regions in 2011 (Atekwana, et. al. (2014)).

# **Specific Conductance**

Pore fluid specific conductance measurements were obtained in the field by the (USGS) personnel as part of the USGS Toxic Substances Hydrology Research program from 1998 to 2012. The cumulative data from the contaminated and uncontaminated locations (Figure 7) were taken from the original specific conductance contour plots available on the USGS Minnesota Water Science Center website (USGS, 2012).



Figure 7: The specific conductance contour plot shows the vertical profiles in the contaminated and uncontaminated zones at the Oil Spill Site in Bemidji, MN. (USGS, 1998)

# 4. METHODS

#### **Field Electrical Resistivity Measurements**

In July 2013, two vertical electrode resistivity arrays (Figure 8a) were assembled and installed at the field site in Bemidji, MN. The control array was inserted into the uncontaminated zone (well 1304), and the other array was inserted into the contaminated zone (well 1308) (Figure 9).

To construct the arrays, wires were attached via 1-inch stainless steel hose clamps to 10 foot sections of 1-inch PVC pipe (Figure 9b). The hose clamps served as electrodes, and each array had 66 electrodes in total. For array 1304 (uncontaminated zone), the first 20 electrodes were spaced 10 cm apart, electrodes 20-34 were spaced 7.5 cm apart, electrodes 34 and 35 were 14 cm apart (due to joint spacing in between PVC pipes), electrodes 35-46 were spaced 7.5 cm apart and electrodes 46-66 were spaced 10 cm apart. When the 1304 array (uncontaminated zone) was installed, electrode 1 was placed at the bottom of the borehole, and electrode 66 at the top. The 1308 array (contaminated zone) was installed in a similar fashion with only minor differences in electrode spacing: electrodes 1-21 spaced 10 cm apart, electrodes 21-33 spaced 7.5 cm apart, electrodes 33 and 34 spaced 14 cm apart (again due to joint spacing in between PVC pipes), electrodes 34-46 spaced 7.5 cm apart and electrodes 46-66 spaced 10 cm apart. Once again, when the array was installed, electrode 1 was placed at the bottom of the borehole, and electrode 66 at the top.



Figure 8a: The 2 Vertical Electrical Resistivity Arrays (VERA) that are pictured here showing M.S. Student Ashley Samuel (left) and Undergraduate Casey McGuffy (right), were eventually installed in order to collect resistivity and IP measurement data collected from the Bemidji, MN Oil Spill Site approximately around July, 2013, August, 2014 and August, 2015 (Photo by Ashley Samuel).



Figure 8b: The 2 Vertical Electrical Resistivity Arrays (VERA) that were eventually installed in order to collect resistivity and IP measurement data collected from the Bemidji, MN Oil Spill Site approximately around July, 2013, August, 2014 and August, 2015 (Pictured on ground with Superimposed Positive and Negative Current and Potential Electrodes, and the Syscal Pro Switch 96 IRIS Resistivity Instrument inset (top right corner) (Photos by Ashley Samuel).



Figure 9: This topographical map has been superimposed with the original oil field contamination layout: including the Uncontaminated and Contaminated Zones, the Middle and South Oil Pools, the BTEX Plume and the Spray Zone as of 2013 (USGS, 2013).

Once each array was installed, the array's electrode wires were connected to a 12 pin terminal block which was then connected to a 96 electrode controller board. The controller board was then hooked up to the IRIS SYSCAL Pro Switch 96 Electrode resistivity and IP instrument. This setup allowed for resistivity and normalized chargeability measurements to be collected automatically by the IRIS instrument. The IRIS instrument combines a transmitter, a receiver and a switching unit and is supplied by a 12V marine battery. The measurements are carried out automatically using a 50V output voltage, 2.5A current, 250W power and 3 stacks (number of readings) per resistivity and IP measurement. The Induced Polarization chargeability (IP) is also measured through 20 windows for a detailed analysis of the decay curves displayed on the graphic LCD screen (IRIS Instruments Brochure, 2016). The measurements were obtained using a basic Wenner configuration due to its higher signal to noise ratio. Using both a = 1 and a = 2 electrode spacings, normal and reciprocal measurements were taken in July 2013, August 2014, April 2015 and August 2015 (Figures 9a-b).

# **Electrical Resistivity Data Processing**

The electrical resistivity data were first processed by performing a thorough error analysis which eliminated the resistance errors greater than a threshold percentage between the normal and reciprocal measurements. These processed data were then inverted using inverse modelling techniques, which use the acquired data to establish a best fit model for those data using R3t inversion software. The resulting inverted resistivities, calculated by R3t, were then visualized using the VisIT software program.

## **Electrical Resistivity Data Error Analysis**

Details on each step are provided below. The Electrical Resistivity data were processed using inverse modelling techniques. Inverse modelling involves using the acquired data in order to establish a best fit model for those data. Before inputting the Bemidji field data into an inversion program, an error model had to be established. Creating an error model allows one to calculate the model errors which are then used for the inversion in order to produce the best possible model for the resistivity data. The normal and reciprocal field data collected at Bemidji were used to calculate the error models. First the normal and reciprocal measurements were lined up side by side according to their Wenner electrode a-spacings, and their corresponding resistances were calculated by using Ohm's Law (Equation 1).

After these resistances were calculated, any unusable data from problematic measurements such as negative resistances were eliminated. From the remaining normal, N, and reciprocal, R, resistance measurements, the absolute error,  $E_{abs}$  was calculated by taking the absolute value of the difference between the two resistance measurements (Equation 20):

$$E_{abs} = |N - R| \tag{20}$$

Then the average resistances (Equation 21) between the N and R measurements were obtained via the equation:

$$R_{ave} = \frac{(N+R)}{2}$$
(21)

The relative reciprocal error, R<sub>recip</sub> was then calculated as:

$$\mathrm{R_{recip}} = 100*(rac{\mathrm{E_{abs}}}{\mathrm{R_{ave}}})$$
 ,

(22)

where any data with  $R_{recip}$  values greater than 10% were eliminated. The logarithm (base 10) of all computed  $R_{ave}$  resistances was then computed and used to sort the  $E_{abs}$  and  $R_{ave}$  values, in ascending order. Then the  $E_{abs}$  and  $R_{ave}$  were divided into bins whose size was roughly determined by dividing the number of resistance measurements by 10. The average  $E_{abs}$  and  $R_{ave}$  values from each bin were then calculated. An error model was then plotted with the average  $E_{abs}$  values as the ordinate and the average  $R_{ave}$  values as the abscissa (Figure 10).



Figure 10: Example of a Resistance Error Model for the resistance data. Model Error Equation based on  $y = 0.016x^{1.0815}$ , where Rave = x (Excel graph by Ashley Samuel)..

