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#### Temporal geophysical signatures due to contaminant mass remediation Vukenkeng Che-Alota<sup>1</sup>, Estella A. Atekwana<sup>1</sup>, \*, Eliot A. Atekwana<sup>1</sup>, William A. Sauck<sup>2</sup>, D.

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## ABSTRACT

Geophysical investigations have documented characteristic changes (e.g., higher bulk electrical conductivity, positive self potential (SP), attenuated ground penetrating radar (GPR) reflections) associated with hydrocarbon biodegradation in field experiments. These characteristic geophysical signatures result from biogeochemical transformations of the bulk properties of the contaminated relative to uncontaminated media. In this study, we present the results of surface geophysical surveys acquired in 1996, 2003, and 2007 that document changes in geophysical signatures associated with removal of hydrocarbon mass in the contaminated zone. Initial investigations in 1996 showed that relative to background, the contaminated area was characterized by higher bulk electrical conductivity, positive SP anomaly, and attenuated

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GPR reflections. Repeated surveys in 2003 and 2007 over the plume showed that in 2007, the bulk electrical conductivity had reverted to near background conditions, the positive SP anomaly became more negative, and the zone of attenuated GPR reflections showed increased signal strength. The removal of hydrocarbon mass in the vadose zone over the plume by a soil vapor extraction system installed in 2001 was primarily responsible for the changing geophysical responses. Although chemical data from groundwater showed a 3 m thick conductive plume in 2007, the plume was not imaged by electrical resistivity. Forward modeling suggests that the apparent bulk electrical conductivity of the saturated zone plume has to be 4-5 times higher than background values to be imaged by electrical resistivity. We conclude that hydrocarbon contaminant mass reduction by natural or engineered (bio)remediation can be effectively imaged by temporal geophysical surveys.

## **INTRODUCTION**

The contamination of groundwater by hydrocarbon from spills and leaky underground storage tanks threatens groundwater resources. Over the last decade, the use of non-invasive geophysical techniques has been instrumental in the detection and delineation of subsurface zones of hydrocarbon contamination. We have previously documented anomalous increases in the bulk electrical conductivity over areas of hydrocarbon contamination (e.g., Sauck et al., 1998, Atekwana et al., 2000; Werkema et al., 2003; Atekwana et al., 2004a, b, & c; Atekwana et al., 2005). Other geophysical studies have also effectively characterized subsurface hydrocarbon contamination using electrical resistivity techniques (e.g., Benson et al., 1997; Halihan et al., 2005; Kaufmann and Deceuster, 2007; Yang et al., 2007), ground penetrating radar (GPR) (e.g., Daniels et al., 1995; Bermejo et al., 1997; Bradford et al., 2007; Cassidy, 2007; 2008) and self 

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potential (SP) (e.g., Minsley et al., 2007). The characteristic geophysical response of hydrocarbon contaminated media has been attributed to a variety of physical, chemical, and biological mechanisms. For example Sauck (2000) attributes the increase in the bulk electrical conductivity to higher pore water conductivity resulting from weathering of aquifer solids by the organic and carbonic acids produced during biodegradation. Other geophysical studies have suggested a variety of mechanisms primarily related to microbial alteration of the hydrocarbon and the host media (e.g., Atekwana et al., 2004b & d; Minsley et al., 2007). Recent geophysical studies also suggest that the growth of microorganisms and their attachment to mineral surfaces and the formation of biofilms are important in the type of geophysical response observed (e.g., Abdel Aal et al., 2004; 2006; Davis et al., 2006). What ever the mechanism that causes the geophysical response, it is clear that the success of geophysical techniques rely on fundamental changes of the physical properties of the contaminated media relative to background caused by physical, chemical, and biological processes following contamination.

We present a conceptual model that illustrates the temporal behavior of the bulk electrical conductivity at a hypothetical hydrocarbon contaminated site (Figure 1). Although the conceptual model uses the bulk electrical conductivity as a measure of the geophysical response, a similar model can be constructed for any geophysical technique that has been successfully applied to hydrocarbon contamination (e.g., electrical resistivity, GPR, SP, etc.). At the initial stage of contamination, fresh spills will be associated with a decrease in the bulk electrical conductivity (e.g., Endres and Redman, 1996; Yang et al., 2007) due to the resistive nature of the petroleum hydrocarbon (Stage A). As microbial degradation of the contaminant mass is initiated, microbial colonization of mineral surfaces, and production of organic and carbonic acid enhance mineral weathering within the contaminated aquifer (e.g., Baedecker et al., 1993; Cozzarelli et

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al., 1990; McMahon et al., 1995; Bennett et al., 1996). This leads to an increase in the electrical conductivity of the pore fluids (electrolytic conductivity) and increase in the bulk electrical conductivity (e.g., Sauck 2000; Atekwana et al., 2004a; b; & d). In addition, the attachment of the microbial cells to mineral surfaces and the growth and proliferation of biofilm (e.g., Abdel Aal et al., 2004; 2006; Davis et al., 2006) adds to the bulk electrical conductivity by increasing the interfacial conductivity component (Stage B). Over time, the bulk electrical conductivity of the contaminated zone increases to some peak value and reaches a steady state related to the availability of terminal electron acceptors, the organic carbon source concentration, and microbial activity (Stage C). With continuous removal of the contaminant mass either by natural attenuation or engineered (bio)remediation, we predict a decrease in microbial activity and accompanying changes induced directly or indirectly by microbial activities in the contaminated environment. We suggest that there will be a decrease in the bulk electrical conductivity to lower values that are close to or at pre-spill conditions (Stage D). The temporal frame required for the above changes to occur depends on several factors such as the mass of hydrocarbon contamination, relative ease of contaminant breakdown, the presence of indigenous microorganisms, the availability of terminal electron acceptors, the mineralogy of the aquifer, the hydrogeology of the site, etc.

