USING GEOPHYSICAL METHODS TO UNDERSTAND,
MONITOR, AND ASSESS A HYDROCARBON-CONTAMINATED AREA

By

Selcen Zehra Yokus

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ABSTRACT OF THE THESIS

USING GEOPHYSICAL METHODS TO UNDERSTAND, MONITOR, AND ASSESS A HYDROCARBON-CONTAMINATED AREA

By
Selcen Zehra Yokus

Thesis Director:
Professor Lee Slater

Hydrocarbon contamination is one of the most significant problems globally. At hydrocarbon-contaminated sites, iron-reducing bacteria may use hydrocarbon as a carbon source and reduce Fe$^{3+}$ to Fe$^{2+}$ to form, for example, magnetite. At an oil spill site near Bemidji (MN, USA), hydro ferric oxide (HFO) transformation to magnetite and, subsequently, magnetite to siderite has been recorded. Being able to detect these transformations with geophysics could help with the monitoring of the progress of biodegradation. Therefore, this study uses two geophysical methods: spectral induced polarization (SIP) and magnetic susceptibility (MS).

SIP is known to be sensitive to specific iron minerals and, therefore, possibly to the transformation of iron minerals. In this study, the sensitivity of SIP to different percentages by volume (between 0.09 % - 5 %) of magnetite, siderite, and HFO was investigated for artificial sand-iron mineral mixtures saturated with groundwater from this hydrocarbon-contaminated site. Additionally, experiments were conducted to understand how the SIP response depends on the
radius of magnetite particles (0.7 mm, 0.4 mm, 0.1 mm, 0.05 mm, 0.02 mm). Our results suggest that the SIP method might be used to differentiate the iron minerals involved in hydrocarbon degradation because the technique is sensitive to iron mineralogy. The SIP response of variations in magnetite concentration and grain size is strong, but it is small (negligible) for the siderite and HFO. The minimal concentrations of magnetite, siderite and HFO likely to be detectable in the laboratory based on the results were respectively 0.09%, 1.5% and 1.5% by volume. SIP might be used to monitor the long-term progress of biodegradation by capturing iron mineral transformations in the future.

MS was examined in both laboratory and field conditions. To understand the sensitivity of MS to different percentages by volume (between 0.0007 % - 100 %) of magnetite, siderite, and HFO, artificial sand-iron mineral mixtures were prepared in the laboratory, and several measurements were recorded. In addition, experiments were conducted to understand if the MS response depended on the radius of magnetite particles (0.7 mm, 0.4 mm, 0.1 mm, 0.05 mm, 0.02 mm). Using these experimental results, synthetic mineral packets were prepared in the laboratory, installed in a hydrocarbon-contaminated area, and monitored monthly using MS. Additionally, MS was applied to cores retrieved from the hydrocarbon-contaminated area in previous years.

As the percentage concentrations increased, an increase was also observed in the MS for all iron minerals in the laboratory study. The minimal concentrations of magnetite, siderite and HFO likely to be detectable in the laboratory were respectively 0.09%, 5% and 12 % by volume. The MS response of variations in grain size is almost the same for all magnetite grain sizes; therefore, no relationship could be established between grain size and MS response. For
synthetic mineral packets, while the MS fluctuated every month, possibly due to magnetite formation and oxidation, in the contaminated zone, a consistent increase in MS was observed in the uncontaminated area in the groundwater fluctuation zone. A decrease in MS was recorded in the mineral packet above the groundwater fluctuation zone in the uncontaminated area. The results obtained from cores retrieved show that the MS value has decreased over the years. These experiments suggest a variation in the MS in the contaminated area that depends on the water level. As the groundwater level increases, the MS value increases and no consistent movement in MS results was observed in the absence of groundwater. The results suggest that the MS method might be used to differentiate iron minerals involved in hydrocarbon degradation because the technique is sensitive to iron mineralogy.
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CHAPTER 1

1.1 Introduction

Hydrocarbon contamination negatively affects the soil and groundwater worldwide, mainly in Europe and the USA (Panagos et al., 2013; Abdel-Shafy and Mansour, 2016). Such areas are well-suited for many chemical transformations to take place. (Haagh et al., 2020; Bennett et al., 2004; Totsche et al., 2003). This situation, which disrupts the chemical properties of the soil and groundwater in the environment, should be examined and monitored (Lari et al., 2018; Tang et al., 2012). Traditionally site characterization relies on the direct method that is a combination of drilling, sampling, and laboratory characterization. Many studies show that this method has limits in identifying and monitoring the contamination (Flores Orozco et al., 2019a; Binley et al., 2015; Cassiani et al., 2014).

Geophysical methods are widely used in the study of solving environmental problems. There are many successful examples in the interpretation of the subsurface (Sumner 1976, Binley 2015, Binley & Slater 2020), identifying the porosity, tortuosity, and clay content (S. Ward 1988, Glover 2015), and determining groundwater remediation (Johnson et al. 2015), contaminant migration (Clément et al. 2010), and groundwater-surface water interaction (Nyquist et al. 2008, A. Ward et al. 2010). This is a significant advantage to understanding and monitoring a contaminated area.

While geophysical methods have these opportunities, there are not enough studies related to the hydrocarbon-contaminated area. Therefore, this study is related to understanding the future
of a contaminated area and monitoring the amount of contamination by using geophysical methods, magnetic susceptibility, and spectral induced polarization.
CHAPTER 2 INVESTIGATING THE SENSITIVITY OF SPECTRAL INDUCED POLARIZATION TO IRON MINERALS INVOLVED IN NATURAL ATTENUATION AT A HYDROCARBON-CONTAMINATED SITE.

2.1 Introduction

Soil pollution negatively impacts human beings and is a growing threat to the health and quality of the environment (Abdel-Shafy and Mansour, 2016). Hydrocarbon pollution, one of the most common and alarming sources of pollutants in the soil, has become more rampant because of activities in the petroleum industry (Marinescu et al., 2011). Leakages from oil pipelines and tanks, as well as emissions from oil refineries, all contribute to hydrocarbon pollution. This contamination may be taken up by plants, including agricultural crops, and can impact groundwater purity by leaching the soils (Rijal et al., 2010). It is essential for human life that the quality of groundwater and soil remains at the level of usability. Therefore, factors that change their quality should be closely monitored.

Identifying the state of hydrocarbon-contamination of the shallow subsurface, often at the hundreds of meter scale with a clear resolution, is a severe problem. Drilling, sampling, and laboratory characterization processes are traditionally used to understand and assess the area (Kingsbury et al., 2021; Trost et al., 2018; Tuccillo et al., 1999). However, hydrocarbon contamination areas are known where biogeochemical processes occur that can cause iron mineral transformation (magnetite, siderite, vivianite, green rust, ferroan calcite) under aerobic and anaerobic conditions (Dippon et al., 2012; Konhauser et al., 2011; Rijal et al., 2010; Prommer et al., 2000; Lovley & Lonergan, 1990; Mortimer & Coleman, 1997). This direct method may disturb the redox-sensitive conditions in the subsurface when a sample comes into contact with oxygen during the sampling and may not represent all the area. Furthermore, the
direct method is limited for some areas, for example, inaccessibility due to ground-surface structures (for example, built infrastructure), hazardous waste sites, and restriction of sampling to protect the environment. Thus, the method can cause the poor estimation of the concentration and of the extension of hydrocarbon plumes and a nonclear contamination map of the area (Cassiani et al., 2014; Algreen et al., 2015; Binley et al., 2015; McCall et al., 2018; Flores Orozco et al., 2019a).

On the other hand, geophysical methods can afford extensive information both laterally and at depth with the required resolution. For example, spectral induced polarization (SIP) method can provide real-time and spatially accurate monitoring and assessment of the processes at the field scale without losing a sample. In this method, the measurements obtained are the electrical conductivity of the ground and the capacitive properties of the subsurface (Binley & Kemna, 2005). It means that the method identifies these physical properties that are indirectly related to contamination. Atekwana and Slater (2009) present a conceptual model of the relationship between geophysical signatures and microorganisms in a hydrocarbon-contaminated area. Figure 1 shows that microorganisms use the carbon source as a nutrient. Microbe-mediated redox reactions occur after microbial growth and proliferation, such as methanogenesis, sulfate-reduction, iron reduction, etc. As a result of mineral dissolution/precipitation, physical and chemical changes occur to the formation. For example, magnetite or iron sulfide can form in the hydrocarbon contaminated area. These minerals have magnetic and electrical properties, which can be identified by using geophysical methods, such as SIP (Figure 1). Many scientists use the induced polarization (IP) method to investigate the iron mineral transformation in the hydrocarbon-contaminated area (Kessouri et al., 2019; Flores Orozco et al., 2019a).
In light of this information, three iron minerals (magnetite, siderite, and HFO) that are common in a hydrocarbon-contaminated area are examined in this article. In addition to the aforementioned minerals SIP anomalies, the response of particular grain radius sizes of magnetite for SIP was analyzed under laboratory conditions.

Figure 1 Relationship Between Micro-organisms at Hydrocarbon Contaminated Sites and Resulting Geophysical Signatures (modified from Atekwana and Slater, 2009).
2.1.1 Project Hypotheses

1) As the magnetite grain radius size increases, the SIP peak frequency will decrease, but the smallest percentile for magnetite at which the anomaly can be received will not depend on the grain radius size.

2) Of the three types of iron minerals studied, magnetite will have the largest phase shift, followed by siderite. Hydrous ferrous oxide-coated sands will not have a significant phase response.

2.1.2 Project Objectives

The primary objectives of this project are:

1. Perform laboratory measurements of the SIP response of magnetite, siderite, and HFO mixed with sands at different volume concentrations.

2. Determine the impact of different grain radius size of magnetite on the SIP response under lab conditions.

3. Discern differences in mineralogy with SIP—for example, conversion of magnetite to other less magnetic minerals, such as siderite.

2.2 Materials and Methods

Iron is the most abundant transition metal in the Earth’s crust (Cotton, 2020). Based on its high surface reactivity and redox chemistry, it has a crucial function during the degradation, mobility, and speciation stages of contaminants (Bjorn and Roychoudhury, 2015). Although having poorly crystalline, iron oxyhydroxides such as ferrihydrite and goethite are the preferred
sources for iron reduction in hydrocarbon-contaminated environments (Villacís-García et al., 2015); however, higher crystallinity minerals such as magnetite can also be used for reduction (Guo and Barnard, 2013; Konhauser et al., 2011). Siderite which is iron carbonate is thought of as a transition mineral in hydrocarbon-contaminated areas.