Either a linear or a power law trendline was then added depending upon which trendline best fit the majority of the data points in the error model, based on the highest calculated R<sup>2</sup> (linear regression) value using Microsoft Excel. If a linear trendline was used, then a slope and y-intercept were obtained from the equation for the trendline (Equation 23) and used to calculate the model errors. If a power law trendline was used, a slope and exponent were obtained from the equation of the trendline (Equation 24) and used to calculate the model errors. These trendline equations and their corresponding slopes, y-intercepts and exponents were then used to calculate the model errors according to either one of the following formulas:

$$\varepsilon_{\text{model}} = m * R_{\text{ave}} + b \tag{23}$$

$$\varepsilon_{\text{model}} = m * (R_{\text{ave}})^{a}$$

These model errors were eventually inputted into the R3t Inversion program, however in certain cases where the solution did not converge in less than 5 iterations, an additional 2% error was added to all  $R_{error}$  values according to the following equation:

$$R_{error} = E_{abs} + 0.02(R_{ave})$$

This additional 2% error allowed the solution to converge in less than 5 iterations using the R3t inversion program (described in the following sections).

## **Phase Data Processing**

(24)

(25)

After completing the error analysis for the resistance data as described previously, the phase data were calculated by multiplying the chargeability, M by a factor of - 1.3 (Mwakanyamale, et. al, 2012). The phase error,  $\phi_{error}$ , was then calculated (Equation 26) and an error analysis for the phase data was performed using a similar method to that used for the resistance data error analysis.

$$\phi_{\text{error}} = |N - R| \tag{26}$$

The only difference between the two error analyses is that for the phase error analysis, instead of plotting the error model in terms of the average  $E_{abs}$  values as the ordinate and the average  $R_{ave}$  values as the abscissa, the average  $\phi_{error}$  values were plotted as the ordinate and the  $R_{ave}$  values as the abscissa (Figures 11a-b).



The phase model errors were also obtained from the equation of the trendline from the phase data and were eventually inputted into the cR3t inversion program which is described in the following sections.

# **Mesh Generation**

As part of the inversion process, a structured 3D tetrahedral mesh was created in order to define the geometry for the discretization of the region surrounding each borehole array as well as the position of the borehole array with respect to elevation. In mathematics, discretization concerns the process of transferring continuous functions, models, and equations into discrete counterparts. The mesh allows the R3t inversion program to calculate the resistivities at each node within the mesh based on the inputted resistances. The structured 3D tetrahedral mesh consists of a series of defined elementary entity points or nodes, which must coincide with the position of the electrodes (Figures 12a-b).



Figures 12a-b: Tetrahedral mesh generated by program gmsh (12a, left) and visualized using VisIT with surfaces created (12b, right) (Graphs created by Ashley Samuel).

Lines connecting these elementary entity points are then created, and closed loop planar surfaces are created from these lines which are then extruded to form the final structured 3D tetrahedral mesh. The mesh can be finely discretized in the user defined foreground region closest to the borehole electrodes, and coarsely discretized in the background region. The finely discretized foreground region contains nodes, lines and surfaces within the mesh that are closer together when compared to the coarsely discretized background region, which has nodes, lines and surfaces that are spread further apart. The foreground region of the mesh allows for better resolution of the resulting inverted resistivity image. The mesh is broken up into a foreground region closer to the borehole electrodes due to the fact that resolution, or the ability of a resistivity measurement to resolve changes within the subsurface, is also always better closer to the borehole electrodes. This is due to the fact that resolution and current density diminish as the distance away from the borehole electrodes increases, therefore only a coarsely discretized background region is required the further away the mesh is from the borehole electrodes.

The structured 3D tetrahedral mesh was defined using the gmsh mesh generator program (Christophe Geuzaine and Jean-Francois Remacle). The gmsh program allows the user to define the mesh graphically or by entering in code into the geometry file (.geo). The process for creating the mesh involves first defining the borehole electrodes as elementary entity points or nodes, and including the elevations of these electrodes within the borehole. Mesh boundaries with elementary entity points (electrodes) are then defined, and the lines connecting each entity are created, which in turn create closed loop planar surfaces. These 2D geometrically closed loop planar surfaces are then extruded to create volumes which form the structured 3D tetrahedral mesh. The term tetrahedral mesh applies because all four node vertices of the resulting 3D discretized section are the same distance from each other, and the planar surfaces have no parallel faces, the shapes of which defines a tetrahedron. The 3D tetrahedral mesh is called "structured" because all of the mesh elements align along a single vertical axis, and in this case the axis refers to the vertical alignment of the borehole electrodes.

The final mesh file (.msh) was then converted into a mesh3d.dat file required by the R3t inversion program by running it through a MatLab script. The MatLab script reads the following data from the mesh file in order to convert it into the proper mesh3d.dat file format required for the R3t inversion program: total number of triangular prism elements, total number of nodes, triangular prism node numbers and node coordinates. This mesh3d.dat file was used for both the field resistivity and phase inversions that are described in the following sections.

### **Resistivity Inversion and Visualization**

Inverse modeling is the science of finding a model to fit the observed data. There are many methods for achieving this goal however the inversion software used for the purpose of this research is R3t version 1.8, which was developed by Andrew Binley of Lancaster University, England. R3t is an inverse solution software program for 3D current flow in a tetrahedral mesh. The inverse solution is based on a regularized objective function combined with weighted least squares (an 'Occams' type solution) as defined in Binley and Kemna (2005). The R3t program uses an iterative process which solves the following equations repeatedly until satisfactory convergence has been achieved:

$$\left(J^{T}W_{d}^{T}W_{d}J + \alpha R\right)\Delta m = J^{T}W_{d}^{T}\left(d - f(m_{i})\right) - \alpha Rm$$
(27)

$$m_{i+1} = m_i + \Delta m \tag{28}$$

where the parameters in Equations 27 and 28 are defined as: J is the Jacobian, such that  $J_{i,j} = \partial d_i / \partial m_j$ , d is the data vector,  $m_i$  is the parameter vector at iteration i,  $W_d$ 

is the data weight matrix, assumed to be diagonal, with  $W_{i,i} = 1/\epsilon_i$ , where  $\epsilon_i$  is the standard deviation of measurement i,  $\alpha$  is the regularization (or smoothing) parameter, R is the roughness matrix, which describes the connectivity of parameter blocks,  $\Delta m$  is update in parameter values at each iteration and f(m) is the forward model for parameters m. Satisfactory convergence is achieved once the data misfit reaches a required tolerance. The data misfit is expressed as a root mean square error:

$$RMS = \sqrt{\frac{1}{N}} \sum \left(\frac{d_i - f_{i(m)}}{\epsilon_i}\right)^2$$
(29)

where N is the number of measurements and the target data misfit (RMS) is equal to 1.

The R3t inversion program requires three input files: R3.in, mesh3d.dat and protocol.dat. In the R3.in file, parameters for the inversion are set based on the desired type of inversion selected. For this inversion, background regularization was used. Background regularization is when changes in resistivity are constrained against a background model rather than a model in order reduce structure in the image. The mesh3d.dat file requires the parameters for defining the 3D tetrahedral mesh as described in the previous section. The protocol.dat file contains the number of measurements as well as the electrode spacings, average resistances and their associated model errors as calculated from the error models. After all of these input files including the resistances were run through the program, R3t then outputted the inverted resistivities into a file (f001.vtk). This file was then used to

visualize graphically the 1D (along the vertical borehole axis) radial inverted resistivities using the VisIt software program. In a radial inversion, a 3D model is achieved but there is only variation in resistivity as a function of depth (distance along the vertical) and also with radial distance away from the well. Resistivity variations occur as a function of radial distance but there is no information on how resistivity changes as a function of azimuth, i.e. the resistivity structure is identical regardless of the azimuthal direction (Figure 13a-b).



