TEMPORAL GEOPHYSICAL AND GEOCHEMICAL

SIGNATURES DUE TO CONTAMINANT SOURCE

REDUCTION AT WURTSMITH AIRFORCE BASE IN

OSCODA MICHIGAN, USA

By

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TEMPORAL GEOPHYSICAL AND

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CONTAMINANT SOURCE REDUCTION AT

WURTSMITH AIRFORCE BASE IN OSCODA,

MICHIGAN, USA

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This thesis is organized in two sections. Section one gives an outline of the thesis and introduces the problem. This section also presents the 1 journal paper. Paper 1 "*Temporal geophysical signatures due to contaminant source reduction*" which focuses on the geophysical signatures was submitted to GEOPHYSICS for review and is currently being revised. Paper 2 describes the impacts of biodegradation and weathering products over time at the FT-02 site in Oscoda, Michigan is still being revised for submission. Section two summarizes the major conclusions of the work

ACKNOWLEDGMENTS

TABLE OF CONTENTS

Page

PAPER 2

SECTION 2

VITA

LIST OF FIGURES

Paper 2

LIST OF TABLES

SECTION 1

This section gives an overview of the research objectives. A general introduction to the study area including previous work done in the area is also given. Also presented in this section are two papers. The first paper "Temporal geophysical signatures due to contaminant remediation" is a peer review journal paper. This paper has being submitted to GEOPHYSICS and is currently being revised for corrections. This paper reports and summarizes the results of geophysical surveys (electrical resistivity, self potential and ground penetrating radar) collected in 1996, 2003 and 2007 at the Wurtsmith Air Force Base in Oscoda, Michigan, USA. The results show that significant alteration of the surface had occurred post the installation of a soil vapor extraction system in 2001, thereby affecting the geophysical responses observed in 2007 compared to 1993 and 2003. The second paper is still work in progress and is being prepared for submission to a journal. It describes the biodegradation and weathering products at the FT-02 site and also shows the effects of the soil vapor extraction system on the plume length.

GENERAL OVERVIEW

The process of bioremediation causes an increase in the bulk electrical conductivity of hydrocarbon contaminated soil that is readily detectable by integrated geophysical methods (Maxwel and Schmok, 1995; Atekwana et al., 1998; Sauck et al., 1998; Grumman and Daniels, 1995; Lucius, 2000; Suck, 2000). The increase in bulk electrical conductivity is attributed to bacterial production of organic and carbonic acids as they degrade hydrocarbons. These acids leach ions from the surrounding soil matrix, causing an increase of the ion content in the pore water that accelerates the dissolution of minerals in the contaminated matrix materials (Sauck, 2000). This results in etching of the grains of the soil matrix observed by Bennett et al. (1996). The dissolved ions, organic acids and pore water bacteria attach to the matrix, causing an increase in the electrical conductivity and a reduction in the bulk resistivity (e.g., Atekwana et al., 1998; Sauck et al., 1998; Sauck, 2000; Abdel Aal et al., 2004; Davis et al., 2006). Sauck (2000) predicts higher TDS for groundwater in sediments contaminated with hydrocarbon and undergoing intrinsic biodegradation. However, both field and laboratory studies models show that in vertical distribution high conductivities are coincident with the zone of free product contamination compared to the saturated zone with contamination in the dissolved phase (e.g. Werkema et al., 2003; Atekwana et al., 2004).

Source removal is one of the most common stems in the process of contaminant remediation. Over time, the bulk electrical conductivity of contaminant plumes are being altered due to removal of source. The removal of the source will result to physical,

chemical and biological changes of the geologic environment. Such changes are readily imaged by geophysical methods such as ground penetrating radar (GPR), electrical resistivity (ER), self potential (SP) and electromagnetic (EM). Several studies have documented these geophysical responses associated with high conductive anomalies (e.g. Bermejo et al., 1997; Sauck et al., 1998; Atekwana et al., 2000; Smart et al., 2003; Bradford e al., 2007; Cassidy et al., 2007; Yang et al., 2007, etc.). Also, laboratory studies have shown that microbial processes change the electrical properties of unconsolidated sediments rich in organic carbon as a result of increased real and imaginary conductivity (Abdel Aal et al., 2004).

Numerous case studies that have been presented to describe geophysical anomalies observed in a contaminant plume (DeRyck et al., 1993; Benson et al, 1995; Maxwell et al., 1995; Bermejo et al., 1997; Sauck et al., 1998; Atekwana et al., 1998; Atekwana et al., 2000; Lucius et al., 2000; Naudet et al., 2003; Naudet et al., 2004; Smart et al., 2004; Cassidy et al., 2007). However, to date there are no studies that have examined the long-term changes including source removal on the geophysical signatures. We are therefore faced with the problem of what happens geophysically as contaminant mass declines over time either due to natural processes or artificially by human intervention. The result of this study should therefore give us an understanding of the geophysical signatures associated with hydrocarbon source removal.

This study was carried at the Wurtsmith Air Force Base in Oscoda, Michigan. This site has been the focus of several geophysical and geochemically studies (e.g.

Chapelle et al., 1996; Bermejo et al., 1997; Sauck et al., 1998; Atekwana et al., 1998; Atekwana et al., 2000; McGuire et al., 2000; Skubal et al., 2001; Moody et al., 2003; Smart et al., 2004; Bradford et al., 2007). Sauck et al., (1998) in 1996, observed a high conductive anomaly at the FT-02 site using geophysical techniques (ground penetrating radar, self potential and electrical resistivity). This area of high anomalous conductivity was coincident with the area of the hydrochemically defined plume. In 2003, similar geophysical studies conducted by Smart et al., (2004) shows a decrease in conductivity over the plume compared to observations by Sauck et al., (1996). Smart et al., (2003) also observed a slight shift to the right of the plume. In the first paper, we compare results of a survey that was carried out at the FT-02 site in 2007 using the geophysical techniques to results carried out in 1996 (Sauck et al., 1998) and in 2003 (Smart et al., 2004). The grids used in the 1996 and 2003 survey were re-established in 2007 for better comparison.

Groundwater investigation at the FT-02 site by Chapelle et al., (1996) showed high dissolved oxygen which was indicative of methanogenesis. This work was supported by Mcguire et al., (2000) and Skubal et al., (2001). Their results suggested that active biodegradation was still occurring at the FT-02 site. The second paper focuses on the biodegradation products observed in 2007 compared to 1996. Also, we present results that show that enhanced mineral weathering is occurring at the plume as a result of biodegradation. We also redefine the outline of the plume in 2007 using groundwater geochemistry data collected from monitoring wells.

DEFINITION OF TERMS

Biodegradation: Decomposition of a substance into more elementary compounds by the action of microorganisms such as bacteria

Self potential (SP): Naturally occurring electric potential difference in the earth, measured between a reference electrode and a roving electrode either at the surface or in a borehole

Soil vapor extraction system: A Soil Vapor Extraction System (SVE) is an in situ unsaturated (vadose) zone soil remediation technology, designed to remove hazardous vapors from the subsurface by drawing air through the contaminated soil, and then volatilizing the liquid, dissolved or absorbed phase pollutants from the soil

PAPER 1

Temporal geophysical signatures due to contaminant remediation

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1.1 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 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.

1.2. 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., Daniels et al., 1995; Benson et al., 1997; Halihan et al., 2005; Kaufmann and Deceuster, 2007; Yang et al., 2007), ground penetrating radar (GPR) (e.g., Bermejo et al., 1997; Bradford et al., 2007; Cassidy, 2007; 2008) and self 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 al., 1990; McMahon et al., 1995; Bennett et al., 1996). This leads to an increase in the electrical conductivity of the pore fluids 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) enhance the electrical properties of the contaminated media (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
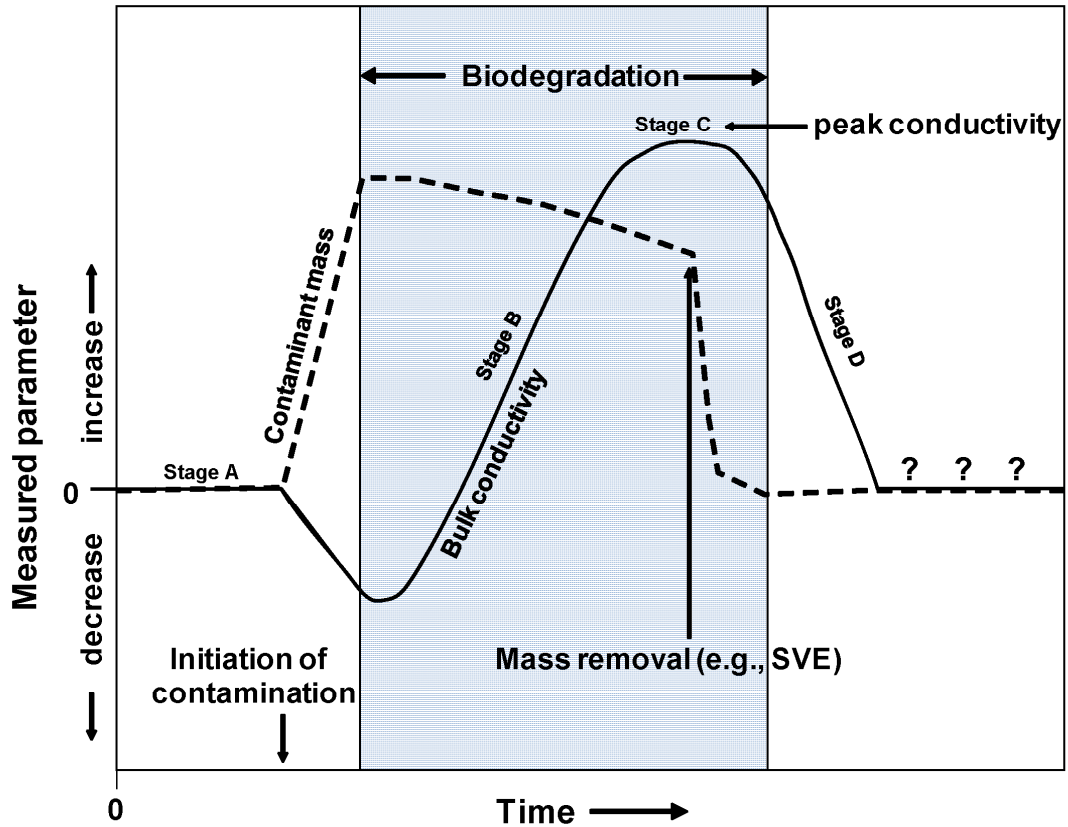
Figure1. Conceptual model of petroleum hydrocarbon contamination illustrating the temporal behavior of bulk electrical conductivity due to contaminant mass reduction by biodegradation, natural attenuation, or engineered remediation.

