Application of Stable Isotope Geochemistry to Assess TCE Biodegradation and Natural Attenuation in a Fractured Dolostone Bedrock

by

Justin Allen Clark

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Isotopic analyses have been developed over the last 10 years as a method for determining chemical interactions of chlorinated solvents. These methods are especially promising for chlorinated ethenes, such as TCE and DCE. This study further develops and employs TCE and DCE compound specific isotopic analyses, along with chemical analyses, to characterize the degradation of TCE in a fractured bedrock aquifers. The site chosen, in Smithville, Ontario, was contaminated by extremely high levels of TCE that is currently undergoing monitored pump-and-treat remediation. A collection of historical data and a extended description of the site are provided for potential use in other research. From December 2008 until April 2010 samples were collected from the site to provide additional data, including isotopic data.

The redox conditions at the site are anoxic to reducing, with sulfate reduction and methanogenesis as dominant terminal electron accepting processes. Redox data indicates that electrochemical conditions are highly variable within the site, including areas near the source zone that are less reducing. Documented changes in groundwater conditions to much more reducing environments indicate that increased oxidation of organic matter is occurring at the Smithville site in select wells.

Chemical analyses of potential TCE degradation products are employed to identify degradation. Many wells on site have dechlorination products. Combined chemical and redox shows that degradation seems to be a removal process for TCE at the Smithville site. Reductive dechlorination is shown to be a significant process forming degradation products such as DCE, VC, ethene and ethane. Production of DCE in significant amounts, above 1.0 ppb, was observed to only occur after 2003. In addition to this, DCE data shows that the percentage of DCE made up of cDCE is above 96%. This indicates that microbes most likely mediate the processes that formed DCE from TCE.

The isotopic data had a high range in both carbon and chlorine isotopes. Chlorine isotopic data ranges from a $\delta^{37}Cl_{TCE}$ of 1.39 to 4.69, and a $\delta^{37}Cl_{cDCE}$ of 3.57 to 13.86. Carbon isotopic data ranges from a $\delta^{13}C_{TCE}$ of -28.9 to -20.7, and a $\delta^{13}C_{cDCE}$ of -26.5 to -11.82. Samples collected in the well closest to the source zone returned the lightest carbon and chlorine isotopic signatures. The range in values indicate varying degrees of degradation throughout the site, however the same wells have similar isotopic trends. Based on isotopic evidence, degradation past DCE to more degraded compounds also occurs at the Smithville site. However, determination of the degree of degradation of TCE and DCE was not implemented due to the variability in isotopic data.

Acknowledgements

Dedication

I would like to dedicate this thesis to my grandpa, Richard P. Holgin, and my mother, Consuelo F. Holguin, as well as all those who have supported me through these many years of school.

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Chapter 1:
Introduction & Problem Statement

Chlorinated solvents are one of the most prevalent classes of contaminants at industrial sites in North America and Europe (Alvarez and Illman, 2006). These contaminants are often released as Dense Nonaqueous Phase Liquids (DNAPLs) and tend be very pervasive in the subsurface. There is often considerable uncertainty as to the fate of DNAPLs in the subsurface due to geologic heterogeneity, complex chemical interactions and unknown release histories. DNAPL source zones and plumes of aqueous phase contaminants resulting from DNAPL release can contribute to long-term groundwater contamination, potentially for centuries; thus, their management and potential remediation is of high importance (Pankow and Cherry, 1996).

Over the two past decades, considerable effort has been expended towards understanding the fundamental processes affecting the fate of DNAPLs spilled or released in heterogeneous unconsolidated geologic materials. Research in this area has focused on such things as DNAPL dissolution mechanisms, the role played by geologic heterogeneity on DNAPL source zone architectures, aqueous-phase plume migration, chemical evolution of DNAPLs, and natural attenuation processes. Chemical models and physical flow models are sometimes employed to aid in describing the chemical transformations and physical transport of DNAPL plumes. However, contaminated natural field sites with complex geologic material, including fractured rock, often require large amounts of physical analyses and chemical data collection to characterize. While progress has been made in understanding DNAPL migration and fate in heterogeneous unconsolidated deposits, there remains a paucity of knowledge on the behavior of DNAPLs in fractured bedrock environments. In spite of the efforts by many scientists, it is widely recognized that few, if any, sites contaminated by DNAPLs have been fully remediated with respect to either the dissolved contaminants contained in the aqueous phase or the removal of the DNAPL source (Alvarez and Illman, 2006).

The organic contaminant trichloroethylene (TCE) is a DNAPL that was commonly used in industrial processes in the last 50 years. Although its use is more restricted today, release of TCE to the natural environment has made it one of the most ubiquitous organic contaminants in industrial nations. Once released to the environment, TCE tends to be resistant to degradation. However, TCE can be transformed into a small number of different compounds through chemical degradation reactions; which are often catalyzed by microbes. Due to the different chemical processes affecting

degradation TCE as well as a variety dispersal methods and source zone types, complex plumes consisting of many different organic solvents can develop from TCE spills (Huang et al., 1999). Loss of contaminant mass, formation of degradation byproducts, and microcosm data have been used as evidence for degradation (Illman and Alvarez, 2009). However, these methods are limited and often cannot be used to fully verify whether biodegration is occurring, determine the degree of biodegradation or determine the mechanisms of degradation.

In recent years isotopic methods have been developing as tools to determine and to better understand the physical and chemical processes affecting TCE degradation, especially at complex field sites (Freedman and Gossett, 1989; Holliger et al., 1998; Bloom et al., 2000; Chapelle and Bradley, 2003; Meckenstock et al., 2004). These isotopic methods, when combined with other methods, have led to promising advances in characterizing organic degradation. Isotopic analyses have been employed as a method of determining the source of TCE and/or verifying the occurrence of degradation of TCE at a given contaminated field site. Isotopic analyses have also been studied as a means of potentially determining the mechanisms of degradation of TCE.

This thesis studies the applicability of isotopic analyses, in conjunction with more common chemical methods, to verify the occurrence of degradation and potentially determine the degree of degradation in a fractured bedrock network. For this study compound specific carbon and chlorine isotopic analyses are employed to better understand the geochemical evolution of TCE and its degradation products. Investigating the applicability of isotopic analyses to characterize the dominant degradation mechanisms for TCE is also a goal of this thesis. The fractured bedrock geology field site, which is located in Smithville, Ontario, was contaminated in 1985 by a large DNAPL spill and is currently undergoing pump-and-treat remediation. Field sampling, which began in 1987, has indicated that the most abundant organic contaminants at the site are PCB, TCE, and TCA. For monitoring purposes aqueous phase VOC concentration analyses have been consistently completed from selected wells near the source zone of the spill for approximately 15 years. Near the source zone of the spill 14 wells, sampled from December 2008 until April 2010, are analyzed in great detail using the results of additional chemical and isotopic analyses.

The research presented in this thesis is connected to a larger project studying the contaminant plume response to DNAPL source zone architecture at natural field sites. The Smithville site was characterized and serves as an example of a contaminated field site undergoing remediation. A goal of this project was also to form an understanding of the hydrogeology of the site and to develop a

dataset that pertains to the site. Data collected is currently being incorporated into a modified computer model for this site. Using this model physical and chemical data will be used to further understand the transport and degradation of TCE. This study, and future modeling, will be used to provide a performance assessment of the existing plume control strategy as well as to examine the potential for bioremediation and/or natural attenuation. The research completed as part of this thesis may also help to guide potential management scenarios.

Chapter 2:
Chemical Background

To understand how TCE and other chemicals behave in the subsurface it is important to have an understanding of the geochemical processes controlling TCE transport and degradation. This section provides some background information on TCE and its behavior in the subsurface. The potential chemical and physical processes that affect and control aqueous concentrations of TCE (and the products of its degradation) in groundwater are discussed in this section. A description of the techniques commonly used to characterize the distribution of TCE and its products of degradation is also presented.

2.1 TCE and Chlorinated Solvents

TCE is a chlorinated aliphatic hydrocarbon (chlorinated alkene) and is one of 14 VOCs identified as Priority Pollutants by the United States Environmental Protection Agency (US EPA). TCE is toxic and a known human and animal carcinogen (US EPA, 2002). TCE is produced as an industrial solvent and first began being manufactured in the 1920s, though production has slowed in recent years. Today TCE is a common pollutant in subsurface environments throughout the world (Pankow and Cherry, 1996; Alvarez and Illman, 2006). It is especially dangerous due to its high potential for transport in subsurface groundwater.

TCE can be chemically transformed into a number of different compounds, including the chlorinated ethenes dichloroethene (DCE), and vinyl chloride (VC). Chlorinated ethenes resemble the chemical structure of ethene ($H_2C=CH_2$) but with chlorine replacing one, two, three, or four hydrogen atoms for VC, DCE, TCE, or tetrachloroethylene (PCE), respectively. DCE is more toxic than TCE, though toxicological research is still being conducted on this compound (US EPA, 2002). DCE has three isomers, 1,1-DCE, cis-1,2-DCE (cDCE) and trans-1,2-DCE (tDCE). VC is more toxic than both DCE and TCE. DCE and VC can be degraded to more innocuous compounds that are acceptable in much higher concentrations in the natural environment. For example, CO_2, ethene and ethane are often formed as a result of chemical transformation of DCE and VC. Table 2.1 presents valid physical and chemical properties of TCE and some of the most common byproducts of its degradation.

**Table 2.1. Physical and selected chemical properties of TCE, cDCE,
VC, ethene and ethane. Table created with data from Yaws (1999).**

Mol. Formula	Substance Name	Mol. Wt.	Density	Henry's Law const.	solubility (mass basis)	log K_{OW}
Units of measurement -->		(g/mol)	(g/cm3)	(atm·L/mol)	(ppm w)	(-)
C_2HCl_3	trichloroethylene	131.39	1.458	11.565	1100	2.42
$C_2H_2Cl_2$	cis-1,2-dichloroethylene	96.94	1.265	7.3644	3500	1.86
C_2H_3Cl	vinyl chloride	62.50	0.903	22.387	2697	1.62
C_2H_4	ethene	28.05	0.568	207.27	131.0	1.13
C_2H_6	ethane	30.07	0.315	481.86	60.4	1.81

Tracking the distribution, transport and degradation of TCE released to the natural environment can be difficult, even if it is in a relatively homogenous aquifer. This is due, mostly, to complex source zones as well as the fact that TCE plumes can have quite different biological and chemical processes affecting its transport and transformation (Huang et al., 1999). TCE released into fractured rock is even more difficult to track due to the complex nature of fluid flow through fractured aquifer matrices. To characterize a plume resulting from TCE released to a given location, such as the Smithville field site, it is important to understand how physical transport and, potentially, degradation control the distribution of TCE and the resulting degradation products.

TCE released to the surface as a DNAPL often percolates through unconsolidated porous media and/or fractured material through unsaturated surface zone to the groundwater table. Given the density of TCE, physical transport of non-aqueous phase TCE can distribute contaminants deep into the local water table and down gradient of the source zone. As this occurs non-aqueous phase TCE can mix with infiltrated water and groundwater, dissolving it into the aqueous phase. As DNAPL and aqueous TCE are transported through the subsurface many processes can affect its concentration. For example, mixing and dilution with uncontaminated water are known to cause a reduction in the aqueous concentration of contaminants in the subsurface. Many of the processes that remove TCE from the subsurface or reduce its aqueous phase concentration do not remove the contaminant by changing its chemical composition. These processes, known as non-destructive processes, simply transfer organic compounds to another phase or location or they dilute the organic contaminant being

studied (Wiedemeier et al., 1999). Non-destructive processes include volatilization, mixing, dilution, sorption, and pump-and-treat methods. Correspondingly, destructive processes are processes that degrade contaminants by means of abiotic or biologically mediated chemical processes.

2.1.1 Non-Destructive Processes

Organic contaminants such as solvents released at contaminant sites are often very volatile. As DNAPLs, such as TCE, migrate down into the saturated zone of a porous media loss to the atmosphere via vaporization (evaporation from pure phase or volatilization from aqueous phase) is a non-destructive process that removes some of the contaminant from the subsurface. TCE and its degradation products may be affected by the process of vaporization to varying degrees depending on the release history and atmospheric interaction. TCE is volatile and (according to Table 2.1) the value of the Henry's Law constant (K_H) for TCE is 11.6 atm·L/mol (at standard temperature and pressure), which is a intermediate value when compared with the K_H for many other organic contaminants (Yaws, 1999). The Henry's Law constant is much smaller for cDCE (and all DCE isomers, though others are not shown), meaning that it is less volatile than TCE. VC, ethene and ethane, on the other hand, are more volatile than TCE. Significant vaporization of TCE (as well as the other compounds discussed) may occur at some contaminated field sites given the proper conditions, such as extended exposure to atmosphere. However, vaporization often does not remove a significant portion of released contaminant masses and large quantities of these contaminants often persist into the subsurface groundwater environment.

Generally DNAPLs are classified by the fact that at large concentrations they are immiscible in water. However, TCE, as well as other DNAPLs, released to subsurface groundwater can be dissolved given mixing with a large enough volume of water. As is shown in Table 2.1, TCE, cDCE and VC all have aqueous phase water solubility values that are relatively high when compared with permissible levels. Upon release non-aqueous phase TCE subsequent dissolution into the aqueous phase is often a significant process that distributes contaminants into the subsurface groundwater environment.

Advection is the physical transport process by which solutes are transported along with flowing groundwater. Velocity variations on a small scale affect hydraulic mixing and can cause solutes to move slower or faster than the ambient groundwater. This process; known as dispersion, causes

mixing and dilution of contaminants into a given aquifer. Another physical process known as molecular diffusion occurs when concentration gradients develop in subsurface groundwater. When concentration gradients develop mixing occurs on a molecular scale due to the kinetic energy of molecules, this tends to draw chemicals from areas of high to low concentration. The mixing of contaminated groundwater, native uncontaminated groundwater and infiltrating surface water controls dilution and is governed by dispersion and diffusion. Therefore, groundwater migration can have a significant effect on the dispersal of solutes in subsurface aquifer material. However, advection is the dominant transport mechanism and controls solute distribution. This is one reason why the pump-and-treat system has been maintained at the Smithville site. The pumping of the eight recovery wells (R1 through R8) also removes contaminants by treating the water extracted.

Sorption is a non-destructive reversible process that can also remove contaminants from the aqueous phase. Adsorption is a type of sorption in which solutes attach to a solid surface, such as the surface of a sand grain or a fracture. Adsorption and subsequent de-sorption can retard the downgradient transport of some organic compounds as well as contribute to long term contamination of an aquifer. As can be calculated from Table 2.1, TCE has an octanol-water partition coefficient (K_{OW}) value of approximately 263, which is an intermediate value when compares with observed K_{OW} values for other organic contaminants (Yaws, 1999). The degree of adsorption for a given aqueous concentration on a given surface is proportional to the fraction of organic carbon (f_{OC}) and the K_{OW}. However, the f_{OC} of the porous media underlying a given site can be highly variable. Depending on the amount of organic carbon, adsorption may also be a significant non-destructive process removing TCE from the aqueous plume as well as retarding subsurface TCE transport.

2.1.2 Abiotic Destructive Processes

Once released to the subsurface TCE has been shown to be quite recalcitrant; however, there are some processes known to remove TCE contamination from the subsurface through degradation. These destructive processes degrade contaminants by means of chemical reactions, some of which are catalyzed by microbes. Destructive removal is the dominant removal mechanisms for TCE and its degradation products at the majority of field sites (Wiedemeier et al., 1999).

Persistent source zone have characterized many TCE plumes and can contaminate local groundwater supplies for decades to centuries (Alvarez and Illman, 2006; Wiedemeier et al., 1999).

Thus, plumes of chlorinated ethenes are commonly elongated in the direction of groundwater flow due to a small amount of intrinsic degradation (Meckenstock et al., 2004). Early research on chlorinated ethenes indicated that they are recalcitrant or nonreactive in the subsurface (Chapelle and Bradley, 2003). However, there are some processes that can reduce the mass of TCE and its degradation products in the subsurface system by transforming TCE to other compounds or elements (e.g., Freedman and Gossett, 1989; Bloom et al., 2000; Meckenstock et al., 2004; Abe et al., 2009). Indeed, many organic contaminants including the chlorinated ethenes have been shown to degrade given the proper chemical conditions. However, degradation of TCE to permissible levels will occur only if the proper hydrogeologic and geochemical conditions are maintained; which is anticipated to occur at few sites (Alvarez and Illman, 2006).

The degree of TCE degradation and the rate of removal at a particular contaminant site or in a laboratory study can vary greatly (Wiedemeier et al., 1999). This is because the mechanisms of degradation can be quite different under different geochemical conditions and more than one process of degradation may be occurring at a specific site or in a particular experiment. Having an understanding of the potential reactions that may occur at a field site is important in order to characterize the reactions that are occurring.