The materials part of this section mentions how these minerals are formed naturally and in which environments they need to develop. Apart from these natural occurrences, mineral transformations in the hydrocarbon-contaminated area for these minerals is mentioned.

2.2.1 Materials: Magnetite, Siderite, HFO

2.2.1.1 Magnetite

Magnetite (Fe$_3$O$_4$), one of iron's oxides, is the most magnetic mineral in nature. It is naturally formed and settled in as a result of the gradual cooling of magma containing silicate and sulfide or precipitation at lower temperatures in hydrothermal fluids (Dare et al., 2012; Boutroy et al., 2014). It is a common mineral in both igneous and sedimentary rocks. Furthermore, it is well known that the reduction of Fe$^{3+}$ by bacteria contributes to biogenic magnetite produce in sediment and the deep sea (Gibbs-Eggar et al., 1999; Bazylinski et al., 1988; Lovely & Phillips, 1987). In addition to these occurrences, some iron-reducing bacteria can use hydrocarbons as a source of carbon in hydrocarbon-contaminated soil. The biodegradation of hydrocarbon (reduce Fe$^{3+}$ to Fe$^{2+}$) results in the formation of ferrimagnetic minerals (Lovley et al., 2000; Lovley et al., 1989; McCabe et al., 1989), one of which is magnetite. The findings from most scientific research have verified the creation of magnetite in hydrocarbon-contaminated environments. For example, the hydrocarbon microleakage in the oil fields of western Venezuela caused a magnetic anomaly. This anomaly had been proven to be the
result of new magnetite in the field (Aldana et al., 2011). In a contaminated area, the relationship between the groundwater fluctuation zone and magnetite is explained in Rijal et al., 2010. Modelling studies also support a relationship between the groundwater fluctuation zone and magnetite formation (Mortimer & Coleman, 1997).

2.2.1.2 Siderite

Siderite can form as a result of sedimentary precipitate in three types of environments: in hydrothermal veins, in metamorphic rocks, and rarely in pegmatites. It arises from areas where sulfur is less abundant (Glasby and Schultz, 1999). In more detail, the rapidly accumulating, organic-rich, fine-grained, anoxic, non-sulfuric deposits in which CO\textsubscript{2} is formed as a result of the oxidation of organic matter (partly due to the reduction of Fe-oxyhydroxides) are suitable environments for siderite formation (Frederichs et al., 2003). The contribution of biological factors in these processes cannot be denied (Konhauser, 1998; Nealson and Saffarini, 1994).

In a contaminated area, siderite has generally been observed to form under conditions of iron reduction if carbonate is present in the surrounding area (Fredrickson et al., 1998; Kukkadapu et al., 2001; Liu et al., 2001). It is an observation that is increasingly supported by more evidence in a hydrocarbon-contaminated area. The easy conversion of this mineral to iron oxides (Morad et al., 1998) strengthens this claim. For example, some scientists have studied the idea of having siderite in the contaminated area and found siderite inside of Bemidji, MN, hydrocarbon-contaminated area (Bennet et al., 1992; Tuccillo et al., 1999; Zachara et al., 2004).
2.2.1.3 HFO

Ferrihydrite, one of the initial corrosion products in the oxidation of iron takes place by the hydrolysis of ferric species (Fe$^{3+}$) in solution, resulting in a blood-red precipitate (Michel et al., 2007). Two kinds of ferrihydrite, six-line ferrihydrite and two-line ferrihydrite, are conventionally recognized; although, there are many controversies about the structure (Michel et al., 2007). Two-line ferrihydrite is often referred to as HFO (Cornell and Schwertmann 1996).

HFO is a mineral that exhibits considerable disorder (Gilbert and Banfield, 2005) and is common in many natural environments (Cornell and Schwertmann, 2003), so it can be generally considered the dominant electron acceptor. Even if ferric iron has a surface barely soluble electron acceptor, iron-reducing bacteria solves this problem to use three different strategies to transfer electrons from a cell to the surface: 1) physical contact between cell surface compounds and ferric iron, 2) iron chelator, which increases the solubility, and 3) electron-shuttling compounds (if physical contact is not possible) (Hernandez and Newman, 2001; Lovley et al., 2004). Due to the reasons mentioned above, ferrihydrite, for Fe$^{3+}$-reducing microorganisms, is used extensively in laboratory studies, and it can come up as a product in cultures of Fe$^{2+}$ oxidizers (Kappler and Straub, 2005). For a contaminated area, it is considered a source of bioavailable Fe$^{3+}$, and magnetite is one of the possible products of its reduction (Porsch et al., 2010).

2.2.2 Spectral Induced Polarization Method

It is discovered that the IP effect reveals the degree to which the subsurface can store electric charge, analogous to a leaky capacitor. To put it more clearly, Schlumberger (1920) explains that while an electric current passes through rock or soil, if the current is interrupted, a
difference in potential, which decays with time, is occurred. The lithology of the rock, its pore geometry, and the degree of water and hydrocarbon saturation can change the rate of this potential (IP potential). Also, physicochemical processes, such as redox reactions, can cause disseminated iron minerals to occur, and this process contributes to the IP effect (Bucker et al., 2018; Placencia-Gómez et al., 2013; Wong 1979; Angoran and Madden 1977; Marshal & Madden 1959).

SIP is an extension of the conventional IP method to cover a range of frequencies. The SIP method is a technique in which an alternating current is injected, and measurements of the impedance \( Z \) and phase shift \( \varphi \) between the current and voltage and amplitude are measured. Measurements at different frequencies are defined in terms of a complex conductivity \( \sigma \):

\[
\sigma(\omega) = \rho^{-1}(\omega) = \sigma'(\omega) + i\sigma''(\omega) \tag{2.1}
\]

where \( \rho \) is the complex resistivity,

\( \sigma' \) is real conductivity,

\( \sigma'' \) is imaginary conductivity,

\( \omega \) is angular frequency,

\( i = \sqrt{-1} \)

In SIP measurements, \( \varphi \) and \( Z \) are obtained over a range of frequencies. A phase shift means that the sinusoidal electric current injected into the medium and the measured voltage are at different points of their cycle at any given time. It is measured as the angle (in radians)
between these two points (injected current and measured voltage) on a circle simultaneously. The ratio of the voltage amplitude to the current amplitude defines the impedance magnitude. The impedance ($Z$) multiplied by the geometric factor (units of m) is the magnitude of complex electrical resistivity $|\rho|$, hence the conductivity magnitude $|\sigma|$:  

$$|\sigma| = \frac{1}{|\rho|} = \frac{1}{Z \times K} \quad (2.2)$$

The real and imaginary parts of the complex conductivity are given by,

$$\sigma' = |\sigma| \cos(\varphi) \quad (2.3)$$

$$\sigma'' = |\sigma| \sin(\varphi)$$

When SIP is measured on a rock or soil that includes iron minerals, the phase shift is considerably greater than the native rock and is often characterized by a specific peak (Figure 2).
The peak is close to symmetric, as shown in Figure 2. In this example, magnetite is 3% of the total sample holder volume (0.7 mm mean grain radius)-sand mixture saturated with 0.0588 S/m groundwater. This peak is called the frequency peak point \( f_{\text{peak}} \).

**Figure 2** Impedance and conductivity magnitude of the mixture of which 3% of the total sample holder volume is magnetite, with a pore fluid conductivity of 0.0588 S/m. The square represents the conductivity magnitude, and the triangle is the phase shift.

\[
y = f(x) = ax^2 + bx + c
\]

\( f_{\text{peak}} \) can be determined by the maximum of a polynomial equation of points around the peak of the phase shift:

\[
\frac{-b}{2a} \quad \text{is equal to } f_{\text{peak}} \quad \text{and} \quad \frac{4ac-b^2}{4a} \quad \text{is the maximum phase shift value in the experiment.}
\]
The relaxation time ($\tau$) that is associated with distinct polarization processes in porous media can be identified in different ways. One approach is to directly define it from $f_{\text{peak}}$ (Revil et al., 2015),

$$\tau = \frac{1}{2\pi f_{\text{peak}}}$$ (2.5)

Pelton et al. (1978), Peltoniemi and Vanhala (1992), and Siegel et al. (1997) are early studies focusing on the idea of differentiating the mineral composition of metallic particles and the ore texture from SIP relaxation spectra. New theories have since been put forward in light of these studies. Gurin et al. (2015) proposed a simple empirical model to describe how grain size ($r^2$) and pore fluid conductivity ($\sigma_w$) affect the relaxation time for polarization of electron-conducting minerals:

$$\tau = a_s \times \left(\frac{r^2}{\sigma_w}\right)$$ (2.6)

where $a_s$ depends on particle mineralogy and surface chemistry and is termed the specific volumetric capacitance of the rock (units of Fm$^{-3}$). In this study, this semi-empirical equation will be examined in detail.

The Wong Electrochemical Model (1979) describes the SIP response of a medium containing disseminated electron conductors saturated with an electrolyte using eight parameters.
Geometrical parameters are amongst the eight, including the diameter and the volume concentration of the particle.

The chargeability has been defined (Binley & Slater, 2020; Saneiyan, 2019; Revil et al., 2014; Binley & Kemna, 2005; Ward, 1988; Wong et al., 1979; Pelton et al., 1978) by using the low frequency ($\sigma_L$), and high-frequency ($\sigma_H$) values of the conductivity, as shown in Figure 2. Wong (1979) developed a model where the chargeability ($m$) depends solely on the volume fraction of the electron-conducting particles ($v$) in the case of an unpolarizable matrix,

$$m = \frac{\sigma_H - \sigma_L}{\sigma_H} = \frac{9v}{(2 + 5v + 2v^2)} \quad (2.7)$$

By means of this equation, metallic content ($v$) can be predicted from the asymptotic values of the conductivity (Wong, 1979).
2.2.3 Column Set Up

![Image of SIP columns with electrodes and tubing](image)

**Figure 3** a SIP column with electrodes b) SIP columns and tubing, groundwater bottle which was covered with the folio and conductivity meter and pump used for the experiment.

Synthetic magnetite in five different radius sizes for measurements: 0.7 mm, 0.4 mm, 0.1 mm, 0.05 mm, 0.02 mm were used. Siderite (BOC Science brand), HFO and clean sand (Fisher brand) were limited to the only grain radius size available in the laboratory, 0.1 mm.