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, 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.

1.3. SITE GEOLOGY AND SITE HISTORY
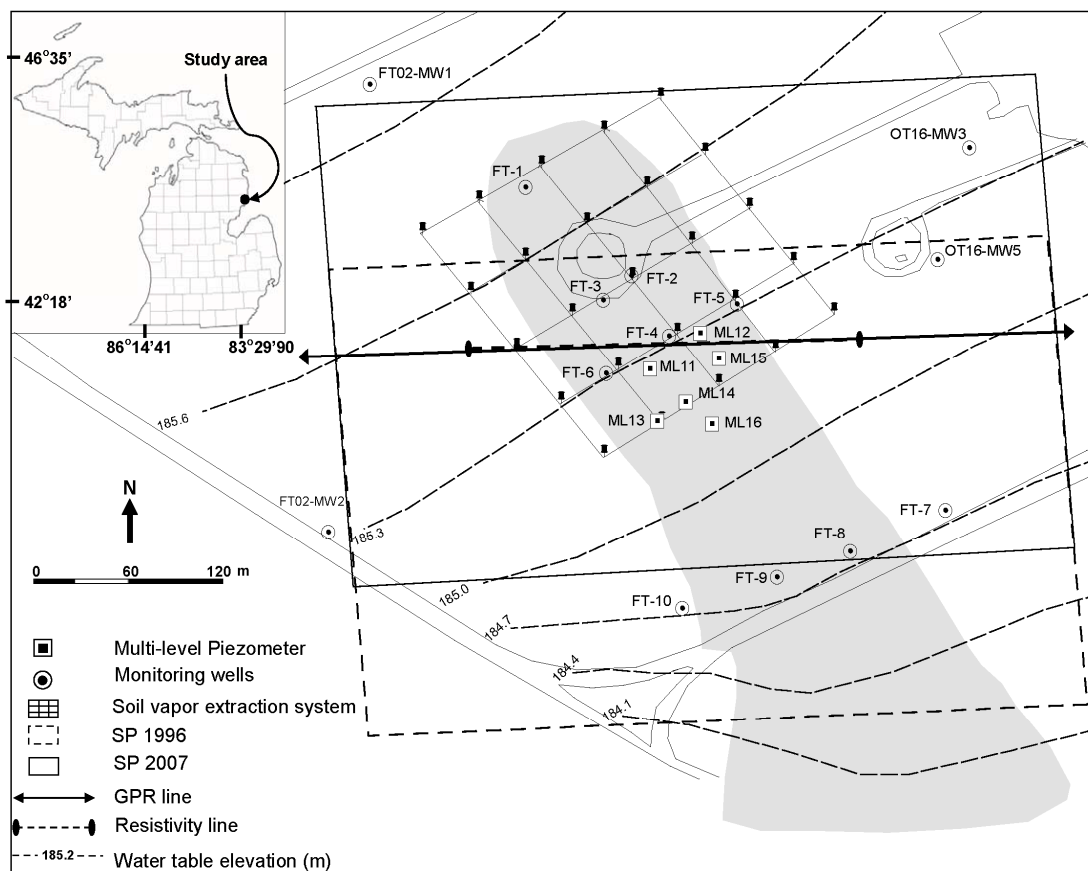
Figure 2. Map of the FT-02 site showing locations of electrical resistivity and ground penetrating radar (GPR) lines, the self potential (SP) grids, multi-level piezometers, monitoring wells, and soil vapor extraction system. The gray area represents the outline of the FT-02 contaminant plume defined in 1996. Insert is the map of Michigan USA.

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 clean, 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 3.47×10^{-4} to 5.32×10^{-4} m/s and groundwater flow varies from 0.03–0.2 m/day (USGS, 1991).

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 seeping 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).

1.4. METHODS

1.4.1. 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 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 match the depth of the 2007 survey. 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$_4$ 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 using Kriging and contoured using SURFER$^®$ (Golden software, 1983). 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).

1.4.2. 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 multi-level 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 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^oC 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.

1.5. RESULTS

1.5.1. 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

17
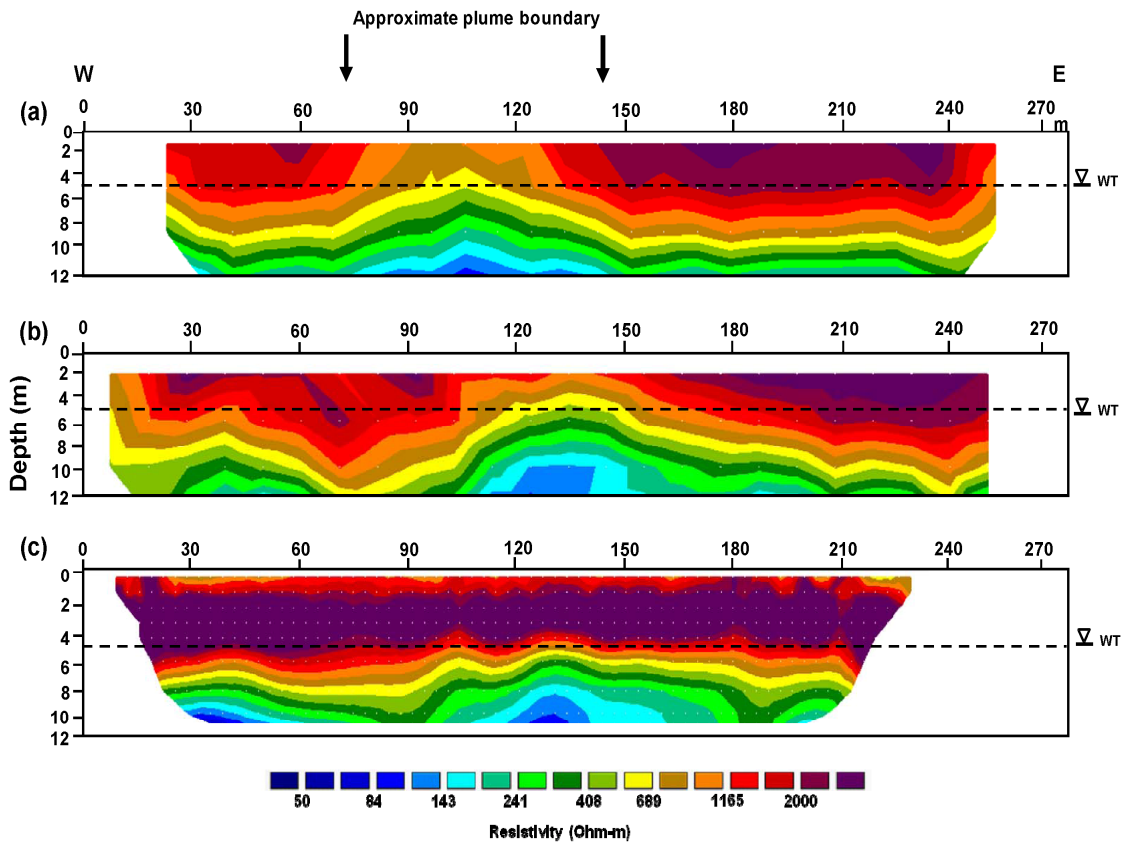
Figure 3. Inverted dipole-dipole resistivity profiles along the contaminant plume for (a) 1996, (b) 2003, and (c) 2007 respectively. The approximate lateral extent of the contaminant plume is indicated by the arrows. Note the change in conductivity in the contaminant plume over time.

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 ~150 m (Figure 3b). However, the highest resistivity values

within the contaminated region of ~700 Ohm-m in the 1996 survey, increased to ~1200

18

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 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.
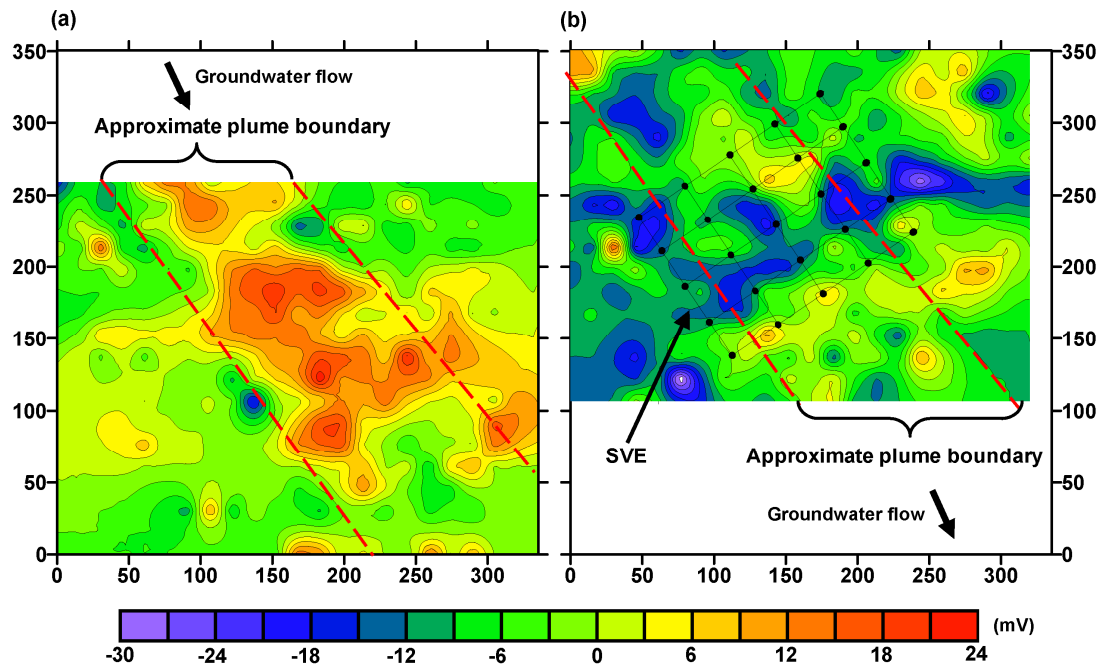
Figure 4. Self potential (SP) anomaly map of a portion of the FT-02 measured in a) 1996 and b) 2007. A grid showing the soil vapor extraction (SVE) system is superimposed on the 2007 SP grid.