Figures 13a-b: Radial resistivity schematic as a function of radial resistivity (13a, left) and in the z direction (13b, right) (Schematic created by Ashley Samuel).

## **Phase Inversion and Visualization**

Several attempts were made to invert the Bemidji field phase data using a process similar to that used to invert the sistivity data. The phase data were b inverted usi Figure 13a-b: Resistivity displayed as radial resistivity (a) and in the Z direction (b). Lancaster University, England. The phase inversion was performed with a similar procedure to what I have described in the previous resistivity section, except that

the resistivity is now considered as a complex variable defined in the data as a magnitude and phase.

For this inversion, background regularization was used. The mesh3d.dat file requires the parameters for defining the 3D tetrahedral mesh as described in the previous section. The protocol.dat file contains the number of measurements as well as the electrode spacings, average resistances and their associated model errors, average phase values and their model errors as calculated from the error models. These input files were run through the cR3t program, which outputted the inverted resistivities and phase values into a file (f001.vtk). This file was then used to visualize graphically the 1D (along the vertical borehole axis) radial inverted resistivities and phase values (Appendix A) using the VisIt software program.

The phase inversion attempts were not successful for all data sets due to the fact that the solutions did not converge in the required number of iterations. Therefore, for almost all of the phase inversion attempts, a solution was not obtained. For the phase inversions that did successfully converge, the results can be found in Appendix A.

## **Ratio Resistivity Inversions**

The Bemidji field data were analyzed using ratio inversions to measure changes in resistivity over time at each of the two borehole arrays. Ratio inversions require combined model errors calculated from each of the two borehole array data sets collected during two different time periods. In order to calculate the combined model error for the ratio inversion the following equation is required:

$$d_{error} = |d| * \sqrt{\left(\frac{a_{error}}{a}\right)^2 + \left(\frac{b_{error}}{b}\right)^2 + \left(\frac{c_{error}}{c}\right)^2}$$
(30)

where the variables in Equation 30 are as follows: a = Year 1 Resistance Data,  $a_{error} =$  Model Error from Year 1 Resistance Data, b = Year 2 Resistance Data,  $b_{error} =$  Model Error from Year 2 Resistance Data, c = Forward Model Resistance Data for a 100 Ohm Homogeneous Earth,  $c_{error} =$  Model Error from Forward Model Resistance Data and d = (Year 2 Resistance Data)/(Year 1 Resistance Data).

The a = Year 1 Resistance Data or background data, can be taken from any of the available data sets from any individual year. The same is true for the b = Year 2 Resistance Data, however it must be from a different year or time period from Year 1. The a<sub>error</sub> and b<sub>error</sub> model errors are calculated from the individual error models for each year's data set. A forward model is used by the R3t inversion program to create resistance data based on a synthetic model for a 100 Ohm-m homogeneous earth. These forward model resistance and calculated transfer resistance data are then used to compute the forward model errors. These transfer resistances and forward modeling errors are calculated from the following formulas:

$$R_{transfer} = \frac{\rho a}{4\pi a} \left[ \frac{1}{AM} - \frac{1}{MB} - \frac{1}{AN} + \frac{1}{NB} \right]$$
(31)

$$c_{error} = |R_{transfer} - c|$$
(32)

where the variables for Equations 31 and 32 are defined as follows:  $\rho a = apparent$ resistivity,  $R_{transfer} = Transfer Resistance, c = Forward Model Resistance Data, <math>4\pi a$ = Geometric Factor for a Borehole Configuration, a = Electrode Spacing for the Wenner Configuration (for these data there are both a=1 and a=2 measurements), AM = Distance Between the Positive Current Electrode (C+) and the Positive Potential Electrode (P+), MB = Distance Between the Positive Potential Electrode (P+) and the Negative Current Electrode (C -), AN = Distance Between the Positive Current Electrode (C+) and the Negative Potential Electrode (P -) and NB = Distance Between the Negative Potential Electrode (P -) and the Negative Current Electrode (C -).

After all of these calculations are performed, the resistance data that are inputted into the R3t protocol.dat file are computed from the relationship:

$$R_{ratio} = d * c \tag{33}$$

As previously defined, d is the ratio of the Year 2 Resistance Data divided by the Year 1 Resistance Data, and c is the Forward Model Resistance Data calculated from a synthetic 100 Ohm homogeneous earth. In addition to the protocol.dat file, a R3.in file containing the parameters for the inversion are set based on the desired type of inversion selected. In this case background regularization was used, and the mesh3d.dat file containing the parameters were used to define the 3D tetrahedral mesh as described in the previous sections. Once these files were run through the R3t inversion program, the resulting f001.vtk file containing the inverted ratio resistivity was used to visualize changes in resistivity in the VisIt software program.

## **Laboratory Methods**

A set of column laboratory experiments was set up in order to observe the SIP response of uncontaminated Bemidji, MN cores mixed with magnetite and saturated with two different pore fluid conductivities. The purpose of the laboratory experiments was to determine the effects of mineralization and pore fluid conductivity on geophysical SIP signatures. These data were then plotted using MatLab in order to view the plotted phase, resistivity, real conductivity and imaginary conductivity versus frequency.

#### **SIP** Measurements on Sample Filled Laboratory Columns

For the supporting laboratory research, a core was taken in 2014 by the USGS personnel from the uncontaminated region just outside the free phase plume area in Bemidji, MN. The core number was 1408-17, which was taken from the soil region around the water table (approximate depth 1.7 - 2.5m from ground surface), and it was approximately 24 inches in length when fully retrieved. Two soil samples were taken from the top of the core while they were still encased in the original plastic cylindrical core casing. The soil samples and their casings were placed in a vice and cut using a Porter-Cable Saber saw. The resulting lengths and diameters of each cut core were approximately 50mm and 45mm, respectively.

Although no thorough chemical analysis on the two samples could be obtained, both samples were assumed to be identical geologically due to the fact that they came from the same core and did not have any apparent visual differences. One soil sample was designated as the relatively undisturbed control sample, and was temporarily left inside its original plastic core casing so that laboratory magnetic susceptibility measurements could be obtained (see following Magnetic Susceptibility section for the procedure). The relatively undisturbed control sample and casing were weighed prior to being packed into the first laboratory column. The plastic casing was also weighed individually after the soil was extracted so that an accurate mass of the soil sample by itself could be calculated by subtracting the casing weight from the total sample with casing. The second soil sample was weighed in a similar fashion while it was still in its casing and then extracted to be mixed with 1% (by mass) abiotic magnetite with grain size  $<106 \mu m$ . Once the magnetite was mixed into the soil sample and a homogenous mixture was achieved, the 1% magnetite soil sample was temporarily placed back into the original plastic core casing so that magnetic susceptibility measurements could be obtained. These two soil samples were then eventually transferred into two separate laboratory columns for the purpose of comparing the effects with and without mineralization on geophysical SIP signatures (Figure 14). The flowchart describing the main experimental procedure and goals for the two different laboratory columns can be found in Figure 15.

The columns were made of Lexan, which is a brand name for a polycarbonate, or a thermoplastic polymer containing carbonate groups in its chemical structure. Polycarbonate columns were used in this experiment because they are strong and optically



Figure 14: Typical PSIP Laboratory Column Setup (Photo by Ashley Samuel).