After preparing the minerals, clean sand was mixed with minerals to provide the disseminated iron mineral particles. To avoid an uncertainty associated with differences between samples and sample holders, measurements were taken with the same sample and sample holders (e.g., Slater and Lesmes 2002; Breede et al. 2011). In addition to this precaution, to get more consistent measurements, the volume of the sand (55g) was kept constant, and measurements were taken by adding iron minerals due to volumetric calculations. To saturate the sand-iron mixture, the groundwater, which came from Bemidji hydrocarbon contaminated well 533, was utilized. The information for groundwater sampling and usage is explained in section 2.2.4.
The mixture was compressed into the sample holder with a suitable tool so that the sample could be tight without shaking it. This process aimed to obtain more accurate and repeatable results (Kemna et al., 2012), and it succeeded. Before starting the measurements, the graphite electrode and the Al-Al electrode were compared to each other, and there were no differences observed for the measurement. The graphite electrode was used for all measurements in this study. The temperature was controlled and was kept constant (25 °C) in the lab.

pH and the conductivity of the groundwater were recorded every measurement day. Information on water conductivity, temperature and pH measurement during the SIP process can be found in section 2.2.5.

The SIP of four samples were studied simultaneously, and the clean sand holder was the background for each of the four samples. To give an example, 1% magnetite, 1% siderite, and 1% HFO and clean sand measurements (total four measurements) went through at the same time. After that, different grain size magnetite measurements followed the same procedure.

The current resistor was 100 Ohms, and the number of steps was 36. The amplitude was 5 Volt. Those were the same inputs for all experiments. For all-grain sizes, 35 frequency between 0.01 and 10000 was tested, and this frequency range was constant for all measurements. However, the range of frequency for 0.02 mm magnetite was different. Five measurements for 0.02mm; for 0.09 %, 0.19 %, 0.39 %, and 0.78 %, 1.56 % the frequency was between 0.01 Hz to 10000 Hz. After that, it was chosen between 0.01Hz and 50000 Hz for 3.2 %, 5 % to visualize the peak point as more accurate. Each measurement was repeated at least twice. It has been observed that the margin of error from repeated measurements was smaller than 2% for impedance and 1% for phase shift if the measurements were reliable. Especially in siderite measurements, these reliable repetitions were of great importance to ensure that the sample
reached saturation. It was clear that as the percentage of siderite of the sample increased the waiting time for the chemistry in the column to equilibrate.

2.2.4 Groundwater Sampling and Usage

Groundwater from the Bemidji, MN hydrocarbon-contaminated area (well 533E) was taken to saturate the sand mixture. This water had a heterogeneous texture with red particles on the bottom of the bottle. After obtaining groundwater, it was stored in the bottle, not in contact with air and light and labelled date and well name. These bottles were put in the big box with ice and shipped at 4 °C to Rutgers Newark laboratory to use for the SIP measurements as a saturation fluid.

Four holes were drilled into the cap of these bottles for pipes, and the liquid transfer was obtained with these holes at SIP measurements. Groundwater contact with air and light was restricted on the measurements process as possible.

2.2.5 Water Conductivity, Temperature, and pH on SIP Process

The conductivity of groundwater waiting in the refrigerator (5°C) was approximately 0.060 S/m. After one day of rest in the laboratory (25°C), the conductivity value increased to 0.065 S/m, and after that, no change was observed. The rested groundwater was used with only sand to understand how to change its conductivity for the clean sand. Although the conductivity of the effluent increased slightly at first, it remained almost constant after one hour of waiting. The groundwater conductivity was recorded for input and output values at every measurement day. At iron-sand mixture measurements, for smaller percentages (0.007%-0.09%), there were no significant differences in conductivity of input and output groundwater (except sand conductivity change).
Nevertheless, bigger percentages iron sand mixture had an increase in the conductivity of output groundwater. However, it was noted that the fine grain size (0.045 mm) affects the output groundwater even if smaller percentages. Since the holes in the mesh covering the sample were larger than 0.02 mm, it could be interpreted that magnetite of this grain size may have passed through it.

Groundwater conductivity varied between 0.0423 and 0.0939 S/m throughout the measurements.

The room temperature was kept at 25°C during all measurements, and the pH value was recorded for each one. pH changed between 6.4 and 8.8 through the process.

2.3 Results

SIP results of different radius sizes (0.02mm- 0.7 mm) and different percentages (0.09-5 %) of the magnetite could be seen in Figure 4. Even though the measurement was started with 0.007 % by volume; the formation of a peak point for magnetite was obtained with 0.09% by volume, which was different from the sand conductivity (background). Figure 4-a shows 0.02 mm grain radius size, which has the most remarkable phase shift and the highest frequency. As the grain size enlarged, the peak frequency value and the phase shift value decreased. For example, the grain size of 0.7mm (Figure 4-e) could be compared to the grain size of 0.02mm (mixture of 5%); the $f_{\text{peak}}$ for 0.7mm magnetite was 39.81 Hz, and relaxation time is $2.52 \times 10^{-5}$ s whereas these values were 9999 Hz and $3.9 \times 10^{-3}$ for 0.02 mm magnetite. As expected, as the percentage of the magnetite increased, the phase shift of the sample increased. Overall, high-frequency dispersion for small particles, which is more representative of biogenic magnetite, may be limited for field applications (Figure 4).
Fluid conductivity was crucial for the real conductivity. On days when the higher fluid conductivity was recorded, the real conductivity values as a result of the SIP measurement were also higher, without being affected by the amount of magnetite (Figure 5).
Figure 4 SIP measurement results for different radius size of magnetite minerals a) 0.02-milimeter, b) 0.05-milimeter, c) 0.1-milimeter, d) 0.4-millimeter, e) 0.7-millimeter. Groundwater conductivity varied between 0.0423 and 0.0939 S/m.
Figure 5 Real conductivity measurement results for different radius size of magnetite minerals a) 0.02-milimeter, b) 0.05-milimeter, c) 0.1-milimeter, d) 0.4-milimeter, e) 0.7-milimeter. Groundwater conductivity varied between 0.0423 and 0.0939 S/m.
HFO and siderite percentage results are shown in Figure 6. Figure 6 – a represents the HFO which was less conductive than siderite. Significantly, 1.5% by volume was the lowest value obtained for both minerals, different from the conductivity of sand, and this value was very close to each other for siderite and HFO. Though it was not shown in this study, 5% and above siderite had a bigger phase shift value than 5% HFO. On the other hand, increasing the percentage amount increased the MS value of HFO less.

Even though there was no peak point as it was in magnetite for HFO and siderite, the phase shift value lightly increased with the increasing percentage of minerals in the mixture. This increment was considerable in siderite after 3%. Higher percentages results were also used to make this inference, but they were not shown in this study.
Figure 6 SIP measurement result for various minerals with different percentages comparison of them. a) between 1.56%-5 % by volume sand HFO mixture, b) between 1.56% - 5 % by volume, sand siderite mixture. Their saturation fluid conductivity varied between 0.0743 and 0.0770 S/m through the measurement

The phase shift values of three minerals (at 0.1 mm radius size for all) used in this study were demonstrated in the same graph in Figure 7. As was known, magnetite was the dominant mineral and had a phase shift value far above the siderite and HFO values. The smallest phase shift values belonged to HFO and were slightly lower than siderite.
Figure 7 Comparison of 1.56 % by volume HFO, siderite and magnetite, which were all the same radius size - (0.1-millimeter). Their saturation fluid conductivity was 0.0749 S/m through the measurement.

Many scientific studies prove that the chargeability increases with the particle content increase (Gurin et al. 2013; Slater et al. 2005; Pelton et al. 1978). Figure 8 displays how chargeability depends on the volumetric particle content in this study. Wong’s prediction for a non-polarizing matrix is symbolized with a black line, and colored symbols represent the different percentages of magnetite minerals.

Wong fit is obtained by using Formula 2.7. The products of these studies validate Wong’s prediction. However, as the percentages of the magnetite decrease, the data coherency for Wong’s prediction reduces, such as 0.09% data. Furthermore, as a result of applying Formula 2.7 to this magnetite data, it appears that the increase in chargeability with decreasing radius size is not very significant. However, as the radius size increases, a slight decrease in chargeability is observed at higher volume contents (5% and above).
Figure 8 Dependence of chargeability on the concentration of magnetite (with different radius size). Graph representation and fit to Wong’s (1979) prediction for a non-polarizing matrix. Radius is 0.7mm, 0.4mm, 0.1mm, 0.05mm, 0.02mm. Fluid conductivity is given above in Figure 2. Solid line shows Wong’s fit, obtained by using the volume fraction of magnetite.

The relaxation times of the magnetite minerals depending on the radius are represented in Figure 9.

Relaxation time was obtained from Formula 2.5, and groundwater resistivity was multiplied with radius square for axis X. In that way, the volumetric capacitance coefficient can be obtained, and from the graph, this coefficient was determined as $4.6 \times 10^2 \text{ Fm}^{-3}$. However, $a_s$ was varied between $7 \times 10^2$ and $3 \times 10^3 \text{ Fm}^{-3}$ for Gurin (2015), and $a_s$ obtained from Slater (2006) data was $3 \times 10^2$.

As many studies supported (e.g., Gurin et al. 2013; Mahan et al. 1986; Grissemann 1971), there was a linear correlation between grain size and relaxation time; in other words, as the radius size increased, the relaxation time had a higher value in this study.
Figure 9 Relaxation time versus radius square multiplied by water conductivity. The dark red line is high limit $3 \times 10^3$, and the light red line is low limit $7 \times 10^2$ for Gurin (2015) as.

2.4 Discussion

Laboratory experiments were conducted using clean sand mixed with known magnetite, siderite, and HFO concentrations. Measurements were limited to 5%, just over 2%, representing the magnetite concentration found in natural environments (Thompson & Oldfield, 1986). The results showed that the phase response increased with the increasing metallic content. However, Samuel (2016) added 1% magnetite in the Bemidji hydrocarbon contaminated area soil and took SIP measurements. She claimed that the addition of magnetite did not impact the phase in SIP, while our results showed that even 0.9% magnetite has a phase response. This result may be due to the field soil structure being much more complex than clean sand or the non-compliance with
the procedures mentioned by Slater and Lesmes 2002, and Breede et al. 2011. When these two situations are compared, it is seen that validating this study with sand taken from the natural environment will be more efficient for field studies. In Samuel (2016) experiment, two artificial solutions with the highest and lowest conductivity value belonging to the Bemidji field was used for saturation. Our study confirmed that real conductivity was more affected by saturation fluid conductivity, not mineralization, as Samuel claimed (can be seen in Figure 5).