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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 (ε_r ~9) to saturated sand (ε_r ~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 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).
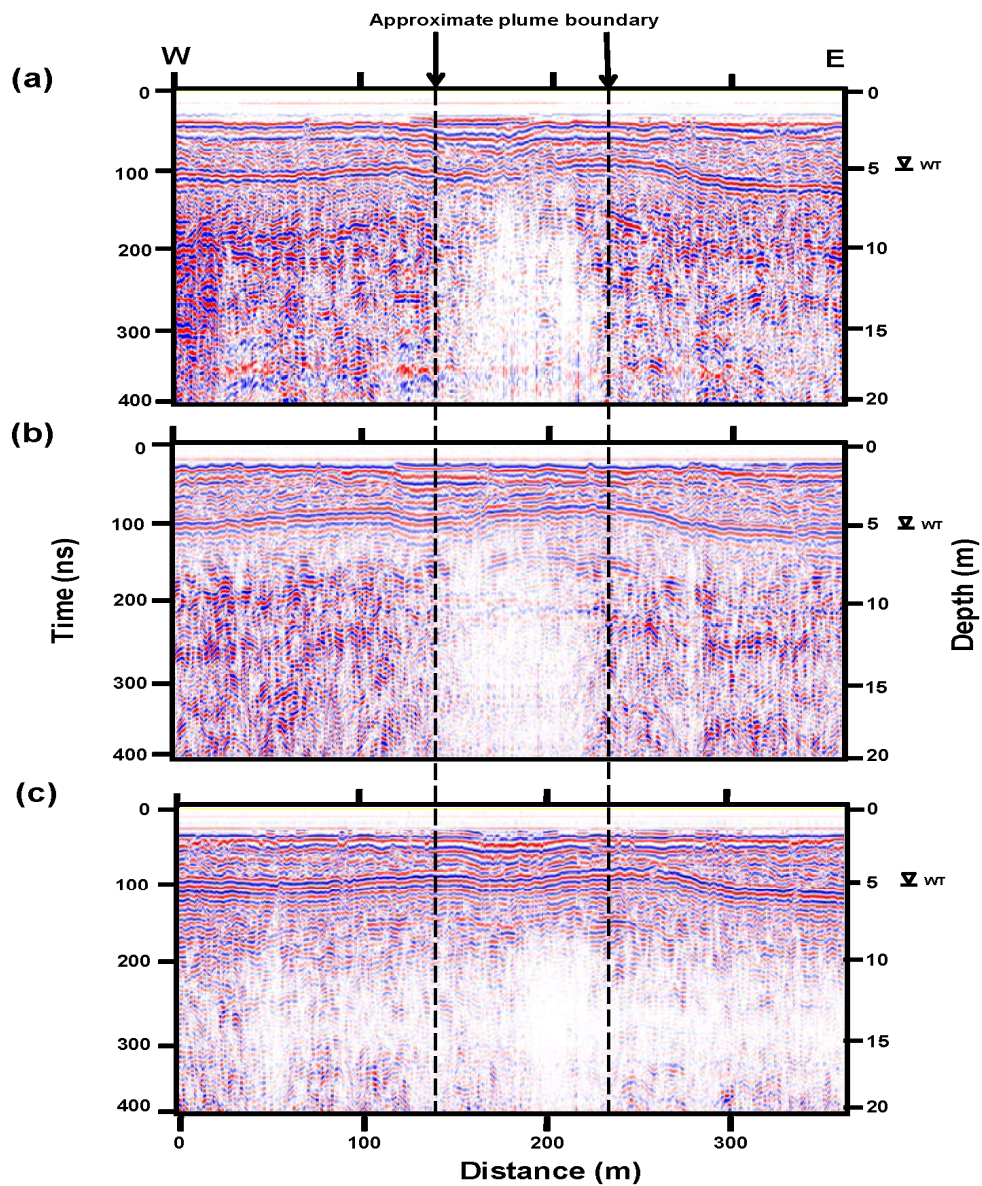
Figure 5. GPR profile over FT-02 contaminant plume measured in a) 1996, b) 2003, and c) 2007. The approximate lateral extent of the contaminant plume is indicated by the arrows. Note the change in the water table reflectors around 100 ns and the change in the depth of the shadow zone in the contaminant plume over

1.5.2. 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
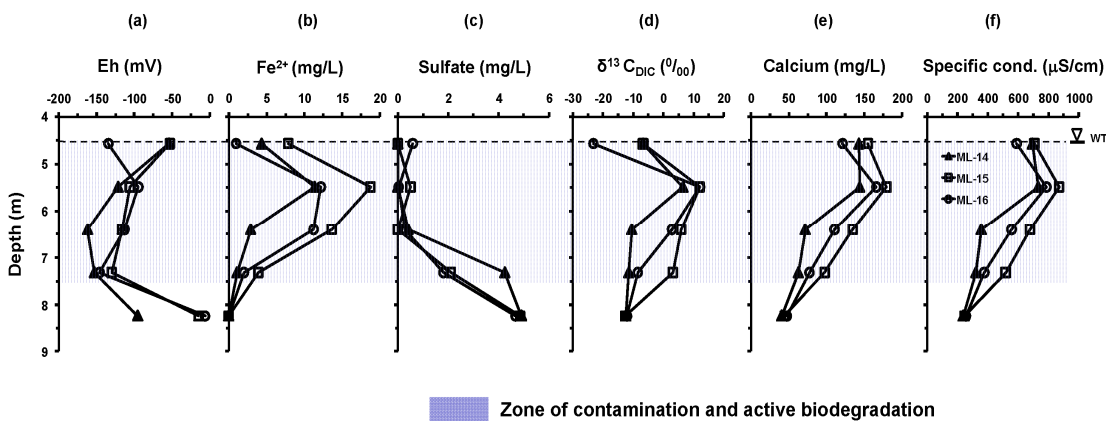
Figure 6. Depth variations of select chemical parameters a) oxidation reduction potential, b) dissolved iron (Fe^{2+}), c) sulfate, d) carbon isotope of dissolved inorganic carbon ($\delta^{13}C_{DIC}$), e) calcium, and f) specific conductance measured in the contaminated aquifer in 2007 at the FT-02 site from multi-level wells 14, 15 & 16 (Figure 1). The water table is at 4.5 m. The zone of active biodegradation was estimated from multi-level wells to be about 3 m.

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 zone defined by Eh, Fe^{2+}, 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).

1.6. DISCUSSION

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 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 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).

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

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_2, N_2), 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 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

26

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 with 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 in 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

27

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 zone by the SVE system. We argue that the removal of volatile and semi-volatile hydrocarbon in the contaminated vadose zone caused a decrease in organic carbon (electron donor to the microorganisms) which decreased microbial activity. The decrease in the microbial activity and its direct and indirect effects in the contaminated environment impacts the physical property of the contaminated environment and the geophysical signatures (e.g., Figure 1). We argue below for why the geophysical response imaged during our surveys is most likely due to 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 cannot 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 ℃ from 2003 to 2007 (Figure 7b). Additionally, the groundwater ionic 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^{o} C in 1996, 16.6^{o} C in 2003, and 18.0^{o} C in 2007
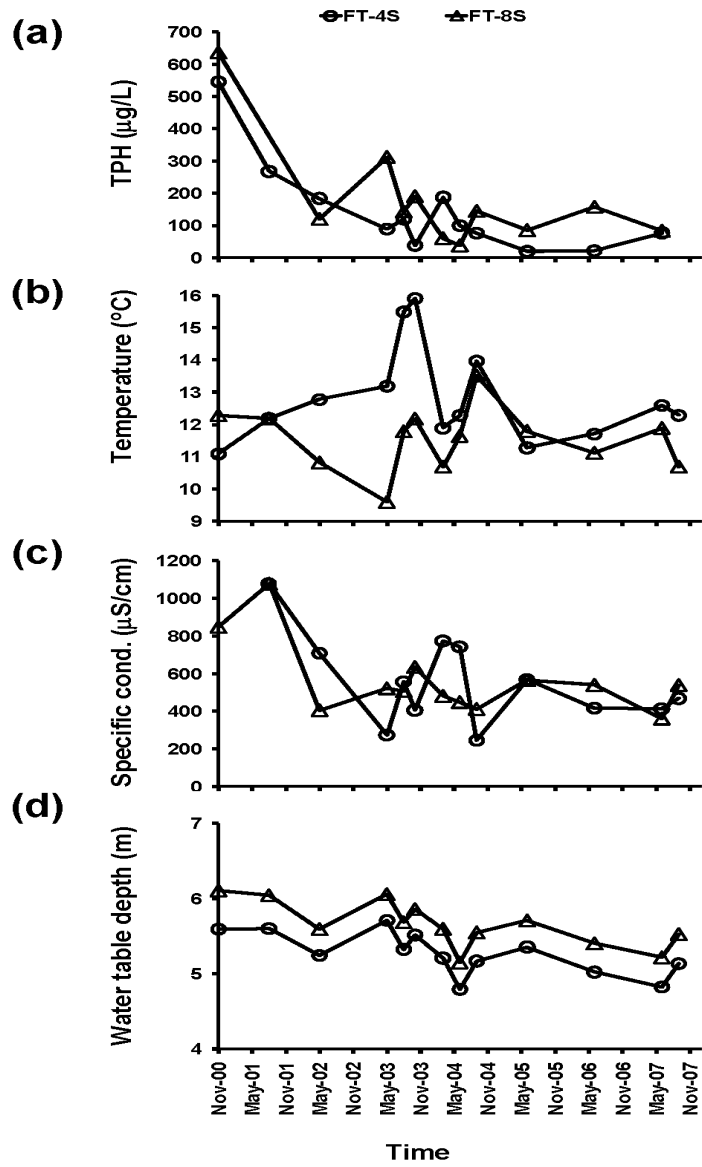
29

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 measured from monitoring wells 4s located in the source area, and 8s located downgradient.

