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Jennifer Therese McGuire

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QUANTIFYING REDOX REACTIONS IN AN AQUIFER CONTAMINATED WITH WASTE FUEL AND CHLORINATED SOLVENTS

By

Jennifer Therese McGuire

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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Department of Geological Sciences

ABSTRACT

QUANTIFYING REDOX REACTIONS IN AN AQUIFER CONTAMINATED WTH WASTE FUEL AND CHLORINATED SOLVENTS

By

Jennifer Therese McGuire

The evolution of redox conditions in an aquifer contaminated with waste fuels, chlorinated solvents, and fire fighting foams was evaluated at the former Wurtsmith Air Force Base in Oscoda, Michigan. Geochemical indicators of terminal electron accepting processes (TEAPs) were evaluated over 5 years in conjunction with hydrogeologic and microbiologic parameters to describe the spatial and temporal variability in redox processes. Observed redox variability was linked to transport processes, particularly recharge events, which deliver terminal electron acceptors (TEAs) to the reduced groundwater plume. To understand how recharge affects groundwater biogeochemical processes, multivariate statistics and graphical tools were used to analyze geochemical data before and after a major recharge event (spring snow melt, 2000) at both small (single well) and large (whole plume) scales. Results show that average TEA concentrations increased within the aquifer and that changes in TEAPs were initiated not in large redox zones but in smaller zones at the interfaces of plume boundaries. Important plume boundaries include the interfaces between the reduced plume and 1) surrounding groundwater, 2) the capillary fringe zone, and 3) recharge waters. Due to the small and transient nature of these important zones, it is difficult to directly measure changes. Therefore, a series of field experiments were designed to replicate as closely as

possible a recharge event in the aquifer. These experiments revealed that, when TEAs are introduced simultaneously into an anaerobic aquifer where fermentative products such as acetate and H₂ gas have accumulated, TEAs could be consumed simultaneously and at similar rates. However, consumption rates were more rapid than observed in natural-gradient, large-scale experiments, likely due to a lack of readily available electron donor (i.e., accumulation of fermentative products) in those systems.

Results from the aforementioned analyses and experiments led to the development of a model for the evolution of redox zonation in contaminated aquifer systems. The conceptual model proposes that during initial contaminant plume development, the rates of TEAPs and therefore redox zonation are controlled by the production of readily available electron donors (e.g., acetate, H_2) and therefore by fermentation rates. As the plume continues to evolve, TEAs are depleted sequentially based on thermodynamically predicted free energies. Once a system has reached a state of maturity where organic carbon inputs balance biodegradation reactions, a stable plume length is achieved. Under these conditions, TEAs will continue to be depleted and fermentative products will accumulate such that distinct redox zones down flow path cannot be sustained. Spatial variability in TEAPs occurs in small interface zones near plume boundaries where TEAs are introduced either by diffusion and dispersion from the sides of the plume or by recharge from precipitation and upgradient flow. TEAP rates are no longer limited by fermentation rates but rather by TEA reduction rates. In addition, TEAs would not necessarily be degraded sequentially given the excess of available donor. The conceptual model was verified by incorporating its key elements and linkages in a 3-D flow and transport model, which successfully represented the early stages of plume evolution.

DEDICATION

I would like to dedicate this dissertation to Erik Wilson Smith without whose continued support, love, and understanding this work could never have been possible. You have been an unbelievable source of strength to me every day. Thank you for being there through all the tears and all the excitement. There isn't anyone else I would have wanted to take this ride with. I love you.

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A special thanks to my family for all their love and support especially during the hard times. Mom and Dad, thank you for believing in me and always being there to listen when I needed to talk things out. Grandma and Grandpa, thank you for your unconditional love, endless toasted cheese sandwiches and support. Our visits always provided me a refuge from stress and helped me to remember what's important in life. Jeanette, you are an amazing friend, sister, and scientist. Thank you for everything, I hope we are always this close. I am looking forward to watching our science careers grow together.

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INTRODUCTION

Understanding the means by which interconnected geochemical and microbiological cycles combine with hydrogeological processes in evolving aqueous systems is fundamental to identifying how environments change over time. In anaerobic systems, one of the main controls on system evolution is the reduction-oxidation (redox) potential of the system. Many elements in nature exist in more than one oxidation state. The major elements (typically at concentrations greater than 1 mg/L) exhibiting redox sensitivity include H, O, C, S, N, Fe, and Mn. Other minor (less abundant) elements include U, Cr, As, Mo, V, Se, Sb, W, Cu, Au, Ag, and Hg. Although these minor elements occur in lower concentrations, many can have serious effects on human health and the environment. Considering conventions developed from traditional physical chemistry, redox can be thought of as the tendency of particular chemicals to donate or accept electrons. This tendency can be described in terms of the standard hydrogen electrode (Stumm and Morgan, 1981). This convention serves to define a thermodynamic scale to which free energies of dissolved species can be compared. Based on this scale, at a given pH and temperature, redox reactions can be ranked into redox reaction sequences based on free energies describing thermodynamic favorability. In nature, microorganisms become involved in electron-transfer reactions to maintain life functions, grow, and reproduce. These activities are often kinetically controlled and therefore represent another important consideration besides thermodynamic free energy when attempting to study the redox state of a system. In addition to considering

thermodynamic and kinetic biogeochemical considerations, systems may be limited by the transport of chemical constituents necessary for systems to evolve. In groundwater systems, the rate of supply of electron acceptors, growth substrates for microorganisms, and nutrients are controlled by both the hydraulic gradient and aquifer properties such as hydraulic conductivity, dispersivity, effective porosity, and sorption coefficients. Therefore, understanding the redox state of aqueous systems requires knowledge of the interconnectivity of hydrogeological, microbiological, and geochemical processes making it an ideal concept to study how these interconnected processes allow systems to evolve.

The characterization of redox potential is of both scientific and practical interest. Redox state controls the form, mobility, toxicity and persistence of many chemicals in the environment. Without an awareness of how redox state evolves and the conditions under which it may change, we cannot adequately evaluate health and safety concerns such as chemical routes of exposure, natural attenuation capabilities, and the means by which we can manage redox sensitive systems. Understanding redox evolution is particularly important to the fields of bioremediation and natural attenuation. These fields of study seek to find efficient ways to remediate contaminated systems. Much effort has been expended to try to understand and implement these important remediation strategies, which in many instances present a more effective and cost efficient means of dealing with hazardous contaminated environments. These strategies make use of redox state by coupling organic contaminants, which serve as electron donors, to available terminal electron acceptors (e.g., O_2 , NO_3 , Fe^{3+} , and SO_4). It is through these microbially mediated terminal electron accepting processes (TEAPs) that organic contaminants are

degraded. In contaminated systems, TEAPs have been observed to distribute themselves into redox zones down flow path based roughly on free energy such that the most reduced conditions occur nearest the contaminant source (e.g., methanogenesis) and more favorable TEAPs (e.g., NO₃ reduction) occur farther down flow path. Unfortunately, understanding the redox state of a system is complicated because redox is very difficult to assess and it is also both spatially and temporally dynamic.

Redox conditions and TEAPs have traditionally been estimated through measurement of Eh or by redox couples which compare the relative concentrations of reduced to oxidized species (e.g., Fe²⁺/Fe³⁺). Such approaches are thought to be unreliable because of problems such as redox disequilibrium and lack of specificity of Eh measurements. The H₂ concentration in aquatic systems has been proposed as a more accurate indicator of *in-situ* TEAPs than the above approaches. Dissolved hydrogen is known to be a fleeting but important intermediate in the decomposition of organic matter. Dissolved hydrogen is produced and consumed in anaerobic environments such that each TEAP maintains a characteristic H₂ concentration. However, other *in-situ* reactions such as homoacetogenesis (production of acetate from hydrogen and carbon dioxide) and dehalogenation reactions can affect concentrations of H₂ in contaminated systems making its use as a TEAP indicator more complicated to apply to real-world environments. In addition to these complexities, even if a specific TEAP can be identified this state is not static but rather highly dynamic both in space and time.

An ideal study site to examine redox variability was found at the former Wurtsmith Air Force Base (Fire Training Area 2 – FTA-02), where a shallow sandy aquifer is contaminated with common petroleum hydrocarbons (BTEX compounds),

chlorinated solvents, surfactants, and fire-fighting foams. Given the complicated nature of the contaminants, hypotheses regarding the possibility of additional reactions interfering with redox indicating parameters (H₂) could be tested. Hydrogeologically, there is relatively little heterogeneity for a natural system, making transport arguments more reliable. Geochemically and microbiologically, a database of relevant parameters at three points in time (October 1995, June 1996, and October 1996) already existed. These preliminary data suggested that the site was experiencing redox variability both spatially and temporally.

The first step was to document the variability of redox processes at FTA-02 and attempt to link those changes to variations in hydrogeologic, microbiologic and geochemical processes, and thereby identify the most important drivers of change in redox state. Chapter 1 of this dissertation documents the spatial and temporal variability of TEAPs as interpreted from combinations of the above mentioned redox determination methods. Results suggest that TEAP processes are variable on relatively short time scales (months) and that the observed variability was related at least in part to recharge events delivering new terminal electron acceptors (TEAs) to the system. Results also identify the importance of considering how changes in transport processes affect the chemistry of the aquifer. The groundwater plume at FTA-02 has experienced relatively cyclical changes in groundwater flow direction of up to 10 degrees related to recharge events. These shifts can introduce new TEAs to previously reduced portions of the aquifer and also have implications for evaluating changes at a static sampling point over time. These findings suggest that, although a complicated relationship exists between

recharge events and the resulting biogeochemical processes operating in the aquifer, recharge inputs of solutes are a major driver of change in TEAPs.

Examination of water table elevation profiles over time revealed that spring snowmelt recharging the aquifer had a major impact on aquifer processes. To explore the role of recharge, statistical and graphical tools were used to examine the groundwater chemistry before and after a major snowmelt event in 2000. The results of these analyses are presented in Chapter 2. Geochemical changes were evaluated at small (single well) and large (plume) scales. Large-scale chemical averages indicated that the influx of recharge water introduced more energetically favorable TEAs to the plume. Based on these inputs, one would expect to observe a shift in dominant anaerobic groundwater microbial processes to more energetically favorable reactions and thus observe changes in redox zonation. However, further data examination by factor analysis, cluster analysis, and graphical techniques revealed that when viewed in greater detail, the changes in TEAPs initiated by recharge may be preferentially occurring on a smaller scale. Evaluation of chemical changes at a single well provided further evidence that many TEAP reactions initiated by recharge events occur in small interface zones and not in large redox zones as we traditionally envision. Since the zone over which these reactions occur is likely small it is very difficult to directly measure these processes. Nonetheless, recharge effects are likely most prevalent at plume boundaries, especially in the organicrich capillary fringe zone. This is important because initiating more favorable TEAPs in zones with high contaminant concentrations may significantly increase the rates of natural attenuation and bioremediation.

The next step was to evaluate the importance of small-scale changes in TEAPs initiated by recharge to the evolution and dynamics of redox conditions by quantifying the observations described above with a numerical model. However, construction of a meaningful model to test hypotheses regarding redox evolution was limited by our understanding of specifically how TEAP reactions were initiated by recharge and the rates at which these reactions would proceed. To address these issues a series of *in-situ* field experiments were conducted. The results of these experiments are presented in Chapter 3. These experiments were specifically designed to evaluate reactions initiated when a recharge solution containing various combinations of TEAs $(O_2, NO_3, and SO_4)$ comes in contact with a highly reduced aquifer. The experiments evaluate which reactions will be initiated, the order in which acceptors will be consumed if introduced simultaneously, and the rates of TEA consumption. In a tandem field experiment, the roles of the aqueous and solid phase portions of the aquifer and their associated microbial communities on these reactions were evaluated. Results suggested that TEAPs initiated during recharge events would not occur in the aqueous phase without the influence of the sediments and their associated microbial communities. It was also observed that if introduced simultaneously, TEAs could be consumed simultaneously and not according to the traditional thermodynamic sequence based on free energy. These findings, in conjunction with the relatively rapid rates obtained during the experiments, led to the development of a conceptual model regarding the evolution of redox conditions in contaminated aquifers.

This conceptual model suggests that initially, when a contaminant is introduced to an aquifer system and a plume begins to develop, the rates of TEAPs and thus redox

zonation are controlled by donor availability and consequently by the rate of fermentation. Fermentative bacteria convert large organic molecules into more readily available electron donors such as acetate and dissolved hydrogen, to be coupled to the traditional sequence of electron acceptors. As the organic plume moves through the system, TEAs are depleted sequentially according to their thermodynamically predicted free energies. Once a system has reached a state of maturity such that organic carbon inputs balance biodegradation reactions, a stable plume length is achieved. Within this framework, TEAs are depleted and fermentative products such as acetate and H₂ will accumulate. Under these conditions, no mechanism exists to maintain stable, distinct redox zones down flow path within the plume. Rather, spatial variability in TEAPs will likely occur in small interface zones near plume boundaries where inputs of TEAs can occur either by diffusion and dispersion from the sides or recharge from precipitation and upgradient flow. At this point, the system has evolved to a state where it is no longer donor (fermentation) limited in terms of rates but is instead acceptor limited in terms of TEAP reaction rates. Under this model, TEAs are consumed rapidly and would have no reason to be degraded sequentially given the excess of readily available donor, which is exactly what we observed at FTA-02 during our field experiments. To evaluate the feasibility of this conceptual model and test hypotheses regarding redox evolution, a three-dimensional partial equilibrium flow and transport model was constructed. Preliminary results from this modeling effort, as well as a description of the work to be done in the near future using this mode, l is presented in Chapter 4.

CHAPTER I.

McGuire, J. T., Smith, E. W., Long, D. T., Hyndman, D. W., Haack, S. K., Klug, M. J., and Velbel, M. A., 2000. Temporal variations in parameters reflecting terminal-electron-accepting processes in an aquifer contaminated with waste fuel and chlorinated solvents, in K. Konhauser and G. Southam (eds.), Geomicrobiology - Technical Session 06, 110th Geological Society of America Annual Meeting. Chemical Geology, 169:471-485.



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Temporal variations in parameters reflecting terminal-electron-accepting processes in an aquifer contaminated with waste fuel and chlorinated solvents

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Abstract

A fundamental issue in aquifer biogeochemistry is the means by which solute transport, geochemical processes, and microbiological activity combine to produce spatial and temporal variations in redox zonation. In this paper, we describe the temporal variability of TEAP conditions in shallow groundwater contaminated with both waste fuel and chlorinated solvents. TEAP parameters (including methane, dissolved iron, and dissolved hydrogen) were measured to characterize the contaminant plume over a 3-year period. We observed that concentrations of TEAP parameters changed on different time scales and appear to be related, in part, to recharge events. Changes in all TEAP parameters were observed on short time scales (months), and over a longer 3-year period.

The results indicate that (1) interpretations of TEAP conditions in aquifers contaminated with a variety of organic chemicals, such as those with petroleum hydrocarbons and chlorinated solvents, must consider additional hydrogen-consuming reactions (e.g., dehalogenation); (2) interpretations must consider the roles of both in situ (at the sampling point) biogeochemical and solute transport processes; and (3) determinations of microbial communities are often necessary to confirm the interpretations made from geochemical and hydrogeological measurements on these processes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aquifer biogeochemistry; Terminal-electron-accepting process; Temporal variation; Redox zonation; Recharge

1. Introduction

The development of redox zones in natural aquatic and groundwater systems is based on the activities of microorganisms. which first use O_2 , and then a 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, 1988; Chapelle, 1993). The succession of terminal electron accepting processes (TEAPs) in order of decreasing redox potential and free energy yield is generally: oxygen reduction,

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nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis (Table 1). In most closed groundwater systems, the sequence of TEAPs follows this succession (i.e., increasingly reduced conditions occur further down the flow path) (Champ et al., 1979). In groundwater systems contaminated with hydrocarbons, redox zonation has been identified (Baedecker and Back, 1979; Barcelona et al., 1989; Bennett et al., 1993; Vroblesky and Chapelle, 1994; Chapelle et al., 1995). In contaminant plumes, the sequence of TEAPs is reversed (Lovely, 1991; Chapelle, 1993). That is, the most reduced conditions (e.g., methanogenesis) occur near the contaminant source due to the greater availability of electron donors, while less reducing conditions (e.g., iron reduction) occur down flow path from the contaminant source.

TEAP conditions and redox zonation affect the chemical form, mobility, and persistence of many groundwater contaminants (e.g., Stumm and Morgan, 1981; Christensen et al., 1994; Davis et al., 1994). Natural biodegradation of many petroleum-derived aromatic hydrocarbons occurs under most redox conditions (Chapelle, 1993; Vogel, 1994). However, the efficiency and rate of hydrocarbon and chlorinated solvent degradation varies with redox environment (Norris, 1994). Microbial degradation of petroleum

hydrocarbons is most efficient under aerobic conditions, but has also been demonstrated to occur under methanogenic, sulfate-reducing, ferric-iron-reducing, and nitrate-reducing conditions (Grbic-Galic and Vogel, 1987; Hutchins et al., 1991; Beller et al., 1992; Edwards et al., 1992; Baedecker et al., 1993; Rabus et al., 1993; Lovely, 1994; Lovely and Lonergan, 1990; Lovely et al., 1995). Redox zonation also affects the nature and distribution of chlorinated aromatic and aliphatic compounds. Chlorinated ethenes are common in groundwater and some degradation occurs under a variety of field and laboratory conditions (Norris, 1994).

Accurate modeling of biodegradation processes and redox zonation in groundwater requires understanding the scales of temporal changes in TEAP conditions (e.g., Essaid et al., 1995; Hunter et al., 1998; Keating and Bahr, 1998: Salvage and Yeh, 1998). Over long time scales (years), changes in redox zonation in groundwater have been attributed to successional changes in TEAP conditions (Berner, 1981). For example, Baedecker et al. (1993) attributed the observed 5-year change in redox zonation in oil-contaminated groundwater to a successional change in TEAP conditions from iron reduction to methanogenesis. Less is known about changes in TEAP conditions on shorter (months to year) time

Table 1

R	eactions	and	free	energies	discussed	in	this	paper
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Reaction	Equation	ΔG (kJ/mole)	
Denitrification	$2NO_3^- + 5H_2 + 2H^- \rightarrow N_2 + 6H_2O$	-1120°	
Nitrate reduction to ammonia	$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ 3H_2O$	- 600°	
Manganese reduction	$MnO_2 + H_2 \rightarrow Mn(OH)_2$	- 163ª	
Iron reduction	$2Fe(OH)_3 + H_2 \rightarrow 2Fe(OH)_2 + 2H_2O$	- 50°	
Sulfate reduction	$SO_4^2 + 4H_3 + H^4 \rightarrow HS^- + 4H_3O_1$	- 152*	
CO ₂ methanogenesis	$HCO_{1}^{-} + 4H_{2} + H^{+} \rightarrow CH_{1} + 3H_{2}O_{1}$	-136°	
Aceticlastic methanogenesis	$CH_1COOH \rightarrow CH_1 + CO_1$	- 53 ^b	
Dechlorination	$PCE^1 + H_2 \rightarrow TCE^2 + H^2 + C1^-$	- 173°	
Dechlorination	$TCE^2 + H^2 \rightarrow DCE^3 + H^2 + C1^2$	- 170°	
Dechlorination	$DCE^3 + H_2 \rightarrow VC^4 + H^2 + Cl^-$	- 140°	
Dechlorination	$VC^4 + H_2 \rightarrow ethylene + H^+Cl^-$	- 150°	

^aLovley and Goodwin (1988).

^bCRC (1993).

^cDolfing and Beurskens (1995).

¹Tetrachloroethvlene.

²Trichloroethylene.

³Cis-1,2-dichloroethylene.

⁴Vinyl chloride.

scales, but these are thought to be related to solute transport including recharge events (e.g., LeBlanc et al., 1991; Hess et al., 1992). Vroblesky and Chapelle (1994) studied temporal variations in TEAPs at a shallow petroleum hydrocarbon-contaminated aquifer. They observed TEAP changes in individual wells over periods as short as 2 months. Although these observations show short-term changes in TEAP variables, they may not necessarily indicate short-term changes in the TEAP conditions of the plume because they do not account for the influence of changes in water table elevation or groundwater flow direction (McGuire et al., 1999). They did, however, assess areal variations in TEAP conditions in the plume, and reported changes over 15 months. They attributed the temporal changes in TEAP conditions to variations in recharge and lateral transport, which influenced the availability of terminal electron acceptors such as SO_4 .