An important question to consider is whether or not the geophysical signatures associated with biodegradation of hydrocarbons will revert to background conditions with removal of the contaminant mass (Stage D; Figure 1) and if geophysical techniques can be used to ascertain such changes. Published results of field geophysical investigations of hydrocarbon contamination show a variety of geophysical responses (e.g., Daniels et al, 1995; Bermejo et al., 1997; Benson et al., 1997, De La Vega, 2002; Orlando, 2002; Cassidy et al., 2007; Kaufmann and Deceuster,

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2007; Yang et al., 2007). Thus, it is not apparent from published geophysical surveys whether the measured response is an indication of a specific state of hydrocarbon contamination evolution i.e., Stage B, C, or D. Understanding the geophysical response to hydrocarbon contaminant mass attenuation is likely to make non-invasive geophysical surveys a regular regimen in the approaches used to monitor natural and engineered bioremediation. In this study, we investigate the effects of hydrocarbon source removal in the vadose zone on the geophysical signatures of a site undergoing biodegradation. The installation of a soil vapor extraction system (SVE) within the source zone provided an opportunity to investigate geophysical signatures associated with contaminant mass reduction.

### SITE GEOLOGY AND SITE HISTORY

This study was conducted at the Fire Training Area 2 (FT-02) located on the decommissioned Wurtsmith Air Force Base in Oscoda, Michigan, USA (Figure 2). The Air Force Base lies on an 8 km wide sandy plain that is part of the Oscoda Lake Plain (USGS, 1991). The subsurface stratigraphy consists of well sorted fine to medium sands that grade downward to gravel. Underlying the sand and gravel deposits at approximately 20 m is a brown to gray lacustrine silty clay unit ranging in thickness from about 6.1 to 30.5 m. The silty clay unit is underlain by a thin glacial till deposit that rests upon bedrock consisting of Mississippian Marshal Sandstone and Coldwater Shale. The average depth to water table at the site ranges from 3.7 to 5.3 m and groundwater flow is to the southeast, towards a large wetland located 366 m in the floodplain of the Au Sable River (Robbins et al., 1995). Aquifer hydraulic conductivity is  $3.47 \times 10^{-4}$  to  $5.32 \times 10^{-4}$  m/s and groundwater flow varies from 0.03–0.2 m/day (USGS, 1991). 

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The U.S. Air Force used the FT-02 site for bi-weekly fire training for a period of 33 years from 1958 to 1991. Typical activities included combustion of several thousand liters of jet fuel and other hydrocarbon fuels. Waste and other combustion products seeped directly into the ground. In 1982, a concrete fire containment basin with an oil-water separator was installed to reduce the amount of fuel sipping into the ground. However, an unknown quantity of the fuel had already infiltrated into the subsurface. In the early 90s the site was used as the National Center for Integrated Bioremediation Research and Development (NCIBRD) and therefore has been the focus of several geophysical and geochemical investigations (e.g., Bermejo et al., 1997; Chapelle et al., 1996; Sauck et al., 1998; Skubal et al., 1999; McGuire et al., 2000; Skubal et al., 2001; Moody et al., 2003; Bradford et al., 2007). A contaminant Light Non-Aqueous Phase Liquid (LNAPL) plume (Figure 2) has been defined by chemical analyses of groundwater, spreading both upgradient and downgradient relative to the concrete pad. In the downgradient direction, most of the contamination is concentrated in the upper portion of the water table and within the capillary fringe (e.g., 1998; McGuire et al., 2000; Skubal et al., 2001) with significant impact of the vadose zone occurring near the source area. In 2007, the size of the FT-02 plume defined geochemically was approximately 75 m wide and extended 30 m upgradient and about 450 m downgradient to the south east of the source area (Figure 2).

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#### **METHODS**

134 Geophysical surveys

The geophysical surveys were conducted near the source area. We conducted electrical resistivity surveys and GPR along the same profile and the SP survey in a grid (Figure 2). Our survey lines and grids based on permanent grid markers established by the University of

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Michigan are located at 15.24 m intervals across the entire site. The electrical resistivity surveys (see Figure 2 for profile location) conducted in 1996 and 2003 used a dipole-dipole array with a 10 m electrode spacing. A single channel IRIS Syscal R2 resistivity system with 4 electrodes was used to acquire these data. In 2007, a dipole-dipole resistivity array was conducted at 3 m electrode spacing using a 10-channel IRIS Syscal Pro resistivity system with 72 electrodes. The apparent resistivity data were inverted using RES2DINV (Geotomo software) and a least-squares inversion technique was used for the inversion subroutine (Loke and Baker, 1996). Although the resistivity data for 2007 was collected at 3 m electrode spacing, the main difference compared to the 1996 and 2003 data collected at 10 m spacing was formation resolution and depth imaged. The data acquired at 3 m spacing had a higher resolution. Re-sampling this data at an equivalent 10 spacing and modeling the data showed no major difference in the resistivity structure of the subsurface. In terms of depth imaged, a survey using a 10 m spacing is about 50 m, while the 3 m electrode spacing survey imaged about 15 m of the subsurface. Because of the differences in the acquisition parameters (10 m vs. 3 m electrodes spacing), a difference image between the different surveys was not produced. The survey data collected in 1996 and 2003 were retrieved and clipped to display parts of the survey common with that of 2007. The data from all the surveys were plotted using the same color scale to allow for direct comparison.