Figure 15: Flowchart depicting the objectives of the Laboratory Column Experiments (Flowchart by Ashley Samuel).

transparent. Each column consisted of a main hollow cylindrical body which had two equally spaced holes on its exterior in order to allow for the placement of two silver wire potential electrodes. Two circular, flat current electrodes made of sintered silver and silver chloride (Ag-AgCl), were glued with an epoxy to the inside of the column end caps which were then soldered to a small thin insulated copper wire which protruded outside of the center of the column end caps to allow for current injection. These column end caps were designed to be fitted perfectly to the main cylindrical body of the column and prevent leakage. The column dimensions were: inner column diameter = 23.52mm, outer column diameter = 29.89mm, total assembled column height = 92.88mm, AM (or the distance between C+ and P+ electrodes) and NB (distance between P- and C- electrodes) = 48mm, MN (distance between P+ and P- electrodes) = 25mm, MB (distance between P+ and C- electrodes) and AN (distance between C+ and P- electrodes) = 71mm and AB (distance between C+ and C- electrodes protruding from column end caps) =  $(1 + 1)^{-1}$ 119mm.

In order to pack the samples, one of the bottom column end caps was first attached to the bottom of the main cylindrical body, and a circular cloth mesh was placed on top of the current electrode in order to protect it from the soil sample. The soil sample was slowly and carefully packed into the base of the column until it completely filled the entire column. Another cloth mesh was placed on top of the second current electrode within the top column end cap and this end cap was fitted to the top of the column in order to seal in the soil sample. Two silver wires were coated to become silver and silver chloride (Ag-AgCl) potential electrodes, and were encased in protective rubber fittings, necessary to prevent current from flowing anywhere other than within the soil sample itself. The rubber encased silver wire potential electrodes were then placed into plastic screw fittings. These plastic screw fittings were then screwed into the preexisting threaded holes outside of the main cylindrical body of the column in order to prevent leakage around the potential electrodes.

Tygon Poly Vinyl Chloride (PVC) tubing (3.5mm inner diameter), selected for its resistance to flex-fatigue and abrasion, was then attached to plastic screw fittings which screwed into a preexisting threaded hole that went through each column end cap. Each tube was attached to a manual shut off valve in order to control inflow and outflow through the column. The tube connected to the base of the column was placed in a pyrex flask filled with artificial groundwater, and held in place using parafilm and electrical tape. The tube was also attached to a peristaltic pump which drew the artificial groundwater from the flask into the column, with inflow from the bottom of the column to become saturated. Saturation was achieved by allowing 5 pore volumes of artificial groundwater to flow through each column. The volume of fluid equivalent to 1 pore volume was calculated using the following equation:

$$PV\% = \varphi(\pi r^2 h),$$

(34)

where  $\varphi$  is the estimated porosity, r is the radius of the soil sample packed into the column and h is the height of the soil sample packed in the column. For both column setups, the estimated porosity was 0.4, the radius of the soil sample was 23.48 mm and the height of the soil sample was 92.48 mm. Equation 34 was multiplied by 5 in order to calculate the equivalent volume of fluid needed to equal 5 pore volumes, which was equivalent to ~80 mL. The top column tube was placed into a graduated pyrex flask so that the total volume of fluid outflow equivalent to 80mL could be measured to ensure full sample saturation.

Once full saturation was achieved, the contact resistances between all current and potential electrodes were checked using a multi-meter and found to be less than 100 K-Ohms. Obtaining lower contact resistances is a way to verify that current will be allowed to flow through the entire sample before any SIP measurements are taken. Both the control sample and the 1% magnetite sample were fully saturated inside the column using lab created artificial groundwater.

The artificial groundwater was created by adding the following masses of chemicals to 1 L of deionized (DI) water in a large flask: 1.07mg Ammonium Chloride (NH<sub>4</sub>Cl), 74.55mg Potassium Chloride (KCl), 98.59mg Magnesium Sulfate (MgSO<sub>4</sub>), 58.81mg Calcium Chloride (CaCl<sub>2</sub>), 112.06mg Sodium Lactate (C<sub>3</sub>H<sub>5</sub>NaO<sub>3</sub>) and 3,353.7mg or 3.35g Pipes Buffer (C<sub>8</sub>H<sub>16.5</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·1.5Na). After the addition of these chemicals, a magnetic stirring rod was placed inside the fluid filled flask and set on top of a magnetic stirrer plate for approximately 1 hour in order to thoroughly mix the chemicals with the DI water. Two different types of

artificial groundwater were created, with two different fluid conductivities equivalent to the Bemidji, MN naturally occurring minimum (0.025 S/m) and maximum (0.085 S/m) field pore fluid conductivities. These two different fluid conductivities were created in order to saturate the columns and observe the effects of using two different pore fluid conductivities on laboratory geophysical signatures. The first artificial groundwater solution originally had a fluid conductivity of 0.149 S/m which was diluted with DI water until a fluid conductivity of 0.085 S/m was measured by the conductivity probe. A portion of the 0.085 S/m artificial groundwater solution was then diluted with DI water in order to reduce the fluid conductivity to 0.025 S/m. SIP measurements were taken immediately after each column was fully saturated with the lower fluid conductivity (0.025 S/m) artificial groundwater solution and had low contact resistances. After these SIP measurements were taken on both columns, they were then re-saturated with the higher fluid conductivity (0.085 S/m) artificial groundwater solution and checked for low contact resistances before additional SIP measurements were obtained. Additionally, the fluid conductivities of the column outflow were recorded (control column = 0.026 S/m and 0.086 S/m respectively, magnetite column = 0.027 S/m and 0.088 S/m respectively) and were found to be similar to the inflow conductivities. This slight increase in resulting outflow versus original inflow conductivity indicated that there was only minor mineral dissolution occurring due to the saturation procedure.

SIP measurements were obtained by first attaching wires with alligator clips to the current and potential electrodes of each column. These wires were plugged into the Portable Spectral Induced Polarization (SIP) Field/Laboratory Unit (PSIP), which is a multi-channel geophysical instrument designed by Ontash and Ermac. The PSIP has a 10V output voltage, 10 mA stimulating current and measures phases less than 1 mRadians over a 1 mHz to 1 KHz frequency spectrum. The PSIP recorded a series of phase and resistance measurements over a 0.01 Hz to 10 KHz frequency spectrum on both laboratory columns from December 2015 to January 2016. The final laboratory column setup for obtaining SIP measurements can be observed in Figure 14.

## Laboratory SIP Data Processing

The PSIP instrument recorded the frequency, phase and relative resistance of each laboratory column for every measurement. A MatLab script was written in order to process these data to obtain the resistivity, real and imaginary conductivity and can be found in Appendix B. First the geometric factor was calculated for each column using the following formula:

$$K = \frac{\pi r^2 h}{MN} , \qquad (35)$$

where K is the geometric factor for the laboratory column, r is the inner radius of the column, h is the height of the column and MN is the distance between the potential electrodes. The geometric factor was found to be equal to 0.0173 mm<sup>2</sup>, and was then used to calculate the resistivity, real and imaginary conductivity based on the following relationships:

$$R = 100^*(R_{rel})$$
 (36)

$$\rho_a = K * R \tag{37}$$

$$\phi = (-1) * \phi_{\text{rec}} \tag{38}$$

Where R is the resistance calculated from multiplying the Relative Resistance,  $R_{rel}$ , by 100,  $\rho_a$  is the apparent resistivity and  $\phi$  is the calculated phase for the purpose of plotting it on a positive ordinate (y-axis) obtained by multiplying the recorded negative phase,  $\phi_{rec}$ , by a -1 from the PSIP instrument. The real conductivity and imaginary conductivity were calculated in the MatLab script using Equations 7 and 8, respectively, where in this case the  $\rho$  is actually the apparent resistivity,  $\rho_a$ .