Solute transport and, therefore, the rate of supply of electron acceptors, growth substrates, and nutrients is controlled by both the hydraulic gradient and aquifer properties such as hydraulic conductivity, dispersivity, effective porosity, and sorption coefficients. Spatial variations in hydraulic conductivity determine the predominant zones of solute transport since groundwater follows the path of least resistance. Dispersion causes lateral and longitudinal solute spreading due to small-scale variability in groundwater velocity, which is a critical factor in accurately describing the geometry of the redox zones. Also, seasonal fluctuations in the direction of groundwater flow may increase transverse dispersion in the study area, and must also be accounted for (Goode and Konikow, 1990).

The purpose of this paper is to describe the temporal variability of TEAP conditions in a shallow groundwater system contaminated with both waste fuel and chlorinated solvents. Few studies have examined TEAP conditions or changes in TEAP conditions in such complex contaminant systems. We examine changes in dissolved hydrogen (H_2) concentrations and other selected TEAP variables (e.g., dissolved methane (CH₄) and dissolved iron (II) (Fe²⁺)) and non-TEAP variables (e.g., potassium (K⁺)). Redox conditions and TEAPs have traditionally been estimated through measurement of Eh or by the relative concentrations of reduced to oxidized

species (e.g., Fe^{2+}/Fe^{3+}). Such approaches are thought to be unreliable because of problems such as redox disequilibrium (Keating and Bahr, 1998) and lack of specificity of Eh measurements (Lovely and Goodwin, 1998). The H₂ concentration in aquatic systems has been proposed as a more accurate indicator of in situ (at the sampling point) TEAPs than the above approaches (Lovely and Goodwin, 1988). Dissolved hydrogen is known to be a fleeting but important intermediate in the decomposition of organic matter. Dissolved hydrogen is produced and consumed in anaerobic environments such that each TEAP maintains a characteristic H₂ concentration (Lovely and Phillips, 1987).

Interpretations of TEAPs from H_2 concentrations, as measured in marine and freshwater sediments and in aquifers, are as follows: methanogenesis, greater than 5 nM; SO₄ reduction. 1–4 nM; Fe³⁺ reduction, 0.2–0.6 nM; and Mn (IV) or nitrate reduction, less than 0.05–0.1 nM (Lovely and Goodwin, 1988). Chapelle et al. (1996) demonstrated the use of H_2 concentrations in delineating redox zonation in the plume at the study site described in this paper. They concluded that delineating redox zones based on H_2 concentrations is more reliable when H_2 concentration are interpreted in the context of other TEAP variables such as Fe²⁺ and CH₄, a strategy we have adopted here.

We suggest that the presence or absence of TEAP variables in water samples from a well may not indicate microbiological reactions that are occurring in situ. Concentrations of TEAP variables may be the result of their transport to the well from an upgradient source since CH_4 and Fe^{2+} are mobile in aqueous environments. Our samples were collected over a 3-year period and include quarterly measurements. Thus, both short-term and long-term changes were studied including influences of solute transport.

2. Description of study area

The study site is a shallow sandy aquifer contaminated with petroleum hydrocarbons and chlorinated solvents at the former Wurtsmith Air Force Base (AFB), Michigan, USA (Fig. 1). Wurtsmith AFB lies on a sandy plain of glacial lake sediment approxi-



Fig. 1. Map showing the location of the study site.

mately 2 km west of the Lake Huron shoreline in Michigan's Lower Peninsula. Geologic units at the site consist of Mississippian sandstones, siltstones and shales, overlain by unconsolidated glacial sediments and surficial deposits. Glacial deposits range in thickness from 30.5 to 76.2 m and consist of gravel, sand, silt, and clay. Surficial deposits include lacustrine sediments, ice-contact sediments, and alluvium. The principal water-bearing unit at the site is a surficial sand and gravel aquifer approximately 20 m thick. The unconfined aquifer is underlain by at least 30.5 m of silty clay. The water table ranges from 3.5 to 5.0 m below land surface (184-186 m above sea level) and fluctuates 0.3 to 0.7 m annually. The aquifer at the study site is comprised of highly permeable alternating aeolian sands and glacial outwash material. Hydraulic conductivities of these deposits are on the order of 30 m/day. The water table gradient ranges from 3 to 5 m/km. Assuming an effective porosity of 30%, average groundwater velocity is approximately 0.5 m/day.

The study site Fire Training Area-2 (FTA-2; Fig. 2) at Wurtsmith AFB was used for fire training exercises from 1952 to 1986. During these exercises. waste fuel and solvents were ignited in the proximity of a mock-aircraft located at the "pad" (Fig. 2). Various compounds were used to extinguish the fires, including aqueous film-forming foam, a multipurpose dry chemical, potassium bicarbonate based soda, and Halon 1211. The majority of contaminants occur within the capillary fringe and have caused an extensive plume approximately 50 m wide and 400 m long (Fig. 2). The plume is complex in that it contains both BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and chlorinated solvents (e.g., dichloroethane). Concentrations of BTEX compounds in the plume range from 20 to 1000 μ g/l while concentrations of dichloroethane, chloroethane, and vinyl chloride range from 2 to 1000 μ g/l. Most of the contamination is associated with aquifer solids between 4.5 and 5.7 m below land surface, which have an average concentration of total hydrocarbons



Fig. 2. Plume map for the Fire-Training Area 2 (FTA-2) at the former Wurtsmith Air Force Base, Michigan. The concrete pad was the site of fire-training activities.

of 13,650 mg/kg (U.S.G.S., 1991). Because the direction of groundwater flow is influenced by recharge, lateral shifts in the plume location at the well array (see below) of up to 10 m have been observed (Smith et al., 1999).

3. Methods

Seasonal measurements of water levels and biogeochemical parameters are being collected at the site, adding to a dataset started in 1995 by Chapelle et al. (1996). To document the vertical distribution of contaminants within the plume, researchers at the National Center for Integrated Bioremediation Research and Development (University of Michigan) installed a series of multilevel sampling wells at this site. The wells were constructed of 2.5-cm-inner-diameter PVC casing, with 0.33-m PVC screens at the bottom. The vertical spacing between the screens varied from 0.5 to 2 m. The multilevel wells are oriented in an array perpendicular to groundwater flow located approximately 100 m downgradient from the suspected source. This array of four wells was used to collect groundwater chemistry samples presented in this paper.

Each level in a well was purged with a peristaltic pump at a rate of approximately 400 ml/min. A flow cell was used to continuously monitor temperature, pH, dissolved oxygen, Eh, and specific conductance until readings became stable. H, samples were taken using the bubble-stripping method (Chapelle and McMahon, 1991). Water was continuously pumped through a standard 400-ml-glass gas-sampling bulb with an introduced nitrogen bubble. After time, the H_2 concentration in the water equilibrates with its concentration in the gas bubble. A gas sample was taken from the gas bubble in the bulb with a gas-tight glass syringe at approximately 10min intervals to monitor the approach to steady state H, concentrations. Enough gas sample was taken with each syringe for three replicates of 7.5 ml and analyzed in the field with a RGA3 reduction gas analyzer (Trace Analytical). Concentrations of H₂ in the aqueous phase were calculated using Henry's Law. The detection limit of this method is approximately 0.08 nM. Although stable readings of flow cell measurements were obtained within 20 to 30 min, H_2 concentrations often required an additional 20 to 90 min to equilibrate.

In the field, samples were collected for a variety of geochemical measurements. Selected measurements discussed in this paper include dissolved sulfide by colorimetric spectroscopy using Chemetrics Company Vacu-Vials[™], Fe²⁺ by phenanthroline colorimetric analysis, major cations by flame atomic adsorption spectrometry, SO₄ by capillary electrophoresis, and CH₄ by flame ionization detection gas chromatography. When applicable, samples were filtered through 0.45 µm polyethersulfone membrane filters. Field blanks were collected for each sampling trip. Samples for major cations were preserved with ultra-pure "optima" nitric acid, SO₄ samples with formaldehyde, and CH₄ samples with mercuric chloride crystals. Sulfide and Fe²⁺ were measured in the field immediately after sample collection. Water level measurements were collected from three hourly recording pressure transducers triangulated approximately 300 m apart about FTA-2 (Fig. 2). Individual water level measurements were taken manually from all available wells at FTA-2 (about 20 wells) during sampling events.

Plots of the spatial distribution of solutes were created using a krigged grid method with a linear variogram model in Surfer (Golden Software). Surfer plots of H₂ were constructed with color divisions indicating TEAP process. In addition to the TEAP variables, spatial and temporal concentrations of K⁺ are presented to help define the loci of the plume since one component of the contaminant plume is potassium bearing fire-fighting foam. The contours of the spatial plots of Fe^{2+} , CH_4 , and K^+ reflect concentrations and do not imply an interpretation of process, with intervals chosen to best show trends in the well array. Spatial plots of other TEAP variables, such as SO, or sulfide, are not presented because their concentrations were too low to generate interpretable diagrams.

4. Results

Over the 3-year sampling period, H_2 concentrations were highest in October 1995 and generally decreased through August 1998. Concentrations then began to increase in November 1998 (Fig. 3). In



Fig. 3. Spatial distribution of H_2 concentrations and inferred terminal electron-accepting process (TEAP) at the FTA-2 well array from October 1995 to November 1998. Vertical axis is depth below water table and horizontal axis is lateral distance across the plume. Upper surface of each image reflects water table position. Groundwater flow is out of the page.



Fig. 4. Spatial distribution of dissolved methane concentrations at the FTA-2 well array from October 1995 to November 1998. Vertical axis is depth below water table and horizontal axis is relative distance laterally. Upper surface of each image reflects water table position. Groundwater flow is out of the page.



Fig. 5. Spatial distribution of dissolved iron concentrations at the FTA-2 well array from October 1995 to November 1998. Vertical axis is depth below water table and horizontal axis is lateral distance across the plume. Upper surface of each image reflects water table position. Groundwater flow is out of the page.



Fig. 6. Spatial distribution of dissolved potassium concentrations at the FTA-2 well array from June 1996 to November 1998. Only limited data were available for October 1995 to create a spartical plot. Vertical axis is depth below water table and horizontal axis is lateral distance across the plume. Upper surface of each image reflects water table position. Groundwater flow is out of the page.

October 1995, the highest H₂ concentrations were localized around the shallowest depths at ML3 and ML5. These high concentrations indicate a potential zone of methanogenesis by CO₂ reduction (Chapelle et al., 1996). Hydrogen concentrations decrease away from this zone suggesting a change in process from methanogenesis to SO_4 reduction to Fe^{3+} reduction (Chapelle et al., 1996). Throughout the well array, the TEAP inferred by H₂ measurements changed from a large area of methanogenesis in October 1995 to predominantly SO₄ reduction in June 1996, to predominantly Fe³⁺ reduction in August 1998, and then to predominantly SO₄ reduction in November 1998. The overall decrease in H₂ concentrations from October 1995 until August 1998 suggests that a long-term change in general TEAP conditions occurred over the 3-year period across the transect. TEAP conditions as defined by H₂ concentrations also varied on short time scales as evidenced by the change from predominantly Fe³⁺-reducing conditions observed in August 1998 to SO₄-reducing conditions in November 1998.

Methane concentrations varied on short time scales throughout the 3-year sampling period but did not parallel the long-term pattern of H_2 concentration (Fig. 4). In October 1995, the highest concentrations of CH₄ were found in the shallow wells at ML3 corresponding to the area in the well array of highest H_2 concentrations. This is consistent with the interpretation of methanogenesis by CO₂ reduction occurring in this area (Chapelle et al., 1996). However, changes in dissolved CH₄ concentrations in the well array did not always parallel those predicted by H_2 concentrations. Similar to H_2 , CH₄ concentrations were highest in October 1995 and decreased in June 1996. After June 1996, H_2 concentrations continued to decrease, while CH₄ concentrations did not.

High Fe²⁺ concentrations were present over the 3-year period, but the loci of highest concentrations changed (Fig. 5). For example, in October 1995, the highest concentrations of Fe²⁺ were found in the easternmost portion of the well array at ML8. In June 1996, the highest concentrations of Fe²⁺ were found in the westernmost portion of the well array at ML4. Similar to H₂ and CH₄, the pattern of Fe²⁺ concentrations was found to be variable on monthly timescales. In addition, the spatial pattern for Fe²⁺ appears to be similar to that of CH₄.

Dissolved potassium concentrations in the contaminant plume were elevated throughout the 3-year period compared to concentrations in the surrounding groundwater (Fig. 6). The source for K^+ in the plume is suspected to be from the KHCO₃ used to extinguish the fires during the fire training exercises. Therefore, the elevated concentrations of K⁺ in the groundwater of the well array indicate water that has moved through the contaminant source near the pad. As can be seen, the area of elevated K⁺ concentrations matches the spatial patterns of H₂, CH₄, and Fe^{2+} (Figs. 3-5). In addition, the changes in the concentration levels of K⁺ at the well array roughly match the changes in H₂ concentrations. Spatial plots of K⁺ could not be constructed for groundwater samples taken in October 1995 because of a limited dataset; however, K⁺ concentrations were some of the highest recorded (29 mg/l) at ML3. This corresponds to a time of high H, concentrations (Fig. 3). After October 1996, K⁺ decreased similarly to H₂ (Figs. 3 and 6). In November 1998, K concentrations increased, as did the H₂ values.

5. Discussion

The influence of groundwater recharge on the spatial and temporal variability of H₂, CH₄ and Fe²⁺ concentrations can be examined by comparing the spatial maps (Figs. 3-5) to changes in the elevation of the water table at FTA-2 (Fig. 7). It can be seen from Fig. 7 that groundwater samples from October 1995 were collected after a period of a steadily declining water table. Without recharge, electron acceptors such as O_2 , Fe^{3+} , and SO_4 would be depleted allowing for the development of an extensive methanogenic zone within the plume resulting in elevated H_2 and CH_4 concentrations. In contrast, samples from June 1996 were collected shortly after a recharge event and H, and CH₄ concentrations decreased. Dissolved hydrogen and CH₄ concentrations in the well array might decrease during recharge events as a result of either (1) dilution by recharge water or (2) by limiting methanogenesis via the introduction of more energetically favorable electron acceptors such as SO₁ to the system. Lower concentrations of other ions (e.g., Na⁺) during this time period were not observed.



Fig. 7. Graph depicting water table elevation as a function of time at FTA-2. Data were taken from water level recorder 2 (solid line) and manual measurements (dotted line). Periods when groundwater samples were collected are also shown. Circles represent samples collected by the U.S. Geological Survey and S's represent samples collected in this study.

This suggests a change in TEAP conditions and not dilution was the dominant cause for changes in H_2 and CH_4 concentrations between October 1995 and June 1996. Recharge events in June 1996, October 1996, November 1997, February 1998, and May 1998 could, in part, explain the low hydrogen concentrations during these time periods.

Based on these observations, we argue that under conditions of declining water table, the tendency of the system will be toward the development of more reduced (e.g., methanogenic) TEAP conditions, while recharge events will push the systems to less reduced conditions (e.g., iron reduction). Although such changes have been observed at other sites (e.g., Vroblesky and Chapelle, 1994), predicting specific TEAP conditions (based on H_2 concentrations) from knowledge of when recharge occurred and the elevation of the water table remains a challenge. For example, the August 1998 samples were collected after a period of prolonged water-table decline similar to the conditions that occurred during the October 1995 sampling (Fig. 7). In addition, the water table elevation was similar to that of October 1995. Thus, it was anticipated that H₂ concentrations in August 1998 would be similar to those of October 1995. However, H₂ concentrations in August 1998 were much lower than in October 1995. Conversely, in November 1998, with continuing decline in the water table, H_2 concentrations increased. A major difference between 1998 and 1995 periods was that the recharge event preceding the declining water table in 1998 was significantly larger than in 1995. This suggests that the magnitude of recharge may play a role in how H_2 responds to recharge events. For example August 1998 the water table elevation was similar to those measured in 1995.

Methane concentrations did not parallel the overall decline in hydrogen concentrations over the 3-year period. Methane and hydrogen patterns may not be coupled because CH_4 may be produced by a mechanism that does not rely on H_2 such as aceticlastic methanogenesis (Table 1). Another possibility for the decoupling is differential transport of the solutes. Methane and other solutes such as Fe^{2+} can be mobile in groundwater while H_2 is highly reactive; thus, transport in groundwater is likely minimal (Lovely and Goodwin, 1988).

We hypothesize that for the majority of the 3-year period, the contaminant plume at the well array was undergoing aceticlastic methanogenesis in combination with various intensities of SO₄ and Fe³⁺ reduction. Methane in this system may be produced by

two separate mechanisms. Hydrogen-oxidizing methanogens can produce methane from hydrogen and carbon dioxide (CO2 reduction) and aceticlastic methanogens can produce methane and carbon dioxide from acetate (aceticlastic methanogenesis). Only in October 1995 and one sample in June 1996 were H₂ concentrations found to be high enough to indicate the production of CH_4 by CO_2 reduction. Unlike CO₂ methanogenesis, which requires high concentrations of H2, aceticlastic methanogenesis has no relationship to H₂ concentrations. A result, methane may be produced by aceticlastic methanogenesis, while other microbial processes such as SO₄ reduction occur. This hypothesis is supported by recent studies, which indicate that at temperatures lower than 20°C. CH₄ production occurs predominantly by aceticlastic methanogenesis and not by CO₂ reduction (Nozhevnikovs et al., 1994; Schultz and Conrad, 1996). Groundwater temperatures at the site appear to have remained below 20°C throughout the 3-year period. Furthermore, Dojka et al. (1998) identified aceticlastic methanogens by a culture-independent molecular phylogenetic approach (on sediments collected from ML-3, see Fig. 2, in 1996), which supports the possibility of in situ CH₄ production.

Over the 3-year period, the threshold for H_2 concentrations was maintained below that necessary for CO₂ methanogenesis. A possible explanation for the low H_2 concentrations is its consumption by homoacetogenesis (the production of acetate from hydrogen and carbon dioxide) (e.g., Chin and Conrad, 1995) and/or dechlorination (Sulfita et al., 1982) processes. Evidence of microbiological communities associated with both processes were found by Dojka et al. (1998). Fennell and Gossett (1998) examined the competition for hydrogen in a dechlorinating culture. They clearly show how low H_2 levels driven by dechlorination reactions favor aceticlastic methanogenesis over CO₂ methanogenesis.

If H_2 is consumed by in situ reactions such as dechlorination, then its low concentration throughout most of the 3-year period is not indicative of other in situ processes such as SO_4 and Fe^{3+} reduction (Mc-Guire et al., 1999). In fact, Dojka et al. (1998) did not find microbial evidence for SO_4 and Fe^{3+} reducers in sediments collected from ML-3 in 1996. Iron sulfide staining was observed on the lower portions of the tubing used to collect samples from the multilevel wells in November 1998, indicating that in situ sulfate reduction has occurred in the past. However, it is possible that this staining is related to processes occurring locally at the well screen not related to processes in the aquifer as a whole.

The influence of solute transport on concentrations of TEAP parameters in the well array is suggested by the relatively high concentrations of Fe^{2+} , and the lack of microbial evidence for in situ Fe^{3+} reduction. The high concentrations of Fe^{2+} throughout the well array indicate Fe^{3+} reduction has occurred within the plume. Similarly, the low sulfate concentrations detected in the plume at the well array indicate sulfate reduction has occurred. However, we have found only traces of dissolved sulfide in the plume. Except for SO₄ inputs from rain (less than 3 ppm), there are few sources for SO₄; and, thus, the high concentrations of Fe^{2+} effectively remove any sulfide produced as iron sulfides.

The high concentrations of Fe^{2+} in groundwater at the well array can be explained by the fact that in the anaerobic groundwater dissolved Fe²⁺ can be transported along the flow path. Dissolved iron (II) would mainly be removed by oxidation to Fe^{3+} and precipitation of oxyhydroxides. Such oxidation could occur at the interface between the anaerobic plume water and the oxic native groundwater (along the fringes of the plume and at the water table). The newly formed iron oxyhydroxides could then become a substrate for iron reducers. Recharge events and changes in water table elevation and groundwater flow direction would drive iron cycling at the interface. A similar argument can be made for the fate, occurrence and transport of dissolved CH₄ throughout the well array. The similarity in the spatial extents, but not necessarily concentration patterns of Fe^{2+} and CH_4 (Figs. 4 and 5, respectively) support this argument. Thus, Fe^{2+} and perhaps CH_4 could have been produced upgradient and transported to the well array and, therefore, their concentrations would not reflect in-situ processes.