The chargeability of magnetite sand mixtures increased linearly as in previous studies (Gurin et al., 2013; Nordsiek & Weller, 2008; Slater et al., 2005) with the increase of the metallic particle content (Figure 8). Moreover, the results were consistent with the Wong model (Figure 8). As a result of these facts, we can say that the results obtained were consistent.

The fact that the metallic grain radius controls the relaxation time is undeniable. On the other hand, there was a discrepancy between the $a_s$ information that Gurin found separately for each material and the results obtained for magnetite from this study. Gurin claimed that $a_s$ varies between $7 \times 10^2$ and $3 \times 10^3$ Fm$^{-3}$ for magnetite, whereas the results of this study show that as were not in this range and indicate a smaller number ($4.68 \times 10^2$), as can be seen in Figure 9. The first probability is that $a_s$ can change depending on the shape of the material. The second probability could be that while the $a_s$ range in this formula is more suitable for smaller grain sizes, the range may need to change $a_s$ the grain size increases. The Figure 9 shows that 0.02mm gave a consistent result with this interval. This difference for $a_s$ is crucial as it may cause misinterpretations in estimating grain size using Formula 2.6.

I need to stress that a critical aspect of the SIP study and testing of the Wong and the Gurin models is that I applied the models to a very small range of particle size - and showing that they can fit these small ranges of volume concentration.
SIP data can potentially shed light on the magnetite content and morphology of different grain sizes and distinguish them from conventional iron minerals with the help of their unique frequency response. As supported by the results of this study, previous studies in lab-scale (Personna et al., 2008; Ntarlagiannis et al., 2005;) and field scale (Williams et al., 2007b) validate that the potential exists to employ the SIP method to monitor a contaminated area.

Although it is not certain, there is a judgment that the magnetite grain size in the contaminated area is nanoscale. This may limit the use of the method in the field since the SIP method used at high frequencies have some problems.

2.5 Conclusion

To better understand the contaminated area and using SIP response, I analyzed clean sand mixture with three potential compounds (magnetite, siderite, and HFO) of hydrocarbon-contaminated environments. SIP data was measured for different volume contents of magnetite, siderite, and HFO and various radius sizes of magnetite. As expected, the SIP peak frequency decreased when the magnetite grain radius size increased, but the smallest percentile for magnetite at which the anomaly could be obtained did not depend on the grain radius size. Moreover, magnetite had the most considerable phase shift for the second hypothesis, followed by siderite, of the three types of iron minerals studied. HFO-coated sands had a minor phase response compared to others.

In this study, I examined homogenous mixtures of magnetite-sand, siderite-sand, and HFO-sand for different percentages of the minerals, and different percentages of various magnetite grain sizes by using SIP. Also, a quantitative comparison of three minerals was showed. In future work, it can be tested for a heterogeneous mixture of the mineral-sand instead
of the homogenous mixture of them. To be more clear, specific percentages of minerals can be
deposited in the specific place of the sample holder and other parts of the sample holder can be
filled up with the sand instead of the homogenous mixture, and the response of SIP can be
compared to homogenous mixture. Furthermore, different minerals can be mixed and studied,
such as magnetite-HFO-sand, magnetite-siderite-sand, siderite-HFO sand mixture for SIP
response. Lastly, magnetite pieces that are, at least, two different grain sizes can be mixed with
sand and analyzed. Merge of 0.7mm magnetite-sand mixture with 0.4 mm magnetite sand
mixture at specific percentages can be an example.

This study showed that a scientific prediction could be made on the magnetite grain size
and percentage in the field by using SIP. This could be used as pioneering work to investigate
mineral transformations associated with hydrocarbon degradation in places like Bemidji, MN. In
such regions, which are observed for a long time, where magnetite formation occurs more, or
decreases can be determined by periodic SIP measurements. Furthermore, knowing which part
has the most magnetite can help collect more efficient samples for chemical experiments. This
method can also be used to determine the degree and boundary of contamination by comparing
measurements of the contaminated area and the surrounding uncontaminated area.
CHAPTER 3 IRON MINERAL TRANSFORMATION AT A HYDROCARBON CONTAMINATED LONG-TERM RESEARCH SITE INFERRED FROM MAGNETIC SUSCEPTIBILITY

3.1 Introduction

Water is used in all biological life and all human activities, from smallest organism to the largest living creatures. Ninety-seven-point five percent of the water resources on earth consist of saltwater and 2.5% fresh water. Sixty-eight-point seven percent of the freshwater consists of glaciers while 29.9% of it is groundwater. Surface water resources such as lakes and rivers cover only 0.26% (Shiklomanov, 1998). Based on this information, it is seen how important groundwater is to obtain fresh water. In the United States, the use of groundwater as a source of drinking water is more than 25% (Dieter et al., 2018). Therefore, it is essential for human life that the quality of the groundwater remains at the level of usability.

Hydrocarbon contaminated media has a negative effect on soil productivity and plant growth (Kayode et al., 2009; Wild et al., 1991); in addition, this pollutant may cause major threats to groundwater resources through leaching the soils (Rijal et al., 2010). On the other hand, hydrocarbon contamination areas, which result from human activities, such as petroleum production and refining, hydraulic fracturing, underground storage tanks, and pipeline ruptures, can be found all over the world. After the oil/fuel seep the subsurface, it creates a series of degradation intermediate compounds that are more polar than the basics hydrocarbons from which they are derived, and as a result of these, biodegradation starts (Podgorski et al., 2018; Islam et al., 2016; Zemo et al., 2013). This biodegradation of hydrocarbon might lead to the formation of oxidation processes that are more toxic than the main contaminant (Tian et al.,
or can help to remediate contaminated soil (Bekins, 2019; Cozzarelli et al., 2001). In these subsurface, biogeochemical activities such as combining electron acceptors and electron donors occur in the ground water table fluctuation zone (GWTF) which is one of the classic environmental transition environments. It is well known that during the biodegradation of oil, ferromagnetic minerals are formed (McCabe et al., 1989) and this process progresses even faster with the help of soil microorganism (Borch et al., 2010; Hamamura et al., 2006; Lovley et al., 1989).

Lovley et al. (1989) hypothesizes that some bacteria can reduce Fe$^{+3}$ to Fe$^{+2}$ by using hydrocarbons as carbon sources and hence magnetite can be created, which is consistent with the findings of other studies (Dippon et al., 2012; Konhauser et al., 2011; Rijal et al., 2010; Prommer et al., 1999a; Lovley & Lonergan, 1990; Mortimer & Coleman, 1997). These scientists conclude that existing magnetite seeds set off further magnetite formation during oxidation of Fe$^{+2}$ by bacteria (Dippon et al., 2012) in the neutral pH (6.5-7) (Konhauser et al., 2011), and anaerobic (Lovley & Lonergan, 1990) or aerobic (Kappler and Straub, 2005) conditions. The amount of magnetite formation is in direct proportion to hydrocarbon and inversely with groundwater, and as a result, the strongest bacterial activity occurs at the top of the GWFT (Rijal et al., 2010); this produced magnetite is ultrafine (Mortimer & Coleman, 1997). Both organic and inorganic contaminated areas are associated with iron transformation (Thamdrup 2000; Straub et al. 2001; Cornell and Schwertmann 2003). This strong influence of iron transformation must be monitored to understand and remediate the contaminated environment.

The geophysical response of hydrocarbon-contaminated area has been tested many times in the field and in the laboratory. (Kaufmann and Deceuster, 2007; Yang et al., 2007; Atekwana et al., 2005; Halihan et al., 2005; Atekwana et al., 2004a, b, and c; Werkema et al., 2003).
Therefore, geophysical signatures can be used to monitor the natural attenuation of oil spills. Atekwana & Slater (2009) interpret a diagram to summarize the relationship between geophysical signatures and microorganisms in a hydrocarbon-contaminated area. In Figure 1, it explains that microorganisms use the carbon source as a nutrient. After microbial growth and proliferation, microbe-mediated redox reactions occur, such as methanogenesis, sulfate-reduction, iron reduction, etc. As a result of the mineral dissolution/precipitation, it is observed that physical and chemical changes occur in the formation. For example, magnetite or iron sulfide can emerge in the hydrocarbon-contaminated area. These minerals have electrical and magnetic signals which can be identified by using geophysical methods, such as magnetic susceptibility.

3.1.1 Use Of Novel Mineral Packets To Investigate Iron Mineral Transformations

Because of bacterial activities, and long-term migration of hydrocarbon, this hydrocarbon-based alteration is highly complex. Many techniques are used to monitor and understand the area, such as soil carbonates methods, magnetic and electrical methods, radioactivity-based methods, and remote sensing methods (Schumacher, D., 1996). Kappler and Straub (2005) set up an environment for observing the iron transformation that bacteria cause, but his results suggest that monitoring this conversion is difficult in laboratory conditions. He explains the poor growth of many iron-metabolizing bacteria could be because bacteria need complex natural systems that host a wide variety of microenvironments.

Furthermore, Baedecker et al. (2018) results show that "starting oil concentration" cannot be used to monitor processes that impact its fate and the transport of hydrocarbons in groundwater after being in a subsurface for a few years in Bemidji, MN. Because of these types of problems, a new approach is necessary to monitor the hydrocarbon contaminated areas.
One of the main subjects of this thesis is the usage of mineral packet, which is the new method to interpret the future of the contaminated area. In the usual methods, a sample is taken from the field and this sample is examined with chemical and physical experiments and compared with the sample of the non-contaminated region, and anomalies are interpreted. However, in this new method, the sample prepared in the laboratory are placed in the contaminated area and uncontaminated area. Magnetic sensitivity measurements are taken at certain periods, and the magnetic changes of the minerals, based on the iron transformation, are observed.

To better understand the iron transformation at a hydrocarbon-contaminated area, two hypotheses for MS method will be explored in this thesis.

3.1.2 Project Hypotheses

The hypotheses that will be explored in this project are:

1) The MS of mineral packets installed in the smear zone of the hydrocarbon-contaminated wells and the MS of cores retrieved at different times will change due to iron mineral conversions between ferrihydrite, magnetite and siderite.