There are few known abiotic chemical reactions capable of degrading TCE. Recent research may suggest that abiotic degradation can be significant in certain natural settings (Brown et al., 2006). However, it is generally accepted that, although degradation reactions can occur by abiotic means, abiotic reactions are not sufficiently fast and do not usually completely degrade TCE and its daughter products to environmentally acceptable compounds. Microbes often may increase the rate at which degradation occurs and can lead to more complete degradation of chlorinated solvents. Vogel et al. (1987) noted that the chemical reactions capable of degrading chlorinated ethenes abiotically can be put into four groups of reactions; substitution, dehydrohalogenation, oxidation, or reduction.

Substitution reactions occur when a functional group in a specific compound is replaced by another element or group. Substitution reactions do not involve the transfer of electrons. In the context of degradation of TCE, DCE, and VC substitution refers to the replacement of a halogen with a hydrogen ion. The most commonly studied substitution reaction that affects chlorinated solvents is hydrolysis (Pankow and Cherry, 1996; Wiedemeier et al., 1999; Alvarez and Illman, 2006). Hydrolysis refers to a substitution reaction in which the hydrogen is separated from the hydroxide ion of water and exchanged with a chlorine molecule of a chlorinated ethene. Compound with less

halogen atoms may be more susceptible to undergoing hydrolysis (Vogel, 1994). TCE degradation daughter products other than chlorinated ethenes may also be susceptible to hydrolysis. Although research on hydrolysis is still being conducted to fully characterize the degree to which hydrolysis may be affecting the degradation of chlorinated solvents at contaminated sites, some have concluded that the rate of chlorinated solvent hydrolysis in nature is slow (Pankow and Cherry, 1996). Substitution reactions, thus, are generally considered not to be dominant reactions involved in the degradation of chlorinated ethenes; however, they may affect the degradation of other compounds formed as a result of TCE degradation (such as chlorinated acetylenes).
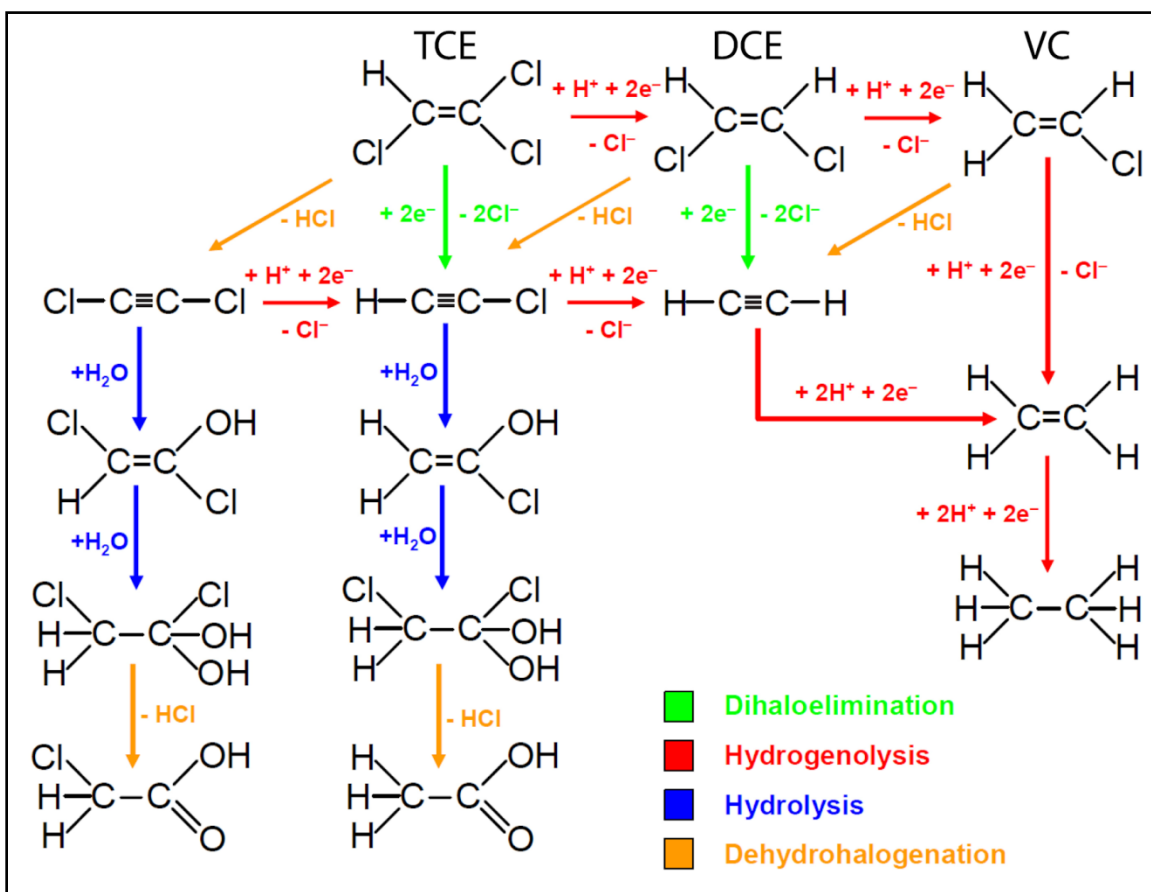
Figure 2.1. Potential abiotic chemical reactions that may be affecting the degradation of chlorinated solvents. Figure modified from Brown, et al (2006).

Some of the proposed abiotic chemical reactions affecting TCE and its degradation products are presented above in Figure 2.1. The molecules with more chlorine molecules (i.e., PCE and TCE)

have been documented as being affected by another chemical reaction, dehydrohalogenation (Vogel et al., 1987). Dehydrohalogenation is a chemical reaction involving elimination, or removal, of a halogen and a hydrogen atom from a halogenated organic compound. In dehydrohalogenation reactions the formal oxidation state of the organic molecule undergoing transformation does not change, therefore no transfer of electrons from other sources is necessary. TCE, DCE and VC can potentially undergo dehydrohalogenation, forming acetylene or chlorinated acetylene products (Brown et al., 2006).

Both substitution and dehydrohalogenation reactions occur only by abiotic means. Reduction reactions, such as dihaloelimination (shown in Figure 2.1) and hydrogenolysis (shown in Figures 2.1 and Figure 2.2), and oxidation reactions are chemical reactions that may occur abiotically, though they are often mediated by microbial activity. These reactions also require the exchange of electrons with external chemicals. Abiotic oxidation reactions are not shown in Figure 2.1. It is important to note that although the pathways of degradation discussed above may be occurring at a given location the potential that other reactions yet to be indentified affect the degradation of chlorinated ethenes by abiotic means (Elsner et al., 2008).

Reactions involving reduction or oxidation of compounds (redox reactions) have been shown to be important in the destructive removal of many organic compounds, including chlorinated ethenes. In addition, these reactions affect the local groundwater electrochemical conditions and govern groundwater microbial survival. For a given redox reaction to occur abiotically the reaction must be thermodynamically favorable. The half-cell reactions shown in Figure 2.2 are currently recognized as the most important redox reactions that degrade TCE (and other chlorinated ethenes). The figure also shows half-cell reactions for natural processes that are important in groundwater systems.

The carbon species in ethene are in a relatively reduced form and ethene is quite susceptible to being oxidized. More halogen molecules in chlorinated ethenes induce a more oxidized state; therefore, the potential for oxidation increases in compounds with less halogen molecules (Vogel et al., 1987). Oxidation of chlorinated ethenes (especially DCE and VC) may occur in oxidizing groundwater or reducing waters. During oxidation of chlorinated ethenes the organic molecule acts as an electron donor (see DCE Oxidation and VC Oxidation in Table 2.2). In a complimentary redox reaction an oxidant would act as an electron accepting process (for example oxygen would accept electrons during aerobic respiration). However, although it is theoretically possible (i.e., thermodynamically feasible) to oxidize chlorinated ethenes microbial mediation is considered to be

required for these reactions to occur (Wiedemeier et al., 1999). Due to this fact oxidation is not thoroughly discussed here, though more is presented in the context of biological degradation of TCE and its degradation products.

Table 2.2. Important Half-Cell Reactions affecting the degradation of TCE and its products of degradation. Data from Wiedemeier et al. (1999).

(Electron Donating)	ΔG_r^o (kcal/mol e⁻)	E° (V)
$C_2H_2Cl_2 + 4 \cdot H_2O \rightarrow 2 \cdot CO_2 + 10 \cdot H^+ + 8 \cdot e^- + 2 \cdot Cl^-$ DCE Oxidation	-16.1	.70
$C_2H_3Cl + 4 \cdot H_2O \rightarrow 2 \cdot CO_2 + 11 \cdot H^+ + 8 \cdot e^- + 2 \cdot Cl^-$ VC Oxidation	-11.4	.50
$.5 \cdot H_2 \rightarrow H^+ + 4 \cdot e^-$ Hydrogen Oxidation	-9.9	.43
$.25 \cdot CH_2O + .25 \cdot H_2O \rightarrow .25 \cdot CO_2 + H^+ + e^-$ Carbohydrate Oxidation	-10.0	.43
(Electron Accepting)	ΔG_r^o (kcal/mol e⁻)	E° (V)
$C_2HCl_3 + 2 \cdot e^- + H^+ \rightarrow C_2H_2Cl_2 + Cl^-$ TCE Reductive Dechlorination	-9.6	.42
$C_2H_2Cl_2 + 2 \cdot e^- + H^+ \rightarrow C_2H_3Cl + Cl^-$ cDCE Reductive Dechlorination	-7.2	.31
$C_2H_3Cl + 2 \cdot e^- + H^+ \rightarrow C_2H_4 + Cl^-$ VC Reductive Dechlorination	-8.8	.38
$O_2 + 4 \cdot e^- + 4 \cdot H^+ \rightarrow 2 \cdot H_2O$ Aerobic Respiration	-18.5	.80
$NO_3^- + 5 \cdot e^- + 6 \cdot H^+ \rightarrow .5 \cdot N_2 + 3 \cdot H_2O$ Denitrification	-16.9	.73
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ Iron (Fe^{3+}) Reduction	-17.8	.77
$SO_4^{2-} + 8 \cdot e^- + H^+ \rightarrow .5 \cdot HS^- + .5 \cdot H_2S + 4 \cdot H_2O$ Sulfate Reducation	5.3	-.23
$CO_2(g) + 8 \cdot e^- + 8 \cdot H^+ \rightarrow CH_4(g) + H_2O$ Methanogenesis	5.9	-.26

There are two main abiotic reduction reactions known that may be affecting the degradation of chlorinated ethenes to varying degrees, dihaloelimination and hydrogenolysis. Dihaloelimination refers to the simultaneous removal of two chorine molecules. During this process the chlorinated ethene will accept 2 electrons and an additional carbon-carbon bond will be formed. The reaction is shown in Figure 2.1, though the thermodynamics are not presented. This is because dihaloelimination

is not commonly observed in natural systems, though induced reducing groundwater conditions can lead to significant abiotic transformation through dihaloelimination (Elsner et al., 2008). Some dihaloelimination reactions that have been documented can occur under aerobic conditions, but hydrogenolysis reactions have only been observed under reducing conditions (Vogel, 1987).

Organic matter in the form of dissolved organic carbon (DOC) is relatively common in groundwater and soils. DOC is an important oxidant in groundwater environments and carbohydrate oxidation (shown in Table 2.2) is a reaction representing DOC oxidation. In highly reducing environments hydrogen oxidation may also act as an electron accepting process. In natural waters, these oxidation reactions are often coupled with the reduction one of the electron accepting processes common groundwater environments. The most important examples of this are reduction of oxygen (aerobic respiration), reduction of nitrogen (denitrification), Iron (III) reduction, and methanogenesis. However, the DOC or H_2 may also be oxidized through the reduction of chlorinated ethenes (Vogel et al., 1987).

During the reduction of TCE, DCE and VC a halogen molecule is separated from the chlorinated solvent and replaced with hydrogen molecule, releasing two electrons (the balanced reactions are shown in Table 2.2). The Gibbs free energy generated as a result of TCE degrading to DCE is approximately the same for all DCE isomers (not shown; Pankow and Cherry, 1996). When reductive dechlorination of chlorinated ethenes occurs abiotically, it is known as hydrogenolysis; however, microbes can potentially catalyze this reaction. Reductive dechlorination of chlorinated ethenes will proceed only if it is thermodynamically favorable, which requires that oxygen and nitrogen must first be removed from the subsurface environment. Though this reaction is probably the most important abiotic mechanism of degradation affecting natural attenuation at contaminated sites, degradation to environmentally acceptable products by abiotic means alone is not likely to be effective (at least on an acceptable time scale).

Determining whether potential reduction reactions are truly abiotic can be complex. For example, dissolved oxygen can be depleted much more rapidly by microbial respiration, resulting in the establishment of anaerobic conditions (Clark and Fritz, 1996) in which abiotic reductive dechlorination of TCE can be thermodynamically feasible. In addition to this, changing the redox conditions (by abiotic or biotic means) can substantially affect the types of microbes that are present in abundance in the subsurface. This could lead to a subsurface environment in which microbes that affect the rate of chlorinated ethene degradation thrive. Thus, some research suggests that microbial

activity at nearly all contaminated field sites is a vital part of the degradation of TCE and its daughter products (Wiedemeier et al., 1999). Redox data can, potentially, indicate which abiotic chemical reactions might be thermodynamically feasible as well as which microbial communities may thrive in a given set of field conditions.

2.1.3 Biologically Mediated Destructive Processes

It has been noted that the kinetic reaction rates of organics (such as carbohydrates) with common electron accepting processes under abiotic conditions are slow. Microbes that gain energy from electron accepting processes can be very important in catalyzing redox reactions in groundwater. In fact, microbes mediate nearly all oxidation of organic compound in groundwater (Clark and Fritz, 1996).

Though some early research indicated that microbial interaction did not affect TCE concentrations at contaminated field sites, more research has provided evidence that the process of reductive dechlorination catalyzed by microbes is quite common in anaerobic aquifers contaminated with chlorinated ethenes (Chapelle and Bradley, 2003). Some chlorinated ethenes may also be affected by oxidizing microbes. In addition to being involved with microbially mediated redox reactions in which microbes receive energy from redox processes, chlorinated ethenes have also been shown to be involved in cometabolic processes that may cause destructive removal (Vogel, 1987). Cometabolism can be defined as the destructive removal of a compound that does not encourage growth of a substrate as a result of reaction that does promote substrate growth. That is, another reaction that microbes draw energy is responsible for the degradation of the chlorinated ethene (Pankow and Cherry, 1996). Biological processes capable of degrading chlorinated ethenes can be divided into direct aerobic oxidation, direct anaerobic oxidation, aerobic cometabolism, anaerobic cometabolism, and direct anaerobic reduction (reductive dechlorination).

Oxidation of chlorinated ethenes by bacterial mediation may be significant in certain groundwater environments. When a microorganism uses chlorinated ethenes as an electron donor in a redox reaction it is known as growth promoting biological oxidation or direct oxidation (Wiedemeier et al., 1999). Oxidation reactions affecting chlorinated ethenes can occur in aerobic and anaerobic aquifers, though DCE and VC are more likely to undergo oxidation than PCE and TCE. In aerobic aquifers where oxygen (a strong reducing agent) is abundant oxidation of organic species including DCE and

VC may proceed relatively quickly. However, aerobic conditions are rarely maintained at organic contaminant sites where large quantities of electron donors are often released. Many plumes created as a result of organic contamination result in a reducing groundwater regime that is maintained for long periods of time (Wiedemeier et al., 1999). In anaerobic environments the direct oxidation of most chlorinated organic compounds has not been observed, though microbes that can use VC for direct anaerobic oxidation seems to be the exception to this (Bradley and Chappelle, 1996). Oxidation in anaerobic groundwater environments is not considered to be a dominant reaction affecting chlorinated ethene degradation, though some exceptions may occur.

Aerobic cometabolism is a process known to affect the degradation of TCE, VC, and DCE. However, as stated above, the plume created by many environment releases of organic contaminants ensures relatively reducing groundwater conditions. For this reason, and due to results presented in Chapter 5, Aerobic cometabolism is not discussed in detail in this report. Anaerobic cometabolism does not occur naturally and typically must be engineered (Wiedemeier et al., 1999).

Certain microbes are able to use chlorinated ethenes as electron accepting processes thus gaining energy and promoting growth of that microbe (Alvarez and Illman, 2006). This biologically mediated direct anaerobic degradation (reductive dechlorination) mechanism is known as halorespiration. During halorespiration chlorinated solvents, including chlorinated ethenes, are directly used as electron accepting processes. Complementing this process dissolved hydrogen often functions as an electron donor. This process has been identified at many natural field sites as being the dominant degradation mechanism for TCE and other chlorinated ethenes (Wiedemeier et al., 1999; Alvarez and Illman, 2006). However, DCE and VC tend to be less susceptible to halorespiration than PCE and TCE. During the halorespiration of chlorinated ethenes the degradation pathway proceeds from TCE to DCE to VC to ethene to ethane (as with abiotic hydrogenolysis). However, microbes tend to reductively dechlorinate TCE to cis-1,2-dichloroethelene rather than the other DCE isomers (1,1-DCE and trans-1,2-DCE; Wiedemeier et al., 1999).