6. Conclusions

The redox environment in a petroleum-derived plume influences the efficiency, rate, and extent of biodegradation (Vogel, 1994). Biodegradation of BTEX compounds is most efficient under aerobic conditions, but has been demonstrated to occur under most redox conditions (Baedecker et al., 1993; Lovely et al., 1995). In aerobic environments, BTEX compounds are degraded to CO₂. In methanogenic environments, the complete transformation of organic compounds to CO₂ and CH₄ requires the combined activities of at least three different functional groups of microorganisms: fermenters, fattyacid degraders, and methanogens. Thus, the effectiveness of groundwater remediation strategies will be influenced not only by our ability to accurately delineate redox zones in a contaminated aquifer, but also to determine the hydrogeological, microbiological, and geochemical factors influencing temporal variations in the zones.

In this paper, we described the spatial and temporal variations of H_2 , CH_4 and Fe^{2+} in shallow groundwater contaminated with both waste fuel and chlorinated solvents over a 3-year period. Results indicate that changes in all parameters occurred on short time scales (months), and that hydrogen concentration also exhibited long-term changes over a longer 3-year period. Recharge events, as indicated by changes in water-table elevation, appear to be related to short-term changes in the concentrations of H_2 , CH_4 , and Fe^{2+} and perhaps long-term changes in the concentrations of H₂. Solute transport (including recharge), in part, controls the availability of organic matter, nutrients, and electron donors and acceptors to the bacteria that carry out many TEAP reactions. These results strongly support the conclusions of Chapelle et al. (1996) that if H₂ concentrations are to be used as an indicator of TEAP processes, they are best interpreted in combination with other TEAP variables.

Our results also show that interpretations of TEAP processes from solute concentrations must consider the roles of in situ (at the sampling point) biogeochemical and solute transport processes. The relative importance of these processes appears to exhibit temporal variability, which is the subject of our on-going studies (McGuire et al., 1998; Smith et al., 1998; Smith et al., 1999). Microbial measurements are often necessary to confirm the interpretations made from geochemical and hydrogeological measurements on these processes. In aquifers contaminated with a variety of organic chemicals (e.g., petroleum hydrocarbons, chlorinated solvents) H_2 concentrations may not be indicative of TEAP processes as they have been traditionally interpreted by other workers such as Lovely and Goodwin (1988) since these previous studies did not consider the effect of dechlorination reactions on H_2 partial pressures.

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CHAPTER II.

Geochemical characterization of the effects of recharge on an anaerobic contaminated aquifer using multivariate statistics

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Introduction

Understanding conditions that can initiate changes in the redox state of anaerobic systems is crucial to evaluating and managing natural and contaminated systems since redox state controls the form, mobility, toxicity, and persistence of many natural and anthropogenically introduced chemical constituents. Spatial and temporal variations in groundwater redox chemistry are well documented (BARCELONA et al., 1989; CRILL and MARTENS, 1987; KENNEDY et al., 1999; VROBLESKY and CHAPPELLE, 1994). It is therefore essential to not only identify the distribution of redox processes at a given point in time but also to understand the conditions under which redox state may vary. In groundwater systems, recharge events are thought to be a significant drive for initiating changes in redox state (VROBLESKY and CHAPPELLE, 1994); however specific influences and responses are not well understood.

The redox state of a system is in part controlled by the activity of microorganisms, which first consume oxygen, and then a succession of alternate terminal electron acceptors (TEAs) to support their growth using a variety of carbon sources (CHAPPELLE, 2001; LOVLEY, 1991; LOVLEY and GOODWIN, 1988; STUMM and MORGAN, 1981). The succession of terminal electron accepting processes (TEAPs) in order of decreasing redox potential and free energy yield is generally: oxygen reduction, nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis. In most closed groundwater systems, the sequence of TEAPs results in redox zones following this succession (i.e., increasingly reduced conditions occur further down the flow path) (CHAMP et al., 1979). However, downgradient of contaminant plumes, the sequence of TEAP zones is generally reversed (CHAPPELLE, 2001; LOVLEY, 1991). That

is, the most reduced conditions (e.g., methanogenesis) occur near the contaminant source due to the greater availability of electron donors, while less reducing conditions (e.g., iron reduction) occur down flow-path from the contaminant source. Since many hydrocarbons, which serve as electron donors, concentrate in the capillary fringe area, more reducing conditions often occur near the water-table interface, resulting in a plume that has vertical as well as horizontal redox zonation (CHAPPELLE et al., 1996). In reduced systems, recharge events can initiate changes in TEAPs by delivering more favorable TEAs such as oxygen (O₂), nitrate (NO₃) and sulfate (SO₄) to the system (VROBLESKY and CHAPPELLE, 1994).

Many aspects of how recharge waters affect TEAPs and redox zonation in reduced systems remain unknown. Direct examination of redox sensitive species, in an aquifer before and after recharge, cannot distinguish the extent to which recharge initiates TEAPs verses a simple dilution of aquifer water with recharge water since both processes result in a decrease in TEA concentrations. It is also unclear the degree to which redox zones are impacted during recharge, the depth to which recharge influences redox, and how subtle differences in topography may enhance recharge effects. One goal of this study is to identify the chemical signature of a recharge event at various scales within an aquifer to evaluate the changes initiated by recharge and examine the spatial pattern of impact. Our hypothesis is that changes in TEAPs, initiated by recharge, occur primarily in small transition zones rather than producing changes in dominant redox zonation. Therefore, changes in biogeochemical parameters, including those indicative of TEAPs, were evaluated at a large plume scale and a smaller single-well scale.

Identifying the chemical changes associated with a recharge event is difficult due to the chemical complexity of contaminated systems. As shown by Suk and Lee (1999) spatial and temporal measurements of chemical and physical properties alone usually do not expose the underlying processes in complex groundwater systems. Traditional geochemical tools such as Stiff and Piper diagrams classify water masses based on patterns of major ion concentrations. These patterns give insight into the chemical evolution a water mass based on water-rock interactions. In contaminated systems, relying solely on the distributions of major ions to classify water masses is ineffective because it neglects many important parameters that represent the hydrogeochemical condition of the water. These traditional analysis methods do not consider redox sensitive species or other indicators of biogeochemical processes that may control waterchemistry variations in contaminated systems. As a result, these tools are inadequate to reveal the underlying associations between chemical and physical parameters that lead us to interpretations of processes during recharge events in contaminated systems.

Multivariate analyses that consider a more complete set of physical and chemical parameters (including: major cations and anions, redox related species, alkalinity, temperature, pH, and redox potential) can provide a better understanding of important parameter associations in contaminated systems than traditional classification methods. Several researchers (e.g., (LEE et al., 2001), (SWANSON et al., 2001), (RITZI et al., 1993)) have used factor and/or cluster analysis to interpret groundwater chemical data. Suk and Lee (1999) demonstrated the effectiveness of combining factor and cluster analyses to reveal the governing processes and hydrogeochemical similarities between measured parameters. One criticism of factor analysis techniques is that they are not directly

observable. This study employs the strategy of combining factor and cluster analysis techniques with a visual representation of the actual chemical signature of the resulting water masses. By examining the chemistry of the resulting water masses from the cluster analysis an important link between the measured parameters and calculated factors is established making process interpretations more meaningful.

Our approach involved first performing factor analysis to determine chemical associations, which allow for the evaluation of the dominant processes controlling groundwater chemistry. Factor scores were then computed for each sample location, which describe the importance (or loading) of each factor on that particular sample. These factor scores were then used in the cluster analysis. Cluster analysis was performed on the factor scores as opposed to the raw chemical data to reduce classification error due to data outliers or multicollinearity. This is effective because factors are independent of one another and indicative of the underlying structure of the original variables. These clusters were then plotted in 3-dimensions to identify the spatial relationship between various water masses within the plume. Once the water masses were defined, they were examined not only in terms of the dominant factors controlling the cluster but also examined the chemical composition to better define the factor loadings.

The primary objective of this study is to evaluate change in a reduced aquifer during a recharge event using statistical and graphical methods, and demonstrate the effectiveness of multivariate statistical techniques for revealing process changes in chemically-complex systems. Specifically, this paper seeks to 1) characterize a reduced groundwater contaminant plume before and after a recharge event in terms of dominant

biogeochemical processes; 2) define the chemical changes associated with the recharge event, and 3) determine the spatial distribution of process changes. These analyses provide a detailed investigation of the role of recharge as a drive for redox state dynamics, which is crucial to the proper understanding and management of natural and contaminated reduced systems.

Materials and Methods

Study Site Description:

The study site is a shallow sandy aquifer contaminated with petroleum hydrocarbons and chlorinated solvents at the former Wurtsmith Air Force Base (AFB), Michigan, U.S.A. Wurtsmith AFB lies on a sandy plain of glacial lake sediment approximately 2 km west of the Lake Huron shoreline in Michigan's Lower Peninsula. The aquifer is approximately 20 meters thick and composed of highly permeable alternating aeolian sands and glacial outwash material. Hydraulic conductivities of these deposits are on the order of 30 m/day. The unconfined aquifer is underlain by at least 30.5 meters of silty clay. The water table varies from 3.5-5.0 m below land surface (184-186 m above sea level), fluctuates 0.3 to 0.7 m annually, and the water table gradient ranges from 3 to 5 meters per kilometer. Assuming an effective porosity of thirty percent, average groundwater velocity is approximately 0.3-0.5 m per day. The plume has lateral direction shifts of 7 to 10 degrees because the groundwater flow direction is influenced by seasonal recharge at this site. Fire training activities performed by the Air Force from 1952 to 1986 at this site contaminated the groundwater. Various compounds were used during the training exercises to ignite and extinguish the fires, including waste fuels, chlorinated solvents, aqueous film-forming foams, a multipurpose dry chemical, potassium bicarbonate based soda, and Halon 1211. An extensive plume approximately 50 m wide and 400 m long has developed, with the majority of contaminant mass residing within the capillary fringe (Figure 2.1). Most of the contamination is associated with aquifer solids between 4.5 and 5.7 m below land surface, which have an average total hydrocarbon concentration of 13,650 mg/kg (USGS, 1991). The plume is complex in that it contains both BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and chlorinated solvents (e.g., dichloroethene). Concentrations of BTEX compounds in the plume range from 20 to 1,000 µg/liter while concentrations of dichloroethane, chloroethane, and vinyl chloride range from 2 to 1,000 µg/liter.

In June 1998, a pilot flow-through bioreactor system was installed near the concrete pad to evaluate the effectiveness of stimulated microbiological activity to remove BTEX and chlorinated solvent contamination from the site. As part of this system, groundwater was extracted, augmented with substrates including nitrate (as NaNO₃) to serve as a TEA for microbial metabolism, and pumped through the bioreactor system. This water was then returned to the test plot near the concrete pad. The extraction well then re-captured the majority of "influenced" water and continued the cycle. This operation ended in June 1999. A slug of bioreactor-influenced water, with increased alkalinity, NH₄⁺ and Na concentrations, reached our monitoring wells ML3 and



Figure 2.1: Plume map for the Fire-Training Area 2 (FTA-2) at the former Wurtsmith Air Force Base, Michigan. The concrete pad was the site of firetraining activities. Grey lines represent plume position during periods of low water table; Red lines represent plume position during periods of high water table. Blue lines are water table contours in feet above sea level.

ML5 between February 1999 and May 1999. The bulk of the influenced water passed through our well grid between October 1999 and January 2000. However, some remnant water may still have been influencing the chemistry at the farthest downgradient wells during January 2000.

The overall reducing conditions in the plume vary historically from Fe-reducing to methanogenic (as determined by H₂ concentrations) on the time scale of months (MCGUIRE et al., 2000). To document the vertical distribution of contaminants within the plume, a series of multi-level sampling wells were installed at this site (Figure 2.2). The wells were constructed of 2.5 cm inner diameter PVC casing, with 0.3 m long, 6.35 mm slotted PVC screens. Vertical spacing between screens is approximately 1 m. This is an ideal site to examine the effects of recharge on reduced systems since a detailed spatial and temporal geochemical, hydrogeologic, and microbiological database for the site has been established (DOJKA et al., 1998; HAACK and BEKINS, 2000; MCGUIRE et al., 2000; REYNOLDS and HAACK, 1999).

Chemical Analysis:

The chemical composition of the groundwater at selected wells within the well grid was evaluated in January and June of 2000 because a significant recharge event occurred between these two sampling events. Groundwater head measurements from 3 hourly-recording pressure transducers indicated that the hydraulic head during January 2000 was still in a seasonal decline due to lack of recharge (Figure 2.3). In May, the



Figure 2.2: Two-dimensional well grid installed near FTA-02.



Figure 2.3: Fluctuations in water table elevation (head) over time. Large gray circles represent sampling events.

groundwater head levels sharply increase due to snowmelt recharge. Peak head conditions occurred in late May and groundwater samples were collected in early June.

Each depth within a well was purged with a peristaltic pump at a rate of approximately 400 ml/min. A flow cell (Yellow Springs Instruments) was used to continuously monitor temperature, pH, dissolved oxygen, Eh, and specific conductance until readings became stable. Dissolved H_2 gas samples were collected using the bubblestripping method (CHAPPELLE and MCMAHON, 1991) and analyzed immediately in the field on a RGA3 reduction gas analyzer (Trace Analytical). Dissolved iron (Fe^{2+}) and sulfide (S²⁻) were measured in the field, by phenanthroline and Chemetrics Vacu-Vials[™] colorimetric analyses respectively. Alkalinity was also measured in the field by potentiometric titration using Gran plots for graphical determinations (DREVER, 1997). Samples for cations and anions were filtered through 0.45 µm polyethersulfone membrane filters and collected for analysis in the laboratory. Major cation samples were preserved with ultra-pure "optima[™]" nitric acid and analyzed by flame atomic absorption spectrometry (Perkin Elmer). Samples collected for anions (Cl, Br, NO₃, and NO₂, SO₄) and NH_4^+ analyses were preserved with formaldehyde and flash frozen respectively, and then analyzed by capillary electrophoresis (Hewlett Packard).

Statistical Analysis:

Factor analysis was performed using SYSTAT (SPSS Inc., 2000) on each standardized dataset to simplify the complex relationships that exist among the observed variables by revealing a reduced set of variables called factors. These factors are neither directly observable nor expressed in terms of the original variables. These factors link together seemingly unrelated variables to give additional insight into the underlying processes operating in the system. In this study, the results of the groundwater chemical analyses are the original variables and the dominant physical and biogeochemical processes operating in the aquifer are the unobservable factors.

Our factor analysis technique involved four steps. The first step was creating a matrix of correlation coefficients for all pairs of constituents. Results showed that specific conductance was highly correlated to many other variables, and was thus eliminated from the datasets prior to performing factor analysis. Measurements of Br, NO_2 , and S^2 were also removed from the datasets due to their low/non-detectable concentrations in the groundwater samples. The second step was estimating the factor loadings. The principal components method was used as the parameter estimation method to transform the observed variables into an orthogonal set of factors. However, initial factor loadings commonly do not reveal the underlying structure of the observed variables due to certain mathematical conditions, such as the variance properties of the principal component (SUK and LEE, 1999). Therefore, the third step was linearly transforming the initial set of loadings into a new set of loadings by factor rotation. Although there are numerous rotation schemes, this study uses Kaiser's scheme of varimax orthogonal rotation, which yields the maximum variance of the squares of the loadings (ABU-JABER et al., 1997). The final step of the factor analysis was computing the factor scores by a simple linear transformation on each of the factored variables. In this study, the factor scores describe the importance of each of the resulting factors on the chemistry of the wells.

Cluster analysis was then performed on the factor scores using JPM4 (SAS Institute). Cluster analysis is an exploratory statistical tool used to divide the entire groundwater system up into smaller groups or clusters. Theoretically, each group would have similar relationships among chemical variables or a similar geochemical signature. Factor scores were clustered instead of the measured variables to exclude unnecessary and mutually dependant variables, which can obscure the underlying data structure. Hierarchical clustering was performed using Ward's method (WARD, 1963). These clusters were then plotted in 3-Dimensions using SYSTAT to visualize the spatial pattern of the clusters. To visualize the geochemical signature of the clusters, z-scores of the raw data were computed and plotted using standard X-Y plots.

Results and Discussion

To examine the large-scale (plume) chemical changes initiated during a recharge event, the average chemical concentration at the shallowest depth of all wells was calculated in January and then again in June 2000 after a major recharge event. Concentrations were averaged from the shallowest depths to avoid misinterpretations based on examination of single-well measurements over time given the observed shifts in groundwater flow direction. During recharge events, groundwater head increases causing the measured changes in the lateral direction of groundwater flow. As a result of these changes, it is often inappropriate to compare a well sampling point before and after recharge since it may be impossible to distinguish the physical movement of a particular water mass away from a sampling point and geochemical changes within a water mass

(MCGUIRE et al., 2000). By averaging chemical concentrations at the shallowest well depths at all wells, the problem of laterally shifting water masses is reduced. This analysis assumes that any changes in the average water chemistry are related to direct recharge inputs and not related to the physical movement of water masses. The percent change in average chemical values between January and June 2000 (before and after recharge) is shown in Figure 2.4. The plot showed that after the recharge event, temperature (T), Eh, dissolved oxygen (O_2) , sulfate (SO_4) and nitrate (NO_3) increased, presumably due to the direct atmospheric inputs from precipitation. A decrease in pH after the recharge event was coupled with increases in calcium (Ca), magnesium (Mg), and alkalinity (primarily HCO_3). This seems reasonable since the recharge water typically has a much lower pH than the native groundwater. Thus, when mixed, recharge would initiate dissolution of carbonate minerals and increase the Ca, Mg, and HCO₃ concentrations in solution. Observed increases in dissolved iron (Fe^{2+}) and conductivity were likely due to inputs from the solid phase. In the case of Fe^{2+} , increases may be caused by a rise in water table elevation allowing reduced water to come in contact with previously oxidized sediments that contain Fe-oxyhydroxides coatings. These Fe (III) rich minerals could then be available for reduction to Fe^{2+} coupled with the oxidation of organic matter (TUCCILLO et al., 1999; VROBLESKY and CHAPPELLE, 1994). The observed increase in Fe^{2+} would not occur in the presence of O₂, which on average increased after the recharge event. These seemingly contradictory observations demonstrate that local chemical changes are important within the plume. The observed increase in average conductivity values is in part due to the increase of solutes from mineral dissolution but may also have contributions from organic contaminants desorbing





from the solid phase into the aqueous phase of the aquifer. Decreases in other solutes such as sodium (Na), potassium (K), ammonium (NH₄), bromide (Br), chloride (Cl), and silica (SiO₂) are likely due to dilution with recharge water, which is depleted with respect to these constituents. The observed average decrease in dissolved hydrogen gas (H₂) concentrations may be due to both dilution and consumption. Dissolved hydrogen can act as an electron donor coupled to the reduction of various TEAs (O₂, NO₃, Fe³⁺, and SO₄), which may have been introduced to the system during the recharge event. These average percent change analyses give an estimation of the inputs to the aquifer during the recharge event. However, this approach cannot be used to infer process and therefore cannot distinguish dilution from consumption by TEAPs.

Factor analysis was used to assess changes initiated by recharge and attempt to discern dilution versus biogeochemical reaction effects. Table 2.1 shows the rotated factor pattern of the five extracted factors for the January and June 2000 sampling events. Initial factor selection was based on the default eigenvalue criterion, which selects any value greater than one. However, in both the January and June datasets, an additional factor with an eignevalue very near one (0.980 and 0.983 respectively) was included to help explain a greater percentage of the variability. Loadings on each of the factors were interpreted such that any association greater than ± 0.75 was considered high loading with respect to that factor, any associations between ± 0.5 -0.75 were considered weaker but still significant loadings and any loading less than ± 0.5 was considered insignificant (WAYLAND et al., in review). The sign designations suggest nothing about the strength of the associations but rather give an indication of inverse relationships among variables if loaded on the same factor.