### Laboratory Magnetic Susceptibility Measurements

Laboratory magnetic susceptibility measurements were obtained on the two sample cores prior to their being packed into the columns. Each core was still in its' original plastic cylindrical casing from the field. As described previously, the control core was kept relatively undisturbed in its original casing, whereas the other core was emptied into a container and mixed with 1% magnetite before being placed back into its original casing. To keep the soil from falling out of the casing, Parafilm and electrical tape were wrapped around the two open ends of each core sample. A Bartington MS2C magnetic susceptibility meter with a circular core sample holder for mounting the core samples vertically, was used to obtain the measurements. An example of this type of MS2C magnetic susceptibility meter and core sample holder can be observed in Figure 16 (Note: these are not the same cores used for the experiment). The laboratory magnetic susceptibility data showed values of  $0.0048 \text{ m}^3/\text{kg}$  for the uncontaminated core prior to being mixed with magnetite and  $0.12 \text{ m}^3/\text{kg}$  for the uncontaminated core after it was mixed with 1% magnetite.



Figure 16: Undergraduate student Tonian Robinson holding a Bartington MSC-2 Magnetic Susceptibility Core Reader (Photo by Judy Robinson).

# **Sample Porosity Calculations**

Upon completion of the SIP measurements, the porosity of each laboratory column soil sample was estimated in order to eliminate the possibility of porosity being a factor in the SIP response. The column was dismantled and the soil sample was carefully extracted onto a plastic tray. The mass of the plastic tray itself was recorded prior to the soil sample extraction, and the total mass of the saturated soil sample and tray were recorded. The saturated soil sample in an open tray was placed into an oven at 40 degrees Celsius for approximately 72 hours. After 72 hours the soil sample was completely dry and the mass of the dry soil sample and tray were recorded. The mass of the plastic tray by itself was subtracted from the recorded masses of the saturated sample and tray along with the dry sample and tray. This calculation was necessary in order to obtain the individual masses of the saturated sample and dry sample. The porosity of each soil sample was then estimated according to the following equation:

(39) 
$$\varphi_{est} = \frac{V_v}{V_T} = \frac{(m_{sat} - m_{dry})}{(\rho_{water})(V_{column})} ,$$

where  $\varphi_{est}$  is the estimated porosity,  $V_v$  is the volume of voids which in this case is equal to the volume of water lost during drying,  $V_T$  is the total volume of the original soil sample in the column,  $m_{sat}$  is the mass of the saturated soil sample by itself,  $m_{dry}$  is the mass of the dry soil sample by itself,  $\rho_{water}$  is the density of water (1g/cm<sup>3</sup>) and  $V_{column}$  is the total interior volume of the laboratory column that held the soil sample. The porosity of the control sample was found to be 0.294 and the magnetite sample's porosity was 0.297, with a percent difference between the two measurements being equal to 1.1%.

#### 5. **RESULTS**

#### **Geological Grain Size Analysis**

Geologically, USGS drillers found that the oil spill site at Bemidji, MN consists of pitted sand and gravel outwash and moderately calcareous silty sand (approximately 20 m thick) and outwash glacial deposits overlying clayey till of unknown thickness (Bennett et al., 1993). A grain size analysis performed by Mewafy, et. al, 2013 concluded that at the uncontaminated location (C1006) the average percentages of gravel, sand, silt and clay were: 4.8%, 93.12% and 2.08% respectively. At the contaminated location (C1010) the average percentages of gravel, sand, silt and clay were: 1.13%, 96.94% and 1.93% respectively (Mewafy, et. al, 2013).

A statistical analysis using a Welch's t-test (Equation 40) was performed to compare the soils between the uncontaminated and contaminated regions. The Welch's t-test is used only when the two population variances are not assumed to be equal (the two sample sizes may or may not be equal) and hence must be estimated separately (The t-statistic to test whether the population means are different was calculated as:

$$t_{\text{value}} = \frac{\mu_1 - \mu_2}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}},$$
(40)

where  $t_{value}$  represents the Welch's t-test parameter which determines the statistical differences between the two different population means,  $\mu_1$  and  $\mu_2$  are the corresponding mean percentages of each soil texture for all sample depths from the uncontaminated and contaminated regions,  $\sigma_1$  and  $\sigma_2$  are the standard deviations of each soil texture for all sample depths from the uncontaminated and contaminated regions and  $n_1$  and  $n_2$  are the sample sizes from the uncontaminated and contaminated regions. The Welch's t-test found that since the calculated t-values were all less than the critical t-scores, the two soils from the uncontaminated and contaminated locations were not statistically different, within a 95-99% confidence level (Figure 17).

Uncontaminated			Contaminated			T-Test Values	
Gravel %	Sand %	Silt & Clay %	Gravel %	Sand %	Silt & Clay %	Gravel %	1.56

Table 1: The Welch's t-test found that since the calculated t-values were all less than the critical t-scores, the two soils from the uncontaminated and contaminated locations were not statistically different, within a 95-99% confidence level (Table created by Ashley Samuel).

# **Raw Apparent Conductivity and Specific Conductance Data**

A preliminary analysis of the raw apparent conductivity data at the research site in Bemidji showed a higher apparent conductivity in the contaminated region compared with the uncontaminated region (Figure 18). This correlated well with higher specific conductances of the pore fluid in the contaminated region versus the uncontaminated region. These preliminary findings justified the need for the use of inverse modelling in this study to improve the data analysis results.



Figure 17: Apparent conductivity, specific conductance and water table vs. elevation at the uncontaminated and contaminated regions (Graph created by Ashley Samuel).

## **1-D Radial Resistivity Inversions**

The 1-D radial resistivity inversion results for the acquired Bemidji, MN uncontaminated (array 1304) and contaminated (array 1308) field data from July 2013, August 2014, April 2015 and August 2015 are plotted in Figure 19 with a scale ranging from 8 to 100,000 Ohm-m.

For all four of the inversion results for the uncontaminated region from July 2013 to August 2015, a lower resistivity ranging from 84 to 891 Ohm-m is observed in the region below the fluctuating water table when compared to the resistivity ranging from 5,000 to 9,440 Ohm-m in the region above the water table. The water table in the uncontaminated region fluctuated between elevations of 423.9 to 424.7m, from July 2013 to August 2015. A similar trend is observed in the contaminated region during the same time period, where the resistivity below the fluctuating water table (also ranging between elevations of 423.9 to





Figure 19: The 2013 Radial 1-D Uncontaminated (1304) Resistivity Inversion (Top Row) and 1-D Contaminated Resistivity Inversions (Bottom Row) taken from the Bemidji, MN oil spill site field data (Graphs created by Ashley Samuel).