2) Changes in MS with time will be large close to the spill site, largest where recharge is focused within the spill zone and smallest in uncontaminated locations.

3.1.3 Project Objectives

The primary objectives of this project are:

- Defining the relationship between the three minerals, at different sizes and content, with MS signals.
▪ Determine the impact of mineral size on MS for different sizes of magnetite and HFO under lab conditions.


▪ Measure MS on cores taken in three different years (2013, 2014, 2016, 2017 and 2019) and compare them to each other to see how MS changes with time.

▪ Repeat MS measurements on 2019 cores three to four times over an 18-month period to see if the MS changes with time.

▪ Capture any changes (at mineral packets that are suspended in four wells) at MS over time due to the transformation of iron minerals.

▪ Compare changes in MS on the iron mineral packets against mineralogical and detailed rock magnetism changes observed by collaborators from the University of Delaware.

3.2 Methods

3.2.1 Groups of Magnetic Susceptibility

All materials are magnetized to some degree when subject to an applied magnetic field. However, depending on several factors, such as the atomic and molecular structure of the material, and the net magnetic field associated with the atoms, they can react quite differently. By looking at the behavior of materials, magnetism can be classified into the following five major groups: ferrimagnetism, ferromagnetism, paramagnetism, diamagnetism, antiferromagnetism.
**Ferrimagnetism:** Neighboring magnetic domains align in opposite directions. In normal conditions, these opposing directions should reduce the effect of the overall magnetic field of material, but in ferrimagnetic materials, such as magnetite, an induced magnetic field is possible due to the small differences between neighboring domains (Goldman, 2006).

**Ferromagnetism:** When exposed to a magnetic field, ferromagnetic materials show a strong magnetization, and even when the external field has been removed, they can retain their magnetic properties. The elements of iron, nickel, cobalt, and many of their alloys experience ferromagnetism (Coey, 2010). Magnetic domains for these elements line up parallel to each other and in the same direction to produce a strong permanent magnet.

**Diamagnetism:** When a diamagnetic substance is exposed to a field, a negative magnetization is produced, and as a result, the susceptibility is negative. An example of this is quartz (Hrouda & Kapička, 1986).

**Paramagnetism:** This is similar to diamagnetism; the magnetization is zero when the field is removed. In the presence of the field, a net positive magnetization and positive susceptibility can be observed. Examples include siderite at room temperature (Pan et al., 2000), and vivianite (Dong et al., 2000; Karlin and Levi, 1983).

**Antiferromagnetism:** Magnetic domains line up in opposite directions with exactly equal moments. As a result, the net moment is zero. An example is Hydrous Ferric Oxide (HFO) at room temperature (Wu et al., 2011).

### 3.2.2 Magnetic Susceptibility Method

MS quantifies the degree of magnetization of a material when a magnetic field is applied. The MS is denoted as a volume-specific susceptibility ($K_m$) or a mass-specific susceptibility ($X$).
The volume specific MS of material $K_m$ (dimensionless), is equal to the ratio of the magnetization $M$ within the material to the applied magnetic field strength $H$,

$$K_m = \frac{M}{H} \quad (3.1)$$

Mass-specific susceptibility $X$ is derived by dividing $K_m$ by the bulk density of the sample ($p$),

$$X = \frac{K_m}{p} \quad (3.2)$$

Mass susceptibility measurement can provide more accurate results for the MS of sediment content because it accounts for variations in the bulk density of the sample (Lascu, 2009). However, according to the Bartsoft Manual MS2_OM0408, cores captured in core liners can include gas and water pockets or have gaps resulting from the coring process. Unless the material is compacted at great pressure, these issues can impact the mass MS measurement. Therefore, when samples were prepared as identical, or there is no option to dry these samples, it is recommended to measure $K_m$ to facilitate comparison between samples. Conversion of $K_m$ to $X$ may be possible, whereas converting $X$ to $K_m$ may be inaccurate in some cases because of compaction issues (i.e., gas, air gaps and water retained during the coring process).

Conversion of volume susceptibility to mass susceptibility is explained for the case of water example in Dearing (1999). A 10 cm$^3$ volume pot is filled with water, and $K_m$ obtained, being $-0.9 \times 10^{-5}$ SI (International system of units, abbreviated from French, Systeme International). The bulk density of water in SI units is 1000 kg m$^{-3}$. Using Equation 3.2, $X$ is equal to $0.9 \times 10^{-8}$ m$^3$ kg$^{-1}$.  

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Mineral packets have been subjected to some preparations so that the MS measurements can be consistent.

The studies were divided into two parts: laboratory studies and field studies. First, experiments were conducted in the laboratory to decide what material and how much to put in the mineral packet. After deciding on the type and amount of mineral in a mineral packet, long-term MS measurements were started in the field.

3.2.3 Laboratory Studies

MS measurements were made on different magnetite grain sizes and a certain percentage of iron minerals (magnetite, siderite and HFO) to decide which mineral grain size and the amount was more suitable for the experiment. Grain sizes of magnetite that were used for this purpose were 1.4 mm, 0.8 mm, 0.26 mm, 0.11 mm, 0.075 mm, 0.045 mm. However, HFO and siderite were restricted to a single grain size (0.26 mm) available in the lab. Amounts of minerals between 0.007% to 100% (0.0007%, 0.0014%, 0.0028%, 0.0056%, 0.011%, 0.022%, 0.045%, 0.09%, 0.15%, 0.35%, 0.75%, 1.5%, 3.5%, 5%, 6.125%, 12.5%, 25%, 50%, 100%) were tested for the experiment.

The methods described in Zachara et al. (1987) and Szecsody et al. (1994) were used to obtain HFO (2-line ferrihydrite) coated sands. Also, ferrihydrite notes described in Brooks et al. (1996) have been considered. Ferrihydrite-coated sand was constituted by using (Fisher brand) clean sand and (Fisher brand) Ferric Chloride (FeCl₃ 6H₂O). After preparing each mineral type, the clean sand was mixed with these minerals to provide the disseminated iron mineral particles. In all experiments (laboratory studies and field studies), the volume of the sand (150 g) was kept constant, and MS measurements were taken by adding specific minerals (magnetite, siderite and HFO) to reach the desired volumetric concentrations. The sand-mineral mixtures were
compacted with a suitable tool into a PVC pipe so that the samples were tight for each measurement and were not affected by shaking during the measurement. Different $K_m$ results were obtained from the experiments performed for the same point initially due to the shaking of the PVC during the measurements and the fact that the material was not tight. Experience has proven that measurements made on compacted mineral packets without shaking gave the same results. So, this compression process was applied to all samples.

In addition to this, all measurements were repeated three times at three different points (5 cm, 6 cm, and 7 cm, corresponding to the middle of the 12.5 cm pipe) in order to understand the effect of small changes in the measurement point on the PVC pipe while measuring the MS. In other words, nine measurements were taken from three different points of the PVC pipe.

These measurements were acquired to understand how the variation of the measuring point on the PVC pipe affects the results. These measurements also helped to understand how the $K_m$ results obtained from different points on the PVC changed as the percentage of minerals in the mixture increased. For example, the measurements taken from 3 different points on the PVC in 0.007% magnetite measurement results differed considerably, while 3% and more magnetite $K_m$ results were almost the same. It describes the resolution of the setup. As a result, 5% magnetite with a 0.8 mm grain size and 20% HFO (0.25 micron) was selected for the mineral packets deployed in the field experiment.

3.2.4 Field Studies

After deciding the mineral grain size and amount, three 156 cm long PVC pipes were prepared to hold the mineral packets. These pipes were drilled at regular intervals (2.54 cm=1 inch) to facilitate groundwater flow. Upon completion of all laboratory work, all necessary materials (PVC pipe, mineral-magnetite, siderite, HFO-, mesh for mineral packets) were shipped
to the Bemidji site. In order to minimize shaking after assembly, Bemidji State University collaborators packed the PVC pipes in the field. Before setting up the mineral packets, 30 cm of sand was filled at the bottom of a 156 cm long PVC pipe. Sand (2.54 cm thickness) was added to separate the 12.5 cm HFO and magnetite (mineral packets) within the PVC pipe. After repeating this process three times, the top of the PVC pipe was filled with sand (30 cm of sand at top and bottom, Figure 10). A total of three PVC pipes were prepared as identical, and 32 mineral packets (11 magnetite, 13 HFO, 8 sand) in these 3 PVC pipes were placed in the Bemidji hydrocarbon contaminated area. In Appendix 1, it was given in the table at which depths the mineral packets were placed and their relationship with groundwater.

To summarize, the mineral packets installation procedure in the field:

1) Mineral packet mixes were created in the laboratory.

2) Materials required for mineral packet (PVC pipe, mesh, sand, and iron-sand mixtures) in Figure 10-a-b were transported to the Bemidji field.

3) Mineral packets were assembled in the field (Figure 10-d).

4) Mineral packets were deployed in wells.

As a note, during the installation of the mineral packets, small magnetite particles accidentally migrated into the HFO mineral packets, so the MS measurements in the HFO mineral packets could not be made properly. Additionally, mineral packets in borehole 310 had a
filling issue. There was a gap between the mesh and the PVC pipe. Accordingly, a correction was applied to all the measurements of mineral packets in 310.

Figure 10 a) PVC arrays (mineral packets) constructed for suspension in wells at the Bemidji field site b) mesh used to keep the mineral packets separated from each other c) mesh divided area d) schematic of the four pipes.

The aims of these laboratory studies can be listed as follows section.

3.2.5 Magnetic Susceptibility Measurement Purposes

MS measurements were performed for three purposes:

1) Checking the accuracy and precision of measurements,
2) Identifying MS response of different minerals (magnetite, siderite, HFO) and the suitable grain size of and percentages of the magnetite for the suspended mineral packets, and

3) Monitoring anomalies in cores retrieved from the field and suspended mineral packets, periodically.

Some external factors can affect the measurements, so temperature changes, PVC pipe diameter differences, different iron mineral responses should be analyzed,

3.2.6 External Factors

Due to the prolonged measurement (more than two years), factors such as the temperature of the environment, the core diameter as an input for the instrument, and the measurements that should be taken from the same location can affect the accuracy and precision of MS measurements. Therefore, these parameters were tested under laboratory conditions.