January 00	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Т	0.05	-0.66	0.12	0.27	0.01
рН	-0.86	0.01	-0.20	-0.02	0.01
Eh	0.52	0.17	0.08	-0.52	0.21
O ₂	-0.23	0.21	0.12	-0.75	-0.12
H₂	0.79	-0.23	0.14	0.13	-0.22
Ca	0.86	0.38	-0.01	0.16	0.04
Mg	0.01	0.93	-0.07	-0.04	0.04
Na	0.11	-0.02	0.90	0.01	0.16
K	0.66	-0.23	0.44	-0.05	0.08
Fe ²⁺	0.80	-0.05	0.36	0.19	0.04
Alk	0.61	0.26	0.68	0.09	0.12
CI	0.04	-0.01	-0.08	0.02	-0.94
SO₄	-0.56	0.24	-0.43	-0.20	0.17
NO ₃	-0.14	0.04	-0.16	-0.83	0.08
NH₄	0.18	-0.23	0.73	-0.04	0.08
SiO ₂	0.25	-0.07	0.71	0.04	-0.18
June 00	Factor I	Factor II	Factor III	Factor IV	Factor V
Т	-0.11	0.10	0.21	-0.55	0.07
рН	-0.48	-0.55	-0.20	0.15	-0.35
Eh	0.11	-0.79	0.26	-0.09	-0.31
O ₂	-0.12	-0.91	-0.10	0.04	-0.10
H₂	0.11	0.18	0.14	-0.06	0.84
Ca	0.47	0.27	0.61	-0.13	0.32
Mg	0.06	-0.02	0.93	-0.07	-0.07
Na	0.89	-0.01	0.03	0.04	0.04
K	0.78	0.16	-0.04	-0.06	0.32
Fe ²⁺	0.80	0.22	0.13	-0.02	0.39
Alk	0.74	0.21	0.51	0.01	0.28
CI	0.02	0.03	0.33	0.75	0.31
SO₄	-0.36	-0.09	-0.17	0.64	-0.32
NO ₃	-0.21	-0.82	-0.18	0.18	0.05
NH₄	0.42	0.10	-0.14	0.06	0.65
SiO ₂	0.74	0.01	0.10	-0.03	-0.05

Table 2.1: Rotated factor pattern of five extracted factors after varimax rotation in January and June of 2000.

The January 2000 dataset (before recharge) was broken down into five factors (1-5). Factor 1 showed high positive loadings on Ca, Fe^{2+} , and H₂, weaker positive loadings on K and alkalinity, high negative loading on pH, and a weaker negative loading on SO₄. These associations suggest active anaerobic microbial processes. In reduced systems, anaerobic processes can allow intermediates such as H_2 and various low molecular weight organic acids, as well as end products such as Fe^{2+} to build up in the system (CHAPPELLE, 2001). As a result of this activity, the pH of the system can be slightly reduced resulting in increased dissolution of minerals such as carbonates and feldspars (BENNETT et al., 1993). Factor 2 showed high positive loading on Mg and weak negative loading on temperature. This factor suggests that Ca and Mg are not associated in the system. The third factor had high positive loadings on Na, alkalinity, NH_4 , and SiO_2 . These associations may suggest the chemical signature of water from bioreactor activities performed at the site 2 years prior to the sampling events. Although the bulk of the influenced water passed through the study area, as indicated by the return to background Na concentrations, these associations suggest that these few down gradient wells may still be experiencing a slight impact. The bioreactor activities stimulated microbial activity by adding NaNO $_3$ to the aquifer system. Increased microbial activity resulted in elevated values of NH_4 (biomass cycling and perhaps dissimilatory nitrate reduction to NH₄) and alkalinity (most likely due to increased production of organic acids) (MCGUIRE et al., in prep). The fourth factor had high negative loadings on O₂ and NO₃ and weaker negative loadings on Eh. This signature suggests aerobic waters with lesser microbial activity, likely due to low organic matter content (uncontaminated water). The final

factor (5) had high negative loading with respect to Cl. This is due to a single well with much higher Cl concentrations than the others, since this factor drops out of the factor analysis when this sample is removed. The elevated chloride concentration may be due to localized dechlorination reactions. Unfortunately, since it is a single sample, contamination cannot be ruled out.

The June 2000 sample set (after recharge) was also broken down into five factors (I-V). Factor I showed high positive factor loadings on Na, K, and Fe²⁺, weaker positive factor loadings on alkalinity and SiO₂ and weak negative loadings on pH. This signature is interpreted to be highly reduced water impacted by recharge water. Prior to the recharge event, the most reduced water had high concentrations of cations, alkalinity, and H₂. The post-recharge associations here are similar suggesting that the water experienced highly anaerobic microbial activity but with one exception; high H₂ values are no longer associated with this group. Since high H₂ concentrations are typically associated with highly reduced waters, this suggests that the system has been "reset" microbially by the introduction of more favorable TEAs (O₂, NO₃ and SO₄) during the recharge event. Factor II was characterized by high negative loadings on O₂, NO₃, Eh, and weaker negative loadings on pH. These associations suggest aerobic water masses. It should be noted that in January the aerobic factor was the fourth most important factor but in June after the recharge event, the aerobic water signature was the second most important factor. Factor III has high positive loadings on Ca, Mg and alkalinity, which suggest the dissolution of carbonate minerals. Interestingly, after the recharge event, Ca and Mg have a higher degree of association than in the pre-recharge water. Factor IV has weak positive loadings on Cl and SO₄, and weak negative loadings on temperature suggestive

of recharge water from snowmelt. Lower temperatures could have resulted as the cold melt-water recharged and mixed with the aquifer water. Sulfate concentrations would have increased due to atmospheric inputs of the precipitation (likely as snow). The Cl is likely from the degradation of chlorinated solvents, which may have washed in with the recharging melt water. The final factor (V) showed a high positive loading on H₂ and a weaker positive loading of NH₄. This factor likely indicates intense anaerobic microbial activity. Dissolved hydrogen is an intermediate of microbially-mediated anaerobic reactions which can build up in highly reduced systems and NH₄ would be present primarily from the cycling of biomass cellular components. These findings suggest that although many of the same processes are operating in the aquifer before and after the recharge event, the relative importance of these processes have changed.

To explore the spatial distribution of process changes inferred by the factor analysis, factor scores describing the relative importance of each of the above factors were calculated at each individual well. Cluster analysis was then performed to group wells together based on factor scores that were used to identify water masses with similar biogeochemical signatures. Figure 2.5 (A&B) shows the resulting dendrograms for January and June. In both datasets, the wells were broken down into 5 smaller clusters. Since factors can be interpreted as processes, a plot identifying the dominant factor(s) controlling each cluster was constructed for both January and June to interpret the processes controlling water chemistry for each cluster (Figures 2.6 & 2.7). However, the factors are limited in that they describe associations and not measured chemical concentrations so these data were considered in conjunction with the average chemistry



Figure 2.5A: Cluster dendrograms for January 2000 showing five clusters

June 2000



Figure 2.5B: Cluster dendrogram for June 2000 showing five clusters









of each cluster. These clusters were then plotted in 3-dimensions to identify if a spatial pattern would exist among the clustered wells and if so, determine the impact of various factors (processes) on the resulting water masses. Figure 2.8 depicts the distribution of clusters in January 2000 prior to the recharge event. This plot shows that clusters of wells with similar chemical associations also cluster together spatially forming distinct water masses. Cluster 4 (C4) is primarily impacted by factor 1 which is characterized by high H₂, cations, alkalinity, and lower values of SO₄ and pH. This water is located in the shallowest portion of the plume. This is the area of greatest contamination and enhanced microbial activity. As microbial processes evolve, TEAs (O_2 , Fe³⁺, NO₃, and SO₄) are depleted and dissolved hydrogen and Fe^{2+} concentrations build up. These processes lower the pH of the water, allowing dissolution of carbonate and aluminosilicate minerals to dissolve. Cluster 1 (C1) is located just below the water table interface and comprises the largest area of the plume. Here the dominant factor is still factor 1 described above but to a much lesser degree than in C4. In some wells within this cluster, factor 4, characterized by higher concentrations of O_2 , NO_3 , and higher Eh measurements, is also a dominant factor. This suggests that these wells exhibit an overall less reduced redox state than those in C4. Cluster 5 (C5) is the water mass that lies at the deepest sampling points. This water mass's most characteristic feature is a negative loading on factor 1. This implies that this water is the least reduced of the three main water packets, which is consistent with the deep, less contaminated, portion of the plume. Cluster 3 (C3) is most influenced by Factor 3, which corresponds to remnant water from the bioreactor bioremediation system. These wells are the only ones affected because they are the





farthest down gradient of the final bioreactor circulation plot. Cluster 2 (C2) is not necessarily a water mass. It is comprised of only one well point and characterized by elevated Cl concentrations. As stated above, this observation may be the result of sample contamination or may be the result of localized degradation of a chlorinated solvent mass. It should be noted that factor 2 (high Mg, low T) and factor 4 (high O₂, NO₃, Eh) are not dominant in any particular water mass and therefore have only minor significance at the plume scale.

The same assessment was repeated in June 2000, after the recharge event. Figure 2.9 shows that, again, cluster of wells with similar chemical associations also cluster together spatially forming distinct water masses. However, the spatial distribution of the resulting water masses is different. Cluster IV (CIV) lies primarily at the surface of the plume but also has some wells located upgradient nearest the contaminant source area. These wells are distinguished by higher values of H_2 and NH_4 . Both of these parameters indicate highly anaerobic microbial activity. It should be noted that the shallowest water mass extends deeper than it did during the January sampling. This suggests that prior to the recharge event (from January until May) the water likely became increasingly reduced influencing a larger zone as anaerobic microorganisms operated without recharge during the winter months. Vertical redox zonation has been observed at this site with the most intense activity occurring near the water table interface (surface of plume) (CHAPPELLE et al., 1996; MCGUIRE et al., 2000). However, the chemical signature of this water mass is more complicated than the observed signature found in January. This mixed chemical signature suggests that within this zone at certain localized points, recharge has stimulated more energetically favorable microbial activity. However, on the





whole, the recharge event was not large enough to significantly reset the system (i.e., the bulk water mass still associates together as anaerobic, microbially active, reduced water). The water mass directly beneath cluster IV is cluster II (CII). The CII signature suggests that this portion of the plume is actually experiencing the most change as a result of the introduction of recharge water. The most likely reason is that this portion of the plume was not as deeply reduced so changes in chemistry may not have shifted microbial processes as dramatically. The observed elevated Cl is likely from an influx of chlorinated solvents from the vadose zone as recharge water moved through the system. Elevated SO₄ values and lower temperature are likely from the recharging melt water. Cluster V (CV) is located at depth within the plume where lower values of Ca, Mg, and alkalinity have been observed. This may be due to precipitation of carbonate minerals or due to comparatively lesser mineral dissolution due to lesser microbial activity (and therefore lower acid production). Cluster III (CIII) is comprised of a small group of wells located at various depths within the plume but never near the water table. Similarly (but opposite) to cluster V, these wells have higher values of Ca, Mg, and alkalinity probably due to the dissolution of carbonate minerals. Cluster 1 (CI) is most influenced by factor I and occurs nearest the contaminant source (surface of plume and upgradient). These samples were likely taken very near the water table where an influx of contamination was likely released to the plume during the recharge event. Therefore, this area likely experienced the greatest increase in microbial activity resulting in lower pH values and higher concentrations of most cations and alkalinity due to mineral dissolution. The lack of H_2 associations in this zone suggests that this may be a location where we are able to observe the small interface where H_2 is consumed coupled to the reduction of TEAs.

These findings suggest that although we know more energetically favorable TEAs were introduced to the plume surface and that the relative importance of various groundwater processes changed as a result of the recharge event, the system was not microbially "reset" in large-scale redox zones within the plume. Rather, many of the specific changes likely occur in more localized areas. To examine localized changes, a single well (ML3) was examined at various depths to establish the vertical distribution of chemical change. Figure 2.10 shows the percent chemical change with depth after the recharge event at multi-level well 3. Since dissolved hydrogen gas is thought to be a sensitive indicator of microbial process (LOVLEY and GOODWIN, 1988), this trend is of great interest. At first glace, it appears that shallowest depth (ML2-22.00) experienced only a slight decrease in H₂. However, since wells ML2-25, ML3-28, and ML3-33 experienced an overall increase in H_2 during this period, it is reasonable to assume that ML3-22 also experienced an increase and then a more significant decrease during the recharge event. This supports the findings of the factor analysis that the plume became more reduced after January but prior to the recharge event. The observed H₂ decrease at ML3-22 and the suspected decrease at ML3-25 (lesser increase than the other wells) are both likely due to a combination of dilution and consumption as an intermediate during microbially mediated processes such as aerobic respiration and denitrification that may have been initiated during the recharge event. The deepest monitoring point (ML3-38) did not experience any change in H₂ concentrations since historically, the concentration has always been below the detection limit and the processes initiated by the recharge event would only decrease the overall concentration. Interestingly, all depths experienced a large percent increase in NO_3 but very low percent increases if at all in SO_4



after the dash represents the depth (in feet) beneath the ground surface. Figure 2.10: Vertical distribution of percent chemical change at a single well (ML3) from January till June 2000. The number

concentrations. Presumably, the chemical concentration of the recharge water was uniform across the site and therefore must have contained dissolved SO₄ since the percent change plots demonstrated that on a plume scale the SO₄ values increased. This suggests that locally the SO₄ was consumed before it could reach the wells sampled, possibly in a very narrow transition zone. These observations imply that although a zone may be characterized as SO₄ reduction by H_2 levels SO₄ may not be available for that reaction to proceed.

Conclusions

Multivariate analyses were performed on groundwater chemistry samples from a contaminated aquifer to characterize the biogeochemical changes initiated during a recharge event. These changes were evaluated at a large (plume) scale and smaller (single-well) scale. Large-scale chemical averages indicated that the influx of recharge water introduced more energetically favorable TEAs to the plume including O₂, NO₃, and SO₄. The resulting rise in water table elevation also may have made available Fe (III) oxyhydroxide coatings as a TEA. Based on the average influx of TEAs, one would expect to observe a shift in dominant anaerobic groundwater microbial processes to more energetically favorable reactions and thus observe changes in redox zonation. However, further data examination by means of factor analysis, cluster analysis, and graphical techniques revealed that when viewed in greater detail, the scale at which changes are initiated by recharge must be considered.

Factor analysis indicated that before and after the recharge event, the dominant chemical associations were very similar. However, the relative importance of each of

these processes was different after the recharge event. Therefore to visualize how these changes in groundwater chemistry/process manifested themselves spatially in the aquifer, cluster analysis was performed on the individual factor scores for all wells. The results of the cluster analysis were then plotted in 3-D space to obtain a visual representation of chemical change. These analyses demonstrated that wells with similar chemistry were spatially distributed such that distinct water masses were observed. Comparison of these resulting water masses before and after recharge indicated that the water masses were altered as a result of recharge but not by initiating changes in dominant redox zones. Rather, reactions seem to be initiated in localized areas, likely at the interface between the reduced water and the capillary fringe zone. Evaluation of chemical changes at a single well provided further evidence that many TEAP reactions initiated by recharge events occur in small interface zones and not in large redox zones as we traditionally envision.

These analyses suggest that recharge events can initiate changes in TEAPs in anaerobic groundwater systems by introducing more energetically favorable TEAs to the system. When coupled to organic electron donors, these more energetically favorable reactions can lead to enhanced microbial degradation of organic contaminants, particularly in the capillary fringe zone where many organic contaminants concentrate. However, since the zone over which these reactions occur is likely very small it is very difficult to directly measure these processes. Nonetheless, recharge effects in this organic-rich zone may significantly increase the rates of natural attenuation and bioremediation. Therefore, to be able to evaluate and design the most effective

bioremediation or natural attenuation strategies, the importance of small-scale spatial changes should be considered.
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CHAPTER III.

McGuire, J.T., Long, D.T., Klug, M.J., Haack, S.K., Hyndman, D.W., accepted March, 2002. Evaluating the behavior of oxygen, nitrate, and sulfate during recharge and quantifying reduction rates in a contaminated aquifer. Environmental Science and Technology.

Abstract

This study evaluates the biogeochemical changes that occur when recharge water comes in contact with a reduced aquifer. It specifically addresses: 1) which reactions occur insitu; 2) the order these reactions will occur if terminal electron acceptors (TEAs) are introduced simultaneously; 3) the rates of these reactions; and 4) the roles of the aqueous and solid phase portions of the aquifer. Recharge events of waters containing various combinations of O₂, NO₃, and SO₄ were simulated at a shallow sandy aquifer contaminated with waste fuels and chlorinated solvents using modified push-pull tests to quantify rates. In-situ rate constants for aerobic respiration (14.4 day⁻¹), denitrification (5.04-7.44 day⁻¹) and sulfate reduction (4.32-6.48 day⁻¹) were estimated. Results show that when introduced together, NO₃ and SO₄ can be consumed simultaneously at similar rates. To distinguish the role of aqueous phase from that of the solid phase of the aquifer, groundwater was extracted, amended with NO₃ and SO₄ and monitored over time. Results indicate that neither NO₃ nor SO₄ was reduced during the course of the aqueous phase study suggesting that NO₃ and SO₄ can behave conservatively in highly reduced water. It is clear that sediments and their associated microbial communities are important in driving redox reactions.

Introduction

Identifying the biogeochemical processes responsible for, the development of and transition between, redox zones and quantifying the rates of these processes is crucial to understanding how many natural and anthropogenic groundwater constituents behave in the environment. Understanding the dynamics associated with the redox state of a system is important since redox controls the form, mobility, and persistence of many groundwater contaminants. Quantifying these dynamics will allow for 1) improved understanding of natural fluctuations of redox processes in pristine and contaminated aquifers; 2) the prediction of rates of natural microbial attenuation of contaminants; and 3) proper design and evaluation of monitored natural attenuation and biostimulation remediation strategies in contaminated aquifers. Although recharge events are thought to be a significant drive for redox dynamics (1), their exact role is not well understood. Few studies have looked at the introduction of recharge solutions to reduced systems and none have examined the effects of introducing a multi-parameter recharge solution as one might expect during a rainfall event. In addition, the roles of aqueous and solid phase portions of an aquifer, and their associated microbial communities, on redox reactions have not been evaluated. To further complicate our understanding of the controls on redox dynamics, laboratory and field measurements of redox reaction rates are often significantly different. This study seeks to quantify the redox reactions associated with the aqueous and solid phase portions of a reduced aquifer during a multi-parameter recharge event.

In pristine and contaminated aqueous systems, redox state is based on the activity of microorganisms, which first consume oxygen, and then a succession of alternate terminal electron acceptors to support their growth using a variety of carbon sources (2-5). The succession of terminal electron accepting processes (TEAPs) in order of decreasing redox potential and free energy yield is generally: oxygen reduction, nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis. In most closed, uncontaminated groundwater systems, the sequence of TEAPs follows this succession (i.e., increasingly reduced conditions occur further down the flow path) (6). Downgradient of contaminant plumes, the sequence of TEAPs is reversed (2,3). That is, the most reduced conditions (e.g., methanogenesis) occur near the contaminant source due to the greater availability of electron donors, while less reducing conditions (e.g., iron reduction) occur down flow path from the contaminant source. Since hydrocarbons (which serve as electron donors) concentrate in the capillary fringe area, more reducing conditions often occur near the water-table interface resulting in a plume that has vertical as well as horizontal redox zonation (7). In reduced systems, it is thought that recharge events can initiate changes in TEAPs by delivering more favorable terminal electron acceptors (TEAs) such as oxygen (O_2) , nitrate (NO_3) and sulfate (SO_4) to the system (1). Thermodynamics would predict that when a recharge solution comes in contact with a reduced aquifer TEAs would be consumed in the order of free energy yield. Although thermodynamics (by evaluation of available free energies) can provide insight into the potential metabolic attractiveness of a reaction, the actual rate and extent of any given redox process is a function of other factors such as activation energy, metabolic kinetics, and the presence of biotic and abiotic catalysts. This suggests that unless competitive pressure exists (e.g., electron donor limitation), there is no reason to assume that TEAs would be consumed in the order of free energy yield. In addition, it is unclear if other biotic and abiotic redox reactions involving TEAs may occur when recharge water comes in contact with reduced groundwater and its associated sediments.