In summary, there are a variety of abiotic and biologically mediated reactions that have been shown to degrade chlorinated ethenes in given conditions. However, many of these reactions only occur in a small variety of locations. Abiotic reactions that occur naturally are recognized as being too slow to significantly degrade chlorinated ethenes, but abiotic reductive dechlorination (and other abiotic reactions) can occur in groundwater. Direct aerobic oxidation and aerobic cometabolism only occur in oxidizing environments, which have been observed to be maintained at few contaminated sites.

TCE and its degradation products are generally unaffected by direct anaerobic oxidation, though it may degrade VC. Sites must be engineered in order for aerobic cometabolism to occur. Halorespiration (biologically mediated reductive dechlorination) has been shown to be a dominant reaction that degrades TCE, DCE and VC at many contaminated field sites, especially in reducing groundwater. The chemical reactions discussed can potentially occur in a subsurface aquifer contaminated with TCE, such as the Smithville site. However, in subsurface environments these reactions are not necessarily easy to identify and many methods have been developed to characterize whether degradation is occurring at contaminated sites and, if so, what degradation mechanisms are dominant.

2.1.4 Identifying Degradation

Over the past 20 years many methods have been used to track the transport and degradation of organic contaminants. As TCE is degraded it reacts to form chemical products whose production and transport are often monitored due to their toxicity and potential role in biogeochemical processes. In some cases mass balance and statistics-based approaches have been employed to track the distribution and transport of TCE. However, documented loss of contaminant mass, formation of degradation byproducts, and microcosm data are the most common chemical methods used as evidence for degradation (Illman and Alvarez, 2009).

Analysis and interpretation of chemical concentration data alone has been used to study transport and, potentially, track the chemical processes affecting some contaminants released into relatively homogeneous subsurface environments. Basic chemical characterization and mass balance approaches are some of the most common methods used to understand the geochemical processes affecting specific organic compounds at a given site (Meckenstock et al., 2004; Mackay et al., 1994). However, mass balance methods often require many wells to adequately track transport and verify degradation. Plumes of the more recalcitrant compounds are often characterized by a large area and long residence times. As a result of these facts, it can often be too costly and requires too much time to collect an adequate dataset to implement mass balance approaches for documenting loss of contaminant mass (Mackay et al., 1994; Alvarez and Illman, 2006). Statistical models that assess historical trends in plume characteristics have also been employed to understand the transport of TCE, including plume stability. However, statistical methods do not give significant insight into the specific biochemical processes affecting degradation of chlorinated ethenes (Ricker, 2008).

Determining the aqueous phase concentrations of chemicals resulting from TCE degradation can useful to verify the occurrence of degradation and, potentially, the chemical processes controlling its degradation. However, interpretation of well-by-well chemical data to determine degradation processes is a complicated task, especially in fractured bedrock environments. DCE, VC, ethene and ethane near contaminant source zones can indicate that reductive ethene species and ethane (either via abiotic dehydrogenation or halorespiration) is a causing destructive removal of TCE. It has been observed that significantly larger fractions of cDCE than the other two DCE isomers may also indicate halorespiration (Wiedemeier et al., 1999). Other analytes that have been proposed as potential chemicals that may help identify processes other than reductive dechlorination that may be affecting degradation. These include alcohols, propane, acetylene, chloroacetylene, di-chloroacetylene, CO_2, and acetic acid. Studying the redox conditions at a particular site, by testing for field E_h or determining the concentrations of the most important analytes commonly found to control redox conditions, can indicate the potential biological communities that may thrive at a given site. However, even with these analyses another potential problem with understanding degradation of chlorinated ethenes is that more than one reaction may be occurring at a given site or the effectiveness of a given mechanism of degradation may be different at different locations of a given field site. Still, knowledge of site-specific and well-specific chemical and electrochemical data can be very useful in determining the potential degradation mechanisms of degradation at a given site.

Various studies focusing on microbial communities have been used to determine the dominant reactions that affect the degradation of TCE and/or the particular microbial communities responsible for the degradation. In some cases DNA studies are employed to determine the exact microbes responsible for chlorinated ethene degradation; the details of this process are not discussed in detail in this thesis due to their current high cost to implement. Another method commonly used to determine whether degradation is occurring and, if so, the dominant degradation mechanisms at a given field site is to collect sediment and/or water samples from a given site and culture the microbial communities collected for laboratory microcosm studies. Experiments can then be done in the laboratory that may confirm the occurrence of TCE degradation, indicate the reactions affecting chlorinated ethene degradation in the field setting, and determine the rates of those reactions. In these experiments, insuring survival of microbial communities and controlling the population of these communities can be very difficult. Although microcosm studies have been useful in collecting data pertaining to biodegradation, they are limited and (due to the fact that interpolation from laboratory to field scale is complex) often cannot be used determine the degree of biodegradation or the mechanisms of

degradation at a given site. Methods based on characterizing the microbial community or experimenting with microcosms are not used in this study.

Employing numerical codes is another method that uses primarily chemical data to better characterize chemical processes and physical transport affecting chlorinated ethenes. Given the original mass distribution and a good understanding of the physical flow regime, such numerical codes can be useful tools (Basu et al., 2008). However, these models often require large amounts of data to calibrate and run, especially in more complex subsurface environments. In the case of insufficient data, such an exercise will not accurately model flow and transport of TCE and its degradation products. Furthermore, given the complex flow through fractured network systems further basic chemical characterization will most likely yield no conclusion as to the dominant chemical processes affecting the plume.

Determining whether degradation is occurring at a given site using only chemical methods can be complex, especially in a fractured aquifer. In addition to this, determining the dominant degradation reaction(s) can also be difficult. However, the more recently developed method of using isotopic analyses to identify degradation and determine the degradation mechanisms has been applied to many sites underlain by unconsolidated porous media. In some cases, isotopic analyses may also help to determine the degree of degradation TCE has undergone.

2.2 Isotopic Analyses

In recent years isotopic methods have been being further developed as a tool to better elucidate and understand the physical and chemical processes affecting TCE degradation, especially at complex field sites (Freedman and Gossett, 1989; Holliger et al., 1998; Bloom et al., 2000; Chapelle and Bradley, 2003; Meckenstock et al., 2004). Isotopic analyses have been employed as a method of determining the source of TCE and/or verifying the occurrence of degradation of TCE at a given contaminated field site. These isotopic methods, when combined with the chemical methods discussed above, have also led to promising advances in determining the mechanisms of degradation and the degree of mass removal (removal rate) of TCE and other chlorinated ethenes.

2.2.1 Background

Isotopic analysis identifies the isotopic signature of a compound by measuring the ratio of isotopes of one or more elements in a compound. The ratios generated can be used to better understand physical and chemical processes that those chemicals have undergone. Atoms are defined by the number of protons in their nucleus, which equals their atomic number and defines the characteristics of the element. Nuclides are defined as species of an atom characterized by the number of neutrons in the nucleus. A set of nuclides with an equal number of protons (i.e., the same element) but different numbers of neutrons are called isotopes of the element. Many elements have multiple isotopes that are stable and abundant in nature. Unstable isotopes, or radioactive nuclides, are also found in nature but tend to be much less abundant due to their radioactive decay. For example, chlorine has many unstable isotopes, but two stable isotopes: ^{37}Cl (which has a terrestrial abundance of 24.23%) and the more common ^{35}Cl (which makes up 75.77% of terrestrial chlorine) (Clark and Fritz, 1997). Stable environmental isotopes are often measured as the ratio of the two most abundant isotopes of a given element. These ratios are usually expressed as the ratio of the heavier to lighter isotope. The ratio, R, for the elements used in this study are R = $^{13}C/^{12}C$ (for carbon) and R = $^{37}Cl/^{35}Cl$ (for chlorine).

Variations in stable isotope concentrations are measured by gas source mass spectrometry in comparison to a known standard (Clark and Fritz, 1997). Standards are either absolute references used by laboratories all over the world, or internal laboratory standards. Due to this convention, isotopic data is usually presented as isotopic mass ratios expressed with the commonly used delta notation, measured relative to a standard as follows:

$$\delta^{13}C_{sample} = \left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{reference}} - 1 \right) \cdot 1000 \; \permil \; VPDB \qquad \textbf{(Equation 1)}$$

$$\delta^{37}Cl_{sample} = \left(\frac{(^{37}C/^{35}C)_{sample}}{(^{37}C/^{35}C)_{reference}} - 1 \right) \cdot 1000 \; \permil \; SMOC \qquad \textbf{(Equation 2)}$$

, where δ indicates a relative mass ratio. The subscript "sample" denotes the isotopic ratio of the sample that was analyzed. The reference ratios, $(^{13}C/^{12}C)_{reference}$ for carbon and $(^{37}Cl/^{35}Cl)_{reference}$ for

chlorine refer to the standard used to compare relative isotopic ratios. The absolute reference standard VPDB (Vienna Pee Dee Belemnite) is the reference standard for carbon isotopes, and SMOC (Standard Mean Ocean Chloride) is the reference standard for chlorine isotopes (Kaufmann et al., 1984).

Fractionation is occurs as a result of any process in which, for a reservoir of a given compound, different mass isotopes are removed or added at different rates. The change in total mass of the reservoir also imparts change in the isotopic ratio (or δ value). Isotopic fractionation can be triggered by chemical reactions or physical processes and imparts a change in the isotopic signature of both the product and reactant chemicals. In nature it has been found that significant fractionation occurs in many of the chemical reactions that are mediated by microbes (Clark and Fritz, 1997). Any thermodynamic reaction in which there are differences in the rates of reaction for different molecular species (isotopes), results in the formation of unequaled concentrations of isotopes in the product and a corresponding removal of concentration of isotopes from the reactant. Thus, the degree of fractionation imparted upon reactants and products is commonly expressed as the fractionation factor, α, which is defined as follows:

$$\alpha_{r\text{-}p} = R_{reactant}/R_{product} \qquad \textbf{(Equation 3)}$$

,where R refers to the ratio of heavier to lighter isotopes. The fractionation factors associated with various processes have been determined for many commonly occurring natural elements. The values for α that are commonly observed in nature are often relatively close to unity, meaning that very little fractionation occurs as a result of many processes. Therefore, the degree of fractionation corresponding to a particular reaction is often expressed as an enrichment factor, ε, which can be calculated as follows:

$$\varepsilon_{r\text{-}p} = (\alpha_{r\text{-}p} - 1) \cdot 1000 \qquad \textbf{(Equation 4)}$$

Many reactions that cause isotopic fractionation in groundwater contaminants have been found to have an exponential enrichment (of the heavier species) or depletion in the reactant reservoir as that reactant it is converted to a new product. The reactions that fit this trend can be modeled using the

Rayleigh equation (eq. 5a). Equation 5b shows the Rayleigh fractionation of TCE expressed in delta notation for carbon isotopic analysis. Using eq. 5b, the enrichment factor (ε_{r-p}) can be calculated for a variety of processes that fractionate carbon isotopes (or other isotopes). The fractionation factors observed in the field are often similar for similar chemical processes; therefore, tracking the processes degrading contaminants using the Rayleigh equation may be possible.

$$R = R_o \cdot f^{\,(\alpha-1)} = R_o \cdot f^{\,(\varepsilon/1000)} \qquad\qquad \textbf{(Equation 5a)}$$

$$\ln(\delta^{13}C + 1000) = \ln(\delta^{13}C_o + 1000) \cdot (\varepsilon/1000) \cdot (\ln f) \qquad \textbf{(Equation 5b)}$$

2.2.2 Application of Isotope Geochemistry

The isotopic signature of a given compound from different sources (such as different manufacturers) is often quite variable. This has made isotopic analyses a useful method of fingerprinting the source of a contaminant and or chemicals released to the natural environment. Therefore, isotopic analyses have often been employed in determining the source or sources of organic compounds, such as TCE.

Once released to the environment organic compounds often are affected by destructive or non-destructive removal, imparting isotopic fractionation upon products and reactants. Observations of significant isotopic change have been employed as a method of verifying the occurrence of degradation of TCE at a given contaminated field site. For example, in the biodegradation of organics, microbes preferentially consume compounds containing lighter molecules (those with less neutrons), as it requires less energy to break those bonds. This imparts a greater rate of reaction to reactants containing lighter isotopes, inducing isotopic fractionation. Under the assumption of Rayleigh distillation, the fractionation factor estimated for these reactions have been shown to be characteristic of specific processes (Meckenstock et al., 2004). Therefore, determining fractionation factor for individual elements at a given field site may lead to discovering the dominant process affecting degradation, though results have often been shown to be ambiguous. Abiotic processes have shown especially variable trends in fractionation, though less isotopic data is available (Elsner et

al., 2008). Table 2.3 presents the enrichment factors, both carbon and chlorine, associated with the removal of TCE via reductive dechlorination by different bacteria.

Table 2.3. Carbon and chlorine fractionation factors associated with commonly observed degradation processes.

Compound	ε_{Carbon}	$\varepsilon_{Chlorine}$	redox conditions	process	Bacteria/Culture	Reference
TCE		-5.5	sulfate reducing	reductive dechlorination	Strain T	Numata et al., 2002
TCE		-5.6	anoxic	reductive dechlorination	Consortium N	Numata et al., 2002
TCE		-5.7	anoxic	reductive dechlorination	Consortium F, nitrate reducing	Numata et al., 2002
TCE		-30	anoxic	reductive dechlorination	Strain T, consortium N, consortium F	Numata et al., 2002
TCE	-6.6		methanogenic	reductive dechlorination	Enrichment culture KB-1	Bloom et al., 2000
TCE	-7.1		anoxic	reductive dechlorination	Mixed facultative anaerobic culture	Lollar et al., 1999
TCE	-13.8		anoxic	reductive dechlorination	Consortium (MeOH)	Slater et al., 2001
TCE	-3.3		anoxic	reductive dechlorination	Dehalobacter restrictus strain PER-K23	Lee et al., 2007
TCE	-16.4		sulfate reducing	reductive dechlorination	Sulfurospirillum multivorans	Lee et al., 2007

Determining the mass ratio of different elements within a compound (such as oxygen and nitrogen of nitrate) can also indicate the mechanisms affecting mass removal. This method has proven useful in quantifying the relative contribution of two pathways of (bio)chemical reactions or to isolate a single mechanism that may not be easy to detect (Abe et al., 2009). The dual-isotope approach is well established for determining the origin and fate of inorganic compounds. This method is often referred to as the two-dimensional isotope approach when it is applied to organic compounds. Graphs showing one isotopic ratio relative to another are sometimes referred to as delta-delta plots. During the last 10 years, the dual isotope method has been applied to the characterization of field sites with a variety of contaminants including aromatic hydrocarbons (such as MTBE) and chlorinated solvents (such as TCE) (Chapelle and Bradley, 2003; Meckenstock et al., 2004). This method is quite promising in determining whether degradation is occurring and the dominant mechanism(s) of degradation, especially in relatively homogeneous aquifers. By measuring the isotope ratios of two elements in a compound simultaneously a unique correlation will be observed, influenced by the different fractionation rates of each isotope affected by the same reaction mechanism (Abe et al., 2009). This correlation is presumed to be independent of chemical concentrations and has been used to study isotopic fractionation associated with many chemical and physical processes. An average slope of for values plotted in a delta-delta plot is also a function of the fractionation factors (α values) for the isotopes being analyzed. In a graph of $\delta^{37}Cl$ vs $\delta^{13}C$ for TCE samples with varying degrees of degradation, the slope is equal to the ratio of enrichment factors or ($\varepsilon_{Cl} / \varepsilon_C$) (Abe et al., 2009). In

some cases, by observing the magnitude of the fractionation along with the slope of the delta-delta plot, it is possible to better understand what processes are affecting the destructive removal of organic compounds including chlorinated ethenes.

Measuring the isotopic mass ratios of multiple compounds involved in degradation reactions (compound-specific isotopic analysis) has also been applied to a variety of degradation reactions. Compound-specific isotopic analyses are often used to track the continued degradation of daughter products formed (Meckenstock et al., 2004). When it comes to identifying specific reaction the results can be ambiguous depending on the natural site conditions and the rates of chemical reaction. However, these isotopic analyses do offer another line of evidence to help determine the process or processes controlling chlorinated ethenes degradation at a given field site.

Though isotopic methods are very promising, they can also be misleading. A problem with applying methods studying Rayleigh-type degradation is that it assumes the reactant reservoir is finite, well mixed and that chemical reactions proceed in a forward direction only (products of degradation do not re-react with the reaction products). A plot of changes in a compound-specific isotope ratio vs changes in compound concentration can also be used to generate a fractionation factor for that compound. For a given chemical and redox condition, compounds may be degraded by different mechanisms, leading to different ratios of isotope fractionation. If a single reaction mechanism is removing chlorinated ethenes the slope of the delta-delta plot can help to determine the process, but multiple processes must be considered individually. Observed isotopic fractionation of compounds at a contaminated field site would reflect the combined effect of the fractionation caused by multiple pathways (Abe et al., 2009).