3.2.6.1 Temperature Change Analysis for MS

In the operational manual for MS2 Magnetic Susceptibility System (OM-0408/50), it was written that the device and the sample must be at room temperature to equilibrate thermally. In this project, the mineral packets would have been suspended underground for a long time (more than two years), and measurements would have been taken monthly, so the temperature would likely change. In this case, it should be tested how the device responds to field temperature conditions. (Dearing, 1994) For this, various measurements were taken in three different environments using a sample with a known magnetic sensitivity value.

In order to observe the effect of temperature change, which was the most significant variable parameter in this measurement, the device was tested for -5°C, 0°C, and 25°C. These
temperature values were chosen because they were the same as the temperature values of the
days when MS measurements were taken at the Bemidji site. In the first experiment, while the
measuring device was in a room at 25°C, four experiments were done by changing the
temperature values of the sample. In the first experiment, the sample was observed at 25°C. In
the second experiment, the sample was held at 0°C for two hours, and then the measurement was
made. In the third experiment, the measurement was taken after the sample was preserved at -
5°C for two hours. In the last experiment, the specimen was left at -5°C degrees for twenty-four
hours before the measurement.

3.2.6.2 PVC Pipe Diameter Analysis on Magnetic Susceptibility Measurement

Before starting the measurement, the PVC pipe diameter was measured and written as an
input to the program (MS2C software). The diameter of the PVC was millimetric (35 mm), and
the diameter value may be different depending on the precision of the caliper and human error.
The diameter difference should be analyzed to get information about the $K_m$ 's response when
the different diameter value was used as an input. The $K_m$ were compared by changing the
diameter value between 36 mm and 43 mm.

3.2.6.3 The Magnetic Analysis of Iron Mineral Types and Grain Size

In lab conditions, using a different percentage of and different types of iron minerals
siderite, magnetite, HFO, $K_m$ values were attained. The purpose of doing this was to learn what
percentages of iron mineral obtained which magnetic susceptibility value so that the results could
be used for anomaly changing for synthetic cores and field cores measurement. In other words,
we could see what percentage and what type of iron the field has and how the synthetic cores
change for their magnetic value while they were in the contaminated area.
For this experiment, the different grain sizes of magnetite (1.4 mm, 0.8 mm, 0.26 mm, 0.11 mm, 0.075 mm, 0.045 mm), single grain size of siderite and HFO (0.26 mm) from 100 % to 0.0007 %, 20-piece percentage measurements (100 %, 50 %, 25 %, 12.5 %, 6.125 %, 5 %, 3.5 %, 1.5 %, 0.75 %, 0.35 %, 0.15 %, 0.09 %, 0.045 %, 0.022 %, 0.011 %, 0.0056 %, 0.0028 %, 0.0028 %, 0.0014 %, 0.0007 %) were taken.

On the one hand, the mineral packets were placed on the field; on the other hand, the cores were extracted from the field and store in the laboratory for magnetic sensitivity studies.

3.2.7 Sediment Core Extraction, Preparation and MS Measurement

Cores from the hydrocarbon-contaminated area were extracted in June 2019. Contaminated area (1905), upland area (1903), and uncontaminated area (1902) cores were taken out using 45- and 50-mm PVC pipes. The first MS measurement of 45 mm cores was fulfilled immediately after drilling. In contrast, the MS measurement tool (core logger) of cores with a diameter of 50 mm was not available, so the MS measurement of these cores in the field could not be performed. All cores were wholly wrapped with aluminum foil to prevent contact with light and put in a de-aired plastic bag to prevent air contact. These cores were placed in icy storage tanks immediately after the wrapped and were sent to Newark for further analysis.

The cores from previous years: 2013 cores; 1304, 1305, 1306, 1308, 2014 cores; 1407, 1408, 1410, 1411, 1415, 2016 core; 1604, and 2017 cores; 1709, 1713, 1714 were preserved in the fridge in Rutgers University-Newark. Even if they were not inside an airless bag, they were in storage tanks in the fridge and had limited contact with air and light in years. You can find information showing where these cores were obtained from in the Bemidji region in Table 1.
Table 1 Contamination of cores retrieved from the Bemidji site places.

<table>
<thead>
<tr>
<th>Years</th>
<th>Contaminated Zone</th>
<th>BTEX Zone</th>
<th>Uncontaminated Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>1305,1308</td>
<td></td>
<td>1304,1306</td>
</tr>
<tr>
<td>2014</td>
<td>1407</td>
<td>1410,1411,1415</td>
<td>1408</td>
</tr>
<tr>
<td>2016</td>
<td>1604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>1709,1713</td>
<td>1714</td>
<td></td>
</tr>
<tr>
<td>2019</td>
<td>1903,1905</td>
<td></td>
<td>1902</td>
</tr>
</tbody>
</table>

Extracted cores were inside different diameter PVC pipes (35mm, 40mm, 50mm, 56mm). There must be a ratio between the pipe diameter and the core logger diameter for measurement accuracy. Because of that, two different diameter core loggers (45mm and 70mm) were used for the measurement.

A specific calibration sample for each core logger was used to control the calibration of the devices. The label values shown on the calibration sample were obtained before starting the measurements. The check with the calibration sample was sufficient to a confidence that the logger was functioning correctly. After this process, the diameter correction algorithm was used to calculate the actual value for the magnetic susceptibility of the calibration sample. The algorithm could be used to do the same for any core that was being measured. It was measured the calibration sample for the 45mm logger using the 70mm logger – and then used the diameter correction algorithm – the value was the same as when you measured the 40mm calibration sample using the 45mm logger (and use the algorithm on that value). By doing this, it could be
checked the calibration between the 45mm and 70mm loggers. Incidentally, Bartsoft company labels the calibration sample with the uncorrected value (diameter correction) so that someone using an MS2 Meter without Bartsoft could efficiently perform a functional check.

### 3.2.8 Magnetic Susceptibility Grain Size Analysis of Samples

Beckman Coulter LS Particle Size Analyzer was used to better understand the minerals' (magnetite siderite, HFO, and clean sand) grain size distribution and analyze the ingredient of products (grain size differentiate). Also, sieve analysis, which was a non-destructive method, was applied to the all-grain size. Because of the limited quantity of products, 0.075 mm, 0.045 mm magnetite samples could not be measured with Beckman coulter LS. However, other samples' analyzed results were so close to sieve results, so sieve analysis values were accepted to identify the grain size of these two-grain sizes.

### 3.3 Study Site

The study site is located about 20 miles northwest of Bemidji, MN. It is known as the USGS managed ‘National Crude Oil Spill Fate and Natural Attenuation Research Site’, located near Bemidji, Minnesota, USA (Figure 11). Geologically, the study site is composed of an approximately 20 m thick layer of moderately calcareous silty sand and outwash glacial deposits overlying a clayey till of unknown thickness (Bennett & Siegel, 1993). With 1 m seasonal fluctuation, the water table depth varies from 0 m (relative to an unnamed lake at 300 m down gradient of the rupture point) to a maximum of 11 m (Delin, 1998). In August 1979, an oil pipeline ruptured, and 1,700,000 L of crude oil were spilt. After cleanup processes, 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). Based on field observations, even though there is no visible evidence of the spill across the area, the subsurface has oil in the vadose zone sediments and on top of the groundwater aquifer (Gunderson, 2014).

In Figure 11, the locations of the wells containing mineral packets are shown with yellow vertical lines, and orange ovals depict the location of cores drilled in 2019. (Brown ovals - 2013, blue ovals - 2014, purple ovals- 2016, green ovals- 2017). The red star represents the pipeline rupture point. The blue outline represents the North oil body (Warren & Bekins, 2015), whilst the red outline indicates the >10 ppb BTEX concentration.
Iron mineral packets were installed into four wells to understand MS signatures arising from the transformation of iron minerals in situ (Table 2).

Figure 11 Study site showing the locations of mineral packets and drilled cores in various years. Blue outline represents North oil plume body (NRE Barry Powers Report, 1998), zone in the red frame shows dissolved phase plume based with >10 ppb BTEX concentration, (1996), yellow vertical lines indicate the location of mineral packets suspended within the smear zone in wells and different color ovals show the location of core drilled in various years-each color represents a year (brown - 2013, blue - 2014, purple - 2016, green - 2017, orange – 2019). (Source: Esri, Maxar, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community)
These mineral packets were placed in well 411 (referred to the Pit location- an oil contaminated area, where recharge is locally enhanced), in well 534A (referred to as the Upland location- an oil contaminated area), in well 925B (referred to as the Downgradient location), and in well 310A (referred to as the Upgradient location) in an uncontaminated area.

Figure 11 shows the location (ovals) of cores drilled in previous years (2013, 2014, 2016, 2017, 2019). For these cores, MS measurements were taken in the laboratory under anerobic conditions.

Table 2 Mineral packet well distances from pipeline rupture site, along with description of the wells and their installation dates.

<table>
<thead>
<tr>
<th>Name</th>
<th>Distance from Rupture Site (m)</th>
<th>Description</th>
<th>Installation Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>-200</td>
<td>Uncontaminated (upgradient)</td>
<td>October 2019</td>
</tr>
<tr>
<td>411</td>
<td>-5.5</td>
<td>Contaminated</td>
<td>November 2018</td>
</tr>
<tr>
<td>534A</td>
<td>24</td>
<td>Contaminated</td>
<td>November 2018</td>
</tr>
<tr>
<td>925B</td>
<td>257</td>
<td>Downgradient</td>
<td>November 2018</td>
</tr>
</tbody>
</table>

Figure 12 represents the geochemical zones across the free phase plume and dissolved phase plume at the North oil pool of the study site as shown. The locations of the mineral packets are shown with respect to the geochemical zones.
Figure 12 Geochemical zones characterized across the free phase plume and dissolved phase plume at the North oil pool and mineral packet locations (310A, 411, 534A, 925B).


3.4 Results

3.4.1 Magnetic Susceptibility for Suspended Mineral Packets

The MS lab measurements at different temperatures concluded that magnetic susceptibility value did not vary among these temperature differences.

For 3.2.6.2 PVC Pipe Diameter Analysis test, it was concluded that when the diameter value was entered smaller than required, the $K_m$ was higher than it should be. And when the radius was entered bigger than necessary, the $K_m$ was lower than it should be. Fortunately, if the
raw data and the correction factor were known, the regulated data finding process could be done quickly.