To understand the biogeochemical processes that dominate during recharge events, it is necessary to not only identify the redox reactions which may be occurring but also to quantify these reaction rates. The determination of rates of TEA consumption is challenging. Many studies use laboratory-based methods including microcosm experiments (8-11), direct observations (radiotracers) (12,13), molecular methods (14), geochemical modeling (5) and kinetic modeling (15). These studies have been performed on sediments from a wide range of aqueous environments including aquifers, lakes, and wetlands. However, these approaches can be limited by possible system disturbances, contamination problems, and often unnaturally high concentrations of substrate. In-situ methods to estimate rates are generally considered to be more representative of actual subsurface conditions. These methods are not as widely used and include natural gradient tracer experiments (16), flowline estimations (17), and push-pull tests (18).

In general, laboratory rate-estimation methods commonly yield zeroth order rates while in-situ field rate estimation methods commonly yield first order rates associated with the TEA concentration. None of the previous laboratory or field studies has examined the localized in-situ TEA consumption rates that would result when natural recharge water, containing multiple TEAs at relatively low levels, is introduced to a reduced groundwater environment. One study by Cunningham at al(19), added multiple TEAs (NO₃ and SO₄) to evaluate possible enhanced biodegradation over longer timer scales (months) in a contaminant plume at Seal Beach, California. They found that although NO3 was utilized preferentially over SO4, the two processes were not strictly sequential. This study utilizes a relatively new technique, in-situ push-pull tests, to examine in detail the localized processes initiated during recharge events.

Push-pull tests have been shown to be useful in obtaining quantitative information on a wide range of in-situ microbial processes in aquifers (20,21) and lake sediments (22).

A test consists of three phases. In the first phase, native groundwater is extracted from the well for preliminary geochemical characterization. This information is necessary to deduce which biogeochemical reactions may already be occurring in the aquifer and to establish background concentrations of the chemicals of interest. Specifically, we wanted to ensure that the groundwater where the tests were performed was reduced. Eh measurements ranged from -150 to -200 mV but due to the lack of specificity of Eh measurements, we chose to rely on concentrations of dissolved hydrogen (H_2) and other selected TEAP variables such as O₂, Fe²⁺, NO₃, NO₂, and SO₄. The H₂ concentration in aquatic systems has been proposed as an indicator of in-situ TEAPs (5). Dissolved hydrogen is known to be a fleeting but important intermediate in the decomposition of Dissolved hydrogen is produced and consumed in anaerobic organic matter. environments such that each TEAP maintains a characteristic H_2 concentration (23). Interpretations of TEAPs from H₂ concentrations, as measured in marine and freshwater sediments and in aquifers, are as follows: methanogenesis, greater than 5 nM; SO_4 reduction, 1-4 nM; Fe³⁺ reduction, 0.2-0.6 nM; and Mn (IV) or nitrate reduction, less than 0.05-0.1 nM (5). Chapelle et al. (7, 24, 25) demonstrated the use of H₂ concentrations in delineating redox zonation in the plume at the study site described in this paper. They concluded that delineating redox zones based on H₂ concentrations is more reliable when H₂ concentration are interpreted in the context of other TEAP variables, a strategy we have adopted here. After the geochemical characterization has been completed to determine initial geochemical condition, the remaining phases of the test can begin. In the second phase, or "push", a well-mixed slug of water containing conservative and reactive solutes is rapidly injected into the saturated zone of the aquifer. A conservative

solute is added as a tracer to account for advection and dispersion and the other added solute(s) are reactive. The third phase, the "pull", begins immediately after the injection is completed. Water is slowly extracted from the well and the concentrations of the solutes are measured over time.

These tests can provide valuable insight into the redox reactions that may be occurring in-situ, but they are limited in that they cannot distinguish the roles of the aqueous and solid phases, and their associated microbiological population in these reactions. The most widely accepted hypothesis for the influence of microbes on redox processes in aquifers is that microbes residing on the solid phase portion of the aquifer are responsible for the majority of the activity (26). This is thought to be due to the much greater concentration of microorganisms in association with the solid phase than in the aqueous phase of the aquifer. However, it is unclear what the role of the aqueous phase is during redox reactions. Based on thermodynamics, abiotic geochemical reactions may occur when oxidized chemical species come in contact with a reduced environment. To determine the significance of the abiotic and biotic redox reactions associated with the aqueous phase of the aquifer, we designed surface reaction vessel (SRV) experiments to run simultaneously with the push-pull tests. The goal of the SRV experiments was to determine what reactions would occur in the aqueous phase and at what rates. Identical control SRVs were amended with formaldehyde and run simultaneously to distinguish microbially-mediated redox reactions from geochemically-driven reactions. The SRVs were filled with water from the aquifer where the push-pull test was conducted and then allowed to react over time to the same addition of solutes as introduced in the push-pull tests. The vessels were designed to maintain aquifer conditions as closely as possible including maintaining the temperature and anaerobic nature of the water.

This study evaluates the biogeochemical changes that occur when a recharge solution comes in contact with reduced groundwater and sediments. It specifically addresses: 1) which reactions occur in-situ; 2) the order in which these reactions will occur if TEAs are introduced simultaneously; 3) the rates at which these reactions occur; and 4) the roles of the aqueous and solid phase portions of the aquifer in these processes. Push-pull tests and surface reaction vessel experiments containing various combinations of solutes to simulate various types of recharge events were designed to address these questions.

Study Site Description

The study site is a shallow sandy aquifer contaminated with petroleum hydrocarbons and chlorinated solvents at the former Wurtsmith Air Force Base (AFB), Michigan, U.S.A. Wurtsmith AFB lies on a sandy plain of glacial lake sediment approximately 2 km west of the Lake Huron shoreline in Michigan's Lower Peninsula. The aquifer is approximately 20 meters thick and composed of highly permeable alternating aeolian sands and glacial outwash material. Hydraulic conductivities of these deposits are on the order of 30 m/day. The unconfined aquifer is underlain by at least 30.5 meters of silty clay. The water table varies from 3.5-5.0 m below land surface (184-186 m above sea level) and fluctuates 0.3 to 0.7 m annually. The water table gradient ranges from 3 to 5 meters per kilometer. Assuming an effective porosity of thirty percent, average groundwater velocity is approximately 0.5 m per day. Because the

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direction of groundwater flow is influenced by recharge, lateral shifts in the plume dire



Fire training activities performed by the Air Force from 1952 to 1986 are the of the source contamination at this Various site. compounds were used during the training exercises to ignite and extinguish the fires, including waste fuels, chlorinated solvents. aqueous film-forming



foams, a multipurpose dry chemical, potassium bicarbonate based soda, and Halon 1211. The majority of the contamination resides within the capillary fringe and an extensive plume approximately 50 m wide and 400 m long has developed (Figure 1). The plume is complex in that it contains both BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and chlorinated solvents (e.g., dichloroethene). Concentrations of BTEX compounds in the plume range from 20 to 1,000 μ g/liter while concentrations of dichloroethane, chloroethane, and vinyl chloride range from 2 to 1,000 μ g/liter. Most of

the contamination is associated with aquifer solids between 4.5 and 5.7 m below land surface, which have an average concentration of total hydrocarbons of 13,650 mg/kg (27).

The portion of the aquifer where the push-pull experiments were performed, multi-level well 3 at the 25 ft (7.6 m) depth (ML3-25), remains in a reduced redox state throughout all groundwater flow regimes. The reducing conditions at this well vary historically from Fe (II) reducing to methanogenic (as determined by H_2 concentrations) on the time scale of months (28). The subject well was constructed of 2.5 cm inner diameter PVC casing, with 0.3 m long, 6.35 mm slotted PVC screens. Vertical spacing between screens is approximately 1 m. This is an ideal site to examine the effects of recharge on reduced systems since a detailed spatial and temporal geochemical, hydrogeologic and microbiological framework for the site has been established (28-31).

Methods

Push-Pull Tests:

Well selection was based on the initial complete geochemical characterization including redox-indicating parameters. A summary of the initial water chemistry from the selected wells is presented in Table 1. All activities were performed at a well with highly reduced water (ML3-25) located roughly in the center of the plume (Figure 1). Three push-pull tests were performed at this well at approximately 1-month intervals. To simulate recharge fluids for the push-pull tests, native uncontaminated groundwater from a well just outside the plume, multi-level well 10 at the 37 ft (11.3 m) depth (ML10-37), was extracted and placed in a 20-liter Nalgene carboy. This fluid was chosen to represent a rain solution which had percolated through the unsaturated zone and

ultimately reached the aquifer. The solution was then amended approximately 10 mg/L of the TEAs which would likely be introduced during a recharge event. Three different types of recharge waters were prepared. The first test solution represented the water resulting from a rain event containing O₂, NO₃, and SO₄. The second test solution represented water which had been depleted in O₂, perhaps upgradient, but still contained NO₃ and SO₄. The third test solution represented recharge water depleted in O₂ and NO₃, but still containing SO₄. To each of these solutions, 100 mg/L chloride (as NaCl) was added as a conservative tracer to account for dilution from mixing, advection, and dispersion. Nitrate and sulfate were added as NaNO₃ and Na₂SO₄ respectively and hand shaken to ensure complete dissolution and homogenization of the solution. Oxygen was removed from test solutions two and three by stripping with inert N₂ gas for approximately 3.5 hours until field test kits could no longer detect O_2 (less than 0.03) ppm). To maintain anaerobic conditions, solutions were kept in an N_2 atmosphere and monitored for O_2 . Before injecting these solutions into the test well, the unscreened interval was packed off to prevent the vertical movement of water up the well casing. The packer was inserted to just above the well screen and inflated with inert N₂ gas to seal off the well. The packer remained in place throughout the test. Once the packer was in place, the anaerobic test solution was "pushed" down the well at a rate of approximately 1 L/min. This was followed by the injection of 2 liters of "chaser solution" (deoxygenated, distilled deionized water) to flush the test solution from the well and force it further into the aquifer. The extraction or "pull" phase began immediately after the injection phase was completed. Effluent from the well was slowly extracted at a rate of approximately 150 ml/min and monitored in the field for Cl, O_2 , NO_3 , NO_2 , S^2 ,

SO₄, Fe²⁺, temperature, pH, and Eh over time. Samples were also collected for anions (Cl, NO₃, NO₂, SO₄) and NH₄⁺ for analysis in the laboratory.

Surface Reaction Vessel Tests:

Water was pumped from the reduced well where the push-pull tests were performed (ML3-25) into a 20L Nalgene carboy attached to a glove bag filled with N₂ to maintain anaerobic conditions. The carboy and attached glove bag were then placed into a temperature-controlled environment (surface reaction vessel) and amended with various TEAs. Control surface reaction vessel experiments were set up in the same manner but inoculated with formaldehyde (to make a final 0.4% solution) to halt microbial activity. The water was then monitored at approximately 5-minute intervals for the duration of the push-pull tests. Real-time measurements of O₂, NO₃, NO₂, S²⁻, SO₄, and Fe²⁺ were taken in the field. Samples were also collected for anions (Cl, NO₃, NO₂, SO₄) and NH₄⁺ for later analysis in the laboratory.

Geochemical Analyses:

A flow cell (Yellow Springs Instruments) was used to continuously monitor temperature, pH, dissolved oxygen, Eh, and specific conductance throughout the push-pull tests. Dissolved H₂ gas samples were collected using the bubble-stripping method (17) and analyzed immediately in the field on a RGA3 reduction gas analyzer (Trace Analytical). In the field, NO₃, NO₂, and S²⁻, were measured by colorimetric spectroscopy using Chemetrics Vacu-VialsTM, Fe²⁺ by phenanthroline colorimetric analysis, and SO₄ by turbidimetric analysis using HACH AcuvacsTM. Samples were collected for anions (Cl, NO₃, NO₂, SO₄) and NH₄⁺ analyses in the laboratory. These were preserved with

formaldehyde and a flash-freezing technique respectively, and then analyzed by capillary electrophoresis.

Rate Determination:

A first-order rate equation was a better fit to the experimental data than the zeroth order rate equation. When the experimental data was plotted over time it formed a curve. Plotting the natural log of the data over time yielded a straighter portion of the curve. Therefore, rates were estimated assuming a first-order process. We followed a method established by Snodgrass and Kitanidis (32) for inferring in-situ reaction rates from pushpull experiments. This analysis assumes the absence of sorption and negligible background concentrations. In our case these are valid assumptions since NO₃ and SO₄ are soluble and relatively non-sorbing and background concentrations were below detection limits. This analysis also assumes the solutes were injected instantaneously as a well-mixed slug. It is reasonable to assume that the injected fluids were well mixed since the test solution was well homogenized prior to injection. Our injection was not instantaneous but this analysis assumes that the rapid injection was negligible compared to the total reaction time. Our approach was modeled after single solute in-situ push-pull tests performed by Haggerty et al. (33) and Schroth et al. (20). We assumed that the injected solutes were transformed within the aquifer according to a first-order rate equation $\partial C_r / \partial t = -kC_r$ so that:

$$C_r(t) = C_r^{\circ} e^{-kt} \qquad (1)$$

where $C_r(t)$ is the reactive solute concentration at time t, C_r^o is the reactive solute concentration at time t=0 and $k [t^{-1}]$ is the rate coefficient. Now assuming that changes in

saturated thickness due to injection and extraction pumping are negligible, the breakthrough curve for a reactive solute $C_r(t^*)$ is given by:

$$C_{r}(t^{*}) = \frac{C_{tr}(t^{*})}{kt_{inj}} \left[e^{-kt} - e^{-k(t_{inj}-t^{*})} \right] \quad (2)$$

where t^* is the time elapsed since the end of the test solution injection, $C_{tr}(t^*)$ is the breakthrough curve for a co-injected tracer (Cl in our case), and t_{inj} is the duration of the test solution injection. Equation 2 can be rewritten:

$$\ln\left(\frac{C_r(t^*)}{C_{tr}(t^*)}\right) = \ln\left(\frac{1 - e^{-kt_{inj}}}{kt_{inj}}\right) - kt^* \qquad (3)$$

This suggests that a plot of $ln(C_r/C_m)$ versus t^* generates a straight line with a slope of – k. Since the determination of k is based on the evaluation of ratios of C_r/C_{tr} , complete tracer mass recovery is not necessary during tracer tests to obtain accurate estimates of k. Similarly, a portion of the breakthrough curve may be used to estimate k. A non-linear least squares regression was used to fit equation 3 to experimental breakthrough data to obtain first order rate coefficients for aerobic respiration, denitrification, and sulfate reduction. For this purpose, C_r in equation 3 is the relative concentration (i.e., the measured concentration divided by the concentration injected in test solution) of reactive solutes (O₂, NO₃, or SO₄) and C_{tr} is the relative Cl concentration. Since the background concentration of the reactive solutes was negligible but the background concentration of the tracer (Cl) was detectable, 1.0-3.5 ppm depending on the test, the measured values of chloride could not be used as a reliable indicator of the degree of mixing without correction. Therefore, C_{tr} was calculated as a mixing proportion between the injected Cl concentration and the background chloride concentration (equation 4) to give a more accurate description of the degree of mixing and other non-reactive processes.

$$C_{tr} = \left(\frac{Cl_m(t^*) - Cl_b}{X}\right) \tag{4}$$

Where $Cl_m(t^*)$ is the measured chloride concentration at time t, Cl_b is the measured background chloride concentration, and X is the slope of the line generated from a plot of the percent input solution (0-100%) versus concentration (background-injection values). This line represents the mixing curve between the injected solution and the background water with respect to chloride concentration. In our case, since the background concentration was very low (< 3.5 ppm) compared to the input test solution concentration (~100 ppm), the slope was near 1.

Results and Discussion

Field vs. Laboratory NO₃ Measurements:

A significant discrepancy was observed between the NO₃ data obtained by field analyses and the NO₃ data obtained by laboratory analyses. Field data obtained from samples collected within the plume gave much lower (often not detectable) concentrations of NO₃ than the corresponding laboratory analyses, which accurately represented the added initial concentrations. Field data obtained from samples collected from outside the contaminant plume largely agreed with corresponding laboratory analyses for NO₃. This suggests that some constituent of the contamination within the plume interfered with the analyses. This field observation was supported by laboratory experiments, which showed that when a known amount of NO₃ was added to the uncontaminated samples (collected outside the contaminant plume), the field method accurately represented the resulting concentration. However, when a known amount of NO₃ was added to the contaminated samples, the field method gave erroneously low and inconsistent readings. One possible explanation for this discrepancy is that the NO₃ field method requires cadmium to reduce NO₃ to NO₂, which is then measured colorimetrically. If the cadmium surfaces were coated with organic contaminants from the plume, they may have been unavailable to reduce the NO₃ and as a result were not able to be measured. For this reason, the NO₃ data presented in this paper will be from laboratory analyses only. Based on these observations, we conclude that caution should be used when interpreting NO₃ data from Cd-reduction field methods in contaminant plumes.

Well ID	Date	H ₂	O ₂	NO ₃	NO ₂	Fe ²⁺	SO ₄	BTEX _{avg}	DCE
ML3-25	6/00	3.55	<0.5	< 0.05	< 0.05	7.12	< 0.05	17-205	5.6
ML10-37	6/00	< 0.05	8.01	19.36	< 0.05	< 0.01	10.7	<0.9	<0.2
ML3-25	7/00	2.68	<0.5	< 0.05	< 0.05	13.7	< 0.05	18-328	<0.2
ML10-37	7/00	< 0.05	6.59	4.3	< 0.05	< 0.01	6.99	<0.9	<0.2
ML3-25	8/00	2.35	<0.5	0.41	< 0.05	7.00	< 0.05	9-314	4.87
ML10-37	8/00	< 0.05	6.43	7.13	<0.05	< 0.01	3.57	<0.9	<0.2

Table 3.1 Initial Chemical Characterization of Selected Wells (mg/L)

DCE: cis 1,2 dichloroethene; reported in ug/L

BTEX: average benzene, toluene, ethylene, and xylene; reported in ug/L

* H2 concentrations are reported in nM

Push-Pull Tests:

The first push-pull test (PP_{ONS}) evaluated oxygen, nitrate, and sulfate consumption rates at well ML3-25 (June 2000). Phase 1, the geochemical characterization, revealed that the aquifer water from that well was reduced (Table 1). PP_{ONS} involved the injection of a test solution containing approximately 100 mg/L Cl (as a conservative tracer), 6 mg/L O₂, 10 mg/L NO₃, and 10 mg/L SO₄. Concentrations of solutes were measured over time (Figure 3.2). As described in the rate determination section, these concentrations were then normalized and divided by the concentration of conservative tracer (Cl) at that point in time to account for non-reactive processes such as advection and dispersion. Rates were then derived from a plot of this ratio versus time (Figure 3). Dissolved oxygen was consumed first at a rate of approximately 0.60 hr⁻¹. In an anaerobic system with excess dissolved iron, oxygen can rapidly be consumed through the abiotic oxidation of Fe(II). After the O₂ was consumed, NO₃ and SO₄ were consumed simultaneously at rates of 0.21 hr⁻¹ and 0.27 hr⁻¹ respectively. The observed lag time for NO₃ and SO₄ reduction occurs because these reactions are biologically mediated. Microbiological response to system change frequently shows a lag time for microbes to adjust to new conditions (3). In addition, our simulated recharge water did not contain electron donors, which may also have contributed to the observed lag phase. The electron donor would have then been supplied through desorption from the solid phase and mixing with the aquifer water. PP_{NS} evaluated nitrate and sulfate consumption rates at well ML3-25 (August 2000). Phase 1, the geochemical characterization, revealed that

the aquifer water was reduced (Table 1). PP_{NS} involved the injection of a test solution containing approximately 100 mg/L Cl (as a conservative tracer), 10 mg/L NO₃, and 10 mg/L SO₄. NO₃ and SO₄ were again consumed simultaneously at rates of 0.31 hr⁻¹ and 0.18 hr⁻¹ respectively (Figure 3.3). PP_S evaluated the rate of sulfate reduction at well ML3-25 (July 2000). Phase 1, the geochemical characterization, revealed that the well was reduced (Table 1). PP_S involved the injection of a test solution containing



Figure 2: Measured concentrations of added solutes versus time. Oxygen (O_2) , Nitrate (NO_3) , and sulfate (SO_4) concentrations are plotted on the left y-axis and chloride (Cl) concentrations are plotted on the right y-axis.

approximately 100 mg/L Cl (as a conservative tracer) and 10 mg/l SO₄. Sulfate was

consumed at a rate of 0.24 hr^{-1} (Figure 3.3).