SP measurements (see Figure 2 for grid location) were conducted in 1996 and 2007 using non-polarizable Cu-CuSO<sub>4</sub> electrodes and a high impedance voltmeter. The potential difference was measured between a fixed reference electrode and a roving electrode placed at grid nodes established every 15.24 m. Because of difficulties in locating the 1996 survey boundary, the 2007 grid is offset from the 1996 grid ~100 m to the north (Figure 2). The SP data was gridded

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using Kriging and contoured using SURFER<sup>®</sup> (Golden Software Inc., Golden, CO). We used the
same color scale to plot both the 1996 and 2007 data.

The GPR survey line established in 1996 was re-occupied in 2003 and 2007 (see Figure 2 for profile location). The survey was conducted using a GSSI Sir 10 A+ (Geophysical Survey System Inc.) system. The system was set up with 100 MHz bistatic antennae recording for a total of 400 nanoseconds. The 100 MHz transmitter-receiver pair was set at a fixed separation of 1.4 m between centers. Acquisition parameters for all three surveys were kept constant at: 512 samples/scan, 20 scans/second (14.7 scans/m), 3-stage vertical (along scan) Infinite Impulse Response (IIR) low pass filter at 120 cycles/400 ns (300 MHz), 4-stage vertical IIR high pass filter at 15 cycles/400 (37.5 MHz). Gains were automatically set at the starting point of the survey which was the same location for all three surveys, to equalize amplitudes to approximately 80% of full scale. The gains were fixed for the entire survey. The data were processed using RADAN (Geophysical Survey Systems, Inc.) and low frequency ringing and high frequency noise across the profiles were eliminated. The data from all surveys were plotted using the same color scale (amplitude to color conversion).

176 Chemical analysis of groundwater

Several monitoring wells and multi-level piezometers were constructed at the FT-02 site by NCIBRD for groundwater sampling (Figure 2). Groundwater from monitoring wells and multilevel piezometers was pumped to the surface using a peristaltic pump. The water was pumped through a flow cell into which a YSI multi-parameter probe was immersed. Water temperature, specific conductance (SPC), pH, and oxidation reduction potential (ORP) were recorded after the readings stabilized. Water samples were filtered using a 0.45 µm pore size in-line filter (Gelman

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Sciences) before collecting water for chemical and isotopic analyses. Ferrous iron ( $Fe^{2+}$ ) was analyzed immediately after filtering in the field by colorimetry using the Phenanthroline method (CHEMetrics, 2004). Samples for major ions were collected in Polyethylene bottles (pre-acidified for cations), cooled to 4°C on ice, and transported to the laboratory. Sulfate and calcium were analyzed by ion chromatography. Water for stable carbon isotope ratio ( $\delta^{13}$ C) was collected and analyzed using the technique described by Atekwana and Krishnamurthy (1998). In addition, historical data (depth to water table, total petroleum hydrocarbons, and specific conductance) used in this study were obtained from the Wurtsmith Air Force Base (WAFB) Authority.

# RESULTS

### 193 Geophysical data

Electrical resistivity (ER) data acquired in 1996 and 2003 were previously reported in Sauck et al. (1998) and Smart et al. (2004), respectively. A compilation of the inverted resistivity profile acquired from 1996, 2003, and 2007 is presented in Figure 3. The 1996 resistivity results show a region of lower resistivity coincident with the zone of contamination (horizontal coordinates 70 m to 140 m) extending from near the surface into the saturated zone (Figure 3a). Within this low resistivity region, the apparent resistivities are <700 ohm-m and decreases with depth to ~100 Ohm-m. The resistivity values in the uncontaminated regions of the vadose zone are greater than 2000 Ohm-m. The 2003 resistivity survey result shows a zone of low resistivity over the plume region between positions ~100 m to ~170 m (Figure 3b). However, the highest resistivity values within the contaminated region of ~700 Ohm-m in the 1996 survey, increased to ~1200 Ohm-m in 2003 (Figure 3a vs. 3b). The results of the 2007 survey (Figure 3c) are markedly different from the 1996 and 2003 surveys (Figure 3a & 3b). The low resistivity

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> anomaly observed in the vadose zone over the plume region in 1996 and 2003 is not evident in the 2007 data. Instead, the previously anomalous conductive zone has become more resistive and reverted to near background resistivity values of ~ 2500 ohm-m (Figure 3c). The anomalous conductive zone within the saturated zone over the plume is barely visible on the 2007 resistivity profile. We observe a uniform (~1.5 m thick) lower resistivity (1000 to 2000 Ohm-m) at the surface which we attribute to precipitation recharge. Up to 4.8 cm of rain had fallen two weeks prior to our survey (www.wunderground.com/history/airport/KAPN, 2008).