Different mineral type experiment results that magnetite was the highest \( K_m \) could be seen in Figure 13. The 0.045% magnetite-sand mixture had a higher \( K_m \) than 100% siderite and HFO. The smallest detection percentage for magnetite was 0.09%. For HFO, it was more consistent after 12%, while for siderite, it was 5%. Additionally, more than 0.0014% of magnetite had a magnetic response bigger than clean sand. The linear regression can be used to check the measurement accuracy, and this value was more than 0.94 for all the minerals (magnetite \( R^2 = 0.98 \), siderite \( R^2 = 0.96 \), HFO \( R^2 = 0.94 \)) while the clean sand did not have a consistent value (\( R^2 = 0.067 \)).

For MS measurements of the sand iron mineral mixture, a specific percentages mixture was put into the PVC pipe, and then clean sand was filled. While the measurements were taken, the mixture was first taken, and then the clean sand measurement was taken. This process was repeated at least three times. The sand indicator on the Figure 13 results from clean sand measurements when taking these HFO sand mixture measurements.
Different grain size magnetite experiment results can be seen in Figure 14. A strong dependence of the $K_m$ on the grain size was not observed, even though there was some variation in the data. However, there is a dependence on grain size in that the gradient of the relationship between $K_m$ and concentration (i.e., the slope) decreases with grain size. This is interesting as others have reported a strong relationship between MS response and grain size (Keating & Knight, 2008; Dunlop, 1972).
Figure 14 Magnetic susceptibility versus the concentration of magnetite (0.09% - 5%) for the different grain size magnetite (0.045mm, 0.075mm, 0.25mm, 0.3mm, 1mm, 2mm) and quartz mixtures by volume.

The variation in magnetic susceptibility of the mineral packet-magnetite in the field over time can be seen in Figure 15. The change in $K_m$, which was in time in the contaminated area, as can be seen in linear regression relationship; $R^2 = 0.0154$ for 411-Mag-1, $R^2 = 0.0953$ for 411-Mag-3, $R^2 = 0.68$ for 411-Mag-5, was not consistent while in the uncontaminated area had a linear relationship with $R^2 = 0.89$ for 310a-MAg-1, $R^2 = 0.80$ for 310a-Mag-5.

For uncontaminated area, $K_m$ of magnetite in Mag-1 had been decreasing systematically for time (Figure 15-g) while Mag-3 and Mag-5 in Figure 15-h, -I showed an increasing trend for MS. On the other hand, the contaminated and upland mineral packets had prominent anomalies for every measurement. Fluctuation movement can be observed clearly, in Figure 15-a, -b, -c, -d, -e, -f.
411 Mag-1, 411-HFO-2, 310 Mag-1, 310 HFO-2, 925b HFO-1, 925b HFO-2, 925b Mag-3, 925b-HFO-4 mineral packets were set up above the groundwater level. Other mineral packets were inside the groundwater.

310 Mag-1 decreased for $K_m$ above the water level while Mag-3 and Mag-5 (that was around the GWFZ) were seen to rise for $K_m$. 411 Mag-1, 411-HFO-2 showed the same decreasing trend while 411 HFO-4 and 411-HFO-6 had an increasing trend and mineral packets 411 Mag-3 and 411 Mag-5 that were inside the groundwater also had a downward trend.

The 310 HFO-2 and 925b-Mag-3 were above the groundwater level, but these mineral packets did not fit this trend.

Percentage change graphs of monthly MS measurements for mineral packets are explained in detail in Appendix 2.
Continued=>
HFO mineral packets (mixed with magnetite) variation over time can be seen in Figure 16. The change in $K_m$ that was in time in the contaminated area; as can be seen in linear...
regression relationship; $R^2 = 0.2518$ for 411-HFO-2, $R^2 = 0.4117$ for 411-HFO-4, $R^2 = 0.0066$ for 411-HFO-6, was not consistent. On the other hand, the uncontaminated area has a linear relationship with $R^2 = 0.98$ for 310a-HFO-2, $R^2 = 0.97$ for 310a-HFO-4 and $R^2 = 0.62$ for 310a-HFO-6. For uncontaminated areas, the $K_m$ of magnetite had been increasing systematically for time. (Figure 16-j and Figure 16-k and Figure 16-l). On the other hand, the contaminated and upland mineral packets (Figure 16- a, -b, -c, -d, -e, -f) had prominent anomalies for every measurement. Fluctuations of $K_m$ HFO packets of the contaminated area can be observed clearly, in Figure 16, as in the magnetite mineral packets of the contaminated area in Figure 15 too.

Mineral packet in 925B had a consistent value with $R^2 = 0.88$ for HFO-2 in Figure 16-g, $R^2 = 0.68$ for HFO-4 in Figure 16-h while 925b-HFO-6 mineral packet had $R^2 = 0.27$, with a limited data (only three data). After September 2020, these mineral packets (925B) were corrupted and could not be taken to measurement.

Since HFO was mixed with magnetite, a low amount of magnetite sensitivity change was observed instead of HFO magnetic sensitivity. The results from these mineral packets agreed with the results from the magnetite packets. While there were up and down movements in the contaminated area, a linear increase was observed in the uncontaminated area.

The mineral packet that had only HFO was 925b-HFO-1, shown in Figure 16- m. This mineral packet did not have a consistent $K_m$ for the MS measurements.
Continued=>
3.4.2 Magnetic Susceptibility for Cores retrieved from the Hydrocarbon Contaminated Area

It was decided to repeat the measurement of all cores retrieved from the field four times (once in 6 months) for their $K_m$ value, but due to the pandemic, the cores from 2019 were measured three times, and the cores from previous years were measured two times. As a result of these measurements, it was determined that there were minor changes in some $K_m$. However, the cavities in the PVC, and as the core was moved, the material inside the PVC was displaced in these cavities and can cause these changes (results were not shown here).

Figure 17 represents cores retrieved from the contaminated area location. Cores from the past (2013, 2014, 2016) had more variability in magnetic susceptibility than cores retrieved in 2017 and 2018 on the groundwater fluctuation zone. Especially 2018 cores had a weak $K_m$. The upper of the GWFZ had more signal than below it. $K_m$ appeared more prominent in the region between 428 and 432 m, except in core 1407. Data from 2014 (1407) and 2017 (1709) had missing cores for this area, as can be seen in Figure 17.
Cores, that belong to different years BTEX zone, are shown in Figure 18. There was insufficient data to interpret the GWFZ in core 1410, while core 1411 and core 1415 had a $K_m$ above the GWFZ. Furthermore, around the 430 m, there was an anomaly for $K_m$ in these cores. Core 1714, the only core from another year, had only data below groundwater level, and this data does not give any information.

Figure 19 represents the uncontaminated area from different parts of the field. Only information of three cores was obtained. These three cores obtained from the different places of the uncontaminated area had high $K_m$ in some points. The cause of this anomaly was explained in the discussion part.

The minimum (MIN) and maximum (MAX) values of all cores are shown in Table 3, Table 4, Table 5. It is clear that there are similar values regardless of whether they are contaminated or uncontaminated.
Figure 17. The magnetic susceptibility measurement results of the cores taken in different years (2013-2019) from the contaminated area and their relationship with the Groundwater Fluctuation Zone.
Figure 18 The magnetic susceptibility measurement results of the cores taken in different years (2014, 2017) from the BTEX contaminated area and their relationship with the Groundwater Fluctuation Zone.

Figure 19 The magnetic susceptibility measurement results of the cores taken in different years (2013-2019) from the uncontaminated area and their relationship with the Groundwater Fluctuation Zone.
Table 3 Comparison of minimum (MIN), maximum (MAX), average (AVRG), standard deviation (STDEV) and relative standard deviation (RSD) of $K_m$ for contaminated area cores

<table>
<thead>
<tr>
<th>Core</th>
<th>1905</th>
<th>1903</th>
<th>1713</th>
<th>1709</th>
<th>1604</th>
<th>1407</th>
<th>1308</th>
<th>1305</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN MS (10^{-4}SI)</td>
<td>2.4</td>
<td>8.7</td>
<td>10.4</td>
<td>5.6</td>
<td>8.0</td>
<td>8.7</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>MAX MS (10^{-4}SI)</td>
<td>93.7</td>
<td>68.9</td>
<td>84.7</td>
<td>244.2</td>
<td>178.8</td>
<td>132.7</td>
<td>319.9</td>
<td>216.6</td>
</tr>
<tr>
<td>AVRGMS (10^{-4}SI)</td>
<td>22.1</td>
<td>25.1</td>
<td>23.7</td>
<td>25.0</td>
<td>27.9</td>
<td>28.6</td>
<td>27.5</td>
<td>21.4</td>
</tr>
<tr>
<td>STDVMS (10^{-4}SI)</td>
<td>13.5</td>
<td>11.8</td>
<td>9.8</td>
<td>20.3</td>
<td>20.6</td>
<td>19.9</td>
<td>26.7</td>
<td>19.8</td>
</tr>
<tr>
<td>RSD %</td>
<td>60.9</td>
<td>46.9</td>
<td>41.5</td>
<td>81.3</td>
<td>73.8</td>
<td>69.9</td>
<td>97.3</td>
<td>92.6</td>
</tr>
</tbody>
</table>

Table 4 Comparison of minimum (MIN), maximum (MAX), average (AVRG), standard deviation (STDEV) and relative standard deviation (RSD) of $K_m$ for BTEX area cores

<table>
<thead>
<tr>
<th>Core</th>
<th>1714</th>
<th>1415</th>
<th>1411</th>
<th>1410</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN MS (10^{-4}SI)</td>
<td>6.0</td>
<td>7.6</td>
<td>7.8</td>
<td>7.5</td>
</tr>
<tr>
<td>MAX MS (10^{-4}SI)</td>
<td>43.1</td>
<td>123.5</td>
<td>47.2</td>
<td>47.4</td>
</tr>
<tr>
<td>AVRGMS (10^{-4}SI)</td>
<td>15.0</td>
<td>23.1</td>
<td>17.3</td>
<td>20.2</td>
</tr>
<tr>
<td>STDEVMS (10^{-4}SI)</td>
<td>7.6</td>
<td>15.2</td>
<td>6.5</td>
<td>7.9</td>
</tr>
<tr>
<td>RSD %</td>
<td>50.8</td>
<td>65.8</td>
<td>37.5</td>
<td>39.4</td>
</tr>
</tbody>
</table>

Table 5 Comparison of minimum (MIN), maximum (MAX), average (AVRG), standard deviation (STDEV) and relative standard deviation (RSD) of $K_m$ for uncontaminated area cores