Figure 3.3: Regression plot for rate coefficient determination, obtained by fitting equation 3 to experimental data. Lines designate portion of dataset used to determine 81 rates.

Obtaining representative rates of in-situ processes is often a limiting factor in the development of geochemical models to evaluate processes in natural environments. Literature values for NO₃ and SO₄ consumption have been calculated based on zero and first order assumptions and estimated primarily by laboratory studies but also by some field experiments. Selecting a representative rate for TEA consumption is difficult since rate estimates range several orders of magnitude (Tables 3.2 & 3.3). Our field-measured first-order rates for aerobic respiration and denitrification are similar to those estimated by in-situ field methods in other locations (Table 3.4). Estimated first-order rates of nitrate and sulfate reduction found by Chapelle (34) and Cunningham (19) were slower than those observed in this study, perhaps due to differences in electron donor utilization. These studies looked at longer-term (months) consumption of NO₃ and SO₄ down flow path, which may have allowed for utilization of a wider range of organic compounds, including more complex fuel constituents, to serve as electron donors. Our study examined the rates of TEA reduction, as they would be initiated during a discrete recharge event that introduced low concentrations of electron acceptors. In this situation, the system was depleted with respect to O₂, NO₃, and SO₄ and had available microbiallymediated intermediates such as H₂ and low molecular weight organic acids to serve as more attractive electron donors. The availability of these donors may have allowed for a greater rate of acceptor consumption. This hypothesis is supported by the observation that during the Cunningham (19) flow path NO₃ augmentation study, the rate of NO₃ reduction decreased over time, presumably due to depletion of more favorable electron donors in the system. Given the nature of the zeroth order laboratory-based methods, it is

impossible to directly compare the rates found in laboratory studies to those found in field studies such as ours. However our in-situ rate estimates for O_2 and NO_3 consumption are similar to in-situ rates estimated found during push-pull tests in another petroleum contaminated aquifer (20), suggesting that these rates may be applicable in other reduced environments where microbial intermediates such as H₂ are available in excess of the amount of TEA introduced.

Environment	Method	Rate (uM/day)	Order	Ref.
UA: Black Creek, USA	flux	1.92-41.1 E-5	zero	(17)
UA: Florida, USA	flowpath	2.74 E-4	zero	(35)
UA: Fox Hills, USA	flowpath	5.48 E-4	zero	(36)
UA: Fuhrberg, Germany	depth profile	3.84 E-2	zero	(37)
UA: Sturgeon Falls, CAN	depth profile	4.38 E-2	zero	(38)
UA: Bocholt, Germany	depth profile	6.3 E-2	zero	(13)
UA: Tuse Naes, Denmark	radiotracer	0.41-1.0	zero	(13)
UA: Romo, Denmark	radiotracer	0.14-12.3	zero	(13)
mixed and pure culture	microcosms	3.04E+4	zero	(39)
Nearshore sediments	radiotracer	6.3 E+2	zero	(12)
UA: Denmark	depth	0.85-2.55	zero	(40)
UA: Denmark	direct	0.55-12.3	zero	(40)
CA: Norman, OK Landfill	microcosms	3.5	zero	(10)
		Rate (umol/g -day)*		
Wintergreen Lake, USA	microcosms	5.50E-2	zero	(9)
Wintergreen Lake, USA	microcosms	3.60E-2	zero	(9)
Ocean Seds, Germany	microcosms	4.30E-6	zero	(41)
Landfill: Norman, OK	microcosms	6.70E-4	zero	(10)
Landfill: Norman, OK	microcosms	0.1-1.3 E-3	zero	(10)
Landfill-Denmark	microcosms	0.1-1.3 E-3	zero	(11)
Landfill-Denmark	microcosms	1.8 E-03	zero	(11)
Wetland Soils	microcosms	0.1-11	zero	(8)
CA: petroleum	push-pull test	5.28 E+3	zero	(18)
		Rate (day ⁻¹)		
CA: petroleum	flowpath	0.02-0.08	first	(7)
CA: petroleum	microcosms	0.02-0.08	first	(7)
CA: petroleum	aug. flow path	0.1	first	(19)
CA: petroleum/Cl solvents	push-pull test	6.48 first		this study
CA: petroleum/Cl solvents	push-pull test	4.32 first		this study
CA: petroleum/Cl solvents	push-pull test	5.76	first	this study

 Table 3.2
 Summary of Rate Measurements for Sulfate Reduction

* umol/gram of dry weight sediment/day

UA: uncontaminated aquifer

CA: contaminated aquifer

Environment	Method	Rate (umol/g-day)*	Order	Ref.
CA: sewage (NO ₃)	microcosms	9.6-22.4E-4	zero	(16)
CA: sewage (NO ₃)	tracer tests	3.1-7.8E-4	zero	(16)
Freshwater Lake Sediments	microcosms	3.10E-01	zero	(42)
Landfill: Denmark	microcosms	1.26 E-3 - 2.33E-1	zero	(11)
Wetland soils: 0-2hrs	microcosms	0.23	zero	(8)
Wetland soils: 1-10days	microcosms	0.5-9.3	zero	(8)
Wetland soils: 10-100days	microcosms	0.2-4.7	zero	(8)
Forest Soil	microcosms	4.8	zero	(43)
		Rate (uM /day)		
CA: petroleum	push-pull tests	1.92E 3	zero	(18)
		Rate (day ⁻¹)		
CA: petroleum	push-pull tests	5.28	first	(20)
CA: petroleum	aug. flow path	0.1-0.6	first	(19)
CA: petroleum/Cl solvents	push-pull tests	5.04	first	this study
CA: petroleum/Cl solvents	push-pull tests	7.44	first	this study

Table 3.3 Summary of Rate Measurements for Nitrate Reduction

* umol/gram of dry weight sediment/day

CA: contaminated aquifer

Table 3.4 Summary of Available First-Order Field Rate Measurements (day⁻¹)

	Aerobic Respiration	Denitrification	Sulfate reduction
Chapelle et al., 1996 (34)	-	-	0.02-0.08
Cunningham et al., 2000 (19)	-	0.1-0.6	0.1
Schroth, et al., 1998 (20)	3.6-40.6	2.16-10.08	-
This study	14.4	5.04-7.44	4.32-6.48

Our results show that when introduced simultaneously, NO₃ and SO₄ are consumed simultaneously at similar rates. This is contrary to the conventional idea that NO₃ will be consumed prior to SO₄ based on thermodynamic arguments. However, it is consistent with the kinetic model of terminal electron accepting processes that suggests that in a non-competitive situation there is no reason why processes should follow the thermodynamic order. Simultaneous redox processes and overlapping redox zones have been observed in pristine and contaminated aquifers systems previously (11,40). It has been suggested that concentration levels of electron acceptor or donor, microniches of various TEAPs, or variability of other parameters such as pH may explain the complex patterns of redox processes observed. In addition to these possibilities, our results suggest that SO₄ and NO₃ may be consumed by microbially-mediated reactions other than the traditional respiratory pathways since NO₃ and SO₄ were consumed simultaneously at roughly the same rates.

Four possible scenarios are proposed. One scenario assumes an abundance of electron donors in a system limited by electron acceptors, NO₃ and SO₄. This is a likely scenario both at this site and many other contaminated systems. During these tests, available H₂ concentrations were high enough (2.35-3.55nM) to support both NO₃ and SO₄ reduction. Under these circumstances, when NO₃ and SO₄ are added simultaneously, they could be consumed simultaneously by an abundance of sulfate reducers in the system. Sulfate reducers have been shown to be ubiquitous in the environment and capable of gaining energy from O₂, Fe (III), and various nitrogen oxides (8.44,45). Similarly, a second possibility is dissimilatory reduction of NO₃ by denitrifiers

under these conditions. A third possible scenario, suggests that if the bacteria present are nitrogen limited, assimilatory nitrate reduction may occur simultaneously with SO₄ reduction. These processes would not necessarily follow the thermodynamic order of processes since they would not be in competition with each other. The assimilatory NO_3 reduction would provide a nitrogen source to the organism while the respiratory SO_4 reduction pathway would provide energy. A fourth possibility is the reduction of NO_3 by green rust (GR). Nitrate has been shown to be stoichiometrically reduced to ammonium while GR is oxidized to magnetite (46). The rate law for this reaction is first order, dependent on Fe (II) concentration, where k=0.072 hr⁻¹. This rate is slower than the observed rate for NO_3 removal at this site however it is not inconsequential. It is unclear if green rust is present at the site since it is difficult to identify with standard mineralogical procedures due to its high reactivity including extreme sensitivity to oxidation by oxygen. However, reduced iron is present in the groundwater and magnetite has been detected in the aquifer material. The possibility of the activity of GR is often indicated in investigations of polluted soils, sediments, landfills, and in remediation techniques using Fe(0) (47,48). Future work needs to be conducted to determine the specific microbially-mediated TEA processes being performed at this site during recharge events.

Surface Reaction Vessel Experiments:

Four variations of SRV experiments were performed. This water was then amended with solutes, hand shaken to ensure it was well mixed, and then allowed to react for the length of the corresponding push-pull test. Samples were collected at roughly 5minute intervals. SRVE 1 was performed using water from ML3-25 (June 2000). Aquifer water was pumped into the SRV and amended with 100 mg/L Cl, 10 mg/L NO₃, and 10 mg/L SO₄. The solution was allowed to react for the length of push-pull test 1, approximately four hours. No changes in NO₃ or SO₄ concentrations were observed over this time period. SRVE 2 and SRVE 2K were performed using water from ML3-25 (July 2000). Aquifer water was pumped into two identical SRVs. Each was amended with 100 mg/L Cl, 20 mg/L NO₃, and 20 mg/L SO₄. SRVE 2K was then amended with formaldehyde (approximately 0.4% final concentration) to serve as a killed control. The solutions were hand shaken to ensure they were well mixed and then allowed to react for the length of push-pull test 2, approximately 4 hours. No changes in NO₃ or SO₄ concentrations were observed in either SRVE 2 or SRVE 2K over this time period. SRVE 3 and SRVE 3K were performed using water from ML3-25 (July 2000). Aquifer water was pumped into two identical SRVs. Each was amended with 100 mg/L Cl, 50 mg/L NO₃, and 50 mg/L SO₄. SRVE 3K was then amended with formaldehyde (approximately 0.4% final concentration) to serve as a killed control. The solutions were allowed to react for the length of push-pull test 2, approximately 4 hours. No changes in NO₃ or SO₄ concentrations were observed in either SRVE 3 or SRVE 3K over this time period. SRVE 4 and SRVE 4K were performed using water from ML3-22, which was similar chemically to ML3-25 in all respects except it contained slightly higher DCE concentrations (4.9 ug/L) (July 2000). Aquifer water was extracted into two identical SRVs. Each was amended with 100 mg/L Cl, 50 mg/L NO₃, and 50 mg/L SO₄. SRVE 4K was then amended with formaldehyde (approximately 0.4% final concentration) to serve as a killed control. The solutions were allowed to react for approximately 4 hours. No changes in NO₃ or SO₄ concentrations were observed in either SRVE 4 or SRVE 4K over this time period. Measured Fe^{2+} concentration remained consistently high (11.3-11.5 mg/L) throughout all SRVEs and dissolved oxygen was below the detection limit of our field kit (<0.03 mg/l) suggesting that the solutions remained anaerobic.

These results indicate that any redox reactions observed in the push-pull tests do not occur in the reduced water without influence of the sediments and their associated microbial communities. This suggests that highly oxidized compounds such as NO_3 and SO₄ may persist in reduced waters. This finding is analogous to the persistence of Cr^{3+} in oxidized water (49). It has been shown that reduced Cr^{3+} is oxidized to Cr^{6+} at a much greater rate by the presence of solid phase manganese oxides than by oxygen (50). In the case of the persistence of NO₃ and SO₄ in reduced water, it is unclear if the absence of the solid phase or its associated microbial population is allowing these oxidized compounds to persist. However, these findings have implications for how geochemical models of reduced systems are constructed and how we interpret the results from such modeling efforts. Geochemical models are driven by free energy yield and consider only the aqueous phase in predicting reactions, disequilibria and other constraints. Even with thermodynamic and kinetic arguments to input into a model, the model would not predict our observed data. Our data clearly demonstrate that in addition to a simple mixing of aqueous solutions, knowledge of the reactions being controlled by the solid phase and their associated microbial population is necessary to understand how NO₃ and SO₄ will behave in the environment.

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CHAPTER IV.

Evolution of redox zonation in a contaminated aquifer: Development of 3-D coupled partial-equilibrium reactive flow-and-transport model.

ſ
Introduction

The concept that terminal electron accepting processes (TEAPs) distribute themselves sequentially into redox zones is often used to interpret how organic compounds will be degraded in the environment. Champ et al. (1979) identified redox sequences in groundwater flow systems associated with a reduction in dissolved organic carbon. Since then, many workers have explored the application of using sequential TEAPs to assist in the clean-up of contaminated sites via bioremediation and natural attenuation strategies (BAEDECKER et al., 1993; BJERG et al., 1995; KONHAUSER, 1994; LEVINE et al., 1997; LYNGKILDE and CHRISTENSEN, 1992)[Vroblesky, 1994 #47. In fact, natural attenuation is quickly becoming an acceptable treatment technology for managing organic contaminant plumes (EPA, 1997). The success of such remediation strategies depends upon a thorough understanding of how TEAPs develop into redox zones in complex subsurface systems and under what conditions redox state and thus zonation may change. This requires the ability to quantify interconnected hydrogeologic, microbiologic, and geochemical processes which contribute to redox including the evaluation of rate limiting steps. The development of tools that adequately quantify the complete evolution of and changes in redox zonation is necessary for the effective design of active remediation strategies and the assessment of the potential for natural attenuation in contaminated systems.

Redox zonation is in part controlled by the activity of microorganisms, which first consume oxygen, and then a succession of alternate terminal electron acceptors (TEAs) to support their growth using a variety of carbon sources (CHAPPELLE, 2001; LOVLEY,

1991; LOVLEY and GOODWIN, 1988; STUMM and MORGAN, 1981). The succession of TEAPs in order of decreasing redox potential and free energy yield is generally: oxygen reduction, nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis. In most closed groundwater systems, the sequence of TEAPs results in redox zones following this succession (i.e., increasingly reduced conditions occur further down the flow path) (CHAMP et al., 1979). However, down gradient of contaminant plumes, the sequence of TEAP zones is generally reversed (CHAPPELLE, 2001; LOVLEY, 1991). That is, the most reduced conditions (e.g., methanogenesis) occur near the contaminant source due to the greater availability of electron donors, while less reducing conditions (e.g., iron reduction) occur father down flow-path from the contaminant source. Since many hydrocarbons, which serve as electron donors, concentrate in the capillary fringe area, more reducing conditions often occur near the water-table interface, resulting in a plume that has vertical as well as horizontal redox zonation (CHAPPELLE et al., 1996; VROBLESKY and CHAPPELLE, 1994).

In principle, as groundwater plumes develop and TEAPs progress, a steady-state balance between source inputs and biotransformation rates can be achieved resulting in a characteristic stabilization of plume length (BUSCHECK and ALCANTAR, 1995; MCNAB and DOOHER, 1998). Precise mathematical descriptions of the necessary factors leading to a characteristic plume length have not yet been worked out. Statistical analyses have revealed that the steady-state plume length is related to the mean site groundwater velocity, and the strength of the contaminant source (MCNAB, 2001). The TEAPs operating in the aquifer, as well as dispersion, have also been shown to have significant impact on steady-state hydrocarbon plume length such that the introduction of more

favorable electron acceptors (e.g., O₂) via groundwater reaeration can reduce plume length by up to 87% (NEALE et al., 2002). Other workers have suggested that the nature of the contaminant can also play a role in the resulting plume length. Statistical analysis of mixed contaminant plumes including chlorinated hydrocarbons at several locations revealed that, in plumes in which active dehalogenation was occurring, plume length was significantly shorter (roughly by a factor of two) than plumes where reductive dehalogenation was not occurring (MCNAB and RICE, 2001). Although, the uncertainty of these factors in complex contaminant plumes makes predicting a steady-state plume length difficult, observational evidence clearly suggests that plumes do achieve a steady state with respect to plume length on relatively short time scales (years). Therefore, as groundwater hydrocarbon plumes evolve, they will reach a point where the front of the plume can no longer advance based on a contaminant source of constant strength.

These concepts lead to the hypothesis that when a plume has stabilized such that it has achieved its maximum spatial extent, horizontal redox zonation (down flow path) cannot be sustained due to the continual depletion of TEAs within the original redox zones. Classic redox zonation patterns suggest that the most reduced zone will occur nearest the contaminant source where more favorable TEAs such as oxygen (O₂), nitrate (NO₃), iron (III) Fe³⁺, and SO₄ have been successively depleted. The boundary between this highly reduced zone (e.g., methanogenic zone) and the adjacent zone where more favorable TEAs are available (e.g., SO₄) over time will not be sustained due to greater fluxes of electron donor moving out of more reduced zone into the adjacent less reduced zone. Following this concept, it can be inferred that ultimately when a fixed plume length is achieved, remaining TEAs will continue to be consumed in each of the zones

until a single highly reduced zone exists. This state is, of course, not static but rather dynamic at least in part due to inputs of TEAs from recharge events and lateral dispersion within the plume (HESS et al., 1992). However, these inputs would result in a more complicated redox pattern within the plume where more energetically favorable TEAPs are stimulated in small transition zones near plume boundaries as opposed to a pattern of larger sequential redox zones. This conceptual model for the evolution of redox state in contaminant plumes has implications not only for basic understanding of redox processes in nature, but also for the evaluation and design of bioremediation and natural attenuation strategies.

Previous work conducted at the former Wurtsmith Air Force Base (WAFB) in Oscoda, Michigan supports the idea that traditional redox zonation may not be sustained in contaminant plumes that have had enough time to evolve to "mature" conditions where TEAs have been successively depleted in each of the zones and changes in TEAPs likely occur in the transition zones at plume boundaries. Multivariate statistical evaluation of geochemical data from the contaminant plume at WAFB, which had 50 years to evolve, has shown that water does not associate into distinct redox zones but rather, dominant variability is influenced primarily by inputs from recharge events (Chapter 2). In addition, microbiological measurements suggest that microorganisms that traditionally perform more favorable TEAPs (aerobic respiration, denitrification, Fe-reduction, and sulfate reduction) do not exist in detectable quantities within the center of the plume (Haack, personal communication 2002, (WEST, 1999)). The primary active microbial community in the aquifer is composed of methanogens (DOJKA et al., 1998), suggesting that all of the more favorable TEAs have been depleted in the center of the plume. Yet,

we know that recharge introduces TEAs to the aquifer, and that they are consumed within the plume because measured TEA concentrations in the aquifer remain near zero. From this we can infer that these reactions are occurring in small regions near the boundaries of the plume where it is difficult to sample and not in large discrete redox zones.

Other workers have recognized the importance of the evolution of redox zones in contaminant plumes as a control on the long-term potential for hydrocarbon transport and degradation and consequently have evaluated changes in redox processes at various scales in a contaminated aquifer (COZZARELLI et al., 2001). With the combined use of small-scale data from aquifer cores and large-scale (plume) geochemical well data, they demonstrated that redox evolution (Fe-reduction to methanogenesis) occurred on very small spatial scales (tens of centimeters) in a contaminated aquifer in Bemidji, Wisconsin. These findings further support our concept that understanding redox evolution not only in large zones which may ultimately disappear, but also at smaller interfaces such as at plume boundaries, is critical to understanding the fate of hydrocarbons in groundwater systems.

Goals and Approach

To evaluate the feasibility of this conceptual model for the evolution of redox zonation in a contaminated aquifer, a numerical model was constructed describing how redox zones evolve after initial contaminant introduction, and how those zones may continue to evolve over time. Numerical models are a common tool to test hypotheses regarding the hydrogeochemical evolution of groundwater systems that link TEAPs and

hydrocarbon degradation (e.g., (ABRAMS and LOAGUE, 1998; COZZARELLI et al., 2000; ESSAID et al., 1995; HUNTER et al., 1998; JAKOBSEN and POSTMA, 1999; KEATING and BAHR, 1998; LENSING et al., 1994; SALVAGE and YEH, 1998; TEBES-STEVENS et al., 1998). Most of the recent modeling of contaminant plume evolution assumes that organic degradation is coupled to the sequential model of TEAPs in redox zones, which according to our data, is not appropriate for describing the contaminant plume at WAFB and may not be appropriate in other evolved systems (ABRAMS and LOAGUE, 1998; ISLAM et al., 2001; PETERSON and SUN, 2000; SUNA et al., 2001).