SP data acquired in 1996 was previously reported in Sauck et al. (1998). The 1996 SP data shows a NW-SE trending positive anomaly (8 to 24 mV) approximately 80 m wide and more than 250 m long, which is coincident with the region of groundwater contamination (Figure 4a) and the zone of anomalous conductivity (Figure 3a). However, in 2007, the survey area (Figure 4b) is characterized by more negative SP values between 18 mV to -34 mV over the plume area observed in 1996.

GPR data acquired in 1996 and 2003 were previously reported in Sauck et al. (1998) and Smart et al. (2004), respectively. The GPR profile for the 1996 survey shows strong reflectors at approximately 100 ns, coincident with the elevation of the water table (Figure 5a). Sauck et al. (1998) suggested that the strong reflectors at the water table was due to the large change in the relative permittivity from moist sand ( $\varepsilon_r \sim 9$ ) to saturated sand ( $\varepsilon_r \sim 25$ ). As noted by Sauck et al. (1998) and Bradford et al. (2007) the most prominent feature of the GPR record is a region of attenuated amplitudes or a "shadow zone". This zone of attenuated reflections approximately 60 to 70 m wide, begins just below the water table and extends the full length of the record. Sauck et al. (1998) used this attenuation anomaly to define the transverse extent of the plume over the entire site (see Sauck et al., 1998; Figure 3). The attenuation anomaly observed in the 1996 GPR

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profile (Fig 5a) is also evident in the 2003 and 2007 records (Figure 5b & c) with some notable differences within the contaminated zone. In the 2007 profile the zone of attenuation occurs deeper in the record (~150 ns) and appears to be wider when compared to the 1996 and 2003 data and the GPR reflectors at the water table and immediately below the water table are stronger when compared to the GPR reflectors in 1996 and 2003 (Figure 5c).

## **Geochemical data**

We present geochemical parameters in groundwater collected from multi-level piezometers in 2007 in Figure 6. We observe negative Eh (Figure 6a) and low dissolved oxygen values within the contaminated aquifer suggesting that anaerobic biodegradation is still occurring within the plume (Chapelle et al., 1996; Skubal et al., 1999; McGuire et al., 2000; Skubal et al., 2001; Moody et al., 2003). We also observe higher  $Fe^{2+}$  (~13 mg/L) and low sulfate concentrations (<2 mg/L) within the contaminated aquifer (Figure 6b and 6c). These redox zones defined by Eh, Fe<sup>2+</sup>, and sulfate is coincident with positive  $\delta^{13}C_{DIC}$  higher concentrations of calcium (>80 mg/l), and higher specific conductance (>400 µS/cm) (Figure 6d; e; & f). The combined geochemical results suggest a 3 m contaminated zone below the water table in which biodegradation is active and where peaks in the different parameters occur about 1 m below the water table (Figure 6).

### DISCUSSION

248 History of hydrocarbon contamination at the FT-02 site

Hydrocarbon contamination at the FT-02 site was initially investigated by ICF Kaiser Technology, Inc. (ICF) in 1995. Chemical analysis of groundwater showed volatile organic and semi-volatile organic compounds (acenapthene, benzene, toluene, ethylbenzene, and xylenes) at

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concentrations ranging from 10 to 2000 mg/L (ICF, 1995). As much as 30 cm of the free product was observed above the water table during the construction of monitoring wells more than 200 m downgradient of contamination source area (Figure 1). As part of the NCIBRD program, several studies have characterized the spatial extent of hydrocarbon contamination and the biological and chemical processes occurring in the contaminated media (e.g., Chapelle et al., 1996; Sauck et al., 1998; Skubal et al., 1999; McGuire et al., 2000; Skubal et al., 2001). These studies were instrumental in the remedial plan developed for the site.

In May 2001, the Wurtsmith Air Force Base Authority installed a Soil Vapor Extraction system (SVE) over the FT-02 contaminant source area (Figure 2). The SVE system consists of 25 extraction points which remove volatile and semi-volatile hydrocarbons by inducing vacuum conditions in the vadose zone. As of March 2003, approximately 2320 Kg of free product had been extracted from the vadose zone (Parsons, 2004). The removal of hydrocarbon contaminants from the vadose zone of the source area by the SVE system is reflected in the temporal groundwater chemistry. We use historical data from monitoring well FT-4S in the source area and along our GPR and resistivity survey lines and monitoring well FT-8S located downgradient (Figure 2) to illustrate temporal changes in the contaminant plume. Prior to the installation of the SVE system, the total petroleum hydrocarbon (TPH) concentration in groundwater was as high as 650 µg/L in 2000 (Figure 7a). After the installation of the SVE system, the TPH concentration in groundwater in the source area at FT-4S decreased steeply to ~100 µg/L in late 2002. Following this decrease, the TPH concentrations fluctuated between 100 and 200 µg/L from 2002 to 2007. The TPH concentration in the groundwater at FT-8S generally mirrors that in the source area (Figure 7a). During the operation of the SVE system, the vacuum created by the system to cause volatilization of the hydrocarbon induces air flow into the vadose zone and

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aquifer. The supply of air provides oxygen which enhances aerobic biodegradation.
Enhancement of biodegradation by oxygen brought to the contaminated zone by this process is
observed in the sharp rise in groundwater temperature at FT-4S by about 5° C between 2000 and
late 2003 (Figure 7b). The water temperature downgradient at FT-8S initially dropped between
2001 and 2003 shortly after the installation of the SVE system, perhaps due to a decrease in the
transport of the contaminant mass to downgradient locations (Figure 7b).