(www.wunderground.com/history/airport/KAPN, 2008). The difference in the mean air temperature ($<1.5^o$ 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 aquifer (Figure 6), evidenced by the terminal electron acceptor concentrations (e.g. Fe^{2+}, SO_4^{2-}). This zone of biodegradation is accompanied by low pH, high CO_2, 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,
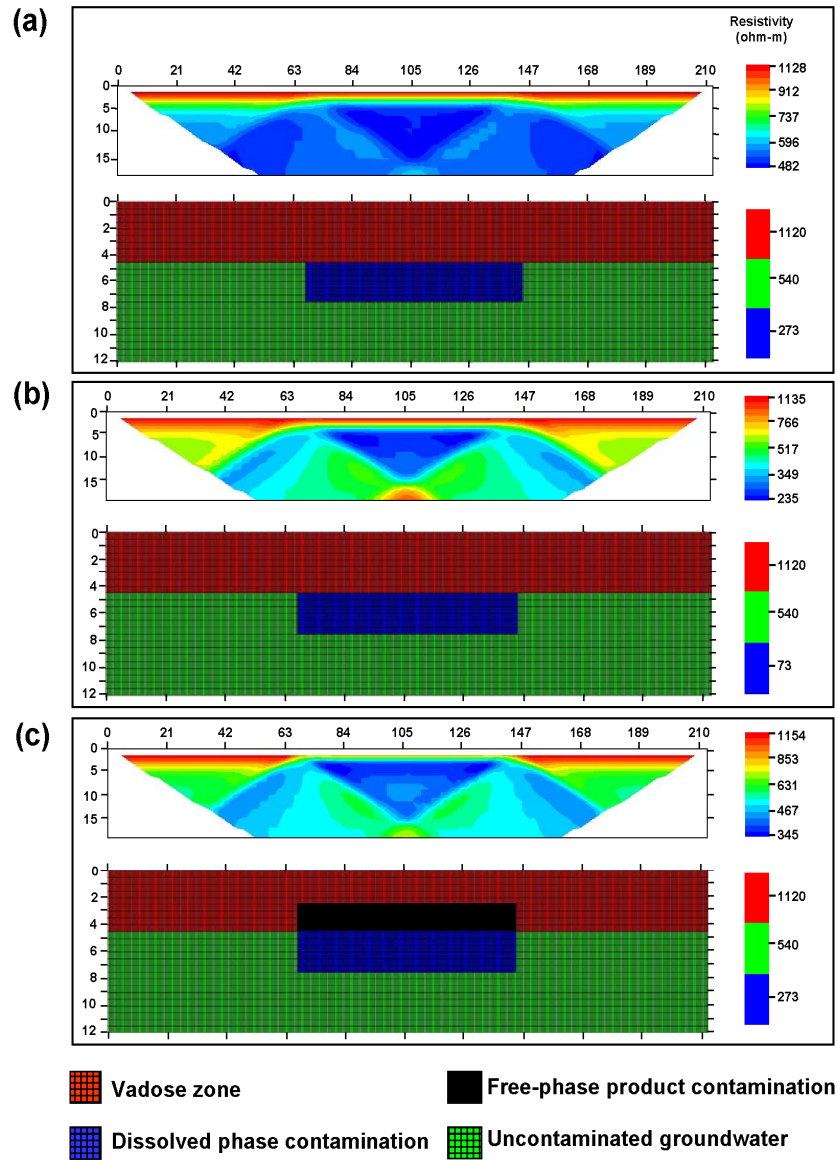
Figure 8. Forward model simulating different conductivity scenarios a) 3 m conductive plume with 273 Ohm-m; b) 3 m conductive plume with 73 Ohm-m; c) 5 m conductive plume extending to the vadose zone.

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 ~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 into 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 background bulk conductivities or be extended into the vadose zone by ~2 m to be observed in the resistivity sections. We therefore conclude that the high bulk

electrical conductivity anomaly observed in the 1996 and 2003 was mainly due to the vadose zone contamination and accompanying biodegradation effects.

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 in organic rich contaminant plumes is 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 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 vadose zone and contaminated saturated zone and between the contaminated vadose and saturated zones and the uncontaminated vadose and saturated zones. This decrease could potentially decrease the diffusion potential between fluids in the contaminated vadose

zone and groundwater and between contaminated and uncontaminated groundwater causing 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 (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 on our 1996 and 2003 resistivity surveys (Figure 3a & 3b). We inferred that the predominant effect to the GRP velocity 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.

1.7. CONCLUSION

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.

1.8. ACKNOWLEDGEMENTS

1.9. REFERENCES

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PAPER 2

Temporal changes in the rate of biodegradation at a hydrocarbon contaminated site undergoing remediation

2.1. INTRODUCTION

Redox zonation in groundwater systems is based on reactions which first use oxygen, and then succession of alternate terminal electron acceptors to support their growth using a variety of carbon sources (Stumm and Morgan, 1981; Lovely, 1991; Lovely and Goodwin, 1998; Chapelle, 1993). In most groundwater systems, the succession of terminal electron accepting processes (TEAPS) in order of decreasing redox potentials and free energy yield is generally: oxygen reduction, nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis (Table 1). Stable carbon isotope ratios of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) has been used to determine terminal electron accepting processes and biodegradation of hydrocarbons in aquifers (Aggarwal and Hinchee, 1991., Conrad et al., 1997; Fang et al., 2000). Atekwana et al., (2004) show that microbial activity enhances mineral weathering which increases the ionic content of groundwater. An increase in the concentration of in biodegradation products increases organic and carbonic acid weathering of minerals in the aquifer, causing an increase in pore fluid conductivity. This leads an increase in the concentration of weathering products (e.g. calcium, silica, magnesium, sodium) in the aquifer depending on aquifer mineralogy.

Studies on TEAP are not unique to this study as the Wurtsmith Air Force base has been a site of several geochemical surveys (Chapelle et al., 1996; McGuire et al., 2000; Skubal et al., 2001; Moody et al., 2003). Most of the studies show evidence of biodegradation and methanogenesis occurring in some parts of the aquifer (Chapelle et al., 1996; McGuire et al., 2000). In this paper, we use TEAPs and stable C isotope ratios of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) to show that active biodegradation occurring in the aquifer. However, unlike previous studies, we present results that show an increase in weathering products as a result of a decrease in terminal electron accepting processes in the aquifer.

Process	Reaction	ΔG (KJ/mole)
Denitrification	$2NO_3^- + 10e- + 12H+ \rightarrow N_2 + 6H_2O$	-1120
Manganese (IV) reduction	$MnO_2 + 2e- + 4H+ \rightarrow Mn_2+ + 2H_2O$	-163
Iron (III) reduction	$Fe(OH)_3 + e- + 3H+ \rightarrow Fe_2+ + 3H_2O$	-50
Sulfate reduction	$SO_4^{2-} + 8e- +10\ H+ \rightarrow H_2S + 4H_2O$	-152
CO_2 methanogenesis	$HCO_3^- + 4H + H^+ \rightarrow CH_4 + 3H_2O$	-136

Table 1. Reactions and free energies of biodegradation products (Lovely and Goodwin., (1998)