424.7m from July 2013 to August 2015), referred to as the smear zone due to the presence of contamination, is lower than the resistivity observed within the region above the smear zone.

A stark contrast in resistivities is observed when comparing the uncontaminated region to the contaminated region for all inversion results from July 2013 to August 2015. For each of the four field dates on which these data were acquired, the inversion results from the uncontaminated region consistently show a significantly higher resistivity ranging from 891 to 9,440 Ohm-m, when compared with the resistivity in the contaminated zone which ranges from 8 to 891 Ohm-m. This trend of higher resistivities in the uncontaminated zone versus the contaminated zone is consistent both above and below the fluctuating water table or smear zone.

#### **1-D Radial Ratio Resistivity Inversions**

The 1-D radial ratio resistivity inversion results for the uncontaminated and contaminated regions in Bemidji, MN allow us to observe the changes in resistivity over time, specifically, from July 2013 to August 2015 (Figures 20a-c). The plotted inversion results represent the percentage ratio of the resistivity data from any year during which the data were collected, to the resistivity data from any background year, usually occurring prior to any of the successive years. As this resistivity ratio is a percentage and therefore multiplied by 100, the scale is set to range from 50 to 150 percent change in resistivity. Data showing a percent change less than 100, indicate a decrease in resistivity over time. Conversely, data showing a percent change greater than 100 indicate an increase in resistivity over time between the

two data sets. If the percent change remains at 100, there is no definitive change in resistivity over time observed for that data set.

In the uncontaminated zone, from July 2013 to August 2014, there is a slight increase in resistivity (100 to 125 % change) within the region below the fluctuating water table, and an even higher increase in resistivity (125 to 150 % change) in the region above the water table (Figure 20a). In addition, there is a small isolated region within the water table fluctuation zone which shows a decrease in resistivity ranging from 50 to 100% change in resistivity. From August 2014 to August 2015, the uncontaminated zone mostly shows no change in resistivity both above and below the water table (Figure 20b). However, a small zone within the water table fluctuation zone showing an increase in resistivity from 125 to 150% is observed. From July 2013 to August 2015, there is a 100 to 150% change in



Figure 20a-c: 1-D Uncontaminated 2014/2013, 2015/2014 and 2015/2013 Radial Ratio Resistivity Inversions, respectively (Graphs created by Ashley Samuel).

resistivity below the water table fluctuation zone and a relatively homogeneous

increase in resistivity (150%) above this water table zone (Figure 20c).
The contaminated 1-D ratio resistivity inversions (Figures 21a-c) show both a decrease and/or increase from July 2013 to August 2014, there is a slight increase and/or decrease in resistivity (100 to 125 % change) within the region below the fluctuating water table, and an even higher increase in resistivity (125 to 150 % change) in the region above the water table (Figure 19a). In addition, there is a small isolated region within the water table fluctuation zone which shows an increase and/or decrease in resistivity ranging from 50 to 100% change in resistivity. From August 2014 to August 2015, the contaminated zone mostly shows no change in resistivity both above and below the water table (Figure 21b). However, a small zone within the water table fluctuation zone showing an increase in resistivity from 125 to 150% change in resistivity is observed. From July 2013 to August 2015, there is a 100 to 150% change in resistivity below the water table fluctuation zone and a relatively homogeneous increase in resistivity (150%) above this water table zone (Figure 21c).



Figure 21a-c: 1-D Contaminated 2014/2013, 2015/2014 and 2015/2013 Ratio Resistivity Inversions, respectively (Graphs created by Ashley Samuel).

### **Phase Data Processing**

The Phase data were processed using a similar error analysis method to the Resistance data processing method. Using the program cR3t, the data were inverted and the results were visualized using VisIT software. This procedure can be found in the Results section.

## **SIP Laboratory Results**

The laboratory SIP results (Figures 20a-d) show the plotted phase, resistivity, real conductivity and imaginary conductivity versus a frequency spectrum of  $10^{-2}$  to  $10^4$  Hz. There is no definitive phase peak or corresponding relaxation frequency observed except for the Control uncontaminated core saturated with 850µS/cm around  $10^{-1}$  Hz. Above a frequency of  $10^2$  Hz, the phases descend in the following order: Magnetite 12-14-15 250µS/cm, Magnetite 12-28-15 850µS/cm, Control 12-28-15 850µS/cm (except just before  $10^4$  Hz, most likely due to SIP measurement errors) and Control 12-14-15 850µS/cm. Below a frequency of  $10^2$  Hz, the phases descend in the following order: Control 12-28-15 850µS/cm, Control 12-14-15 250µS/cm.

The resistivity within each frequency spectrum descends in the following order: Control 12-14-15 250µS/cm, Control 12-28-15 850µS/cm, Magnetite 12-14-15 250μS/cm and Magnetite 12-28-15 850μS/cm. The real conductivity values descend in the exact opposite order as the resistivity. The imaginary conductivity values do not change significantly throughout the entire frequency spectrum.

# 6. **DISCUSSION**

## **Geological Site Conditions and Geophysical Signatures**

According to the Welch's statistical t-test, the grain size distributions of the uncontaminated and contaminated zones are not statistically different. It can be assumed that any differences in grain size distributions between the two regions at Bemidji, MN are not statistically significant. Therefore, changes in grain size are not significantly playing a role in the resistivity and IP results at the oil spill site.



Figures 22a-d: SIP Laboratory results showing Phase vs. Frequency (22a, Top Left Corner), Resistivity vs. Frequency (22b, Top Right Corner), Real Conductivity vs. Frequency (22c, Bottom Left Corner) and Imaginary Conductivity vs. Frequency (22d, Bottom Right Corner) (Graphs created by Ashley Samuel).

#### Magnetic Susceptibility and Geophysical Signatures

The magnetic susceptibility at the Bemidji, MN oil spill site peaks around the fluctuating water table zone at about 13.5 m<sup>3</sup>/kg within the fluctuating water table zone (Figure 21a-b). However, in the contaminated zone, a magnetic susceptibility peak is observed around 15.6 m<sup>3</sup>/kg within the smear zone. This indicates a higher degree of magnetic iron minerals in the contaminated zone due to biodegradation when compared to the uncontaminated zone.

The laboratory cores had a magnetic susceptibility of 0.0048 m<sup>3</sup>/kg for the uncontaminated core prior to being mixed with magnetite and 0.12 m<sup>3</sup>/kg for the uncontaminated core once it was mixed with 1% magnetite. For both the field and laboratory data, the contaminated zones had magnetic susceptibility values 16-24% higher than the uncontaminated zones. This corresponds well with the field magnetic susceptibility values being higher for the smear zone within the contaminated region than the uncontaminated region, due to the fact that it contains more iron minerals such as magnetite.

#### Hydrology and Geophysical Signatures

The 1-D radial resistivity inversion results for the acquired Bemidji, MN uncontaminated (array 1304) and contaminated (array 1308) field data from July

2013, August 2014, April 2015 and August 2015, show changes in their geophysical signatures most likely due to changes in hydrology.