281 Decrease in the specific conductance within the contaminated aquifer measured at FT-4S 282 and FT-8S generally mirrors the decrease in TPH (Figure 7c). Within the source area, specific 283 conductance decreased from ~1000  $\mu$ S/cm in 2001 to <300  $\mu$ S/cm in 2003. However, the 284 specific conductance between 2003 and 2007 fluctuated between 400  $\mu$ S/cm and 600  $\mu$ S/cm 285 which we attribute to seasonal variations in rainfall recharge (Figure 7d). During periods of 286 lower water table, the specific conductance is higher and vice versa.

## 288 Hydrocarbon biodegradation and geophysical response

The physical contaminated environment is altered by the growth and proliferation of microbes, microbial attachment to solid surfaces, and production of biosurfactants, organic carbonic acids and various gases (e.g., CO<sub>2</sub>, N<sub>2</sub>), and mineral weathering and precipitation reactions. The expected geophysical response can vary and depends on the sensitivity of a specific geophysical technique to changes imposed on the physical property of the contaminant environment. The geophysical surveys were conducted near the source area where both the vadose zone and saturated zone were impacted by hydrocarbons (Figure 2). Initial investigations conducted in 1996 showed a distinct geoelectrically conductive anomaly within the saturated and unsaturated zones over the contaminant plume and coincident with the area of positive SP

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anomalies and attenuated GPR reflections (Figure 3a, 4a, & 5a). The Geochemical data from contaminated groundwater at this site documents microbial activity from terminal electron acceptor depletion, elevated pore fluid conductivity and high calcium concentrations (Figure 6), and temporal increase in temperature (Figure 7b). Although we did not investigate evidence of microbial activity within the capillary fringe and vadose zone (smear zone) with free product and residual product in this study, other studies have shown evidence of biodegradation and microbial activity effects on geophysical properties. In a laboratory column experiment where sediments were contaminated with diesel, Atekwana et al. (2004d) show higher bulk electrical conductivity in the region above the water table where sediments had free product and residual product saturation compared to the contaminated saturated zone with dissolved product. The population of microbes capable of degrading hydrocarbon was higher in the zone of highest bulk electrical conductivity above the water table (Atekwana et al., 2004d). Similar observations of higher bulk electrical conductivity and hydrocarbon degrading microbial population have been reported in field settings (Werkema et al., 2003; Atekwana et al., 2004b; Allen et al., 2007). Werkema et al., (2003) estimate pore water conductivity ratios between contaminated and uncontaminated locations of 5.5 in the smear zone (contaminated region with free and residual product saturation that straddles the water table and affected by seasonal water level fluctuations) and between 1 to 2 for the saturated zone contaminated with dissolved product. The geophysical picture that emerges from these studies is one in which hydrocarbon degradation in the smear zone is distinct from that of the saturated zone in terms of the magnitude of the geophysical response. At the FT-02 site, we attribute the decrease in the bulk electrical conductivity, negative SP anomaly and increased GPR signal strength observed in the 2007 survey compared to earlier surveys in 1996 and 2003 (see Figs 3, 4, & 5) to the removal of hydrocarbons from the vadose 

 

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321 zone by the SVE system. We argue that the removal of volatile and semi-volatile hydrocarbon in 322 the contaminated vadose zone caused a decrease in organic carbon (electron donor to the 323 microorganisms) which decreased microbial activity. The decrease in the microbial activity and 324 its direct and indirect effects in the contaminated environment impacted the physical properties 325 of the contaminated environment and the resulting geophysical signatures (e.g., Figure 1). We 326 argue below for why the geophysical response imaged during our surveys is most likely due to 327 microbial effects resulting from contaminant mass removal.

Bulk Electrical conductivity: In the absence of hydrocarbon contamination, the bulk electrical conductivity of the subsurface can vary because of saturation, depth to groundwater table, temperature, and concentrations of ions (salinity) of pore fluids (e.g., Doser et al., 2004; Rein et al., 2004). For example, Rein et al. (2004) documented short to long term variations in resistivity variations in an area of fluctuating groundwater level in response to rainfall events and seasonal and daily changes in temperature. The geophysical structure imaged showed up to 26% change in the resistivity in the uppermost soil layer (<1 m) which is ascribed to varying moisture changes and from strong air temperature variations (Rein et al., 2004). In dry climate settings where salts accumulate in the near surface due to evaporation, flushing of the salts by subsequent rains or irrigation are clearly evident in temporal resistivity imaging (e.g., Doser et al., 2004).