2.3. 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 1). 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 clean, well sorted fine to medium sands that grade downward to gravel. Underlying the sand and gravel deposits at approximately 20 m in depth 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 Paleozoic bedrock consisting of Mississippian Marshal Sandstone and Coldwater Shale. The depth to water table from 1996 to 2007 ranged from 3.7 to 5.3 m in the groundwater monitoring wells. Ground water flow is to the southeast, towards a large wetland located 366 m south- south east of the site in the flood plain of the Au Sable River (Robbins et a., 1995; Sauck et al., 1998). Aquifer hydraulic conductivity is 3.47×10^{-4} to 5.32×10^{-4} m/s and groundwater flow varies from 0.03–0.2 m/day (USGS, 1991).
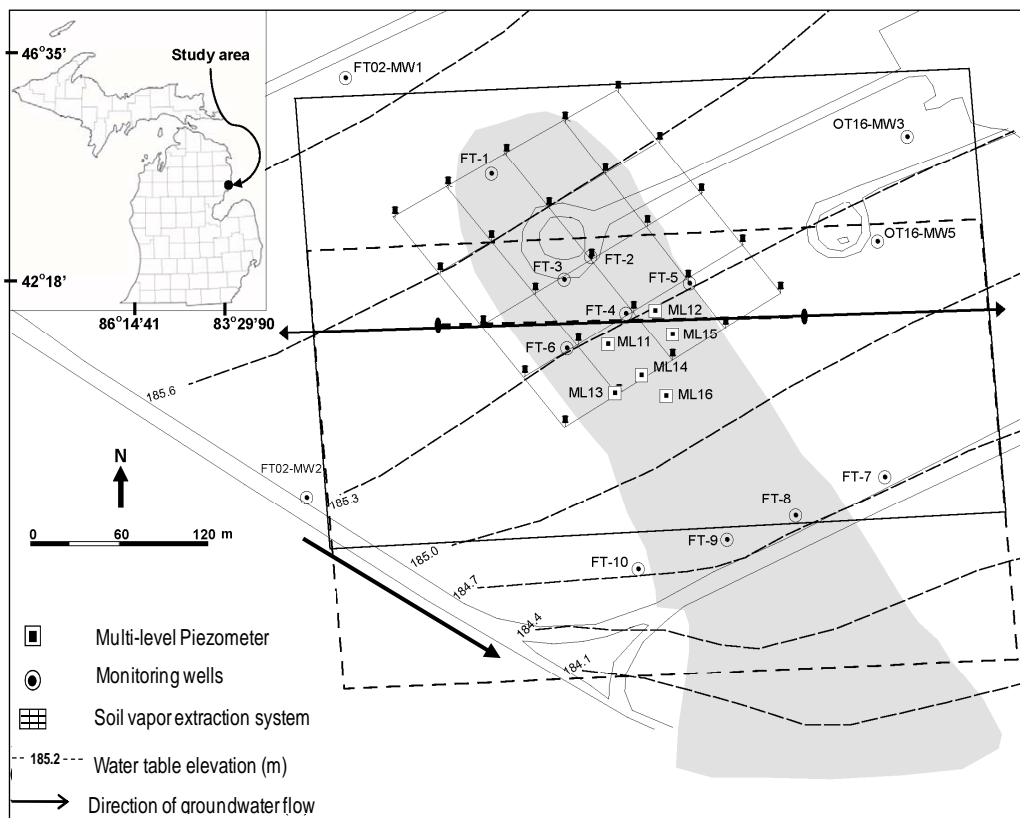
Figure 1. Map of the FT-02 site showing locations of monitoring wells, multi level wells, and soil vapor extraction system. The gray area represents the outline of the FT-02 contaminant plume defined in 1996

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 and 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 help reduce the amount of fuel seeping into the ground. However, an unknown quantity of the fuel had already infiltrated into the subsurface. A contaminant

Light Non-Aqueous Phase Liquid (LNAPL) plume has been defined by chemical analyses of groundwater (Chapelle et al., 1996; Skubal et al., 1999; McGuire et al., 2000; Skubal et al., 2001; Moody et al., 2003). Most of the contamination is concentrated in the upper parts of the water table and within the capillary fringe zone (McGuire et al., 2000; Skubal et al., 2001). In 2007, The contaminant plume at FT-02 is approximately 75 m wide and extends 30 m up gradient and about 450 m down gradient to the south east of the source area (Skubal et al., 2001) (Figure 2). The contaminant plume in groundwater consists of both BTEX (benzene, toluene, ethyl benzene and xylene) compounds and chlorinated solvents.

2.4. Groundwater sampling

A number of monitoring wells and multi-level piezometers were constructed at the FT-02 site by the National Center for Integrated Bioremediation Research and Development (NCIBRD) for groundwater sampling (Figure 1). Groundwater from monitoring wells and multi-level piezometers was pumped to the surface using a peristaltic pump. The water was pumped through a flow cell into which a HydroLab™ down hole Minisonde or Yellow Springs Instrument (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 Sciences) before collecting water for chemical and isotopic analyses. Samples for chemical analysis were collected in

polyethylene bottles (pre-acidfied with nitric acid for cations). The samples were transported on ice stored at $4^{o}C$ to the laboratory until analyses. Samples for DIC extraction and $\delta^{13}C_{DIC}$ measurements were filtered directly into pre-evacuated vials loaded with 85% phosphoric acid and magnetic stir bars and subsequently analyzed using the technique described by Atekwana and Krishnamurthy (1998).

After filtration in the field, alkalinity measurements were conducted by acid titration (Hach Company, 1992); Ferrous iron (Fe^{2+}) and silica concentrations were measured by colorimetry using the phenantholine method (CHEMetrics, 2004). Anions (nitrate and sulfate) were measured by ion chromatography and cations (calcium) were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). DIC was extracted from samples under vacuum and the concentration determined manometricly after cryogenic separation (Atekwana and Krishnamurthy, 1998). The extracted CO_2 was stored in Pyrex® tubes and later analyzed for $\delta^{13}C$ by isotope ratio mass spectrometry at Western Michigan University, Kalamazoo, Michigan. In addition to the 2007 field data, historical data on groundwater physical and chemical parameters were obtained from the Wurtsmith Air Force Base (WAFB) Authority and used in this study.

2.5. RESULTS AND DISCUSSION

The spatial distribution of subsurface redox zones was first characterized at the FT-02 site in 1995 (Chapelle et al., 1996). During that period, the groundwater was

contaminated with high concentrations of BTEX compounds (100-1000 μg/L), with the lowest Eh measurements (-158 mV) in the center of the FT-02 contaminant plume (Chapelle et al., 1996). Chapelle et al. (1996) also illustrated zones at which sulfate concentrations were depleted in the plume relative to surrounding groundwater, which was indicative of sulfate reduction. Also, the presence of dissolved Fe^{2+} in the contaminated plume indicated that active Fe (III) reduction was still occurring in the plume. The presence of nitrite (0.2-1.0 mg/L) at the oxic/anoxic boundary indicated that nitrate reduction was also occurring at this site. In 2007, we observe low Eh measurements (-90 to -160 mV) distributed across the plume which. As demonstrated by Chapelle et al (1996), these measurements alone do not uniquely identify specific redox processes.

Chapelle et al. (1996) observed concentrations of methane that were relatively high (up to 15 mg/L) compared to background lelels suggesting the presence of active methanogenesis in the contaminated plume. They also noted depletion in nitrate, sulfate and iron concentrations in the anoxic plume compared to uncontaminated groundwater values which suggested that nitrate, sulfate and iron reduction was also still occurring in the anoxic plume. The 2007 groundwater geochemistry data contained traces of dissolved oxygen (> 1 mg/l), nitrate (< 1 mgLl), manganese (II) (< 1 mg/L), (< 4 mg/L), Fe^{2+} (< 16 mg/L) and sulfate (< 4 mg/L) in the anoxic plume (Figure 3). This suggests that active zones of nitrate, iron and sulfate reduction were occurring in the plume. However results presented by Chapelle et al. (1996) shows that zones of active biodegradation were more