In addition to fractionation by the degradation mechanisms discussed above, non-destructive processes also may affect the isotopic mass ratio of TCE and its degradation products. For example, sorption may be affecting the natural attenuation and removal of TCE and its associated degradation products. Multiple reports have characterized the degree of fractionation that occurs as a result of sorption. Slater et al., 2000 studied the isotopic fractionation of carbon in TCE and other organic contaminants during sorption. It was found that sorption doesn't significantly fractionate the carbon isotope of TCE, at least when compared to the analytical accuracy of isotopic analysis and the fractionation associated with other commonly observed chemical processes.

Additional analyses of isotopic fractionation associated with aqueous TCE sorption to different materials were conducted in conjunction with this project (Stotler et al., 2011). The degree of

isotopic fractionation during sorption to two commonly studied materials (sand from the Canadian Forces Military base in Bordon, Ontario, and activated carbon) was determined. The amount of chlorine isotopic fractionation associated with TCE sorption to Borden sand and activated carbon are shown in Figure 2.2 (A and B). The results of this laboratory study show that Borden sand caused a small but measurable fractionation of the stable chlorine isotope (ε_{Cl} = -0.074); whereas, activated carbon imparts a larger degree of fractionation (ε_{Cl} = -0.1). The study found that fractionation of carbon isotopes of TCE was negligible (results not shown), in accordance with Slater et al. (2000). Based on these results on the fractionation of TCE associated with sorption, this process is not expected to be significant at contaminated sites. In most cases the variation of in isotopic ratios imparted by sorption will be below the limits of accuracy for measurement.
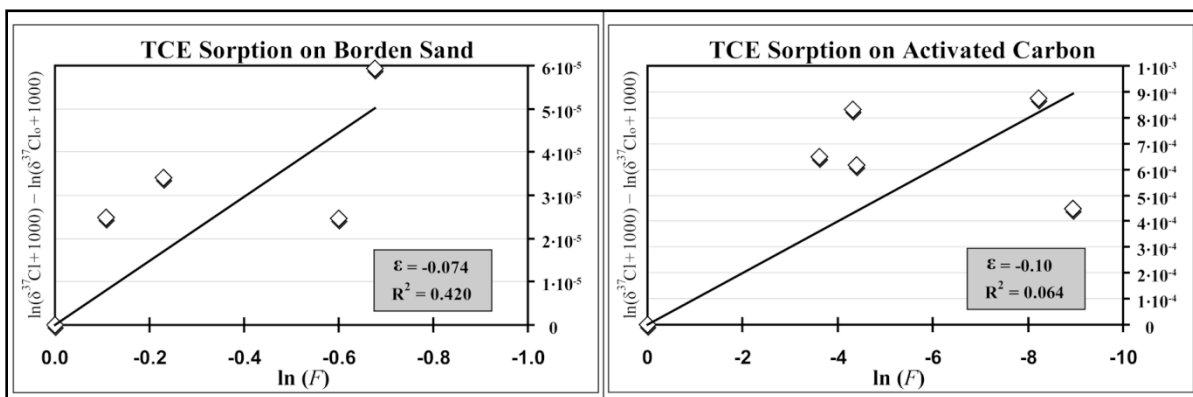
**Figure 2.2. A & B. Chlorine isotope fractionation for TCE sorption
to Borden sand and activated carbon (Stotler et al., 2011).**

Volatilization is a non-destructive removal mechanism for that may affect chlorinated ethenes released to subsurface environments. The isotopic fractionation of TCE associated with volatilization has been scrutinized in other studies. Huang et al. (1999) showed that there is detectable carbon and chlorine isotopic fractionation associated with pure phase evaporation. The chlorine isotopic enrichment factor, ε_{Cl}, calculated for TCE evaporation was +1.82 ‰. This means that as evaporation of TCE occurs the remaining mass is enriched in heavier chlorine isotopes (^{37}Cl) as molecules with lighter isotopes evaporate (^{35}Cl), increasing the δ^{37}Cl value of the mass. The fractionation of chlorine isotopes imparted by the process of evaporation is relatively small when compared to the isotopic fractionation associated with abiological and biological degradation processes. The enrichment

factor, ε_C, for carbon isotopes was reported as -0.31 ‰, indicating an enrichment of the heavier carbon-13 isotope in the remaining TCE reservoir. It is also noteworthy that the enrichment factor for chlorine was in the opposite direction than for carbon.

Poulson and Drever (1999) studied the fractionation of carbon, chlorine and hydrogen isotopes in TCE during volatilization from the aqueous (dissolved) phase at various temperatures. The study found a chlorine enrichment, ε_{Cl}, factor of +1.64 ‰ and a carbon enrichment factor, ε_C, of -0.35 ‰. Results from both studies indicate that as TCE vaporizes the remaining TCE mass increases in $\delta^{13}C$, but the degree of fractionation is very small for carbon isotopes. The fractionation of chlorine in TCE imparted on the reservoir will decrease the isotopic ratio. Both studies also found a larger degree of chlorine isotopic fractionation than carbon isotopic fractionation, however the enrichment factor is still relatively small when compared with fractionation due to degradation. Furthermore, the degree of fractionation for a given reservoir depends on the amount of volatilization which may vary heavily from site to site, but is often less than the mass removal by other processes.

In most cases non-destructive processes do not significantly impact isotopic ratios at a natural field sites. However, degradation by abiotic or biologically mediated processes can significantly alter the isotopic ratio observed in a laboratory or field environment. Due to the variability in isotopic ratios potentially imparted by the processes discussed above, applying isotopic methods to even relatively homogeneous aquifers can be difficult. Therefore, it is often useful to use other methods to narrow down the potential reactions affecting degradation (e.g., characterizing redox conditions may narrow down the potential microbial populations that thrive in a given subsurface environment). Given that different processes fractionate chlorine and carbon isotopes to varying degrees, it may be possible to conclusively verify certain processes that dominantly affect degradation of chlorinated ethenes at the Smithville site. This depends on using available data in the literature on carbon and chlorine isotope fractionation during degradation of TCE (or subsequent degradation products) and comparing that information to delta-delta plots generated from samples collected at the site, then considering all of this in light of site specific chemical conditions.

Chapter 3:
Site Description

Investigations into the potential applicability of isotopic analyses to better understand geochemical evolution of TCE in fractured networks were conducted at a field site previously contaminated by a large spill of DNAPLs along with various other chemicals. The contaminated area, located in Smithville, Ontario, is relatively well characterized and is currently undergoing remediation. To facilitate sampling of rock properties and to monitor contaminants many observation wells have been drilled, and a pump-and-treat system have been installed to control offsite migration of (Golder Associates, 1994).

Consistent quarterly geochemical sampling of polychlorinated biphenyls (PCBs) and other volatile organic compounds (VOCs) at the Smithville site has been conducted since 1987. Data collected through 2001 has been synthesized in several reports (Feenstra, 1989; Golder Associates, 1994, 1999; Slough et al., 1997). Extensive geochemical sampling has been ongoing since 2001, but these results have not been synthesized to date.

In this section a characterization, depending on previously reported data and newly gathered data, of the Smithville site is presented. A basic understanding of the underlying geology, a discussion of the physical properties of aquifer materials, as well as, an analysis of historical trends in physical and chemical data are described.

3.1 Site History

Smithville is a small town located in the Township of West Lincoln which is in the Regional Municipality of Niagara, Ontario. Smithville is about 40 kilometers southeast of Hamilton, Ontario. Figure 3.1 indicates the contaminant source zone (in red), the location of wells sampled for chemical analyses (wells with names labeled are central to the chemical characterization of the site), and the estimated local groundwater flow direction (in green). This axes on the local site map shown have units of meters and are relative to the location of a recovery well in the vicinity of the source zone, R1. The field site is a former industrial complex at the northeastern part of Smithville, but was contaminated by a DNAPL spill and subsequently shut down. The nearest industrial complex is a dry

cleaning facility approximately 50 meters to the west, and the downtown center of Smithville is located approximately one kilometer to the southwest.

The site was operated between 1978 and 1983 as a hazardous waste transfer and storage station by a company called Canadian Waste Management Limited (CWML). After the site was filled to capacity in 1983 the site was maintained as a storage facility while the company deliberated on how to deal with the accumulated waste. In 1980 the Ministry of the Environment (MOE) of Ontario installed five test wells to the north and south of the CWML compound to monitor the site. Soil and water samples collected from these wells did not contain detectable levels of PCBs or other organic contaminants. However, in July of 1985 local environmentalists discovered that PCB was contaminating a shallow lagoon at the site. This soon became the focus of much attention from the media and the public, as it was suspected that DNAPL had been released to the local groundwater. In August of 1985 the Ontario MOE tested water and soil in the area and found detectable levels of PCBs in both on-site and off-site samples. At this time the MOE also tested municipal water supply wells in Smithville and found no detectable PCBs. Later that year the Ontario MOE assumed control of the site and began to implement a program for decommission and remediation of the site (Golder Associates, 1999).
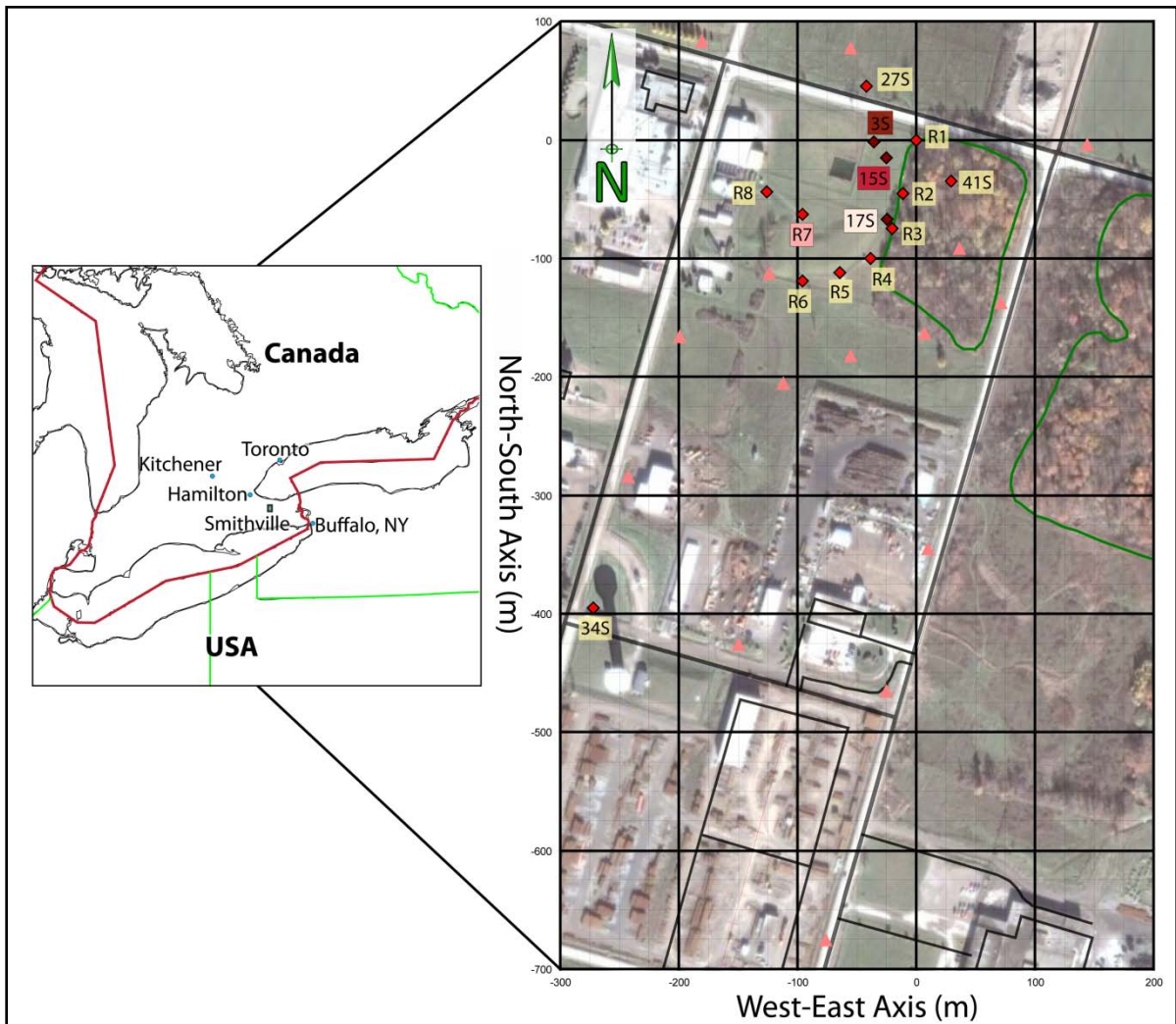
**Figure 3.1. Map of the site in Smithville Ontario, location
denoted by dot in Ontario Regional Map (Google Earth, 2010).**

At the end of CWML operations it was approximated that the Smithville site had stored
approximately 434,000 liters of liquid wastes. This waste was comprised of an estimated 266,000
liters (about 60% of the total volume) of waste from polychlorinated biphenyls (PCBs), 57,000 liters
(about 13% of the total volume) of other organic chlorinated solvents, as well as acids, alkalis, and
inorganic waste sludge (Golder Associates, 1999). It has been estimated that 30,000 - 40,000 liters of
poorly characterized NAPLs were released into the fractured bedrock aquifer underlying Smithville.
The original mass of TCE was released as a DNAPL to the surface and has been percolating through
fractures in surface soils and the Eramosa Member where much of it has now reached the saturated

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zone. However, due to the fact that much overburden layer source zone of the Smithville site has been excavated to the top of the bedrock,this study focuses on the saturated groundwater zone. Field sampling, which began in 1987, has indicated that the most abundant organic contaminants at the site are PCB, TCE, and TCA. Therefore, identifying whether some degradation reactions that commonly affect TCE occur at the Smithville site is also made more complex due to the fact that many other organic contaminants were spilled at the site. Thus, some of the compounds that can be used to verify degradation processes that affect TCE (and its degradadataion products) are occurring were released to at the site or may be created as a result of the degradation of these contaminants. This project focuses on the distribution, transport and degradation of TCE and its degradation products released from the Smithville site.

The exact mass, composition, date and location of contaminant releases at the Smithville site before 1985 are not known. Therefore, TCE and its degradation products may have been affected by the process of vaporization (evaporation from pure phase or volatilization from aqueous phase) during release into the subsurface. However, the surface location of the vast majority of released contaminants has been identified; this is shown as the source zone in Figure 3.1. A report by Slough and others (1997) deduced that fractures and macropores within the overburden allowed for downward migration of DNAPLs released at the ground surface. It has been estimated that 30,000 - 40,000 liters of a poorly characterized mix of NAPLs were released to the bedrock aquifer (Golder Associates, 1999).

Early chemical data collected in 1987 from a well near the source zone, Well 13 (not shown on map), gives an indication of the original chemical composition of contaminants released to the groundwater environment. This is the data, presented in Table 3.1, is the oldest reliable data collected from subsurface groundwater samples at the site and serves as a potential base-case for the concentration of chemicals in the subsurface. Well 13 is located approximately 10 meters away from the suspected source zone, with map coordinates of (2.54, -6.58). As can be seen, the TCE concentration was quite high with smaller concentrations of PCE and 1,1-DCE. The cDCE concentrations were not tested for until much later. VC was also tested for, but was not found in great abundance (i.e., the chemical concentrations were below analytical limits) (Golder Associates, 1999).

Table 3.1. Chemical data from Well 13, collected on August 9, 1987.

Compound	Well 13, Top	Well 13, Bottom	MDL
-	concentration (µg/L)	concentration (µg/L)	concentration (µg/L)
PCE	3.2	1.4	2.0
TCE	1600	1300	2.0
trans-1,2-DCE	3.2	ND	2.0
1,1-DCE	20	27	5.0
Vinyl Chloride	ND	ND	10

The Smithville site strategy was divided into a four phase decommission and remediation project. The Phase 1 achievements involved the immediate action needed to secure the site from further loss, leakage, or escape of organic contaminants from the CWML property (Proctor and Redfern Group, 1989). Phase 2 objectives included constructing on-site secure storage facilities to transfer the accessible contaminants into storage. During Phase 3, which lasted from 1986 to 1993, actions were taken to excavate topsoil layers, removing contaminated surficial materials. At this time all accumulated waste from the cleanup was incinerated. Furthermore, much effort was expended to determine the nature and extent of the DNAPL contamination at the site. The first three phases of the remediation program successfully destroyed the DNAPL waste stored on-site and took steps to remediate the surface of the site; however, a significant quantity of PCB and other contaminants remained in the ground beneath the site and down gradient of the site. Phase 4 actions, which are still ongoing, include monitoring and remediating the contaminants in the bedrock beneath the former CWML site, as well as, tracking contaminants originating from the site (Golder Associates, 1999).