The changes in the resistivity data presented in this study can not be explained by both long term and short term variations in soil moisture, temperature or pore water salinity. Over the long term, groundwater levels have varied seasonally and annually (Figure 7d) but have remained within less than 1.0 m. The water temperature increased between 2000 and 2003 and has only changed by about 1 °C from 2003 to 2007 (Figure 7b). Additionally, the groundwater ionic

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chemistry indicated by the specific conductance has varied little between 2003 and 2007 except due to seasonal water level changes (Figure 7 c). Two weeks before the May 7 1996, June 24 2003, and September 1 2007 surveys were conducted, rainfall events totaling 3.6 cm, 1.3 cm, and 4.8 cm, respectively were recorded at the Alpena weather station (KAPN) 81 km north of the study site (www.wunderground.com/history/airport/KAPN, 2008). The difference in rainfall totals in the two week prior to our surveys indicates a much wetter 2007, which should result in a lower resistivity vadose zone. This is in contrast to our actual observation (Figure 3c). However, we note that the precipitation that occurred prior to the 2007 survey can be seen in the resistivity section that shows a thin (<1 m) shallow lower resistivity layer extending across the entire section. The mean daily temperature for the two weeks prior to each survey were 3.6° C in 1996, 16.6° C in 2003, and 18.0° C in 2007 (www.wunderground.com/history/airport/KAPN, 2008). The difference in the mean air temperature  $(<1.5^{\circ} \text{ C})$  is not sufficient to result in the more than 1000 Ohm-m increase in resistivity between 2003 and 2007. The climate in the study area is humid and there are no reported occurrences of salt formation in the surface soils that can impact the resistivity structure with rain recharge. Finally the resistivity structure of the background areas are all above 2000 Ohm-m, hence, we argue that the temporal changes in the anomalous low to high resistivity over the contaminated zone cannot be explained by long or short term variations in moisture content, temperature, or salinity. We therefore conclude that changes in the bulk electrical conductivity observed within the contaminated zone may be related to the removal of hydrocarbons in the vadose zone and decreased microbial activity.

Although the SVE system was decreasing the mass of the hydrocarbons in the vadose zone, hydrocarbons in the dissolved phase still persists in the saturated zone. The geochemical data suggest that anaerobic biodegradation is occurring within a narrow zone <3 m thick in the

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aquifer (Figure 6), evidenced by the terminal electron acceptor concentrations (e.g.  $Fe^{2+}$ ,  $SO_4^{2-}$ ). 6 This zone of biodegradation is accompanied by low pH, high CO<sub>2</sub>, high silica, and calcium concentrations and high specific conductance. The higher silica and calcium concentration is evidence of enhanced mineral weathering within this zone in the aquifer (e. g., Atekwana et al., 2004b, Atekwana et al., 2005). The ~3 m thick contaminated zone below the water table with higher specific conductance is not clearly evident on the 2007 resistivity profile (Figure 3c). To explain this observation, we performed a simple 3 layer forward model (Figure 8) with a 3 m thick bulk conductive layer in the upper parts of the saturated zone. Resistivity values assigned to the different layers were obtained from measurements made on cores retrieved from the FT-02 site in 2007. Model simulation results suggest that given a saturated plume thickness of  $\sim 3$  m with an apparent resistivity of 273 ohm-m, a background saturated zone apparent resistivity of 540 ohm-m, and a vadose zone apparent resistivity of 1120 Ohm-m, a bulk electrical conductivity anomaly is not evident in the modeled data (Figure 8a). This simulation result is similar to what we observe in the 2007 resistivity profile (Figure 3c). However, when the apparent resistivity of the contaminant plume in the saturated zone is decreased by ~4 to 5 times the background values as suggested by Werkema et al. (2003), the bulk electrical conductivity anomaly is observed on the resistivity section (Figure 8b). Figure 8c shows the result of a forward model where we use an apparent resistivity for the contaminant plume at 273 ohm-m, background saturated zone apparent resistivity of 540 ohm-m, and a vadose zone apparent resistivity of 1120 Ohm-m. However, we extend the 3 m contaminant plume in the saturated zone in to the vadose zone by 2 m. Simulation results show a visible conductive plume in the modeled resistivity sections. The forward model results suggest that the bulk electrical conductivity of the 3-m thick layer in the saturated zone has to be at least 4 to 5 times higher than

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390 background bulk conductivities or be extended into the vadose zone by ~2 m to be observed in 391 the resistivity sections. We therefore conclude that the high bulk electrical conductivity anomaly 392 observed in the 1996 and 2003 was mainly due to the vadose zone contamination and 393 accompanying biodegradation effects.

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Self Potential: Terminal electron acceptor processes during microbial degradation of hydrocarbon are driven by redox conditions in the contaminated media (e.g., Vroblesky and Chapelle, 1994, Cozzarelli et al., 2001). The redox state within a hydrocarbon contamination is significantly different from background conditions. Naudet et al. (2003; 2004) have suggested that SP anomalies in organic rich contaminant plumes are generated in response to redox processes because of good positive correlations between redox potential (Eh) and residual SP. The relationship between SP vs. Eh for the FT-02 site is poor ( $R^2 = 0.0335$ ). Our analysis of the resistivity suggests that the contaminated saturated and vadose zone contribute differently to the geophysical response measured at the surface and that the vadoze zone contribution to the geophysical response may be higher than the saturated zone. In fact, Minsley et al. (2007) show very strong SP (mean of 60 mV) signals for dense non aqueous phase liquids (DNAPL) trapped in the vadose zone in which they attribute to biodegradation. High SP values show close correspondence to high DNAPL concentration although this was not entirely so for all locations at the study site (Minsley et al., 2007). Thus, the poor correlation we observe between SP and Eh at the FT-02 site may occur for two reasons: 1) the redox measurements being compared to SP were collected from groundwater and may contribute only partly to the total SP measured at the surface and 2) redox conditions occurring due to biodegradation in the capillary fringe and lower vadose zone which may contribute to the overall electrochemistry of the system redox, was not