prominent in the west portion of the plume than in the east (refer to Chapelle et al., 1996 Figure 3). Also, the 2007 geochemical data shows active biodegradation is prominent in the eastern portion of the plume as compared to observations made by Chapelle et al (1996). We observe high concentrations of Fe^{2+} (> 11 mg/L) in ML-15 compared to >1 mg/l from ML-13 to ML-16 (Figure 3 c).
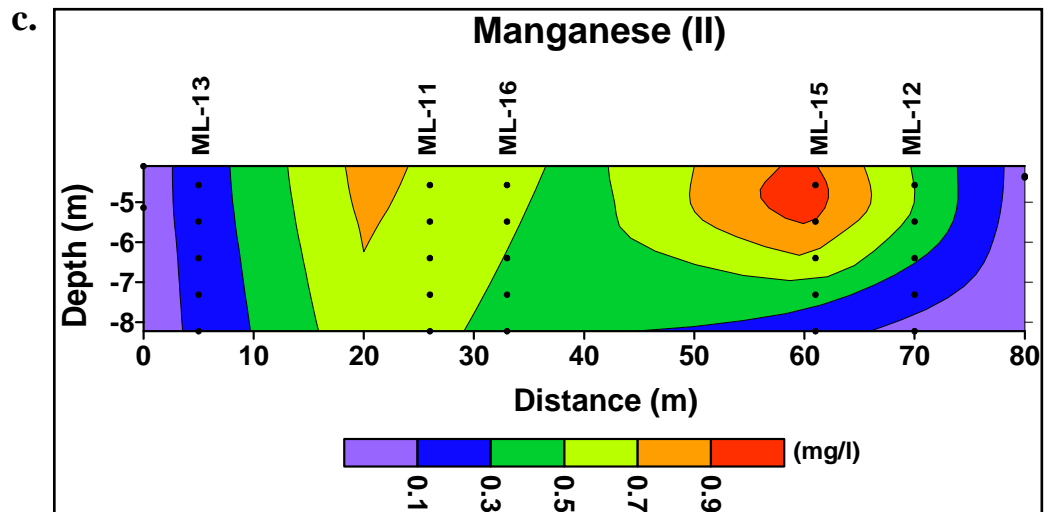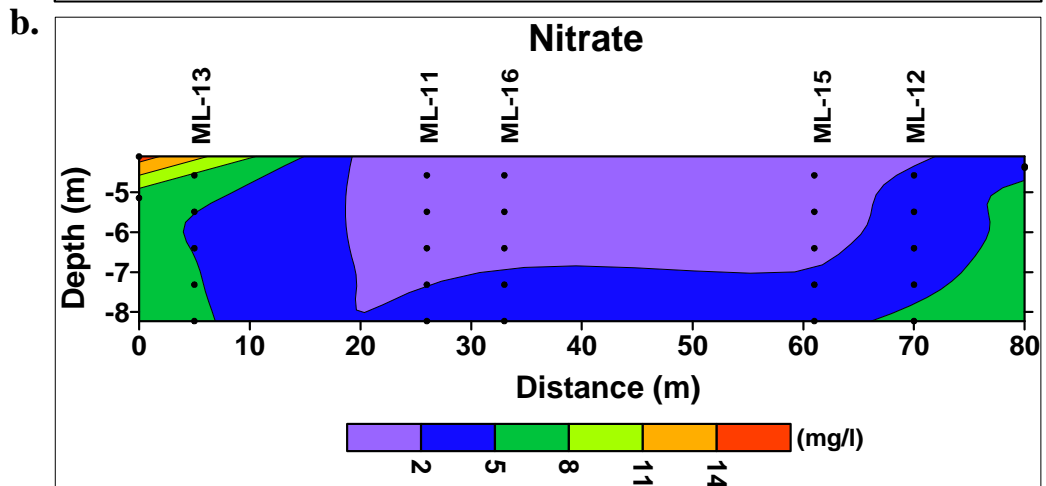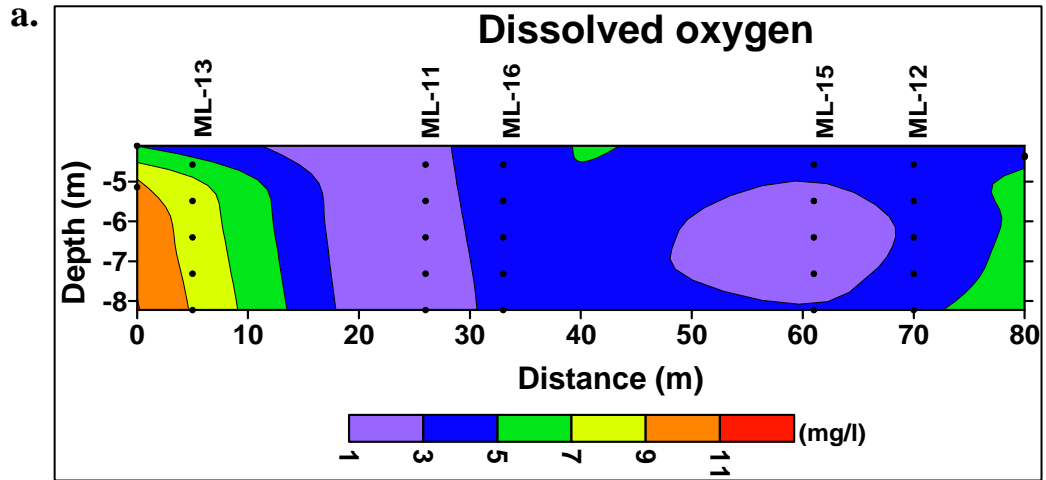
Previous studies have shown that higher microbial activities are associated with bulk conductivities of sediments due to enhanced mineral weathering (Sauck, 2000). This results from bacterial degradation of hydrocarbons which increases CO_2 in the aquifer and produces organic and carbonic acids. These acids increase mineral weathering rates in the subsurface (e.g., Hiebert and Benett, 1992). Between depths of 4.5 to 7.5 m, we observer higher calcium (> 130 mg/L) (Figure 2g), silica (> 8 mg/L) (Figure 2h), Mn^{2+} (> 1 mg/l) (Figure 2c), Fe^{2+} (> 11 mg/l) (Figure 2d) and higher bulk conductivities (between 480 to 650 µS/cm) which decrease with depth (Figure 2i). These trends are accompanied by low pH values of less 7 (Figure 2j). This depth interval is also coincident with depths of lower nitrate and sulfate (Figure 2b & e). These trends suggests that enhanced mineral weathering of grains which results to increase in pore fluid conductivity tracks biodegradation at the FT-02 site.
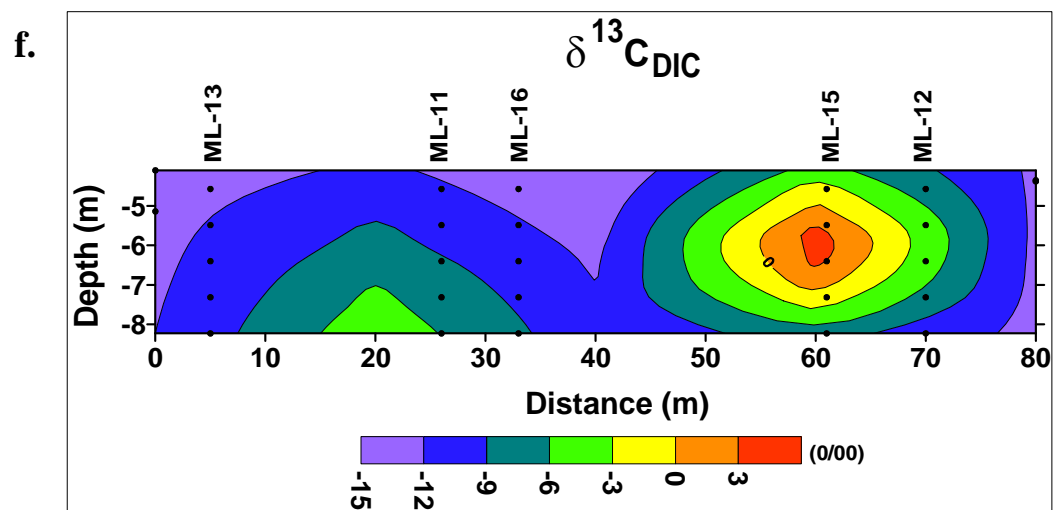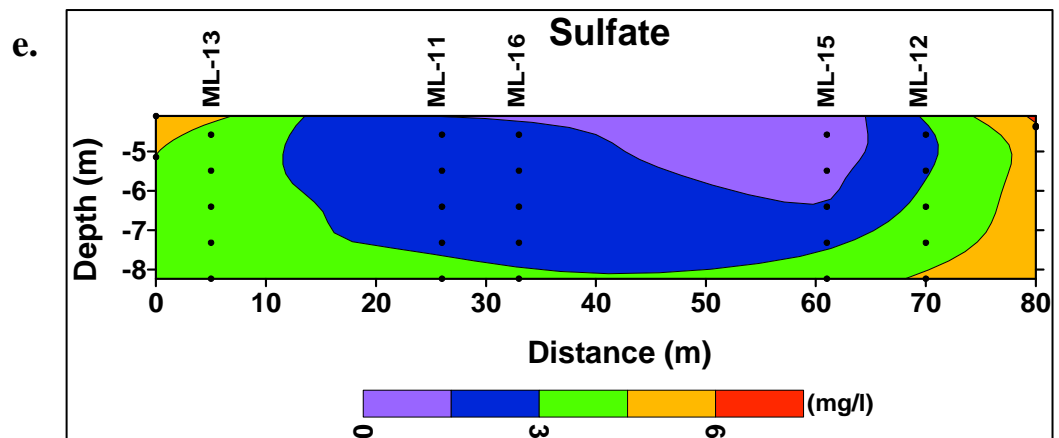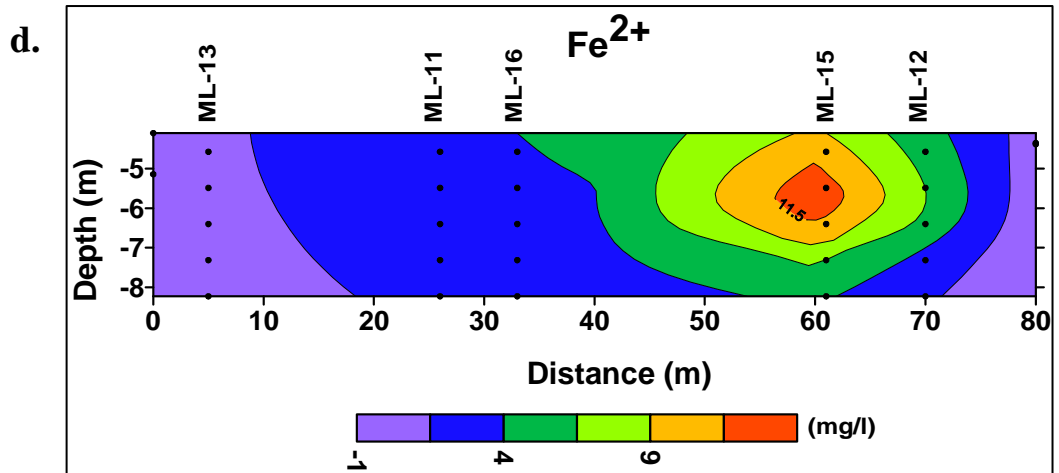
In May 2001, the Wurtsmith Air Force Base Authority installed a Soil Vapor Extraction system (SVE) over the FT-02 contaminant source area. The system consists of 25 extraction points divided into five separate operating groups (Figure 1). As of March 2003, approximately 2320 Kg of free product had been extracted from the vadose zone
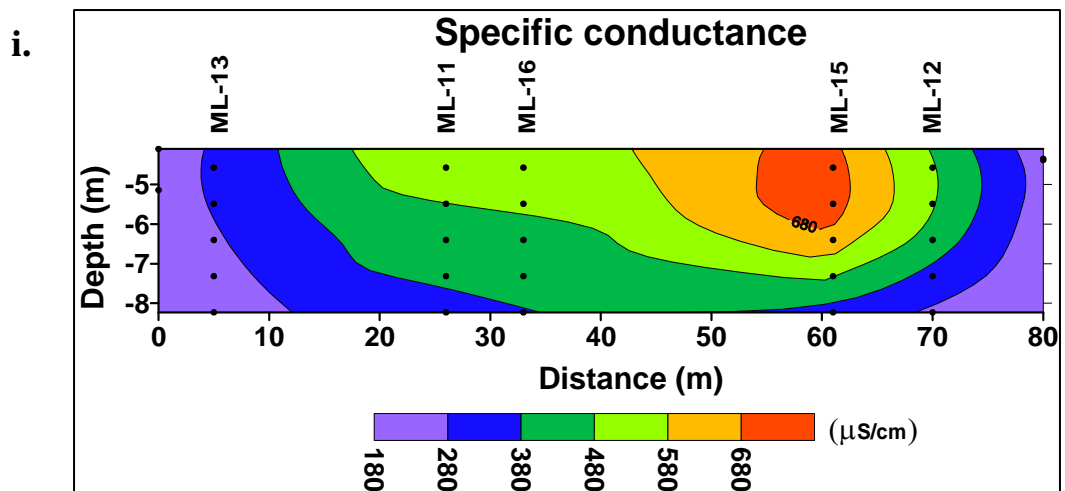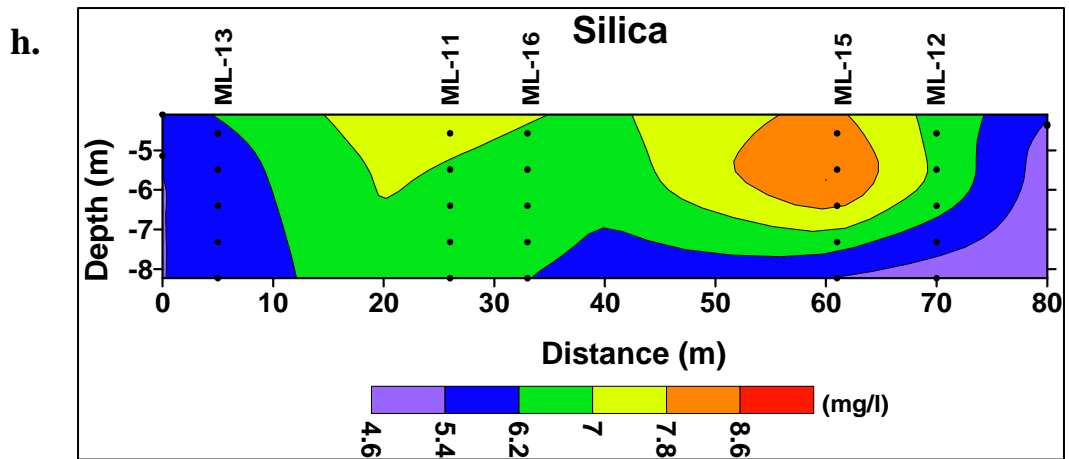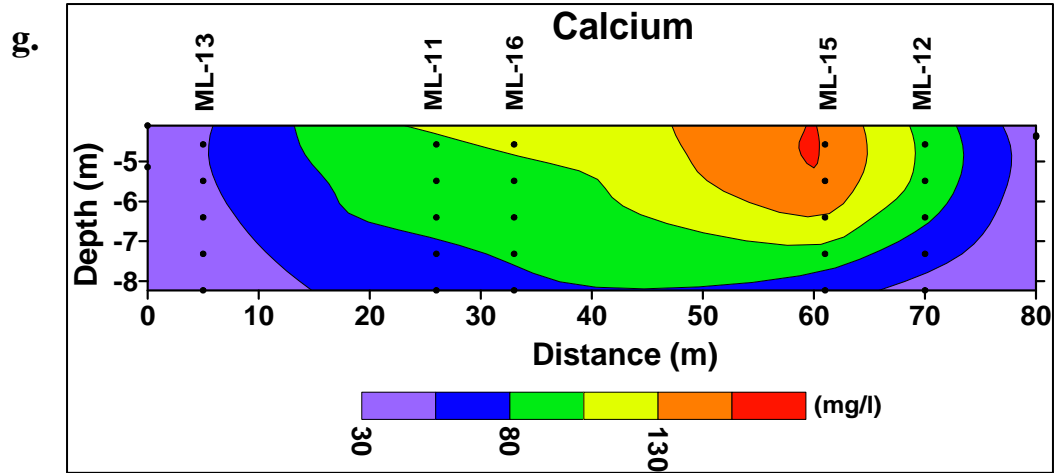
(Parsons, 2004). Groundwater analysis obtained from the WSAFB authority suggest that the total petroleum hydrocarbon (BTEX) concentrations had dropped to ~150-200 mg/l in 2007 (Figure 3) compared to the 1995 BTEX concentrations. Even though the soil vapor extraction system removed several kilograms of BTEX from the vadose zone, the concentration of the TEAP did not significantly change compared to the concentrations observed by Chapelle et al., (1996). This suggests that the effects of the soil vapor extraction system are more prominent in the vadose zone than in the saturated zone. However, as a result of the reduction in TPH over time, our groundwater data shows that the width of the plume has decreased by ~ 20 m in 2007 compared to the ~ 75 m wide plume defined in 1996 by Sauck et al., (1998). We use Fe^{2+}, sulfate, calcium and specific conductance (SPC) (Figure 4) from monitoring wells along a transect from line 185.3 m (OT16-MW3, FT-5, FT-4, FT-6) (Figure 1) to delineate the outline of the plume in 2007. We also show an outline of the hydrochemically defined plume in 1996 (Sauck et al., 1996). From (Figure 2), we observe a general shrinking from east to west in Fe^{2+} sulfate, and calcium concentration as well as the specific conductance from. This shift to the west is also prominent in the multi level wells (Figure 2). Smart et al., (2004) also noted that the plume location defined in Sauck et al. (1998) (Figure 5a; between position ~75 and ~145) had shifted slightly to the east (Figure 5b; between positions ~100 and ~160 m) over the course of several years.