A number of different simulation approaches have been developed, differing mainly in how organic and inorganic processes have been coupled. A summary of these models is provided in a recent review paper (BRUN and ENGESGAARD, 2002). The various types of models comprise two major approaches to quantifying biogeochemical transport; 1) those using a "one-step" biodegradation pathway, where the substrate and electron acceptor have been identified; and 2) those using a "two-step" biodegradation approach that divides the biogeochemical processes into two half-cell reactions, where the first reaction consumes substrate and donates electrons and the second reaction consumes those electrons by coupling them to a TEA. According to Brun and Engengaard (2001), the first group of models (one-step) found support in the classical biodegradation transport models, which consider complex bacterial growth relationships and add geochemical reactions only as needed. This approach tracks a limited number of geochemical species through a system and therefore cannot account for the more complicated interrelations between biogeochemical cycles, which may significantly impact the "real-world" chemical pathways. The second group (two-step) found support

in geochemical transport models that consider a complex suite of geochemical reactions and subsequently add simple degradation reactions such as zero- or first-order processes, neglecting bacterial growth. Although these models do a better job of accounting for the complete geochemistry of the system, they may oversimplify organic biodegradation reactions by neglecting the growth and decay of microorganisms, which is an important control on many microbially mediated reactions. Many of these two-step models adhere to a partial equilibrium approach (PEA) where the second reaction (the TEAP) is allowed to occur instantaneously assuming that the first reaction is the rate-limiting step (MCNAB and NARASIMHAN, 1994; POSTMA and JAKOBSEN, 1996). These models assume that the initial fermentation step (electron production) is the rate-limiting step based on thermodynamic arguments and the general occurrence of very low concentrations of fermentation products. We have adopted this strategy for the development of our model.

Our 3-dimensional model considers both 1) the biodegradation of organic matter based on the influence of transport on microbiological growth and 2) the complex suite of biogeochemical reactions operating in the aquifer. Both are important to consider because, due to the interconnectivity of biogeochemical cycles, the viability of a given degradation pathway is a function of local geochemical conditions which ultimately determine its energetic favorability. For example, subtle changes in pH initiated by one chemical process (e.g. SO₄ reduction) can have profound effects on the pe of a system, thus changing the stability of several other chemical constituents (LANGMUIR, 1997). By considering a more complete geochemical system, which describes how one cycle may impact another, predicted chemical changes may be very different than originally anticipated. For example, the pH changes predicted above during sulfate reduction may

be buffered by the precipitation/dissolution reactions of calcite in the aquifer. In addition to the geochemical processes operating in the aquifer, it is important to consider the impact of microorganisms on the system. Microorganisms become involved in thermodynamically favorable redox reactions to extract energy for metabolic processes. As a result, they can influence the rates of biodegradation processes; however, they cannot influence the overall energetic favorability of such reactions. Therefore, geochemical thermodynamic considerations remain an important control on redox dependent degradation particularly when considered in conjunction with the kinetics of the rate-limiting step.

The model we have developed links the reactive transport codes MODFLOW (MCDONALD and HARBAUGH, 1988) and RT3D (CLEMENT, 1997; CLEMENT and JONES, 1998) with the geochemical modeling code PHREEQC (PARKHURST and APPELO, 1999). Thus flow and transport variables such as advection, dispersion, rate limitation, and microbial growth are considered with the thermodynamic geochemical framework of the groundwater and contaminant plume system. Other attempts have been made to combine flow and transport codes with geochemical modeling codes, for example PHAST (PARKHURST et al., 2001) links the transport code HST3D with PHREEQC. One benefit of our linked modeling code is that that many groundwater flow and transport models already exist in the MODFLOW and RT3D format so they could easily be coupled with all the geochemical capabilities built into PHREEQC.

The goal of this study is to quantitatively evaluate a new conceptual model for the evolution of redox zonation in aquifer systems over relatively long time scales (decades) and demonstrate the necessity of examining the complete geochemical condition of the

system. Specifically, this paper 1) presents an alternative model for the ultimate fate of redox zonation in contaminated aquifers; 2) proposes a new conceptual model describing the importance of TEAs inputs from recharge and dispersion on the redox state of a contaminant plume and; 3) introduces a new tool to quantify the hydrogeochemical evolution of groundwater through the linking of three previously established modeling codes.

Study Site Description

The study site is a shallow sandy aquifer contaminated with petroleum hydrocarbons and chlorinated solvents at the former Wurtsmith Air Force Base (AFB), Oscoda, Michigan, U.S.A. Wurtsmith AFB lies on a sandy plain of glacial lake sediment approximately 2 km west of the Lake Huron shoreline in Michigan's Lower Peninsula. The aquifer is approximately 20 meters thick and composed of highly permeable alternating aeolian sands and glacial outwash material. Hydraulic conductivities of these deposits are on the order of 30 m/day. The unconfined aquifer is underlain by at least 30.5 meters of silty clay. The water table varies from 3.5-5.0 m below land surface (184-186 m above sea level), fluctuates 0.3 to 0.7 m annually, and the water table gradient ranges from 3 to 5 meters per kilometer. Assuming an effective porosity of thirty percent, average groundwater velocity is approximately 0.3-0.5 m per day. The plume has lateral direction shifts of 7 to 10 degrees because the groundwater flow direction is influenced by seasonal recharge at this site.

Fire training activities performed by the Air Force from 1952 to 1986 at this site contaminated the groundwater. This suggests that the groundwater plume has

had nearly 50 years to evolve to its current redox state. Various compounds were used during the training exercises to ignite and extinguish the fires, including waste fuels, chlorinated solvents, aqueous film-forming foams, a multipurpose dry chemical, potassium bicarbonate based soda, and Halon 1211. An extensive plume approximately 50 m wide and 400 m long has developed down gradient from the concrete pad where the fire training activities were performed (Figure 4.1). Most of the contamination is associated with aquifer solids between 4.5 and 5.7 m below land surface, which have an average total hydrocarbon concentration of 13,650 mg/kg (USGS, 1991).

The plume is complex in that it contains both BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and chlorinated solvents (e.g., dichloroethene). Concentrations of BTEX compounds in the plume range from 20 to 1,000 μ g/liter while concentrations of dichloroethane, chloroethane, and vinyl chloride range from 2 to 1,000 μ g/liter. To document the vertical distribution of contaminants within the plume, PVC multi-level groundwater monitoring wells were installed at the site (Figure 4.2). The reducing conditions of the plume vary historically from Fe-reducing to methanogenic (as determined by H_2 concentrations) both spatially and temporally on the time scale of months (MCGUIRE et al., 2000). Dissolved H_2 gas, an important intermediate in the decomposition of organic matter, is thought to be an indicator of TEAPs. In anaerobic environments, H₂ is produced and consumed such that each TEAP maintains a characteristic H_2 concentration (LOVELY and PHILLIPS, 1987). At WAFB, TEAPs indicated by hydrogen gas concentrations do not distribute themselves into sequential zones down flow path but rather, exhibit a more complicated likely related to recharge inputs (Figure 4.3). Despite the complicated nature of the site, WAFB is an ideal location



Figure 4.1 Plume map for the Fire-Training Area 2 (FTA-2) at the former Wurtsmith Air Force Base, Michigan. The concrete pad was the site of fire-training activities. Grey lines represent plume position during periods of low water table; Red lines represent plume position during periods of high water table. Blue lines are water table contours in feet above sea level.



Figure 4.2: Two-dimensional well grid. The dashed arrows denote wells through which chemical transects (T1 and T2) were constructed.





to examine the evolution of redox zonation since detailed spatial and temporal geochemical, hydrogeologic, and microbiological database for the site has been established (DOJKA et al., 1998; HAACK and BEKINS, 2000; MCGUIRE et al., 2000; REYNOLDS and HAACK, 1999).

Methods

Development the Three-Dimensional Partial Equilibrium Numerical Model

The three-dimensional partial equilibrium numerical model couples an existing 3-D flow model (SMITH, 2002) created using MODFLOW with kinetically controlled fermentations reactions (via RT3D) and thermodynamically controlled reactions (via PHREEQC). A schematic of how these three codes work together is presented in Figure 4.4. MODFLOW is used to transport selected geochemical species including original contaminant (C_{org}) from the source area. RT3D then takes the output from the flow model and allows the C_{org} in each cell to be reacted to produce fermentation products to serve directly as electron donors (C_{ace}) for the TEAPs. These outputs are then given to PHREEQC, which evaluates the electron input, speciates the redox sensitive species considering the complete geochemistry of the water, and returns the select chemical species to MODFLOW where transport processes are considered. This loop is repeated for each cell with changes in C_{org} at every time step.

Initial application of the model (Phase I) is to test the hypothesis that under realistic physico-chemical conditions at this site, a steady-state plume length can be achieved and that once a stable plume length is established; redox zonation will no longer



be sustained. It should be noted that this simulation neglects inputs from recharge events, which can directly deliver TEAs and also increase dispersion in increasing TEA inputs. Examining the effects of recharge on mature plumes will be explored in the Phase (II) of the modeling simulations (see Future Work sections). A description of specific model construction inputs for each portion of the three components to the overall model is described below.

Flow Model

A three-dimensional, numerical groundwater flow model was constructed of the surficial aquifer in the area encompassing the former Wurtsmith Air Force Base (SMITH et al., 1999), (SMITH, 2002). The computer program MODFLOW 96 was utilized to solve the approximated partial differential flow equation using a block-centered, finite-difference approach throughout the modeled domain. A graphical user interface program (GUI), GMS version 3.1, was used to construct the model grid, assign parameters, and view model output files. The model was run as both steady-state and transient simulations using a time-varying recharge input. Initial modeling simulations (Phase I) use a steady state model (i.e., neglects differential recharge) and future modeling simulations (Phase II) will use the transient model to evaluate recharge effects. The boundaries of the model coincide with regional surface water features and groundwater divides (Figure 4.5). To allow for accurate placement of surveyed monitoring locations relative to model boundaries, the grid framework was referenced to the state plane coordinate system. This was accomplished by using spatially referenced Digital Line



Figure 4.5: Groundwater flow model output showing location of natural boundaries and approximate location of groundwater plume FTA-2 within this model framework.



Graphs (DLG) of surface water features to establish the model boundaries. A DLG was also used to position an interior sink boundary (drain), representing Allen Lake. Land surface topography was input to the model using an x,y,z data file created from Digital Elevation Model (DEM) files. Each DEM covers a 7.5 minute unit corresponding to the USGS 1:24,000 scale topographic quadrangle map series and is based on 30 by 30 meter data spacing. Two DEM files, representing the Oscoda, MI and Foote Site Village, MI 7.5 minute topographic maps were processed using Arcinfo to merge the files, convert coordinates from latitude/longitude to state plane coordinate system, and output an x,y,z file compatible with GMS. Slightly exaggerated east-west linearity in the topography is an unavoidable artifact of the optical scanning process the USGS uses to create the DEM data sets. Additionally, merging the Oscoda and Foote DEM's was complicated because the west boundary of the Oscoda data set was approximately 15 feet lower than the abutting east boundary of the Foote data set. Comparison to paper copies of the corresponding 7.5 minute topographic maps showed the Oscoda data to be inaccurate along a portion of the west edge of its coverage. This was corrected by mathematically adjusting this portion of the generated x,y,z data set. The topography of the lowermost (no-flow) model boundary, which represents the contact with the underlying clay unit, was generated by using the Surfer program to create a contour surface from elevation data selected from local boring logs. GMS was used to vertically divide the model into four layers by interpolation between the upper and lower model surfaces at each cell. An overall horizontal cell size of 120 by 120 feet was employed with a refinement to 20 by 20 feet in Fire Training Area 2 (FTA-2), located in the south-central portion of the model. A refinement factor of 0.2 was utilized in the transition between the large and small-sized

cells. The model consists of 265 rows by 255 columns by 4 layers for a total of 270,300 cells, approximately 60 percent of which are active, representing roughly ten square miles. Sixty-nine observation wells located at FTA-2 were imported using their surveyed coordinates and a "screened" elevation equivalent to the base of their actual screened intervals.

Hydraulic parameters were initially assigned based on previously collected data from aquifer tests, grain-size analysis and geologic reports; and then refined during model calibration exercises. Horizontal and vertical hydraulic conductivity was estimated at 120 ft/day (USGS, 1990). An organic contaminant source area (C_{org}) was added to layers 2 and 3 in the vicinity of the concrete pad (see Figure 4.1) at a concentration of 0.001 (mol/L) based on measured total hydrocarbon concentrations. Due to the nature of the contamination activities, it is highly unlikely that a single source area exists but rather that it is likely comprised of several smaller source areas that combine to contaminate the region directly surrounding the concrete pad. In addition to the carbon source, average measured background concentrations (determined from wells outside of the contaminant plume) were assigned to each cell in the model as shown in Table 4.1. In the initial model, Fe³ was assigned as an immobile phase to represent solid phase Fe-oxyhydroxide minerals. The flow model tracked these ten components (C_{org} , O_2 , NO₃, NO₂, NH₄, SO₄, S²⁻, CH₄, Fe²⁺, Fe³⁺) for the duration of the simulation.

Species	O ₂	NO ₃	NO ₂	NH4	SO ₄	S ²	CH ₄	Fe ²	Fe ^{3*}
Input	8.0	10	0.1	0	10	0	0	0	20

Table 4.1 Initial concentrations assigned in flow model (mg/L)

*immobile phase

<u>Reactive transport model</u>

The reactive transport package RT3D was used to simulate the kinetically controlled (rate-limiting) reactions occurring in the aquifer. Monod kinetics was used to describe the fermentation of larger organic molecules (C_{org}) to smaller fermentative products such as acetate and H₂ (C_{ace}), which can serve as electron donors for the TEAPs. In the initial stage (Phase I) of the modeling, all of the TEAP reactions are considered instantaneous when compared to the slow rate of fermentation and therefore were evaluated and constrained by thermodynamic arguments in PHREEQC. The fermentation of organic matter was represented by the equation:

$$\frac{dC_{org}}{dt} = -k_{donor} X_{donor} \frac{\left[C_{org}\right]}{Ks_{donor} + \left[C_{org}\right]}$$
(1)

where C_{org} is the total amount of organic matter in the aqueous phase (mol/L); k_{donor} is the maximum specific rate of fermentation (272 µmol/mg of fermenting biomass-day); X_{donor} is biomass available for fermentation (0.003 mg); and Ks_{donor} is the half-velocity coefficient (14.1 µmol/L). Initial estimates of constants were averaged from microcosm studies (FENNELL and GOSSETT, 1998). After calculating the amount of fermentation products (C_{ace}) produced, RT3D calculates the total N, S, and Fe present in each cell and gives this information to PHREEQC where these parameters are speciated according to biogeochemical reactions that consider the total geochemistry of the system.

Geochemical model

A number of geochemical modeling programs exist for predicting inorganic aqueous speciation and saturation based on chemical equilibrium principles, for example WATEQ (TRUESDELL and JONES, 1974), GEOCHEM (SPOSITO, 1980), and MINTEO (FELMY et al., 1983). For our model simulations, we have chosen to use PHREEQC because it can also calculate reversible reactions that include complexation, mineral/amorphous solid, gas, solid solution, surface complexation, and ion-exchange reactions including those that are irreversible reactions. The latter includes kinetically controlled reactions, mixing of solutions, and temperature change. These additional capabilities allow for a more realistic evaluation of hypotheses regarding the evolution of redox state in contaminant plumes by considering a greater number of possible geochemical interactions within the system. The initial PHREEQC chemical input file for the model (Figure 4.6) consisted of average "background" solute concentrations at the study site obtained from average concentrations just outside the contaminant plume. The modeled solution was allowed to equilibrate with calcite since mineralogical studies performed at the site permit this to be occurring (LONG et al., 2000), unpublished data Madden, 2000). After the initial time step, total values of nitrogen (N), sulfur (S), and iron (Fe) and the amount of electron donor (C_{ace}) were assigned by RT3D. PHREEQC then considers these new concentrations in conjunction with the rest of the water chemistry, calculates chemical speciation and sends that output to MODFLOW where transport processes are considered. Although Phase I simulations do not make use of all the capabilities of PHREEQC (e.g., redox sensitive solid phase constraints) as they will



Figure 4.6: Initial PHREEC input file; after the initial time step the total organic (CH_2O), sulfur (S), nitrogen (N), and iron (Fe) are calculated by RT3D and included in the input file as such.

be in Phase II, establishing the linkage between PHREEQC and the commonly used flow and transport models MODFLOW and RT3D allows for much greater hypothesis testing capabilities in future modeling efforts.

Preliminary Phase 1 Modeling Results

Before running the fully reactive 3-D PEA model, a sample 1-D groundwater simulation was run using PHREEQC to evaluate the effects of sequentially adding electron donor (C_{ace}) to our initial background water. Results show that as more electron donor is added to the system, the TEAs present are consumed sequentially based on thermodynamic arguments (Figure 4.7). Immediately as Cace is added to the system, the most energetically favorable TEA oxygen [denoted O(0)] is degraded. This is followed by the degradation of NO_3 [denoted N(5)] and production of N_2 initially (not shown) and ultimately NH₄ [denoted N(-3)]. After nitrate is degraded, iron oxides [denoted Fe(3)] are reduced and Fe(2) is produced. This redox couple is followed by the consumption of sulfate [denoted S(6)] and the production of sulfide [denoted S(2)]. These changes are driven by changes in pe resulting from the input of electrons from the degradation of organic matter. It should be noted that throughout this experiment, pH remained relatively constant. Changes in pH were buffered by allowing the system to be in equilibrium with calcite. These trends suggest that given appropriate organic input (from MODFLOW and RT3D), the coupled model should allow us to observe the 3-D evolution of TEAPs and the resulting redox zonation in the aquifer.





The coupled 3-D reactive flow and transport model was then run for 365 days to determine if TEAPs would be initiated in the aquifer as a result of the contamination input and to test the linkages between the three modeling codes. It should be noted that in this initial model, RT3D was not calculating the total N, Fe, and S but rather PHREEQC was reading the initial total input of N, Fe, and S (see Table 1) and speciating according to the electrons produced during the fermentation step. The model output for each of the chemical components was plotted in 3-D using Tecplot. Two-dimensional slices through layer 2 were created from these 3-D images for ease of viewing the plume.

Figure 4.8 shows the evolution of organic matter (C_{org}) in the aquifer at 10, 200, and 364 days. The initial condition of the aquifer is assumed to have a very low concentration of organic matter. Inputs of contaminant (C_{org}) were then added to a discrete "source" area and transported over time. As a result, the majority of the field shown in Figure 4.8 is blue corresponding to areas without C_{org} inputs and a smaller distinct plume of increased C_{org} can be seen developing down gradient of the designated source area. After 364 days, a contaminant plume roughly 150 feet wide by 1500 feet long has developed. As the plume develops, we would expect that the C_{org} would be fermented into usable electron donors (C_{ace}) which could then be oxidized coupled to the reduction of oxygen (the most favorable TEA). This would result in decreased oxygen concentrations within the plume. Figure 4.9 demonstrates that over the 365-day simulation, oxygen is depleted to concentrations nearing zero within the plume presumably driven by the production of usable electron donors. This demonstrates that the linkages between the three modeling codes are working such that the important hydrogeochemical controls of each portion of the model are operating effectively. Based















on thermodynamics, after the oxygen has been consumed within the plume, NO₃ (the second most favorable TEA) will be reduced. Figure 4.10 shows that NO₃ concentrations decreased within the plume but not to concentrations below which NO₃ reduction cannot be sustained (ISLAM et al., 2001). This suggests that at 365 days, the plume has reached a state of NO₃ reduction. To evaluate the poised redox state at this point in time ammonium (NH₄) and sulfate (SO₄) concentrations were examined (Figure 4.11). The lack of NH₄ production (concentrations near zero throughout the aquifer, denoted in blue) and lack of SO₄ reduction (high initial concentrations present throughout aquifer, denoted in red) suggests that the system is not reduced enough to initiate those reactions and that NO₃ reduction is poised to produce N₂ gas (DREVER, 1997).