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measured. An alternative mechanism that may cause the observed SP is diffusion potentials due to differences in the mobility of electrolytes of different concentrations in the contaminated and background pore fluids and groundwater (Telford et al., 1990; Reynolds, 1997; Nyquist and Cory, 2002). Such diffusion potentials are typically small and positive, consistent with the values observed in this study. Sauck et al. (1998) attributes the high SP source at the FT-02 plume to electrochemical potentials from chemical concentration gradients and ion diffusion. If SP is generated by ionic diffusion potential, then the step decrease in the SP between 1996 and 2007 can not be explained by ionic flushing by fresh water, an explanation used to account for lower bulk electrical conductivity along the profile in 2003 (Smart et al., 2004). For the diffusion potentials to persist in natural settings, there has to be a source/mechanism capable of maintaining imbalances in the electrolyte concentration (in our case, excess organic carbon that drives the hydrocarbon biodegradation) (Reynolds, 1997). Hence, any reduction in the ionic concentration over time will also reduce the magnitude of this potential. Removal of hydrocarbon mass by the SVE system decreases biodegradation activities. The decrease in microbial activities in turn decreases the ionic concentration differences between fluids in the contaminated and uncontaminated zones (vadose and saturated zones) explaining the observed decrease in SP between 1996 and 2007. Although streaming potentials due to fluid flow (Telford et al., 1990) can cause an SP response, we discount this possibility at the site because of low groundwater gradients and velocity. 

 Ground Penetrating Radar: There are two main changes that appear in the GPR records over the FT-02 contaminant plume between 1996, 2003, and 2007: 1) strengthening of the GPR reflection with time and 2) lowering of the depth of the "shadow zone" below the water table

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(Figure 5). In the absence of changing geologic parameters, variations of GRP attenuation over LNAPL plumes occur due to changing dielectric constants (relative permittivity contrast) and the resistivity structure of the subsurface (e.g., Daniels et al., 1995; Orlando, 2002; Cassidy, 2007). The attenuation of GPR reflection amplitude resulting in the shadow zone is explained by increase in the bulk conductivity associated with biodegradation (e.g., Sauck 2000; Bradford 2007). Bradford (2007) suggests that increased conductivity in the contaminated zone pore fluids alters the relaxation characteristics of the bulk formation, masking decrease in dispersion caused by the residual hydrocarbons. In addition, Bradford (2007) noted that dispersion in the zone of contamination was generally higher in the vadose zone than in the saturated zone (Figure 8c; Bradford, 2007). Cassidy (2007) shows enhanced relative GPR signal attenuation associated with the smear zone surrounding the seasonally changing water table interface compared to the saturated contaminated zone. The zone of higher dispersion (Bradford 2007) and enhanced signal attenuation (Cassidy, 2007) in the contaminated vadose zone corresponds to the same region of the vadose zone where we show elevated bulk electrical conductivity in our 1996 and 2003 resistivity surveys (Figure 3a & 3b). We inferred that the predominant effect to the GRP signal attenuation occurs from microbial alteration of the contaminants. Thus, removal of hydrocarbon from the contaminant zone and the reduction in fluid conductivity (Figure 7) may explain the strengthening of the GPR reflections. However, we are unable to explain why the GPR attenuation is deeper and wider below the water table in the 2007 image compared to 2003 and 1996 (Figure 3). There is need for further investigations to explain this phenomenon. 

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### CONCLUSIONS

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The removal of the contaminant mass from LNAPL contaminant alter the physio-chemical and biological properties of the subsurface which can be monitored using chemical analysis of groundwater and integrated geophysical techniques (GPR, SP, and electrical resistivity). Laboratory and field surveys have demonstrated increased bulk conductivities as well as increased microbial activities associated with LNAPL contamination. Geophysical signatures associated with the long term changes in the contaminant reduction (e.g., by natural or engineered biodegradation or source removal), is unknown. In this study, we demonstrate that the removal of the contaminant mass from the source area reduced the total petroleum hydrocarbon available for microbial metabolism, thereby altering the chemical, biological, and physical conditions. By removing the hydrocarbon source from the area, the microbial population and activity also reduces, resulting in changes that can be detected by geophysical techniques. We therefore conclude that contaminant mass reduction by natural bioremediation or enhanced engineered remediation can be effectively imaged using geophysical techniques especially if the contamination is prominent in the vadose zone rather than in the saturated zone.