2.6. CONCLUSION

This study shows the effects on biodegradation on enhanced mineral weathering in the aquifer. Increase in calcium and silica concentration and specific conductance in the aquifer suggest that enhanced mineral weathering is occurring in the aquifer. The geochemical data suggest that active biodegradation is occurring in parts of the plume and is especially prominent on the east. This pattern in the geochemical parameters is also followed by the electrical resistivity response. Although the soil vapor extraction was prominent in the vadose zone, a reduction in total petroleum hydrocarbon over time suggests a reduction in the contaminant mass. Also, geochemical data shows that the overall width of the plume has shrunk by ~ 10 m in 2007.

a. Dissolved oxygen

b. Nitrate

c. Manganese (II)

d. Fe^{2+}

e. Sulfate

f. δ^{13}C$_{DIC}$

56

g. **Calcium**

h. **Silica**
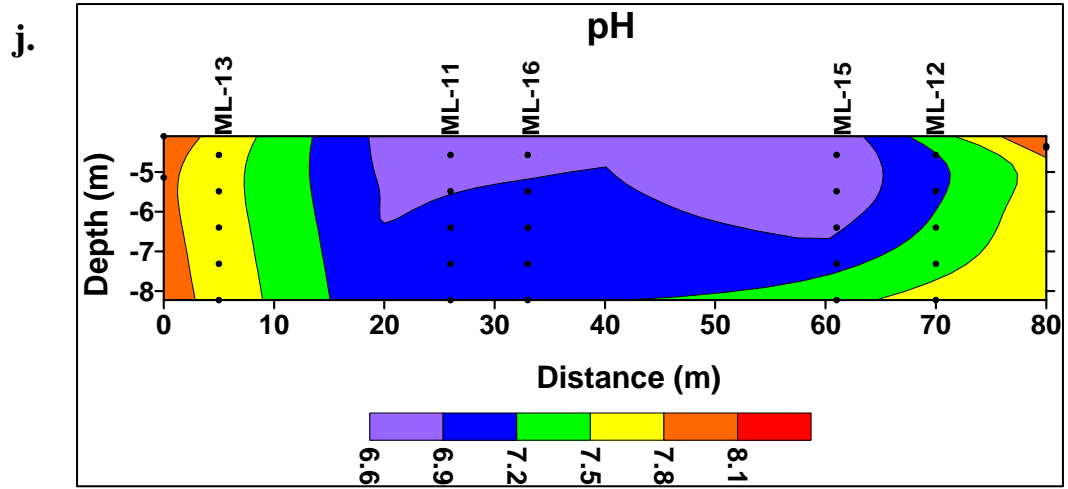

i. **Specific conductance**

57

Figure 2. Spatial distribution of biodegradation and weathering products; Figure 10a to 10f (Spatial distribution of terminal electron acceptor process (TEAP) at the FT-02 site from multi level wells); Figure 10g to 10j (Spatial distribution of weathering products from multi level wells)