For characterization of the site, over 50 observation wells and 8 production wells (R1-R8) were installed in the local area between 1985 and 1990. As part of the cleanup operations the 8 production wells (R1-R8) were connected to a series of groundwater pumps and a treatment system, this pump-and-treat system is still in operation. These production wells influences the local groundwater flow regime and remove contaminants from the subsurface environment. Figure B 10 (in Appendix B) presents pertinent well construction data for 14 of the wells in the proximity of the suspected source zone, information from these wells is emphasized throughout this thesis.

Samples collected from the site were tested for many organic and inorganic contaminants. Groundwater samples analyzed uncovered large quantities of DNAPL as well as high dissolved phase concentrations. Out of the organic contaminants that were sampled for at the Smithville site the most abundant in the recent past are PCBs, trichloroethylene, dichloroethylene (DCE), benzene, vinyl

chloride (VC) and trichloroethane (TCA). Natural attenuation, monitoring of local wells and controlled pump-and-treatment have been the main strategies for the long term control and remediation of the contaminant site.

3.2 Topography & Geology

The upper soil layer at the Smithville site is topographically a flat-lying glaciolacustrine clay plain. This glacial till covers the bedrock in the local area and over much of the Niagara Peninsula in Southern Ontario (Willis et al., 1992; Johnson et al., 1992). This clay overburden varies in thickness from 4 to 11 m in the vicinity of the site. However, during remediation large quantities of this clay layer was excavated and removed from the site (especially in the source zone). A more permeable sandy soil was used to replace the soil removed from the site.

The local geological characterization of the site is quite complete due to wells drilled on site to determine the extent of the plume as well as to study the geology and hydrogeology. For this study, the maximum depth of interest is only about 50 meters because the chemical plume created by contaminants released at Smithville is considered to be isolated from lower layers by multiple locally confining units (Golder Associates, 1999). The hydrogeology of the geological layers is further discussed in section 3.3. The units encountered in the shallow subsurface were first deposited in the middle of the Silurian Period (approximately 420 to 450 million years ago). This period in the geological history of the area was marked by extensive carbonate deposition and some clastic sedimentation (Johnson et al., 1992). The units of interest in the shallow subsurface are the Lockport Formation, the Decew Formation and the Rochester Formation. The fraction of organic carbon (f_{OC}) in the rocks underlying Smithville site is 0.041 % (Golder Associates, 1999). This value is relatively small compared to many other contaminated field sites.

The uppermost bedrock layer is the Lockport Formation. Locally, the Lockport Formation dips at about 0.5% to the South. This geological unit can be divided into 4 members; these members, in ascending order, are the Eramosa Member, the Vinemount Member, the Goat Island Member, and the Gasport Member.

The top member of the Lockport Formation, the Eramosa Member is a dolostone that has been characterized as fine-crystalline, bituminous, and argillaceous. The bedding in this layer is thin to

medium (Telford, 1978; Johnson et al., 1992). This layer contains many cracks and is weathered (Golder Associates, 1999). The Eramosa Member is 11-15 meters thick in the local area. The contact between the Eramosa Member and the underlying Vinemount Member is gradational.

The next unit, the Vinemount Member, is often included as part of the Goat Island Member, but in parts of southern Ontario it is quite distinct from the Eramosa Member (Telford, 1978). The Vinemount Member has been divided into a distinct Upper Vinemount Member and Lower Vinemount Member in local well logs (Golder Associates, 1999). The Upper Vinemount Member is a shaly dolostone that is highly weathered. The Upper Vinemount Member is 4-6 meters thick in the local area. The Lower Vinemount Member is also a shaly dolostone, but it is not as weathered and is tightly bedded (Telford, 1978; Johnson et al., 1992). The Lower Vinemount Member is 3-5 meters thick in the local area.

The layer directly underlying Lower Vinemount Member is the Goat Island Member. The Goat Island Member is a dark to light grey, and crystalline (very fine to micro crystalline) dolostone (Telford, 1978). The Goat Island Member tends to be mineralized with calcite, selenite, sphalerite, galena, and pyrite (Golder Associates, 1999). The layer is 6-8 meters thick and the bedding of this layer is thick and irregular. The contact between this layer and the Gasport Member is gradational to sharp and drawn primarily at the change from the finer grained dolostone to the fossiliferous and coarsely crystalline Gasport Member (Johnson et al., 1992).

The Gasport Member is light grey, generally coarse-grained, dolomitic limestone. This layer is also argillaceous and is massively bedded with discontinuous shale patterns and stylotites (Bolton, 1964; Johnson et al., 1992). The Gasport Member contains many fossils with remains of reef-like development and crinoids (Kilgour and Liberty, 1981). The Gasport Member is 8-11 meters thick in the local area. The lower contact is sharp with the Decew Formation (Bolton, 1964).

The Decew Formation is a very fine-crystalline dolostone that tends to be dark grey in color. Some geologists have considered this to be basal Lockport Formation (Kilgour and Liberty, 1981). This layer is argillaceous and contains some sandstone as well as shale (especially towards the base of the Lockport Formation). This unit is sparsely fossiliferous and has thin to medium bedding. The Decew Formation is less than 2 meters thick in the local area. The lower contact with the Rochester Formation is gradational in the local area (Kilgour and Liberty, 1981; Johnson et al., 1992).

Underlying the Decew Formation, a tight shale sequence, approximately 17 m thick, known as the Rochester Formation, exists. This layer is a dark grey to black, calcareous shale and siltstone with abundant carbonate interbeds (Johnson et al., 1992). The layer contains many fossils including brachiopods, corals and trilobites with signs of bioturbation during formation. The layers have been described as having parallel cut-and-fill structures with cross-lamination. The upper part of the Rochester Formation is known as the Burleigh Hill sub unit. This upper unit of this layer is moderately fossiliferous, blue-grey, calcareous shale with calcisiltite interbeds (Johnson et al., 1992).

Figure 3.2 shows the local Smithville site in a bit more detail, with the location of two cross sections denoted by two purple lines (South-North and West-East). On this map, as with the previous map, the axes shown have units of meters and are relative to the location of RWS1 (also referred to as R1). To prepare the cross sections, local site data has been collected from the approximately 60 wells. Using this data each layer was kriged individually and cross sections were defined. This was completed using Viewlog, a well log analysis program. Figure 3.3 is a cross section which is approximately North-South in orientation. Figure 3.4 is a cross section which is approximately West-East in orientation. These two cross section locations were selected to be in the approximate direction of groundwater flow (South-North) and approximately perpendicular to the direction of groundwater flow (West-East).
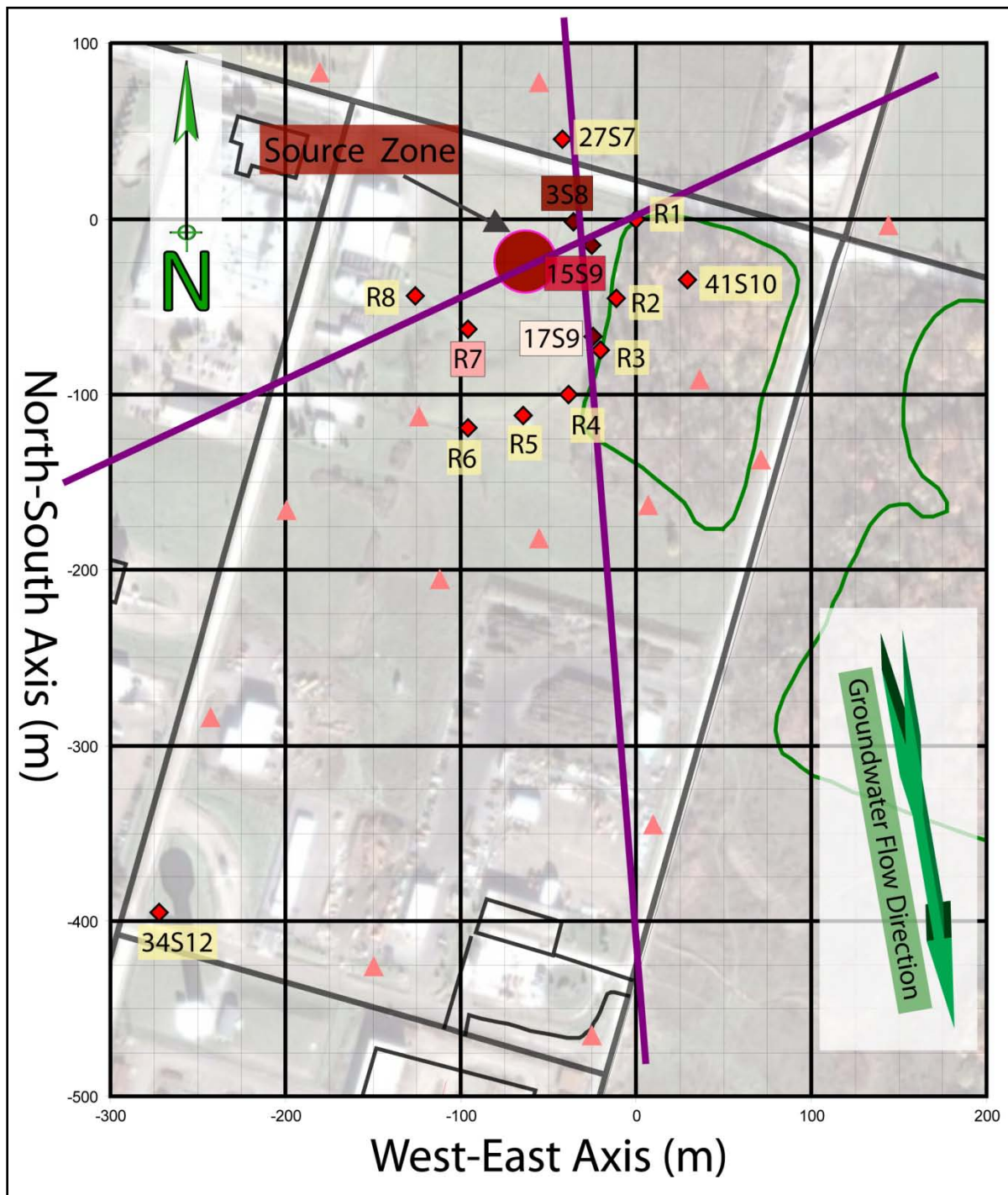
Figure 3.2. Local site map with cross section locations (indicated by purple lines). Contaminant source zone is shown in red and the estimated local groundwater flow direction is indicated by green arrow. Diamonds and triangles denote shallow wells sampled for chemical analyses.
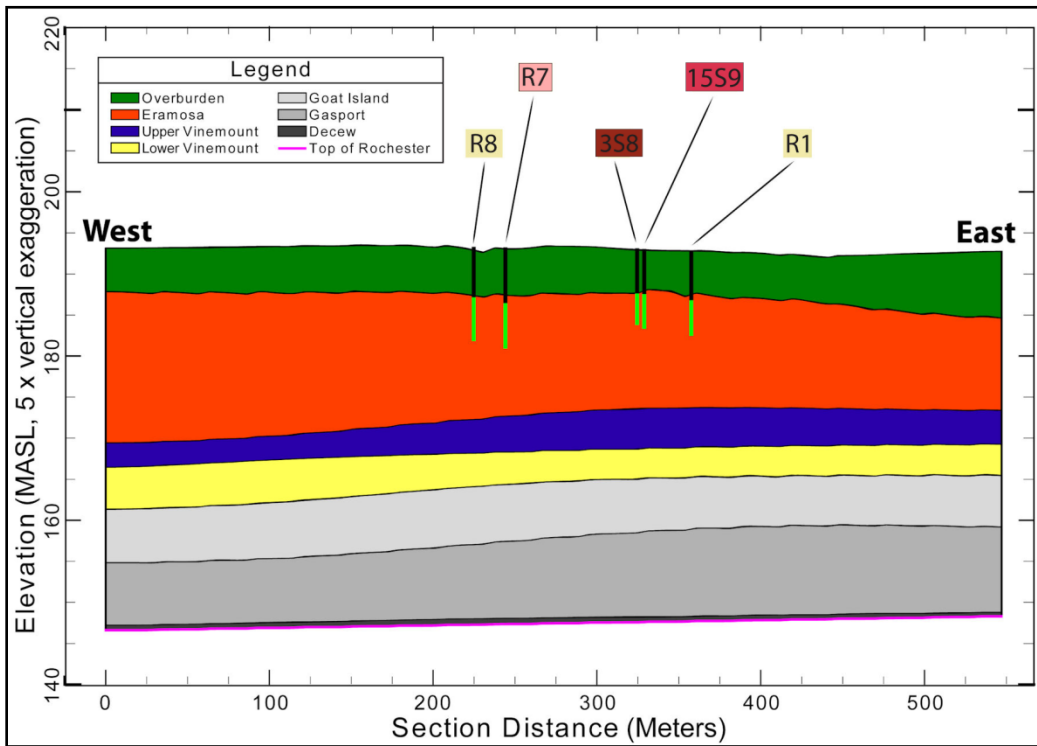
Figure 3.3. North-South cross section view of the Smithville site. A vertical exaggeration of 5 was used. The locations of 7 wells that are central to this study are indicated.
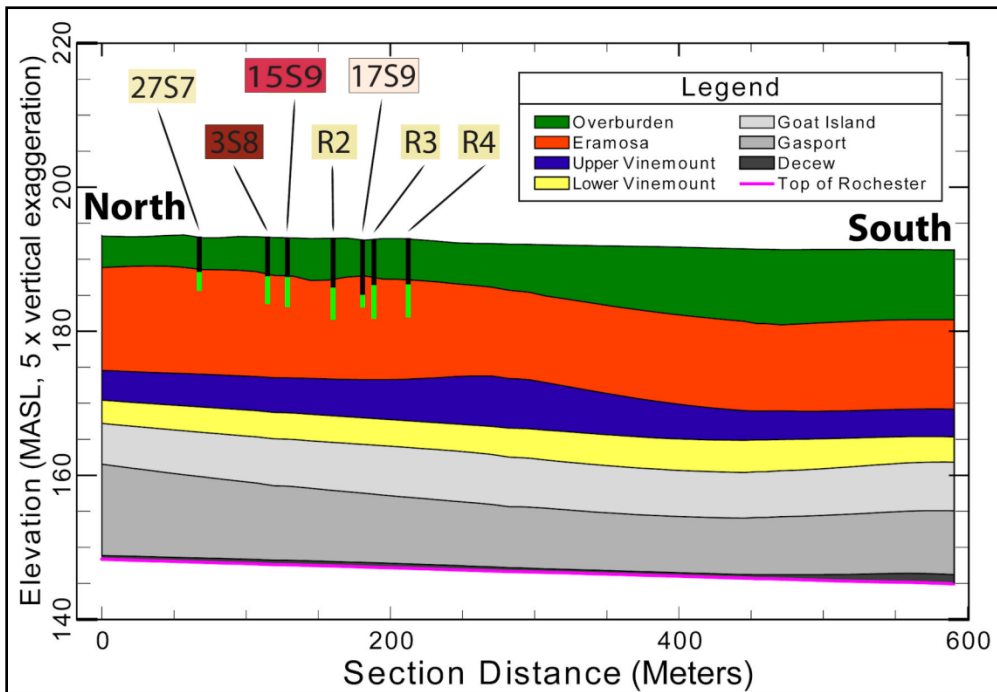
Figure 3.4. West-East cross section view of the local site map. A vertical exaggeration of 5 was used. The locations of 5 wells that are central to this study are indicated.

3.3 Hydrogeology

This study focuses primarily on the chemical characterization of chlorinated organic contaminants released from the Smithville site. However, contaminants released to the groundwater table will be transported through the underlying fracture network. Therefore, to study the geochemistry of a contaminated filed site it is important to understand the hydrogeology of the site. The hydraulic properties of the overburden and geological units underlying the Smithville site are presented in some detail in previous studies (Willis et al., 1992; Lapcevik et al., 1997). During site characterization and previous studies much data was collected. Some of this information is presented to show the potential for contaminant transport in the local groundwater environment. This includes the fracture density, hydraulic conductivity and water levels for select wells. Neither physical data pertaining to the mass of contaminated water removed by the pump-and-treat system, nor, the results of chemical monitoring have been the focus of research since September of 2000.

3.3.1 Flow Through Geologic Media

The conceptual model employed at this site is dependent on a good understanding of the fractured network underlying the Smithville site. Therefore, available data was synthesized to characterize the groundwater flow through each layer. Analysis of the potential for physical transport of water and other fluids through the porous geologic media is primarily based on two reports, one studying fracture density and another in which hydraulic tests were conducted to estimate hydraulic conductivity.

   To study the hydrogeology of the area cores were collected and photographed for fifteen of the wells drilled at the Smithville site. The frequency, size and orientation of fractures in the geologic material removed from the Lockport Formation were recorded. These fractures were classified as bedding plane fractures (relatively horizontal cracks), vertical fractures, or broken-core zones (Lapcevik et al., 1997). Also during site characterization constant-head hydraulic tests were conducted for 23 wells (Golder Associates, 1994). For these wells test intervals of 2 meters were isolated using pneumatic packers. For 6 wells additional tests with .5 meter test intervals were conducted. Transmissivity measurements ranging from approximately 10^{-2} to 10^{-10} m^2/s can be measured using this system. Transmissivity and hydraulic conductivity were estimated for given packer test intervals. A detailed geophysical analysis of the fractured bedrock underlying the site,

including geostatisical analysis, is presented in Lapcevik et al. (1997). Table 3.2 presents the results of packer tests in a simple manner, grouped by geological layer.