For all four of the 1-D Radial Resistivity inversion results for the uncontaminated and contaminated regions from July 2013 to August 2015, a lower resistivity is observed in the region below the fluctuating water table when compared to the resistivity ranging in the region above the water table, due to saturation below the water table. The main difference is that in the contaminated zone, where there is still crude oil present, the fluctuating water table zone or the smear zone has a lower resistivity when compared to the uncontaminated zone. This geophysical effect is most likely due to the fact that the biodegraded crude oil is mixed with the saturated smear zone or fluctuating contaminated water table. Groundwater temperature variations in Bemidji, MN on the dates which the resistivity data were collected were recorded for July 2013, August 2014, April 2015 and August 2015. The mean temperatures in Bemidji, MN increased and then decreased from July 2013 to August 2014, and from August 2014 to April 2015, and then increased from April 2015 to August 2015. Variations in the groundwater temperature don't explain the resistivity variations that are observed in these data. The hydrology data and temperature data are consistent with these findings, however they are not all completely relevant to the individual yearly resistivity measurements. To procure the relevance of these data, the 1-D radial ratio resistivity inversion results must be analyzed in order to examine the effects of time on their geophysical signatures.

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The 1-D radial ratio resistivity inversion results for the uncontaminated and contaminated regions in Bemidji, MN allow us to observe the changes in resistivity from July 2013 to August 2015. In the uncontaminated zone, from July 2013 to August 2014, there is a slight increase in resistivity within the region below the fluctuating water table, and an even higher increase in resistivity in the region above the water table. This is despite the fact that the water levels actually increase from July 2013 to August 2014. One would expect the water levels to decrease if the resistivity is increasing, however, most likely this is due to water quality and not quantity. As water quality data were not obtained, this is merely conjecture. Oil levels dropped from July 2013 to August 2014, having an almost negligible effect on geophysical signatures because they represent an extremely thin layer of oil on top of the smear zone. In addition, there is a small isolated region within the uncontaminated water table fluctuation zone which shows a decrease in resistivity, which is probably due to near electrode effects.

From August 2014 to August 2015, the uncontaminated zone mostly shows no change in resistivity both above and below the water table. However, a small zone within the water table fluctuation zone showing an increase in resistivity is observed, and is again most likely due to hydrology. From July 2013 to August 2015, there is a change in resistivity below the water table fluctuation zone and a relatively homogeneous increase in resistivity above this water table zone which could be due to the decrease in water levels and precipitation data from those two time periods.

The contaminated 1-D ratio resistivity inversions show both a decrease and/or increase from July 2013 to August 2014. There is either no change or a slight increase in resistivity within the region below the fluctuating water table, and an even higher increase in resistivity in the region above the water table. While it is difficult to tell whether these changes in resistivity are due to near electrode effects or are due to changes in hydrology, oil levels and/or groundwater temperature, most likely they are due to hydrology. In addition, there is a small isolated region within the water table fluctuation zone which shows an increase and/or decrease in resistivity. From August 2014 to August 2015, the uncontaminated zone mostly shows no change in resistivity both above and below the water table. However, a small zone within the water table fluctuation zone showing an increase in resistivity is observed. From July 2013 to August 2015, changes in resistivity below the water table fluctuation zone and a relatively homogeneous increase in resistivity above this water table zone are observed. These general increases in resistivity are most likely due to the changes in hydrology.

#### Magnetic Susceptibility Field and Laboratory Results

The field Magnetic Susceptibility data results from Atekwana (2014) show a definitive peak around the smear zone within the contaminated zone and a smaller peak around the uncontaminated water table fluctuation zone. The peak within the contaminated zone most likely corresponds to the higher iron mineral content (or increased ferrimagnetism) and is possibly due to the biomineralization of magnetite. This would also partially explain the increased conductivity of the smear zone region also found in the 1-D Radial Resistivity Inversions. This is due to the fact

that the higher the ferrimagnetism, the higher the conductivity of the iron mineral itself, in this case, magnetite. The smaller peak within the uncontaminated zone is possibly due to a smaller degree of mineralization occurring which is probably not due to biodegradation of any crude oil.

For both the field uncontaminated and contaminated zones, the magnetic susceptibilities were mostly 13.0 m<sup>3</sup>/kg throughout the measured subsurface with the exception of the peaks within the fluctuating water table zone or smear zone. In the uncontaminated zone, a magnetic susceptibility peak of around 13.5 m<sup>3</sup>/kg is observed within the fluctuating water table zone. However, in the contaminated zone, a magnetic susceptibility peak is observed around 15.6 m<sup>3</sup>/kg within the smear zone (Atekwana, 2014).

The laboratory magnetic susceptibility results are consistent with the field data in that for the uncontaminated cores without magnetite, they are showing a much lower value than for the uncontaminated cores with magnetite. This is again due to the fact that the higher magnetite containing core has a higher magnetic susceptibility due to the magnetite's higher ferrimagnetism.

## Laboratory SIP Results

The laboratory SIP results show the plotted phase, resistivity, real conductivity and imaginary conductivity versus a frequency spectrum of  $10^{-2}$  to  $10^4$  Hz. There is no definitive phase peak or corresponding relaxation frequency observed except for the control uncontaminated core saturated with 850µS/cm around  $10^{-1}$  Hz. Above a frequency of  $10^2$  Hz, the phases descend in the following order in terms of their file names: Magnetite 12-14-15 250 $\mu$ S/cm, Magnetite 12-28-15 850 $\mu$ S/cm, Control 12-28-15 850 $\mu$ S/cm (except just before 10<sup>4</sup> Hz, most likely due to SIP measurement errors) and Control 12-14-15 850 $\mu$ S/cm. Below a frequency of 10<sup>2</sup> Hz, the phases descend in the following order in terms of their file names: Control 12-28-15 850 $\mu$ S/cm, Control 12-14-15 250 $\mu$ S/cm, Magnetite 12-28-15 850 $\mu$ S/cm and Magnetite 12-14-15 250 $\mu$ S/cm. There is no indication that either the magnetite or the pore fluid conductivity seem to be controlling the decreasing phase values for any frequency range.

The resistivity within each frequency spectrum descends in the following order: Control 12-14-15 250 $\mu$ S/cm, Control 12-28-15 850 $\mu$ S/cm, Magnetite 12-14-15 250 $\mu$ S/cm and Magnetite 12-28-15 850 $\mu$ S/cm. The real conductivity values descend in the exact opposite order as the resistivity. Both the pore fluid conductivity and iron mineral (magnetite) content seem to be controlling the resistivity and real conductivity values. The higher the pore fluid conductivity and the magnetite content, the lower the resistivity values and higher the real conductivity values.

The imaginary conductivity values do not change significantly throughout the entire frequency spectrum. Perhaps this indicates that magnetite does not affect the imaginary conductivity response.

## **Solid Phase Changes and Geophysical Signatures**

Solid phase changes are not responsible for changes in geophysical signatures at Bemidji, Minnesota. Solid phase changes include mineralization/biomineralization of iron minerals such as magnetite. In the field data, biomineralization of magnetite is not effecting the resistivity changes that are occurring within the smear zone and the uncontaminated fluctuating water table zone. The laboratory data suggest that mineralization (albeit in this case abiotic) does not have a substantial effect on geophysical signatures such as resistivity and real conductivity. The generation of solid precipitates such as magnetite by biodegradation does not produce substantial laboratory electrical spectral induced polarization (SIP) and magnetic susceptibility responses.