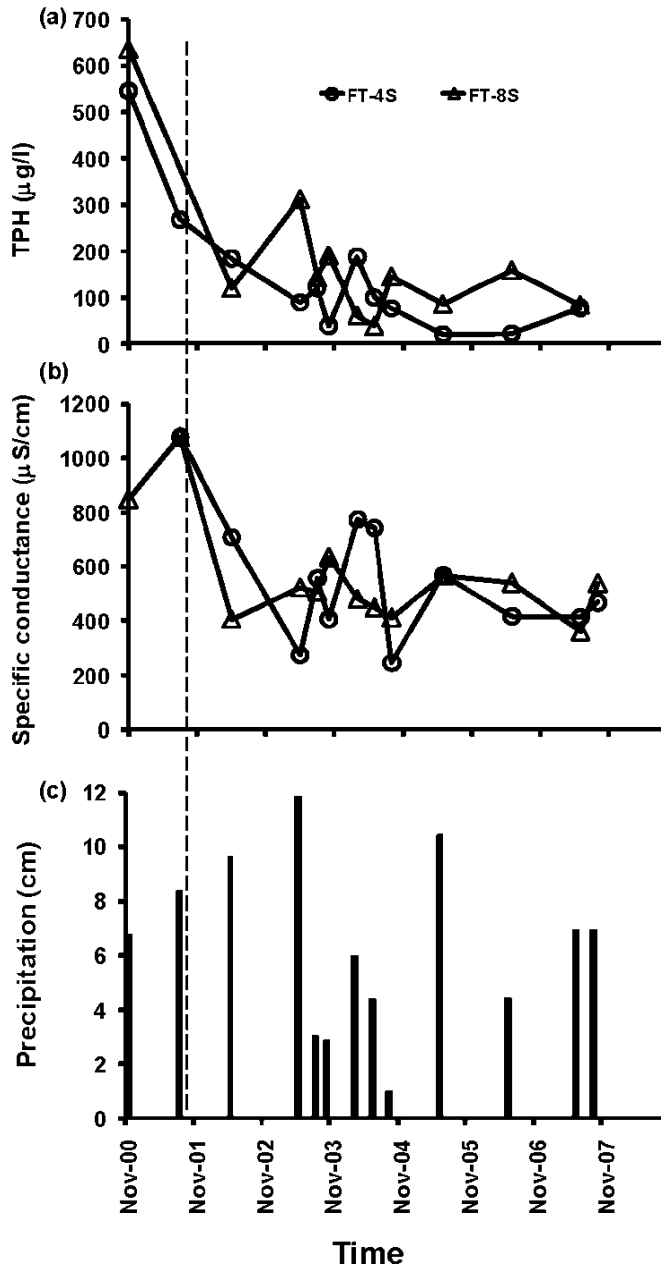Figure 3. Temporal changes in the total petroleum hydrocarbon and groundwater specific conductance in the FT-02 contaminant plume
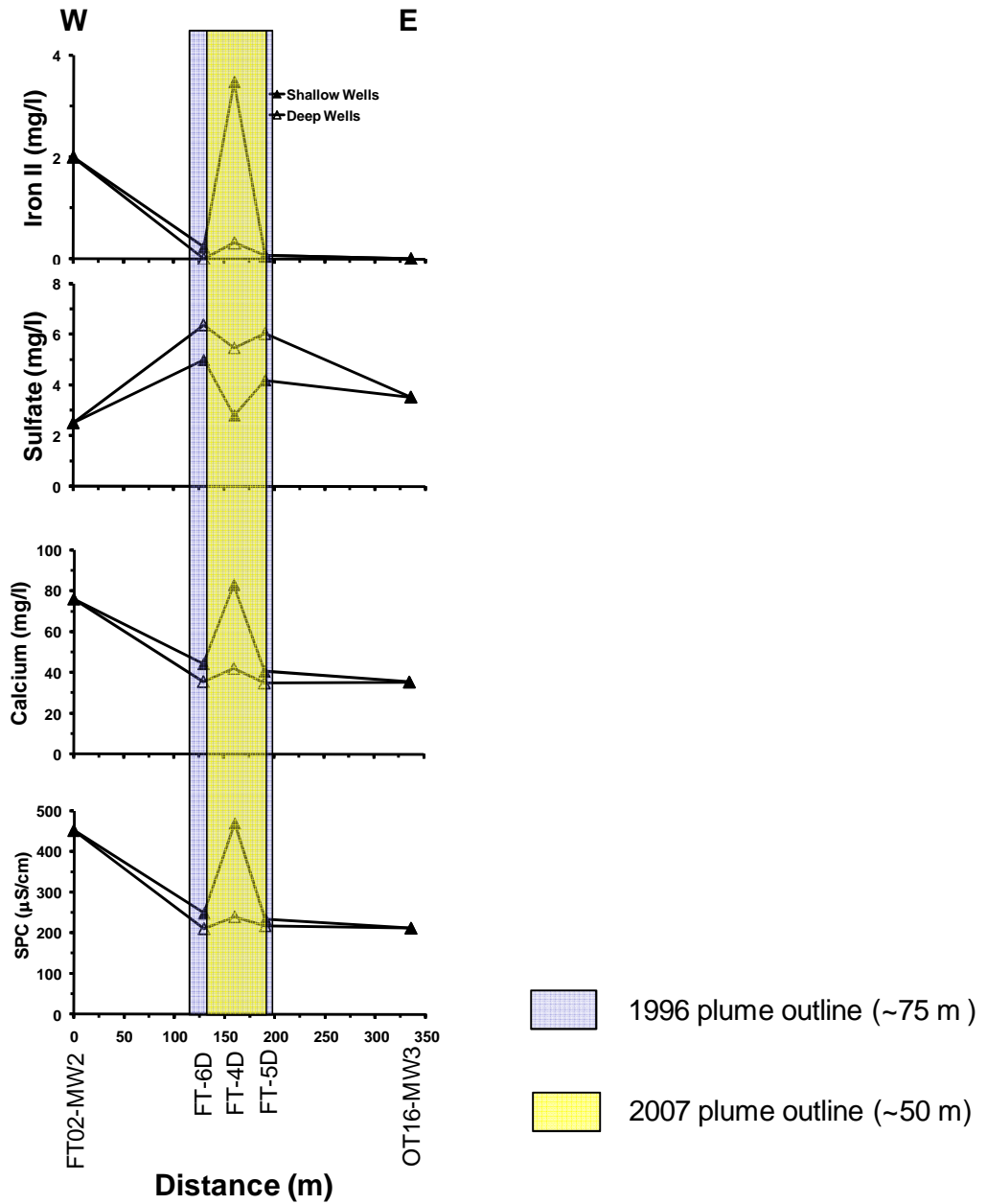
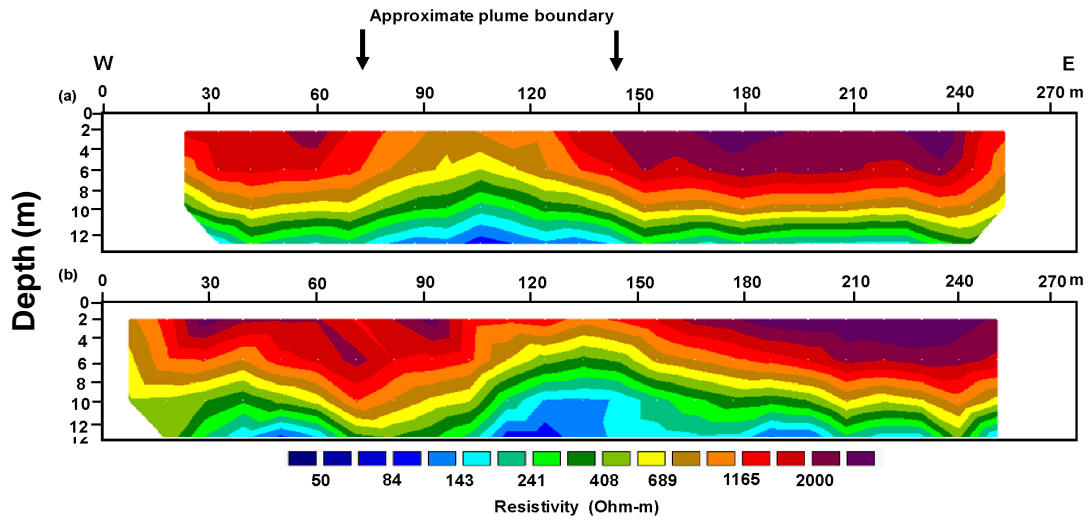Figure 4. Outline of FT-02 contaminant plume defined hydro chemically in
1996 and 2007

Figure 5. Inverted dipole-dipole resistivity profiles along the contaminant plume for (a) 1996, (b) 2003. The approximate lateral extent of the contaminant plume is indicated by the arrows.

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SECTION 2

CONCLUSION

The work documents changes in electrical resistivity, ground penetrating radar and spontaneous potential responses at a hydrocarbon site undergoing biodegradation as the site evolves chemically due to installation of a soil vapor extraction. The study is a continuation of observations reported by the authors in Sauck et al., (1996) and Smart et al., (2004). The high bulk electric conductivity anomaly observed in the 1996 and 2003 was mainly due to the vadose zone contamination and biodegradation effects. Removal of the contaminant mass (LNAPL) by soil vapor extraction decreased the carbon source, altering the physio-chemical and biological properties of the subsurface. With reduction in carbon source, bacteria turns to terminal electron acceptors (nitrate, manganese, iron, sulfate and methane) or other organic source for nutrients. As biodegradation increases, organic and carbonic acid weathering of mineral grains, increases pore fluid conductivity over time. This leads to increases concentration of weathering products (calcium, silica, specific conductance) in the aquifer. Also, compared to background, the specific conductance is high in the plume, which suggests that biodegradation impacts the bulk electric conductivity at the FT-02 site.

Despite a decrease in biodegradation, there is still evidence from geochemical parameters that suggest that intrinsic biorediation is still occurring in the saturated. This implies that changes that occur within the vadose zone as a result of hydrocarbon reduction do not necessarily affect changes in the saturated zone. 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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           DUE TO CONTAMINANT SOURCE REDUCTION AT WURTSMITH
           AIRFORCE BASE IN OSCODA MICHIGAN

Pages in Study: 66   Candidate for the Degree of Master of Science

Major Field: Geology

Scope and Method of Study:
    Electrical resistivity, self potential, ground penetrating radar along with ground
    water analysis to investigate geophysical signatures due to source removal by soil
    vapor extraction system at a hydrocarbon contaminated site in Oscoda, Michigan.

Findings and Conclusions:
    Results show that the high bulk conductivity anomaly observed in the 1996 and
    2003 had become more resistive in 2007; the positive SP anomaly observed over
    the plume in 1996 had become more negative in 2007; In 2007 the zone of GPR
    attenuation is significantly deeper in the section and the water table reflection is
    continuous compared to 1996 & 2003; Geochemical analyses suggest that
    intrinsic bioremediation (sulfate and iron reduction) is still occurring in the
    contaminated aquifer.

    The removal of the contaminant mass from LNAPL contaminant alters the
    physio-chemical and biological properties of the subsurface which can be
    monitored using geochemical and geophysical techniques (GPR, SP, and
    electrical resistivity). The high bulk conductivity anomaly observed in the 1996
    and 2003 was mainly due to the vadose zone contamination and biodegradation
    effects Also, the decrease in carbon source reduced microbial activity, potentially
    explaining the changes in observed geophysical signatures. 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

ADVISER'S APPROVAL: Dr. Estella Atekwana