<table>
<thead>
<tr>
<th>Core</th>
<th>1902</th>
<th>1408</th>
<th>1306</th>
<th>1304</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN MS (10^{-4}SI)</td>
<td>6.7</td>
<td>4.8</td>
<td>2.8</td>
<td>5.6</td>
</tr>
<tr>
<td>MAX MS (10^{-4}SI)</td>
<td>136.5</td>
<td>450.9</td>
<td>112.9</td>
<td>81.7</td>
</tr>
<tr>
<td>AVRG MS (10^{-4}SI)</td>
<td>23.8</td>
<td>20.5</td>
<td>20.4</td>
<td>25.1</td>
</tr>
<tr>
<td>STDEV MS (10^{-4}SI)</td>
<td>14.0</td>
<td>30.3</td>
<td>12.9</td>
<td>21.0</td>
</tr>
<tr>
<td>RSD %</td>
<td>58.9</td>
<td>147.7</td>
<td>63.5</td>
<td>83.7</td>
</tr>
</tbody>
</table>

3.5 Discussion

Zachara et al. (2002) proved that scanning electron microscope (SEM) imaging could not be used as a descriptive method for nano-sized magnetite. However, as understood from the laboratory studies, the MS method can measure the magnetite amount without being sensitive to the grain size. This had led to MS superiority over the SEM imaging method for a contaminated area.
Cores retrieved from the different years also had some anomalies for MS in uncontaminated areas. Baedecker et al. (1992) stated that the magnetite at the Bemidji site was of authigenic origin. Furthermore, Tuccillo et al. (1999) proved that a 0.5% magnetite could be in the original Bemidji site. Moreover, Zachara et al. (2004) advocated that the magnetite in the Bemidji aquifer was detrital magnetite of magmatic or metamorphic origin by using the euhedral morphology of magnetite grains. These pieces of information can explain the high $K_m$ obtained from the uncontaminated area.

According to Atekwana et al. (2014), the groundwater fluctuation zones at the contaminated area had an apparent MS anomaly and an increased MS in the vadose zone directly above the source zone for retrieved cores. In addition, Atekwana et al. (2014) and Lund et al. (2017) explained the decrease in $K_m$ in the contaminated area with the transformation of magnetite to siderite formed by microbial means by iron-reducing bacteria because of the anoxic condition within the plume. However, Bryce et al. (2018) proved the anaerobic oxidation of magnetite by reducing nitrate to N$_2$. This condition can decay the hypothesis that magnetite transformed to siderite in the contaminated area.

Moreover, siderite can be detectable in low temperature magnetometry marked by the presence of Néel transition (TN) at a temperature of ~38K (Jacobs, 1963; Housen et al., 1996). Ohenhen used TN and found no evidence of siderite in all measured magnetite packets and core samples.

The hypothesis of this thesis was that the MS of mineral packets installed in the smear zone of the hydrocarbon-contaminated wells and the MS of cores retrieved at different times would change due to iron mineral conversions between HFO, magnetite and siderite. MS decrease was not observed in this period.
However, it is possible to see an overall decrease in variability of the $K_m$ over the years. A 3-point moving average filter was used to reduce some variability and look at changes in the average profile (data was not shown here). Furthermore, the data's minimum, maximum, average, standard deviation, and relative standard deviation were calculated for all cores. RSD (for bigger percentages value), which indicates that data is more spread out, has calculated between 2013 and 2019 (Table 3). There is no continuous decrease in RSD from 2013 to 2019, although there is some evidence of an overall decline. On the other hand, such an interpretation cannot be made with the available data for the BTEX zone and uncontaminated field (Table 4, Table 5). It is thought that this overall decrease in the contaminated area will be related to the fact that the groundwater level will remain at a low level continuously after 2011.

Mineral packet 310 is in Zone 4 (Figure 11), and it is described as the uncontaminated native groundwater, which is aerobic with dissolved oxygen concentrations between 8 and 10 milligrams per liter (mg/L) (Bennett et al., 1993). Oxidation of magnetite is likely under these conditions 310-MAG 1 is an example, with decreasing $K_m$. On the other hand, 411 mineral packets are in Zone 1, and it is described lower concentrations of $O_2$ (10 – 20%), higher concentrations of $CO_2$ (>10 %) and $CH_4$ (> 10%) and hydrocarbon (>1 ppm) (Delin et al., 1998). 411 MAG-1, which is above the groundwater, slightly decreases $K_m$ because of these environmental conditions.

The results obtained from mineral packets showed that while the $K_m$ increased periodically in the uncontaminated area, fluctuations were observed in the contaminated area. Compared to hypothesis 1, it was not changed due to iron mineral conversions between HFO, magnetite and siderite in the contaminated area. Groundwater level played a crucial role in this. The samples that were in the groundwater and that were not in contact with the groundwater
gave different $K_m$ responses. It shows that groundwater influences the change of $K_m$ value, and therefore, iron transformation. This can be interpreted as microbial activities that increase the $K_m$ value increase when the groundwater level increases. Thus, they cause magnetite formation. When the water level decreased, fluctuations in the $K_m$ value were observed in the region because of oxidation.

Environmental conditions, especially groundwater level, had a big impact on biogeochemical reactions in the contaminated area. In line with the information obtained from the mineral packets, which was a part of this study, it has been observed that the water level affects the mineral transformation.

To be clear, this means that transformation to the magnetite is much more prominent while the groundwater level is high in a hydrocarbon-contaminated area. It can be a cycle in the hydrocarbon contaminated area, and rapid $K_m$ increases can be seen when the groundwater level increases. Sudden decreases in $K_m$ value in the absence of groundwater, such as after 2011, can be presented as evidence for this situation. Therefore, it has to be monitored in the long term to understand how it impacts the environment.

For further studies, groundwater levels should be monitored, and MS measurements should be applied in the highest groundwater level period to understand and monitor the area.

3.6 Conclusion

In order to better understand a region contaminated with hydrocarbons, two approaches were followed in this study. First, three minerals were examined for their $K_m$ value in the laboratory conditions, and after that, these minerals (magnetite and HFO coated sand) were prepared as mineral packets and were placed in the contaminated region. $K_m$ values were measured at certain time intervals. Second, the cores taken from the contaminated area at
different years were examined in the laboratory environment with repeated measurements at 6-month intervals two or three times.

These two approaches have been rigorously used to understand the efficiency of the MS method in better understanding the hydrocarbon-contaminated site. The results obtained from mineral packets showed that while the $K_m$ value increased periodically in the uncontaminated area, fluctuations were observed in the contaminated area.

In fact, the samples that were in the groundwater and that were not in contact with the groundwater gave different $K_m$ responses. It shows that groundwater influences the change of $K_m$, and therefore, iron transformation.

This can be interpreted as when the groundwater level rises, microbial activities that cause magnetite formation increase and thus, the $K_m$ increases. When the water level decreased, fluctuations in the $K_m$ were observed in the region because of oxidation. This means that transformation to the magnetite is much more prominent while the groundwater level is high in a hydrocarbon-contaminated area. Therefore, it has to be monitored in the long term to understand how it impacts the environment.
CHAPTER 4 CONCLUSION

This thesis improves the understanding of using geophysical methods at a hydrocarbon-contaminated area.

First, in laboratory conditions, three iron mineral is analyzed by using SIP. While magnetite is used many times for experiments, there a not enough study for siderite and HFO in the literature. This thesis helps to have an idea how their electrical properties with known phase responses. Also, it is validated that there is a change in frequencies that depend on the grain size of the magnetite. This can improve field data interpretation, especially for an environment to have both natural-occurring magnetite and microbial magnetite. Because of the consistency with the Wong model and discrepancy with Gurin, 2015 volumetric specific capacitance correction, this data can cause more investigation related to the volumetric specific capacitance range.

Second, laboratory MS measurements showed that the method is strongly sensitive to the iron mineral type and percentages. Even 100% siderite cannot reach the $K_m$ value of 0.09% magnetite. HFO has a lower response than siderite. Furthermore, it can be clearly stated that the grain size has a secondary effect based on the results obtained.

Field results demonstrate decreasing in $K_m$ at the groundwater fluctuation zone and vadose zone during years. The results from this study may prompt future studies to examine the relationship between groundwater and microbial activities such as iron mineral transformation.

These two-methods examination show that geophysical methods can help understand and monitor the hydrocarbon contaminated areas with a good resolution.
References


Appendix

1. Suspended Mineral Packet Places

These are elevations above mean sea level.

Table 6  Places of suspended mineral packets in the contaminated area (411 and 534), and groundwater level.

<table>
<thead>
<tr>
<th>Mineral Pack</th>
<th>Mid of Mineral Pack(m)</th>
<th>Taken Sample Places(m)</th>
<th>Mineral Pack</th>
<th>Mid of Mineral Pack(m)</th>
<th>Taken Sample Places(m)</th>
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Table 7 Places of suspended mineral packets in the -background, -uncontaminated area (310 and 925), and groundwater level

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<th>Mineral Pack</th>
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<th>Taken Sample Places(m)</th>
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land surface 433.484m
land surface 432.846m
9.6m is rope length
8.22 is rope length
2. Suspended Mineral Packets Percentage Change

Table 8 Magnetite HFO mineral packets % MS change data

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When the magnetite surface change graphs were examined, the effect of the groundwater level can be seen.

411-MAG-3, MAG-5 534 MAG-1 that were inside the groundwater had similarities related to the monthly change. Between April and June, there was an increasing trend for the period of three years, while a downward trend was observed between September and February.

For the uncontaminated area Mag-1, there was a 3% decrease in MS, while an average 1.8%
increase was observed in Mag-3 and Mag-5 that were inside of the groundwater. 925b for magnetite have limited data with an increase in June.

On the one hand, 411 HFO generally increased between April and September, and there only was a downward trend in February. On the other hand, decreases were observed for all 534 HFO except the October measurement.

A significant increase was recorded in February; 777% for 310 HFO-6 and 178% for HFO-4 in the uncontaminated area. In order to show this trend, the y-scale was numbered differently from the others.

Mineral packet 925-HFO-1 that had only HFO did not have enough data for comparison even if there was a slight downward trend. Although 925 HFO-4 showed an increase in September 2019, the same increase could not be seen in 2020, unlike the contaminated area.
Figure 20 Magnetite mineral packets % MS change
Figure 2: HFO mineral packets % MS change