Table 3.2. Hydraulic conductivity for various layers using synthesized Smithville data (Lapcevik et al., 1997).

Hydraulic Conductivity of Smithville Wells			
23 Wells, 1597 Tests			
Geological Unit	Tests	Geometric Mean K (M/s)	Average ln K (m/s)
Eramosa Mb	70	2.14E-06	-13.05
Upper Vinemount Mb	15	8.71E-07	-13.95
Lower Vinemount Mb	295	1.10E-08	-18.33
Goat Island Mb	227	8.06E-08	-16.33
Gasport Mb	148	1.21E-06	-13.62
Decew Fm	173	9.66E-08	-16.15
Rochester Fm	676	2.73E-09	-19.72

The Smithville site has an overburden layer that is made up primarily of clay material, thus surface water is generally considered to be poorly connected to the groundwater table. However, significant fracturing throughout its entire length made it possible for fluids to penetrate this layer and migrate to lower layers (Slough et al., 1997). Furthermore, the emplacement of a more permeable soil in some areas of the site may have had an effect on the recharge rate of water. This study focuses primarily on the bedrock material and contamination below the overburden due to the fact that much of the overburden and surface material has been remediated.

Underlying the overburden is a series of sedimentary carbonate rocks layers. The geological units contain various cracks, fractures, and vugs that permit groundwater flow. The physical flow of water through this complex fractured network allows for contaminants to be transported along with the groundwater and aqueous mixing of contaminants to occur. This section provides a context for the chemical hydrogeology presented later. Figure 1.5 relates the stratigraphy of a single well (borehole 64) to the hydraulic conductivity estimated from packer testing. In Appendix A two more figures are

presented that show the stratigraphy of individual wells and the variability of hydraulic conductivity with depth (see Figure A 1 and Figure A 2).
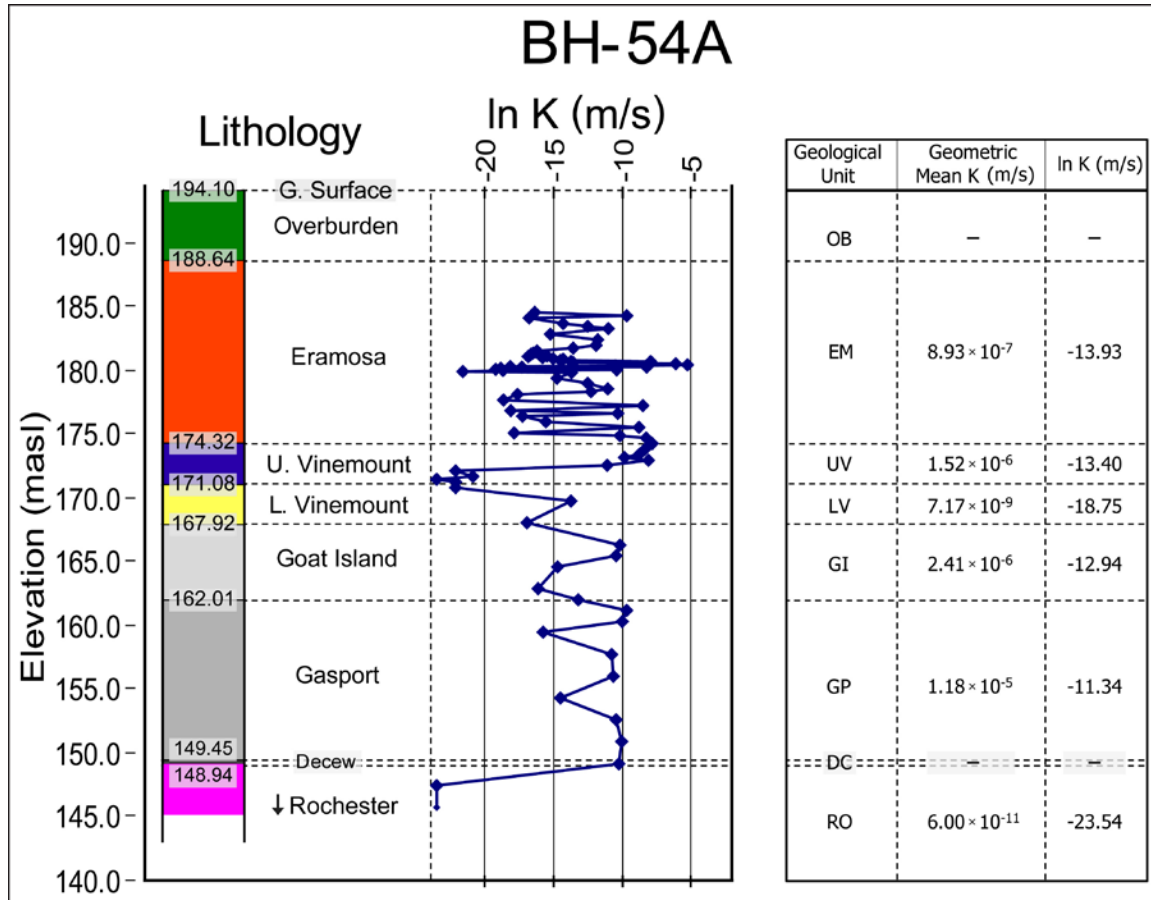
Figure 3.5. Lithology and hydraulic conductivity (m/s) for borehole 54A.

The Eramosa Member is the uppermost bedrock unit and thus is very important in the context of the organic contamination at the site. The geometric mean of the hydraulic conductivity is orders of magnitude larger than for other units. Also, about 50% of all bedding-plane (horizontal) fractures and 40% of all broken core zones recorded from the Lockport Formation underlying the site were encountered in the Eramosa Member (Lapcevik et al., 1997). Looking at the results of hydraulic testing reveals that this layer is quite conductive and is a large potential aquifer. Domestic wells in southern Ontario normally draw their water from this formation and it is very important to understand the potential for flow and contamination of this layer. Therefore, the Eramosa Member is the primary

focus of the geochemical investigation of the site. The Eramosa Member is also the layer in which the vast majority of chemical and isotopic samples were collected.

As can be seen in Figure 3.5 (also in Figure A 1 and Figure A 2 in Appendix A), the conductivity of the Upper Vinemount Member is quite variable. However, the geometric mean of the hydraulic conductivity values collected for this layer is much lower than for the Eramosa Member. Furthermore, about 23% of all bedding-plane fractures and 21% of all broken core zones from the site are encountered in this layer (Lapcevik et al., 1997).

The Lower Vinemount Member is less fractured and less conductive than other layers. The low conductivity in this layer can be seen in Figure 3.5 (as well as in Figure A 1 and A 2) by the reduction of K values through this geological unit. The geometric mean of hydraulic conductivity values is at least two orders of magnitude lower than the conductivity in the Eramosa Member. Furthermore, extremely small hydraulic conductivities were not able to be measured using packer test. Therefore, it is possible that the actual conductivity in the layer is lower than estimated here. The Lower Vinemount Member and Goat Island Member combined account for less than 1% of the total fractures classified during site characterization (Lapcevik et al., 1997). From the information presented above and the lack of chemicals being detected in the layers below this one, the Lower Vinemount Member can be considered a local aquitard.

The Goat Island Member is also a relatively impermeable geological unit (Lapcevik et al., 1997). It is more porous than the Lower Vinemount Member, especially in the lower parts where vugs are common (Bolton, 1964). The geometric mean of the hydraulic conductivity was calculated as $8.06 \cdot 10^{-8}$ calculated for this layer, still significantly lower than the Eramosa and Upper Vinemount Members.

The Gasport Member is a very porous unit (Bolton, 1964). In fact, 20% of bedding-plane fractures and 25% of broken core zones encountered at the site were discovered in the Gasport Member (Lapcevik et al., 1997). The Gasport Member has a high hydraulic conductivity and it transmits groundwater quite well. For this study, however, the Gasport Member is not very important due to the fact that Lower Vinemount Member serves as a barrier for transport to the lower layers.

The Decew Formation is also characterized by a low permeability, with a geometric of $9.66 \cdot 10^{-8}$ m/s. The next layer is the shale of the Rochester Formation. This is a tightly bedded shale layer that also has a low permeability. Once again, these two deeper layers are not central to this study.

3.3.2 Removal And Treatment System

The Smithville site has been implemented with a network of 8 wells situated around the original source zone. These wells are regularly pumped, thus controlling the local head distribution and downgradient transport. The change in the local groundwater head configuration has the potential to re-distribute subsurface contaminants and affect mixing. The removal of water from the subsurface creates local depressions in the water levels near the recovery wells; this is discussed more thoroughly in the next section. The pumping removes contaminants from the aquifer. After extraction water is pumped to a set of four settling tanks and through a series of filters. If the water is below environmental standards it is discharged into a sanitary sewer. If the sample is still contaminated that tank is sent back through the filtration process.
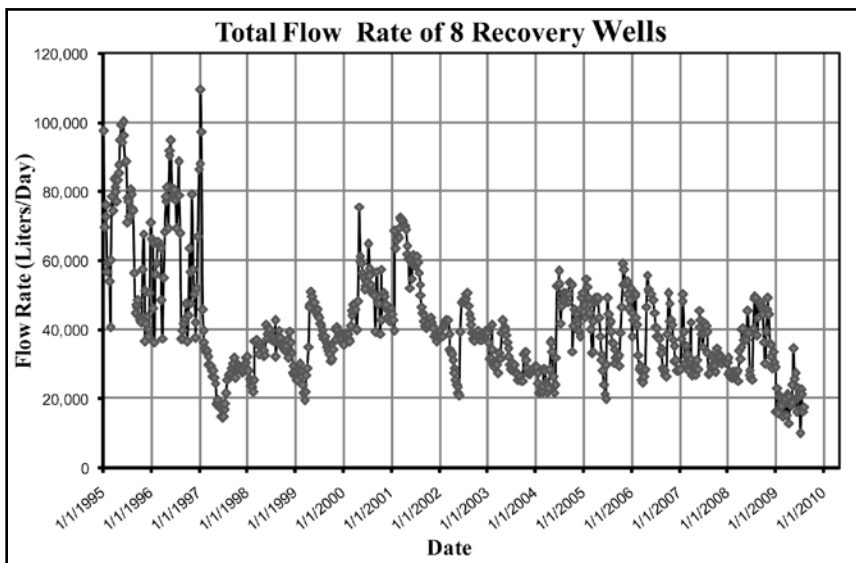
Figure 3.6. Cumulative flow rate (all 8 recovery wells) vs time. Flow rates are given in Liters/Day.

Figure 3.6 is a representation of the cumulative flow rate from all 8 pump-and-treat wells. As can be seen above, the cumulative pumping rate of the 8 wells is quite variable. The pumping rate of each well was varied by site operators to maintain the highest pumping rate (and remove the largest volume of water) without pumping any well to the point of not being able to remove any more water.

This is dependent on the permeability of the aquifer, the connection with the fractured network and well construction; thus the range in rates of pumping for each of the 8 pumped wells is different. There are 8 pump-and-treat wells in total at the Smithville site.

One goal of the project was to assess the effectiveness of the Smithville site pump-and-treat system by determining the total mass of certain contaminants removed by the system. However, determining the mass removal rate by means of the pump-and-treat system can be problematic. This is due to the fact that chemical data from the wells was only collected approximately every three months. Given the variability in chemical concentrations from and the sparse sampling data, the mass removal cannot be verified accurately. By multiplying at the concentration of each well by the volume of water removed during a three month period an estimate of the total mass removed was made using central temporal weighting. Estimates of the total mass of certain contaminants removed from the subsurface due to this system were then calculated. The total mass of TCE removed from the site was estimated to be 15.25 kg. This mass is much lower than expected, suggesting that this may not be an effective method for determining TCE removal from the subsurface. The mass removed was calculated for other chemicals than just the TCE using the same method discussed above. This data is presented in the Appendix B as Figure B 4.

A correlation between the flow rate and concentration values has been noted in more than one of the wells. Figures A 4 (A & B; in Appendix A) show the flow rate vs chemical concentration for wells R1 and R3. A statistical analysis of this correlation was completed to assess this relationship. It was determined that the flow data and TCE concentration data is poorly correlated and that the only pumping well in which a significant correlation was found was well R1. Figure A 5 shows the Concentration of TCE vs the rate of pumping for well R1.

3.3.3 Groundwater Table

As has been stated, the focus of this thesis is the Smithville site geochemistry. However, the transport of chemicals in the subsurface depends on the groundwater head configuration. Water levels were determined approximately every 2 months from 1988 until spring of 2000. The head configuration of the units underlying the Smithville site has been discussed in previous reports (Golder Associates, 1999). Data collected since 2000 relies entirely on 6 wells instrumented with pressure transducers. This data is somewhat hard to interpret due to the fact that the more recent measurements of the head

values in given wells were taken with pressure transducers that were repositioned multiple times. Therefore, this study presents only accessible data prior to the spring of 2000. Future modeling and continued site characterization may warrant further water table sampling and even more data collection.

Figure 3.7 is a representation of the hydraulic head configuration of the upper part of the Eramosa Member on July 27, 1989 and Figure 3.8 shows the head level on July 6, 1999. The specific locations of wells that are used to characterize the head distribution for each of the figures are shown, though some are omitted as they were out of the range of the map). The Eramosa Member is also the dominant flow unit and is; thus, the unit in which this thesis primarily focuses on. The wells sampled to determine the head distribution only penetrate into the first 6 meters of the Eramosa Member, therefore the water table reconstructions shown is only valid for the upper part of the Eramosa Member. The head data collected from the site indicates that the water table is only slightly below the top of the Eramosa Member.