#### **Aqueous Phase Changes and Geophysical Signatures**

Aqueous phase changes are also contributing to changes in geophysical signatures at Bemidji, Minnesota. Aqueous phase changes include pore fluid conductivity changes. Pore fluid conductivity may exert an even greater contributory significance to geophysical signatures than does solid phase changes such as mineralization/biomineralization. Electrolytic conductivity is the electrical conductivity of the pore fluid within the subsurface. At the site in Bemidji, the metabolic byproducts produced by biodegradation such as organic acids are elevating the electrolytic conductivity within the contaminant plume. When the conductivity increases, the resistivity decreases, due to their inverse relationship with one another.

## **Future Research Considerations**

If any additional research were to be performed, there would be numerous possibilities for future research considerations. Perhaps additional laboratory

experiments using the PSIP instrument setup for both SIP and TDIP measurements could be obtained. The Fourier transform could be utilized to convert the field TDIP data to SIP data for comparison purposes. Finally, it would help tremendously to know the exact geochemistry of the field cores using a synchrotron.

## 7. CONCLUSIONS

Site grain size distribution was ruled out as being a factor in changes in geophysical signatures. The addition of magnetite was not responsible for changes in resistivity in the laboratory results. The magnetic susceptibility field and laboratory data agree in that they both show a higher degree of ferrimagnetism within the contaminated zone or where mineralization is present. However, this still does not explain the higher conductivity, or lower resistivity found in these regions for the 1-D Radial Resistivity Inversions. Hydrology definitely plays a role in the 1-D Radial Resistivity Inversion results. The more saturated or more conductive the water is which saturates the uncontaminated water table fluctuation zone or smear zone, the lower the resistivity in those regions. Oil levels, consisting of an extremely thin layer on top of the water table, most likely do not play a significant role in changes in resistivity throughout the uncontaminated and contaminated regions. Groundwater temperature variations most likely do not effect resistivity changes in the field.

The laboratory SIP results lead us to conclude that aqueous phase changes are responsible for changes in SIP response and therefore geophysical signatures and not solid phase changes. The SIP data clearly show that phase is not affected by changes in pore fluid conductivity or the addition of magnetite. However, resistivity and real conductivity are definitely affected more so by pore fluid conductivity and not by mineralization or the addition of magnetite. Imaginary conductivity is not affected whatsoever by the pore fluid conductivity or the addition of magnetite.

The pore fluid conductivity is an example of aqueous phase changes which eventually affects geophysical signatures and the addition of magnetite is an example of solid phase changes which does not affect geophysical signatures at this particular site. These results indicate that the resistivity measurements could be used to monitor long term changes in the aqueous geochemistry associated with natural attenuation however the value of induced polarization measurements were limited at this site.

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## **APPENDICES**

# A) Phase Inversion Attempts

This appendix contains a list of the figures from the phase inversion attempts.



Figure A-1: Phase inversion attempts from the Uncontaminated (1304, Left) region and the Contaminated (1308, Right) from 2013 (Graphs created by Ashley Samuel).



Figure A-2: Phase inversion attempts from the Contaminated 8/2014 (1308, Left), the Contaminated 4/2015 (1308, Middle) and the Contaminated 8-2015 (1308, Right) regions, respectively (Graphs created by Ashley Samuel).

## **B) SIP Data Processing MatLab Script**

% This MatLab script will read in all of the recorded SIP Laboratory Data from one or more Excel spreadsheet files and plot the phase, calculated resistivity, real conductivity and imaginary conductivities versus frequency.

clc; close all; clear all;

% Select one or more Excel spreadsheet files:

```
dName = uigetdir('.', 'Select folder containing Excel CSV files');
if dName==0, error('No folder selected'); end
files = dir( fullfile(dName, '*.csv') );
files = strcat(dName, filesep, {files.name}');
% The following will extract the data from the selected Excel spreadsheet files:
NUM_SHEETS = 1;
                           % Represents the number of sheets per file
for s=1:NUM_SHEETS
% Extract the data from the Excel spreadsheet for all files selected:
   numData = cell(numel(files),1);
   for f=1:numel(files)
     numData{f} = xlsread(files{f}, s);
   end
end
geometric factor = ((.01175)^2*pi)/0.025; % Geometric Factor = (Cross Sectional
Area of
% Interior Column)/(Distance Between Potential Electrodes)
% Extract the data from the Excel spreadsheet files and create matrices containing
the
% frequency, resistance and phase data. Then use these data to calculate the
resistivity, real and
% imaginary conductivities:
for i=1:f
   [pathstr(i).name,name(i).name,ext(i).name] = fileparts(files{i,1})
```

```
Freq(i).name = numData{i,1}(16:52,2)
  ResisMag(i).name = numData{i,1}(16:52,3) % This is really the Relative
Resistance
  Phase(i).name = numData\{i,1\}(16:52,4)
                                                % Phase is in radians
  resistance(i).name = 100*(ResisMag(i).name) % Resistance = 100*(Relative
Resistance)
  resistivity(i).name = geometricfactor*resistance(i).name
  % Resistivity = (Geometric Factor)*(Resistance)
  Phaseforplotting(i).name = Phase(i).name*(-1)
  % Phase = (Phase)* (-1) for plotting on positive y-axis
  imaginaryconductivity(i).name= (((1./(resistivity(i).name))).*(-
1*sin(Phase(i).name)))
  % Imaginary Conductivity = (1/Resistivity)*(sin(Phase))
  realconductivity(i).name = (((1./(resistivity(i).name))).*(cos(Phase(i).name)))
  % Real Conductivity = (1/Resistivity)*cos(Phase)
```

```
% Now to plot everything
```

```
figure(1)
```

```
cc=hsv(6)
subplot(2,2,1)
% This will plot the Phase versus Frequency:
semilogx(Freq(i).name, Phaseforplotting(i).name, '-o',
'MarkerEdgeColor', 'b', 'MarkerFaceColor', cc(i,:))
title('Phase vs. Frequency')
xlabel('Frequency (Hz)')
ylabel('Phase (radians)')
```

```
hold on
```

```
% This will plot the Resistivity versus Frequency:
subplot(2,2,2)
loglog(Freq(i).name,resistivity(i).name, '-
o','MarkerEdgeColor','b','MarkerFaceColor', cc(i,:))
title('Resistivity vs. Frequency')
xlabel('Frequency (Hz)')
ylabel('Resistivity (Ohm-m)')
hold on
```

```
% This will plot the Real Conductivity versus Frequency:
subplot(2,2,3)
loglog(Freq(i).name,realconductivity(i).name,'-o', 'MarkerEdgeColor', 'b',
'MarkerFaceColor',
cc(i,:))
title('Real Conductivity vs. Frequency')
```

xlabel('Frequency (Hz)') ylabel('Real Conductivity (S/m)') hold on

% This will plot the Imaginary Conductivity versus Frequency: subplot(2,2,4) loglog(Freq(i).name,imaginaryconductivity(i).name, 'o','MarkerEdgeColor','b','MarkerFaceColor', cc(i,:)) title('Imaginary Conductivity vs. Frequency') xlabel('Frequency (Hz)') ylabel('Imaginary Conductivity (S/m)') hold on

end

% This will plot the legend with every Excel Spreadsheet filename selected for plotting:

legend(name(1,1).name, name(1,2).name, name(1,3).name, name(1,4).name, 'Location', 'Northwest')