These results suggest that the three modeling codes are communicating appropriately and that the model is going through a sequential TEAP ladder based on thermodynamic arguments. However, the rate at which the sequence of traditional redox zones will be achieved is constrained by the kinetics of the fermentation of organic matter. Allowing the evolution rate of the system to be limited by fermentation is reasonable during the initial stages of redox zonation. However, once the system has reached a state where fermentative products can build up (e.g. methanogenesis), it is no longer appropriate to assume that fermentation is the rate-limiting step and when TEAs are introduced to such a system (e.g. during recharge) their rates of reduction, although comparatively fast, (see Chapter 3) become the rate limiting factor.



Figure 4.10: Nitrate Concentration (mol/L) at 10, 200, and 364 days





Figure 4.11: Ammonium and Sulfate Concentrations (mol/L) at 10, 200, and 364 days



Future Work

Preliminary results demonstrate that combining flow and transport codes with geochemical modeling codes can provide a powerful tool to evaluate hypotheses regarding the evolution of TEAPs in organic groundwater contaminant plumes. The immediate next step is to continue to run the model for longer periods of time until it has reached a "mature" state where plume length has stabilized. This will allow us to test the hypothesis that under such conditions, redox zones will not be sustained but rather TEAs will continue to be degraded sequentially until the plume has reached a state of methanogenesis. Once this hypothesis has been tested, the next step is to increase the geochemical complexity of the model such that we can incorporate realistic, redox sensitive solid phases (e.g., pyrolusite (Mn-oxide), Fe-oxyhydroxides, and pyrite). After these steady state hypotheses have been tested (Phase I), Phase II will examine the more realistic scenario evaluating changes due to recharge introducing TEAs to a mature system. A system that has reached redox maturity will have a build up of fermentative products (acetate and H_2) and thus, it is no longer reasonable to assume that TEAP reaction rates will be limited by fermentation reactions as during the initial evolution. Therefore, the rates of TEA consumption become significant. Rate estimates obtained from push-pull tests (see Chapter 3) will be used to constrain these processes by incorporating them into RT3D.
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CONCLUSION

A conceptual model for the evolution of redox zones in aqueous systems has been proposed. This model makes the distinction between systems in which the rate of TEAPs is controlled by the availability of electron donors (from fermentation) and those in which there is an accumulation of fermentative products and thus the rate of TEAPs is controlled by the availability of electron acceptors. When a contaminant plume is initially evolving, TEAPs will be limited by the concentration of readily available electron donor from fermentative reactions. As the plume becomes more reduced fermentative products begin to accumulate in the system, removing the donor limitation on the TEAP rates. As a result, reactions can proceed at faster rates as was observed during the field experiments. Newly introduced TEAs may also be consumed simultaneously under these conditions because there is no competitive exclusion between TEAPs given low TEA input concentrations (e.g., typical concentrations present in precipitation). Field experiments also demonstrated that the reduction of TEAs observed in the aquifer did not occur in the reduced aquifer water without the influence of the solid phase portion of the aquifer and its associated microbial community. It was also shown that oxidized species such as NO_3 and SO_4 , can persist even in highly reduced waters where thermodynamics predict they would be reduced. This implies that when modeling anaerobic systems, strictly thermodynamic geochemical arguments may not always be appropriate. The geochemistry must be considered in conjunction with transport processes and microbiological properties of the system.

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These findings collectively imply that in a highly reduced system, much of the important TEAPs will be initiated rapidly when TEAs are introduced to the reduced aquifer. Under this scenario, the majority of the TEAP variability will occur in small discrete interface zones near the boundaries of the plume. This idea is supported by graphical and multivariate statistical analyses performed on geochemical data obtained before and after a major recharge event (from spring snow melt). Statistical results demonstrate that although wells with similar chemistry are spatially distributed near one another (denoting distinct water masses in the system), the variability is not related to distinct redox zones in the system. Examination of small-scale (single well) changes suggests that the spatial areas over which recharge has the greatest impact on TEAPs are small (less than 3 feet). It is likely that during recharge events most of these changes occur near the water table-capillary fringe interface where abundant donor and microorganisms exist. Unfortunately, due to the small and transient nature of these zones, directly sampling where the greatest redox variability is occurring very difficult. In addition, our observations of geochemical changes over 5 years suggest that even when sampling within a transition zone where TEAPs are occurring, finding an appropriate indicator of that *in-situ* process may be complicated by redox disequilibria and additional microbial reactions which impact TEAP indicating variables such as H₂.

These findings were utilized to develop a three-dimensional partial equilibrium flow and transport model to test hypotheses regarding redox evolution. The conceptual model was verified by incorporating its key elements

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and linkages in a 3-D flow and transport model, which successfully represented the early stages of plume evolution. This model will be used in the near future to quantify biogeochemical changes due to recharge and will incorporate additional real-world geochemical complexities by including realistic redox-sensitive solid phases (e.g., pyrolusite (Mn-oxide), Fe-oxyhydroxides, and pyrite). The outputs of these modeling efforts will not only improve our basic understanding of redox evolution in natural and contaminated systems but will also aid in the design and evaluation of bioremediation and natural attenuation strategies. APPENDICES



APPENDIX A.

Procedure for Determination of Hydrogen Gas Concentrations Using the RGA-3

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Set-Up

From a cold start-up, the RGA-3 requires at least 2 hours to stabilize prior to sample analysis. The RGA-3 frequently takes longer than 2 hours to stabilize, especially following transportation to the sampling site. Recommendation: set up the RGA-3 at least 24 hrs. in advance of sampling.

- 1. Set analyzer on a stable surface protected from rain, direct sun, etc. Use a power-strip with a surge suppressor to connect RGA-3 to power.
- 2. Remove plugs and caps; make sure to remove red cap from mercury scrubber and plug from sample "out" port
- 3. Hook up connections to integrator (printer):
 a) on integrator (back): red → Ch A+, black → Ch Ab) on RGA-3 (back): red → 1 V out (off set), black → GND
- 4. Attach regulator to N2 cylinder; flush regulator thoroughly with N2 and then fill 1-2 Tedlar bags (you will need these to make your dilutions)
- 5. Attach carrier gas lines, sample injection port
- Adjust regulator to approximately 100 kPa (~20psi)
 ***<u>Never</u> turn on the detector without carrier flow. In the absence of carrier flow, Hg evolved from the oxide bed may plate out onto the detector optics.
- 7. Turn on power switches to RGA-3 and integrator (on backs) and turn on the RGA-3 lamp (switch located on front face).
- Turn on heaters for column and detectors Press "TEMP SEL" button on front panel to toggle between COL (column) and DET (detector); press "TEMP ON/OFF" button to turn heaters on/off. Make sure the "ON" light comes on when you turn on the heaters.
- After 1.5 hours, turn on the lamp. You can remove the top cover of the RGA-3 and observe a faint blue glow from the lamp housing to confirm operation. Wait at least two hours before proceeding to step 8.
- 10. Press "SET/AT" button to toggle between the set temperature and actual temperature. Record set/at values for both column and detector in the logbook (used to monitor integrity of thermocouples). ***Actual values should be within 5 C of set value and stable.
- 11. Press "TEST" repeatedly and toggle through the x1, x2, x4, x8, x16, and x32 positions. Record the values displayed on the LED during each position in the logbook. These values indicate lamp output, baseline levels, etc. (see manual for description)
- 12. Press "RANGE" to get out of test mode; continue to press "RANGE" until you reach the x32 position (indicated by light); use this setting for analyses.
- 13. On printer, press "LEVEL". Record initial value in logbook. On RGA-3, press "ZERO", then press "LEVEL" again (value should drop to either 1000 or 1500.)
- 14. On printer, press "PT EVAL". Wait ~ 1 min. for it to take reading and print value. Record value in logbook. (Values greater than 500 indicate the column might be contaminated and require reconditioning.)
- 15. Proceed with calibration.

Standby Mode

If running samples on consecutive days.....

- 1. At the end of the day, turn off the UV lamp, but leave the heaters on, and leave carrier gas flow on.
- 2. At the start of the next day, turn on the UV lamp and wait 20-30 minutes to stabilize.
- 3. Carry out steps 10-15 in Set-Up.

Calibration/Sample Analyses

Record results from all analyses in logbook...

1. Check operation of valve by completing one cycle. Valve initially should be in "load"

position (check light). On RGA-3, press VALVE to switch valve to the "inject" position

(watch light, listen for sound of valve switching). Wait 1-2 secs, then press VALVE

again to revert back to "load" position (watch light, listen for sound of valve switching).

- 2. Analyze Lab Air:
 - a) Using 25 ml gas-tight syringe, open valve of syringe and push/pull plunger several times to flush the syringe
 - b) Fill syringe with lab air and close valve
 - c) Connect syringe to sample port of RGA-3, open valve on syringe, and slowly inject 7.5 ml of sample into RGA-3.

****Sample loop capacity is ~ 1 ml; you want to inject ~6x volume of sample l loop to properly flush it.

- d) Close valve on syringe; press VALVE on RGA-3 (to switch valve to "inject" position); press INJ/END A on integrator to start run, press start on timer (or mark your stopwatch).
- e) (at 20 psi) Wait 10 seconds, then press VALVE on the RGA-3 (to switch the valve to the "load" position). ***Be sure not to let valve run longer: you may introduce some nasty organics which can poison the mercuric oxide bed, reducing its efficiency.
- f) Wait for H2 and CO peaks to come out. Retention times are approximately 0.27 min and 0.45 min, respectively. Once they have eluted, press INJ/END A on integrator to stop the run and calculate peak areas.
- g) Wait at least 30 seconds before running another replicate. ***You should wait at least 3x the elution time (RT) of your analyte of interest in order to sufficiently backflush the first column.
- h) After 30+ seconds, proceed with next replicate analysis of lab air.
- 3. Analyze N2 carrier gas (from Tedlar bags). This will serve as your calibration blank.

- a) Attach a 22 gauge needle (or finer) to gas-tight syringe; insert needle into septum fitting of Tedlar bag, open valve on syringe and withdraw several ml's of N2. Close valve on syringe.
- b) Remove syringe from Tedlar bag. Open valve and completely expel the gas; close valve when finished (this serves to "flush" the syringe).
- c) Insert needle into septum fitting of Tedlar bag and withdraw 25 ml of N2; close valve.
- d) Remove needle from syringe adapter.
- e) Repeat procedure outlined in steps 2c-2h (above) for N2.
- 4. Standards

You generally do not see H2 concentrations greater than 10ppm (8.0 nM) in nature, so this can serve as a preliminary upper bound for calibration.

- a) Fill Tedlar bag with a certified H2 standard (generally 100ppm H_2 in N_2).
- b) Prepare 25 ml of 10ppm H2. Attach needle to gas-tight syringe and withdraw several ml of H2 standard from Tedlar bag. Remove syringe from Tedlar bag and expel the gas to flush syringe. Withdraw another aliquot of gas (several ml) from Tedlar bag and close valve. Hold syringe vertically, open valve and slowly but steadily expel gas until plunger reaches the 2.5 ml mark, then close valve. Withdraw enough N2 from the Tedlar bag you filled with the carrier gas to fill the syringe to 25 ml (this is now your 10ppm H2 standard). Recommendation: If you prepare 25 ml of 10ppm standard and inject 7.5 ml per replicate, you can run three replicates and still have 2.5 ml left. You can then prepare a 1:10 dilution of the remaining gas to make your 1ppm H2 standard.
- c) Analyze according to procedures outlined above.
- d) In the same manner, prepare and analyze 1ppm, 0.1 ppm, 2ppm, and 0.2ppm H₂ standards. You can also prepare 4 and 0.4ppm standards if desired.
- 5. Sample collection

Once well has been purged for at least 3 well volumes, connect pump tubing to gas-stripping bulbs. Tip upright and fill with groundwater. Return bulb to online position and inject three syringe-fulls of N_2 gas into the bulb to create an inert headspace. Allow at least 15 minutes before collecting first sample. *Note that increasing the rate of groundwater flow will decrease the time necessary to reach equilibrium.

6. Running samples

Once you have successfully calibrated, you are ready to run samples. Where possible, remove enough gas from the gas-stripping bulbs so that you can run three replicates per sample. Continue to run samples until values stabilize.

- 7. Checking calibration
 - a) The RGA-3 does have a tendency to drift, and the calibration should be checked every 3-4 hours. You should also check the calibration if: 1) there is a large shift in the baseline/integrator response, or 2) hydrocarbons have been injected into the RGA-3 (e.g. because valve was left in "inject" position for too long.
 - b) Check calibration by preparing and analyzing 10ppm and 1ppm H2 standards. If results differ from previous calibration by more than 10%, make a new suite of standards and go through a complete calibration.

Shut Down/Pack Up

- 1. Turn off UV lamp and the heaters for both the detector and column.
- 2. Once temperatures are at ambient levels (i.e. detector temperature MUST be less than 100°C, but preferably below 50°C), turn off carrier gas flow. Recommendation: Increase carrier gas flow rate (40-60 psi) to cool detector more quickly.
- 3. Turn off power to the integrator and RGA-3.
- 4. Disconnect integrator.
- 5. Remove sample inlet port and carrier gas line from RGA-3.
- 6. Insert plugs into all open ports to keep particulates from entering the RGA-3; replace red cap on mercury scrubber.
- 7. Pack RGA-3 and integrator into silver carry case; make sure all sides are securely fastened.

APPENDIX B.

Timeline of Project Events

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November 1997	MSU/USGS Reseach Team Sampling Trip 1
January 1998	EFX installed wells in two plots (one set installed 1-27-98 and one set installed 2-9-98)
February 1998	MSU/USGS Reseach Team Sampling Trip 2
	(Geochemistry samples taken from new wells at EFX plot; may not have equilibrated ex. high H2 values)
April 1998	MSU/USGS Reseach Team Sampling Trip 3
	(limited sampling due to restricted team)
May 98	MSU/USGS Reseach Team Sampling Trip 4
June 98	Bromide Tracer Test 6-(8-12)-98
	(First time EFX circulted water through plot. Water did not circulate through the bioreactor.)
June 98	Chloride Tracer Test 6-(17-22)-98
	(First time EFX circulated water through the bioreactor and back to plot.)
August 1998	MSU/USGS Reseach Team Sampling Trip 5
November 1998	MSU/USGS Reseach Team Sampling Trip 6
	(In-situ microcosms placed in ML-3 and ML-1 at various depths.)
February 1999	Micorcosm Retrieval (see notes)-Chemisry taken from ML3(H2) and ML1(noH2)
May 1999	MSU/USGS Reseach Team Sampling Trip 6 (MSU wells only)
	Preliminary Push-Pull Trial performed on ML3 (KNO3 and NaCl added)
	First set GPR transects run-EWS, DWH
June 1999	MSU/USGS Reseach Team Sampling Trip 7(EFX wells only-1 transect)
	(EFX shut down operations at FTA-2)
July 1999	Charaterization of ML3 for taking core for microcosms/ H2 study (see notebook for details)
August 1999	Installation of new MSU wells (ML11-ML16)-EWS,JTM
October 1999	MSU/USGS Reseach Team Sampling Trip 8(Flow paths 1 & 2 and rest of new wells)
	Second set GPR transects run-JDM, DWH; sediment retrieved from ML3-in-situ microcosms (MAV-garnets)
November 1999	MSU/USGS Microcosm study begins (core taken from ML3 to set up 72 laboratory microcosms)
January 2000	MSU/USGS Reseach Team Sampling Trip 9(Flow paths 1&2)
June 2000	MSU/USGS Reseach Team Sampling Trip 10(Flow paths 1&2)
June 2000	Push-Pull Trial 1 and jug experiments performed on ML3 (DO, NaNO3, Na2SO4, and NaCl added)
July 2000	Push-Pull Trials 2 and 3 and jug experiments performed at ML3 (DO, NaNO3, Na2SO4, and NaCl added)
August 2000	Push-Pull Trial 4 performed at ML3 (DO, NaNO3, Na2SO4, and NaCl added)
May 2001	Push-Pull Trial 5 performed at ML3 and ML1
June 2001	Final GPR study and collection of cations-anion-specific conductance

Wurtsmith AFB Timeline (MSU/USGS Research Team Activities after Nov. 1997)

APPENDIX C.

Well Sampling History

	USGS	11/97	2/98	4/98	5/98	8/98	11/98	2/99	5/99	10/99	1/00	6/00
ML1-17.9	X	Х	Х	Х	Х	Х	dry		dry		dry	dry
ML1-20	X	Х	Х	Х	Х	Х	X	Х	Х		X	Х
ML1-22.5	X	Х	Х	X	Х	X	Х	X	Х		X	Х
ML1-24.5	X	Х	Х	X	X	X	Х	Х	Х		X	Х
ML1-25.3	X	X	X	X	Х	Х	Х		Х		X	Х
ML2-20.5			Х									
ML3-17.81	X	Х	dry	dry	Х		dry	dry	dry	dry	dry	dry
ML3-18.31	Х	Х	Х	Х	Х	Х	dry	dry	dry	dry	dry	dry
ML3-22.00	Х	Х	Х	Х	Х	Х	dry	Х	Х	х	Х	Х
ML3-25.03	Х	Х	Х	Х	Х	Х	Х	Х	Х	х	х	Х
ML3-27.99	X	Х	Х	Х	Х	Х	Х	X	Х	х	х	Х
ML3-32.78	X	Х	Х	Х	Х	Х	Х	Х	Х	х	х	Х
ML3-37.59	Х	Х	Х	Х	Х	Х	Х	Х	Х	X	х	Х
ML4-17.50	X	Х	X		Х	Х	dry		dry	dry		dry
ML4-17.75	Х				Х	Х	dry		dry	dry		dry
ML4-21.44	X	Х	X		Х	Х	dry		Х	х		X
ML4-24.44	X				Х	Х	X		Х	x		Х
ML4-27.42	Х	Х	Х		Х	Х	Х		Х	х		Х
ML5-18.42	Х	Х	dry		Х	Х	dry		dry	dry	dry	dry
ML5-18.84	Х	Х	X		Х	Х	dry		dry	dry	dry	dry
ML5-22.64	Х	Х	Х	Х	Х	Х	X		Х	x	x	X
ML5-25.67	Х	Х	Х	Х	Х	Х	Х	CAT	Х	x	x	Х
ML5-28.37	Х	Х	Х	Х	Х	Х	Х		Х	х	x	Х
ML5-33.78	X	Х	Х	Х	Х	Х	Х		Х	х	х	Х
ML5-38.48	Х	Х	Х	Х	Х	Х	Х	CAT	Х	x	x	Х
ML6-12.30			Х		Х	Х	dry	dry	dry	х		dry
ML6-16.02							X	Х	Х	X		Х
ML6-19.04			Х		Х	Х	Х	Х	Х	X		Х
ML6-22.00												X
ML6-28.74			X		X	X	Х	X	X	X		Х
ML6-32.11												Х
ML8-18.70	X				X	X	dry		dry			dry
ML8-19.15	X	Х	X		X	X	dry		dry			dry
ML8-22.80	X				X	X	X		X			X
ML8-25.85	Х	Х	X		X	Х	X		Х			X
ML8-28.80	Х				X	X	Х		Х			X
ML8-33.65	X				X	X	X		Х			X
ML8-38.55	X	X	Х		Х	X	X		X			X
PZ-7		X	X		X	X						
PX-8			X									
PZ-9		X	X		X	X						
PZ-15		X	X		X	X						
ML10-36.99												X

Well Sampling History-complete geochemistry

Well Sampling History-complete geochemistry

	USGS	11/97	2/98	4/98	5/98	8/98	11/98	2/99	5/99	10/99	1/00	6/00
ML11-18										X	X	X
ML11-21										X	Х	X
ML11-24										X	X	Х
ML11-27										Х	X	X
ML12-18										x	X	Х
ML12-21										х	х	Х
ML12-24										х	X	Х
ML12-27										X	frozen	Х
ML13-18										х		Х
ML13-21										x		X
ML13-24										X		X
ML13-27										X		X
ML14-18										x	X	X
ML14-21										x	X	Х
ML14-24										х	Х	X
ML14-27										x	X	Х
ML15-18						-				X	X	Х
ML15-21										X	frozen	Х
ML15-24										X	X	X
ML15-27										X	X	Х
ML16-18										X	X	Х
ML16-21										X	X	X
ML16-24										X	X	Х
ML16-27										X	X	Х