As can be seen in Figure 3.7, the water table as of July 1989 was sloping to the south-southeast. In this figure some evidence of pumping affecting the head configuration is seen. The water table has changed significantly in some parts of the two figures, especially in the area of the pump-and-treatment wells. Drawdown as a result of pumping can be observed, this may help to keep the chemical plume stable and contained within the source area. To emphasize the drawdown in the proximity of the pumped wells and to more clearly show how the head configuration has changed Figure A 4 (in Appendix A) shows the change in elevation of hydraulic head at each location. The change in head in the area near the pumped wells has continued to control the local groundwater head configuration and prevent some offsite transport. There are some wells that are monitored that are much farther down gradient including near Twenty Mile Creek, a local stream that is hydraulically connected to the bedrock aquifer. At this point there is no evidence of transport of TCE or other organic contaminants to Twenty Mile Creek (MOE, 2010).
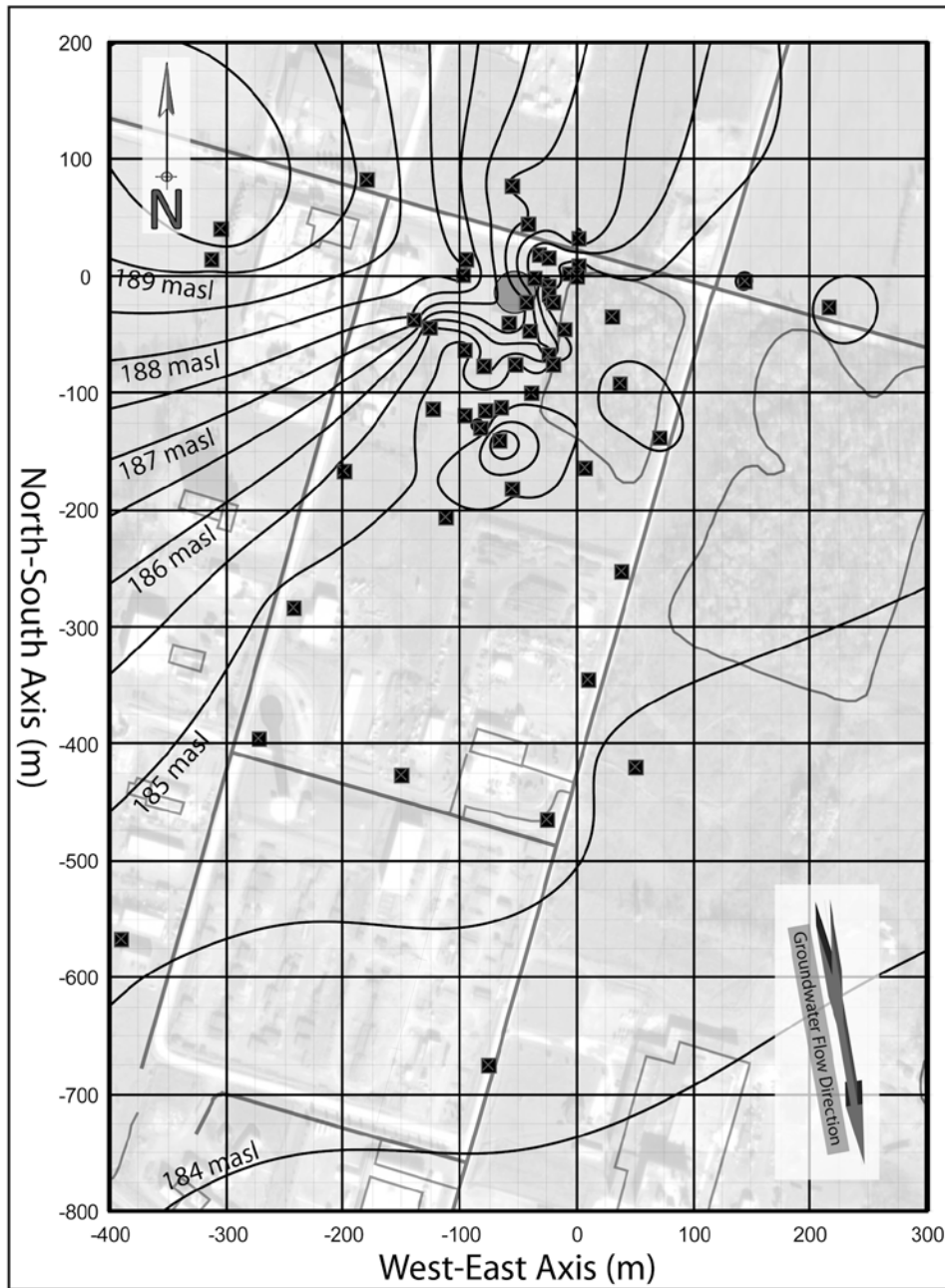
Figure 3.7. Groundwater head distribution on July 27, 1989 in masl. Grid shown is slightly larger than previous figures, the contour interval of .5 meters is used.
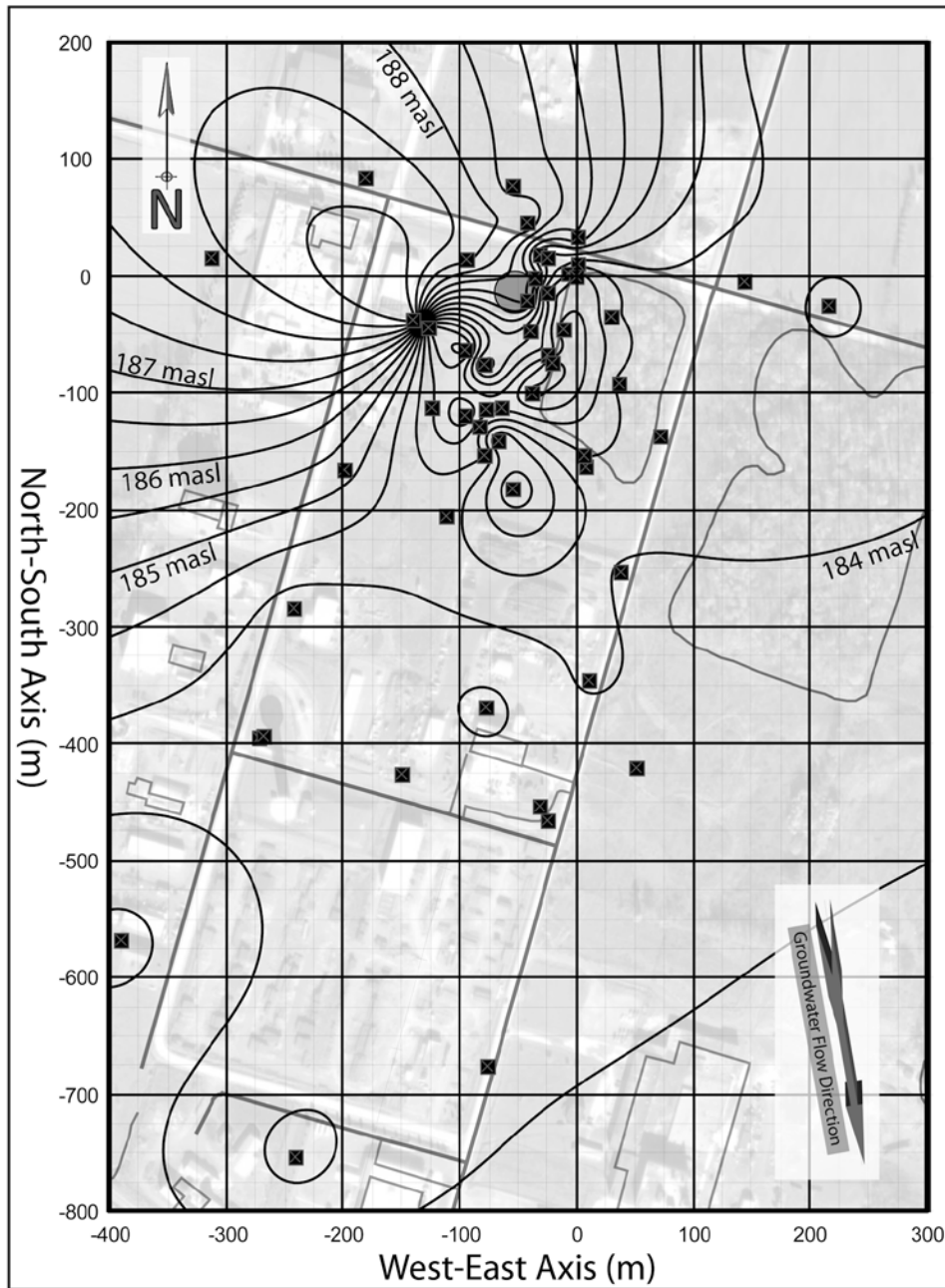
Figure 3.8. Groundwater head distribution on July 6, 1999 in masl. Grid shown is slightly larger than previous figures, the contour interval of .5 meters is used.

Chapter 4:
Analytical Methods

This project depends on accurate and exact chemical and isotopic analyses. To complete analyses and obtain the necessary data many different types of analytical methodologies were used. This section briefly presents the basic chemical methods used. The analytical methods used for determining the isotopic signature of TCE and cDCE samples collected are discussed in more detail.

4.1 Methods for Chemical Analyses

The analytical methods used for basic chemical reactions are not discussed in detail in this thesis. This is due to the fact that the methods used are based on established methods that have been in use for many years. This study uses a standard E_h electrode, calibrated with Zobel's solution (Nordstrom, 1977) and Light's solution (Langmuir, 1971), to analyze the redox parameter E_h.

Presented chemical analyses completed at the University of Waterloo were done on VOCs via a gas chromatograph - flame ionization detector (GC-FID). Samples were analyzed with a Varian 3800 gas chromatograph equipped with a flame ionization detector and capillary injection port. Ethene, ethane, methane and propane were tested for with analytical precisions of .2 ug/L, .2 ug/L, ,3 ug/L, and approximately 2 ug/L, respectively. More specific information on the analytical method used for GC-FID see Kampbell, et al. (1998). For the remaining chemical results completed, Table 4.1 shows the chemical analyzed along with the methods used to determine chemical concentrations. Both the method used internally (by Maxxam analytical testing laboratory) as well as a reference EPA method or Standard Methods and Procedures (SM) method are shown for these analyses.

Table 4.1. Carbon and chlorine fractionation factors associated with commonly observed degradation processes.

Analysis	EPA/SM Method	Maxxam Method
Polychlorinated biphenyl (PCB) and TCB	SM-846 3rd Edition	CAM SOP 00307
Volatile organic compounds in Water	EPA 8260 Modified	CAM SOP-00226
Alkalinity	SM 2320B	CAM SOP-00448
Chloride by Automated Colourimetry	SM 4500 Cl E	CAM SOP-00463
Ferrous Iron in Water by Colourimetry	Based on SM3500FeB	CAM SOP-00409
Dissolved Metals Analysis by ICP	EPA 6010	CAM SOP-00408
Nitrate (NO3) and Nitrite (NO2) in Water	SM 4500 NO3I/NO2B	CAM SOP-00440
pH	SM 4500H	CAM SOP-00448
Orthophosphate	SM 4500 P-F	CAM SOP-00461
Sulphate by Automated Colourimetry	EPA 375.4	CAM SOP-00464
Sulphide	SM 4500-S G	CAM SOP-00455
Organic Acids Analysis in Water Sample	-	CAM SOP-00431

4.2 Methods for Isotopic Analyses

Chlorine stable isotopes of TCE and cDCE were determined by the means of a Continuous Flow - Isotope Ratio Mass Spectrometry (CF-IRMS) following the procedure described in Shouakar-Stash, et al. (2006). The organic compounds were extracted and concentrated by Solid Phase Micro Extraction (SPME), for this the CTC Analytics CombiPAL SPME autosampler and purge-and-trap system is used. The extracted compounds were injected on a GC column to separate the various compounds and only the desired compounds were directed to the IRMS to be analyzed for their isotopic compositions. The analyses were performed on an IsoPrime (Micromass, UK) coupled with an Agilent 6890 GC. The GC was supplied with a DB-5 MS gas chromatographic column (60 m $\times$ 0.320 mm, 1 μm film thickness from J and W Scientific Inc., cat # 1235563).

The chlorine isotopic compositions are reported in permil (‰) deviation from isotopic standard reference material using the conventional δ notation, where $\delta = ((R_{sample}/R_{standard})-1) \cdot 1000$. $^{37}Cl/^{35}Cl$ is the measured isotopic ratio. The $\delta^{37}Cl$ values were calibrated and reported relative to the reference material, Standard Mean Ocean Chloride (SMOC) (Kaufmann et al., 1984). The standard deviation for chlorine isotopic analyses of TCE range from .01 ‰ to .2 ‰; for chlorine isotopic analyses of cDCE it ranges from .01 ‰ to .27 ‰.

To determine the $\delta^{13}C$ values of TCE and cDCE the carbon isotopes lab also used a PT-GC-IRMS setup. The system used is a Tekmar 3000 purge-and-trap unit (Tekmar Company, Cincinatti, Ohio). For Gas Chromotography a Trace GC (Thermo Finnigan, San Jose, CA interface) with a GC-Combustion III interface that operates at $940^{o}C$ is used for carbon isotopic analyses. For separations a 60 meter long DB-624 column with .32mm internal diameter and 1.8μm film thickness is used. The IRMS used is the Delta^{plus} XL isotope ratio mass spectrometer (Thermo Finnigan MAT, Bremen, Germany).

The carbon isotopic compositions are reported in permil (‰) deviation from isotopic standard reference material using the conventional delta notation, where $\delta = ((R_{sample}/R_{standard})-1) \cdot 1000$. $^{13}C/^{12}C$ is the measured isotopic ratio. The $\delta^{13}C$ values were calibrated and reported relative to the reference material, Vienna Pee Dee Belemnite (VPDB) (Clark and Fritz, 1997). The standard deviation for chlorine isotopic analyses of TCE and cDCE using this method is approximately .5 ‰.

Chapter 5:
Results

The existing site database was obtained from EarthFX, a MOE contractor (Earth FX, 2010; Golder Associates, 1994). Just over fifty wells at the Smithville site are currently sampled as part of an ongoing quarterly sampling routine, though not all are sampled every quarter. However, some of the analyses were not introduced until after 1987. Additionally, some of the methods applied were inaccurate and since have been outdated due to relatively high minimum detection limits. Consistent sampling for many species of VOCs has been maintained since 1996. Currently, the database contains the results of over 9,000 chemical concentration analyses pertaining to VOCs and PCBs, some ranging back in time to 1987.

A new sampling campaign commenced in December 2008 to collect additional field data and to begin extended characterization of the processes affecting TCE at the Smithville site. Samples from the 14 wells that are emphasized throughout this thesis were collected during regular quarterly sampling events in December 2008, March 2009, June 2009, September 2009, and December 2009. The chemical samples taken were collected entirely from wells screened in the upper part of the Eramosa Member. Samples analyzed were collected for chlorine and carbon isotopic analyses, concentrations of important redox parameters (CH_4, NO_3^{2-}, SO_4^{2-} and E_h) and additional organic chemical concentration analyses (Ethene, ethane, acetylene, and propane). Other compounds that may help characterize TCE degradation were not analyzed, such as H_2, Cl_2, acetic acid, CO_2, acetylene, chloroacetylene, dichloroacetylene. Most of the wells selected are sampled quarterly by the MOE, thus, some historical concentration information is known. However, three of the 14 emphasized wells had not been regularly used for monitoring purposes. These wells are selected due to their proximity to the source zone and so that transects could be observed perpendicular and parallel to the ambient groundwater flow direction.

The significant results of the analyses completed are discussed in this section. The results of chlorinated ethene concentration analyses and the more recently completed chemical analyses of additional (potential) daughter products of TCE degradation are presented. Results of analyses pertaining to the electrochemical conditions are shown, as are the results of isotopic analyses. For all chemical concentration plots presented in this section (and in Appendix A) the computer software program Surfer[R] was used to visualize the chemical data and interpolate between sample locations.

Interpolation between data collected was done by kriging, which is based upon geostatistical methods. These figures all have units of meters in the N-S and E-W directions and the location of R1 is set to (0,0).

5.1 Redox Conditions

Reactions involving reduction or oxidation of compounds (redox reactions) have been shown to be important in the destructive removal of many organic compounds, including chlorinated ethenes. Characterizing the electrochemical conditions of a site, thus, can be used to better understand the chemical interaction of aqueous chlorinated ethenes. Identify locations where large amounts of organic degradation has occurred can be aided using redox data. The data presented in this section can also be used to constrain the potential mechanisms of biodegradation, by eliminating some of the potential degradation reactions.

A study published in 1997 attempted to characterize the redox conditions of the native uncontaminated groundwater underlying Smithville (Zanini et al., 1997; results not shown). The results of this report indicate that Eramosa Member wells sampled had waters that were suboxic to reducing, with even more highly reducing conditions in layers below the Eramosa Member. This study employed chemical analyses and an E_h electrode to determine the concentration of some important redox parameters and the E_h of samples collected in the field.