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1		Geophysical Response to Contaminant Removal
2 3 4	638	
5 6	639	FIGURE CAPTIONS
7 8 9	640	Figure1. Conceptual model of petroleum hydrocarbon contamination illustrating the temporal
10 11	641	behavior of the bulk electrical conductivity due to contaminant mass reduction by
12 13 14	642	biodegradation, natural attenuation, or engineered remediation.
15 16	643	
17 18 19	644	Figure 2. Map of the FT-02 site showing locations of electrical resistivity and ground
20 21	645	penetrating radar (GPR) lines, the self potential (SP) grids, multi-level piezometers, monitoring
22 23	646	wells, and soil vapor extraction system. The gray area represents the outline of the FT-02
24 25 26	647	contaminant plume defined in 1996. Insert is the map of Michigan USA.
27 28	648	
29 30 31	649	Figure 3. Inverted dipole-dipole resistivity profiles along the contaminant plume for (a) 1996,
32 33	650	(b) 2003, and (c) 2007 respectively. The approximate lateral extent of the contaminant plume is
34 35 36	651	indicated by the arrows. Note the change in conductivity in the contaminant plume over time.
37 38	652	
39 40	653	<b>Figure 4.</b> Self potential (SP) anomaly map of a portion of the FT-02 measured in a) 1996 and b)
41 42 43	654	2007. A grid showing the soil vapor extraction (SVE) system is superimposed on the 2007 SP
44 45	655	grid.
46 47 48	656	
48 49 50	657	Figure 5. GPR profile over FT-02 contaminant plume measured in a) 1996, b) 2003, and c)
51 52	658	2007. The approximate lateral extent of the contaminant plume is indicated by the arrows. Note
53 54 55	659	the change in the water table reflectors around 100 ns and the change in the depth of the shadow
56 57 58 59 60	660	zone in the contaminant plume over time.

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Figure 6. Depth variations of select chemical parameters a) oxidation reduction potential, b) dissolved iron (Fe<sup>2+</sup>), c) sulfate, d) carbon isotope of dissolved inorganic carbon ( $\delta^{13}C_{DIC}$ ), e) calcium, and f) specific conductance measured in the contaminated aquifer in 2007 at the FT-02 site. The water table is at 4.5 m. The zone of active biodegradation was estimated from multilevel wells to be about 3 m.

Figure 7. Temporal changes in a) total petroleum hydrocarbon (TPH), b) temperature, c)
groundwater specific conductance, and d) depth to water table, in the FT-02 contaminant plume.

Figure 8. Forward model simulating different conductivity scenarios a) 3 m conductive plume
with 273 Ohm-m; b) 3 m conductive plume with 73 Ohm-m; c) 5 m conductive plume extending
to the vadose zone.







Conceptual model of petroleum hydrocarbon contamination illustrating the temporal behavior of the bulk electrical conductivity due to contaminant mass reduction by biodegradation, natural attenuation, or engineered remediation. 279x215mm (600 x 600 DPI)





Map of the FT-02 site showing locations of electrical resistivity and ground penetrating radar (GPR) lines, the self potential (SP) grids, multi-level piezometers, monitoring wells, and soil vapor extraction system. The gray area represents the outline of the FT-02 contaminant plume defined in 1996. Insert is the map of Michigan USA. 279x215mm (600 x 600 DPI)





Inverted dipole-dipole resistivity profiles along the contaminant plume for (a) 1996, (b) 2003, and (c) 2007 respectively. The approximate lateral extent of the contaminant plume is indicated by the arrows. Note the change in conductivity in the contaminant plume over time. 279x215mm (600 x 600 DPI)

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Che-Alota et al., Figure 4



Self potential (SP) anomaly map of a portion of the FT-02 measured in a) 1996 and b) 2007. A grid showing the soil vapor extraction (SVE) system is superimposed on the 2007 SP grid. 279x215mm (600 x 600 DPI)





GPR profile over FT-02 contaminant plume measured in a) 1996, b) 2003, and c) 2007. The approximate lateral extent of the contaminant plume is indicated by the arrows. Note the change in the water table reflectors around 100 ns and the change in the depth of the shadow zone in the contaminant plume over time. 279x215mm (600 x 600 DPI)

Che-Alota et al., Figure 6



Zone of contamination and active biodegradation

Depth variations of select chemical parameters a) oxidation reduction potential, b) dissolved iron (Fe2+), c) sulfate, d) carbon isotope of dissolved inorganic carbon ( $\delta$ 13CDIC), e) calcium, and f) specific conductance measured in the contaminated aquifer in 2007 at the FT-02 site. The water table is at 4.5 m. The zone of active biodegradation was estimated from multi-level wells to be about 3 m.

279x215mm (600 x 600 DPI)

OFT-49 +FT-85

(a)

(b)

(c) cond. (uS/cm)

(d)

Water table depth (m)

Temperature (°C)

700

600 TPH (µg/L) 500 400

300 200

100

80

600

400 specific 200

Vov-DI

Time

Temporal changes in a) total petroleum hydrocarbon (TPH), b) temperature, c) groundwater specific

conductance, and d) depth to water table, in the FT-02 contaminant plume.

279x215mm (600 x 600 DPI)

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Che-Alota et al., Figure 7







Forward model simulating different conductivity scenarios a) 3 m conductive plume with 273 Ohmm; b) 3 m conductive plume with 73 Ohm-m; c) 5 m conductive plume extending to the vadose zone.

279x215mm (600 x 600 DPI)