Table B 5 (in Appendix B) presents all of the valid data pertaining to the redox conditions that were collected from the Smithville site in April of 2010 (these analyses were not completed for the other sampling dates). Figure 5.1 and Figure 5.2 show the distribution of two relevant parameters, methane concentration and E_h, that can help to characterize the redox conditions of groundwater underlying Smithville.
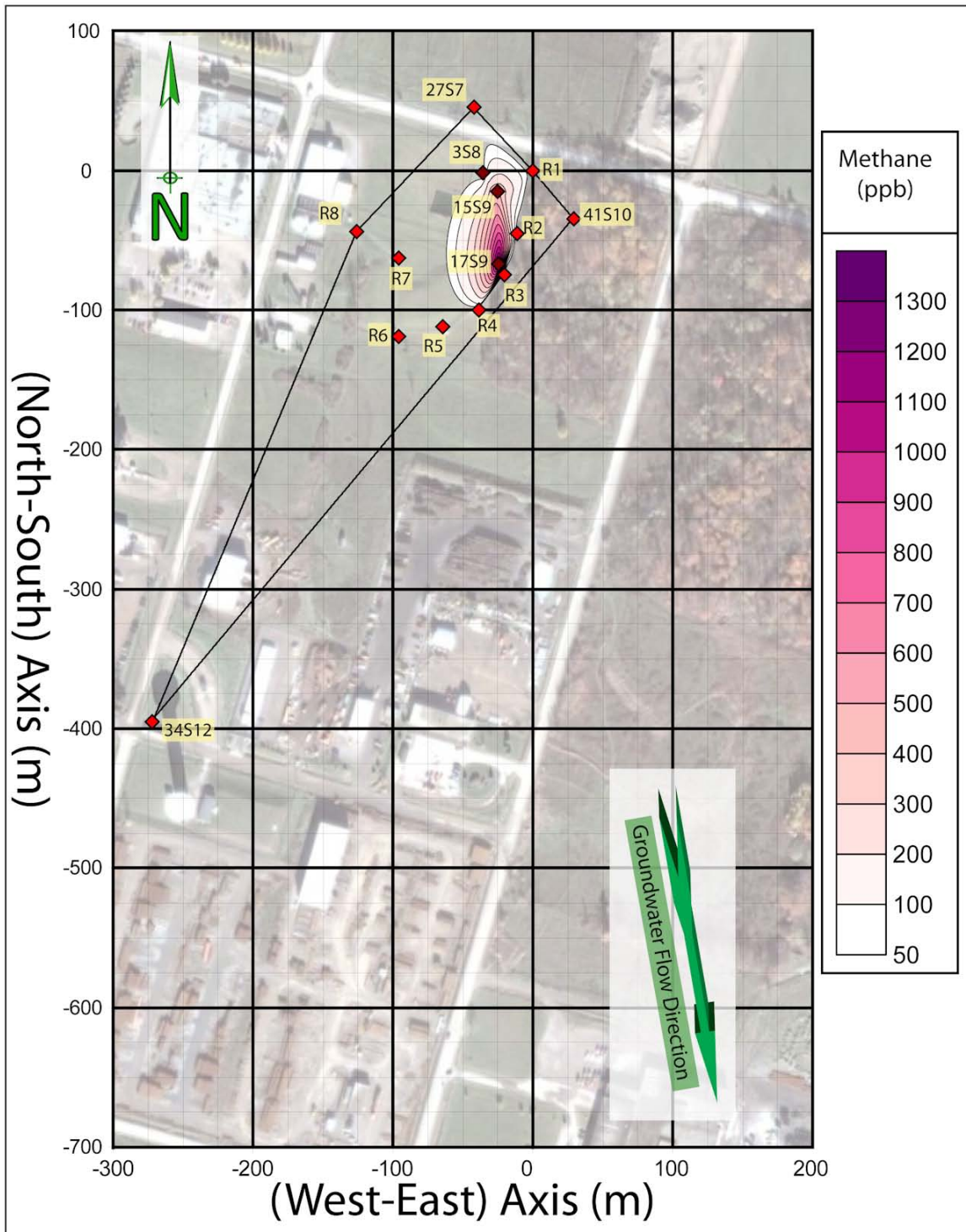
Figure 5.1. The concentration of methane in ppb (ug/L) at the Smithville site. The samples indicating redox conditions were collected in April 2010.
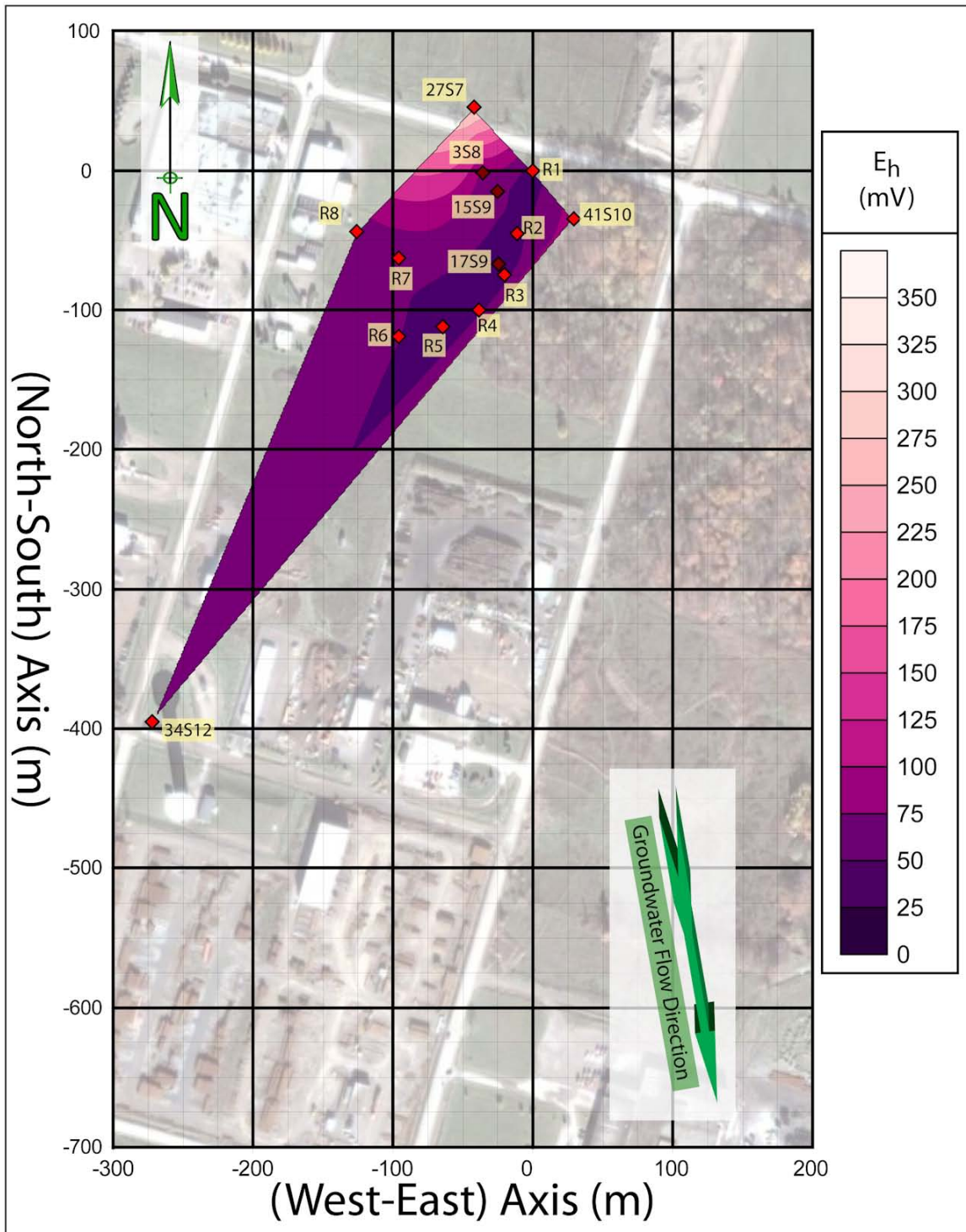
Figure 5.2. The distribution of reduction-oxidation potential (E$_h$ values, in mV). The samples indicating redox conditions were collected in April 2010.

Figure 5.1 presents the results of the methane concentration analyses sampled wells for samples collected in April of 2010. In this figure the highest concentrations of methane are found in wells 15S9 and 17S9, with concentrations well above detection limit for wells R6, and R7. Figure 5.2 shows the field based reduction-oxidation (redox) potential, or E_h, for selected local wells. The E_h observed at well 17S9 and wells R1-R5 is quite low, especially relative to other results from the site. Figures A 11 (in Appendix A) is an additional figure verifying relevant redox conditions on site, it shows a representation of the distribution of Sulfate (SO_4^{2-}) concentrations in wells at the Smithville site for April 2010. Areas of high sulfate, indicative of oxidation of organic matter in a dolostone bedrock, agree well with methane and E_h.

5.2 Chlorinated Ethenes

Studying the concentration of TCE and its products of degradation, especially chlorinated ethenes, often helps to form a general understanding of the geochemical evolution of a TCE contaminated aquifer. At the Smithville site, the earliest TCE analyses date from 1987, but concentration data for PCE, DCE and VC has only been collected since 1996. Not all of the results for chemical analyses of chlorinated ethenes are presented in this thesis. Tables B8 - B15 (in Appendix B) show all available chlorinated ethene concentration data for wells R1-R8. Table B6 (also in Appendix B) shows the chlorinated ethene data collected from December 2008 until January 2010 for the 14 main wells emphasized in this thesis. Chemical concentration analyses of ethene, and ethane were only completed for the 14 wells near the source zone from December 2008 until April 2010.

TCE is consistently observed in many of the sampled wells at the Smithville site. However, it has been found almost entirely in the Eramosa Member and the Vinemount Member. The results of the majority of chemical analyses completed in the units below the Eramosa Member (results not shown) have been found to have concentrations of chlorinated solvents below the limits of detection. However, most of the samples collected on site were taken from wells screened in the upper 5 meters of the Eramosa Member.

To present the data for TCE concentration on site, available data from approximately 30 wells was kriged to create representations of the TCE plume for the 6 sampling events during this study. These figures (Figures 5.3, A-F) show the concentration of TCE in parts per billion (micrograms per liter).

Many of the wells sampled are at least 100 meters from the source zone. Both historically and today the, majority of these wells do not have detectable concentrations of chlorinated ethenes. However, some wells, especially well 34S12, are relatively far from the source zone and yet have had measurable concentrations of TCE for many years (starting in 2001). While this result was not entirely unexpected, since TCE can be quite mobile (Pankow and Cherry, 1996), it is somewhat surprising given the remediation and containment activities that have been ongoing since the 1990s. Well 34S12 (in the southwest corners of Figures 5.3 A-F) is the only well out of the immediate source zone to consistently have TCE concentrations above detectable limits. In fact, the TCE concentrations detected have consistently been above the EPA regulatory limit of 5 ppb (USEPA, 2002). Groundwater table data also indicates that in the Eramosa Member the direction of groundwater flow and contaminant transport from the source zone is not directly toward well 34S12, though water transported downgradient most likely moves in the same general direction.

Chlorinated ethene data collected on site, some of which is presented in Figures 5.3 A-F, shows that the highest concentrations of TCE, in the wells sampled, correspond to samples collected from wells 3S8 and R7. However, well 3S8 was only sampled from December 2008 until April of 2010. Samples collected in June 2009, September 2009, and Jauary 2010 showed extremely high TCE concentrations in well 3S8. March 2009 is the only sampling event in which a TCE sample from well R7 was higher in concentration than the corresponding sample from 3S8. It is also noteworthy that the TCE concentrations observed in well 15S9 are substantially lower than in 3S8 even though they are quite close to each other; this is in part due to the proximity of well 3S8 in relation to the original source zone. However, samples collected from wells 15S9 and 17S9 did consistently have TCE concentrations that are relatively high (between 200 and 800 ug/L)
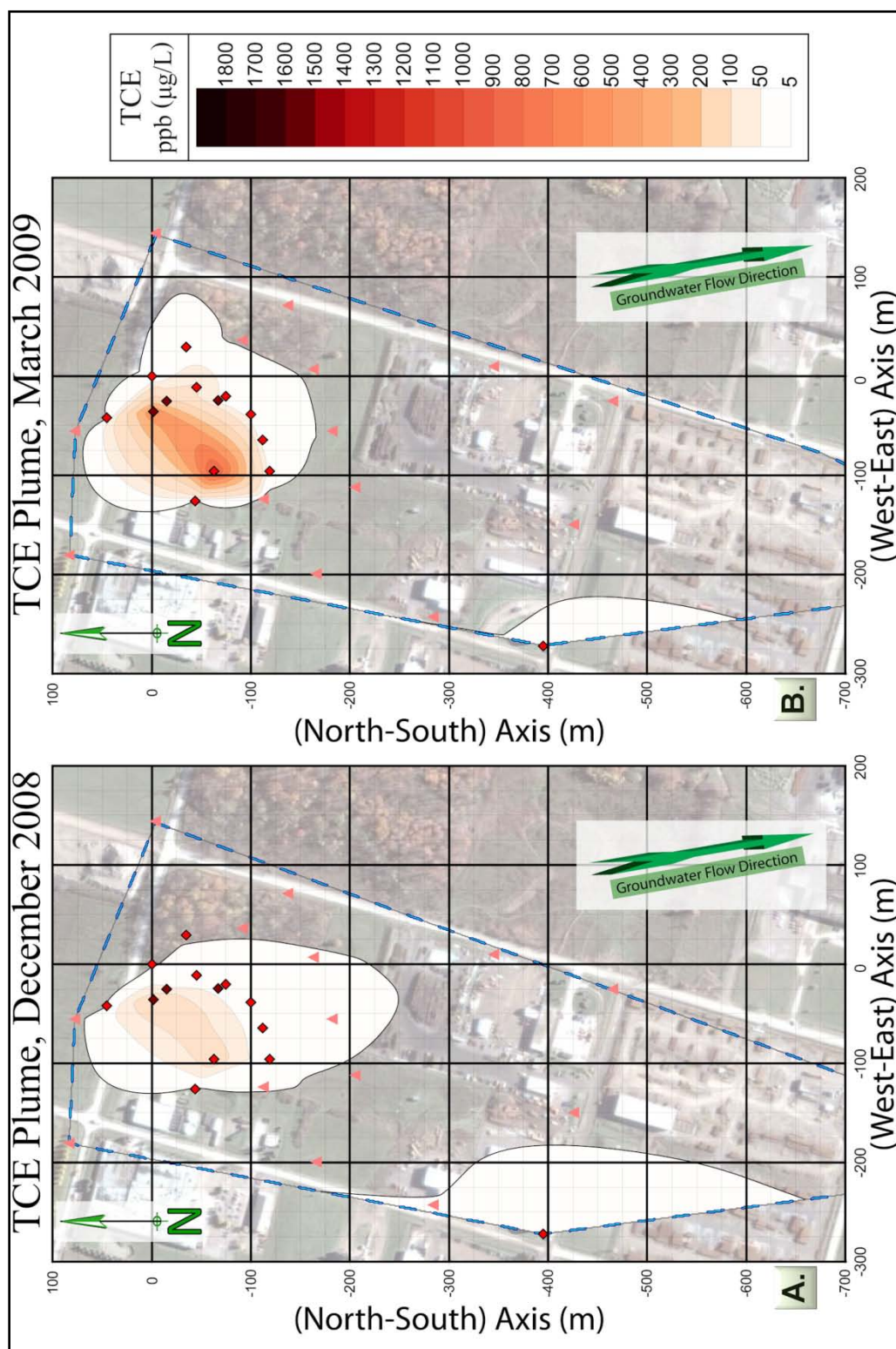
Figure 5.3, A & B. Contour map showing TCE concentrations in ppb (µg/L), December 2008 and March 2009. Sampled wells are shown as diamonds for the 14 wells primary to the study and triangles for other wells used to characterize the chemical concentrations. Groundwater flow direction is indicated by the green arrow.
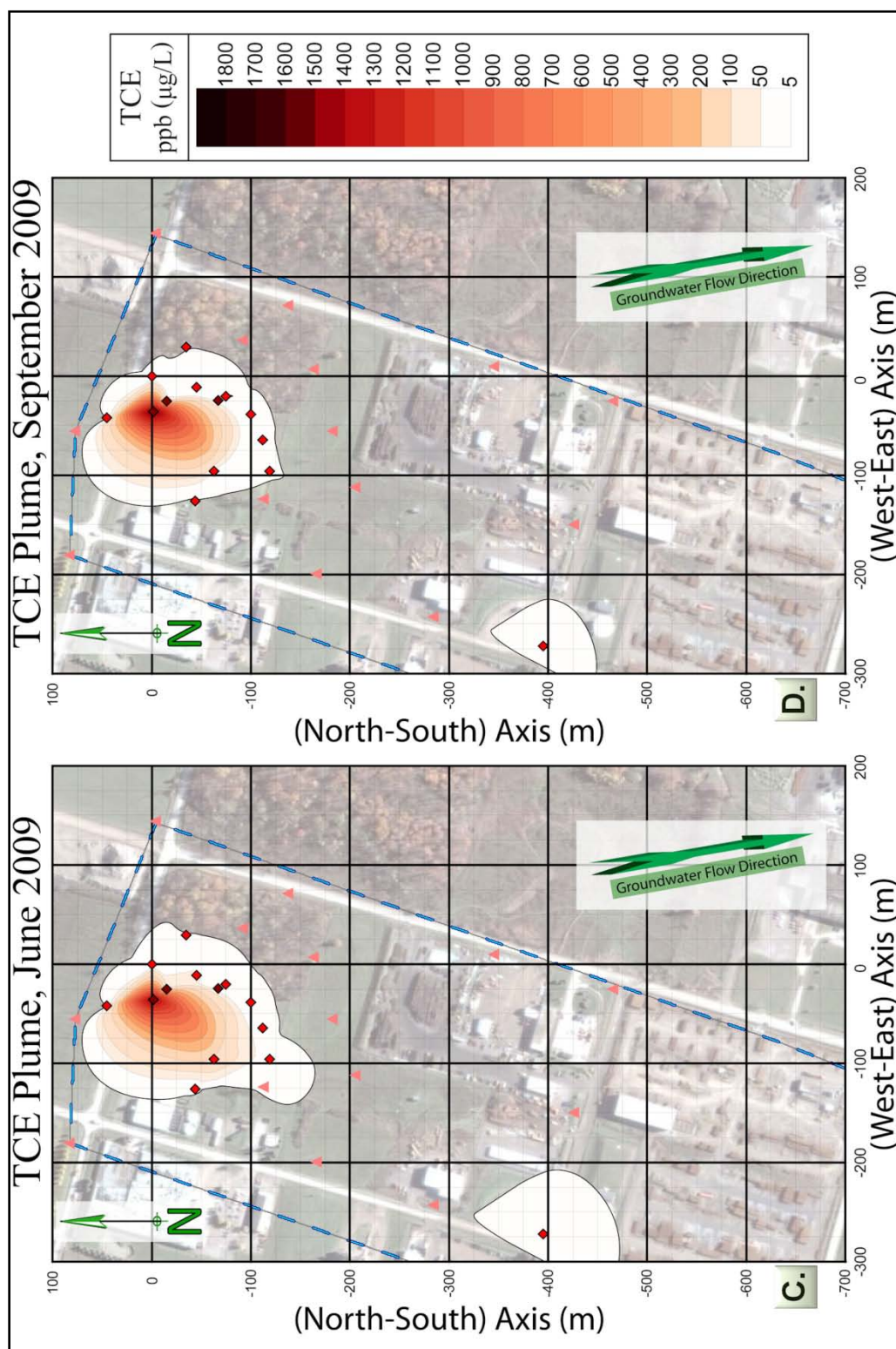
Figure 5.3, C & D. Contour map showing TCE concentrations in ppb (µg/L), June 2009 and September 2009. Sampled wells are shown as diamonds for the 14 wells primary to the study and triangles for other wells used to characterize the chemical concentrations. Groundwater flow direction is indicated by the green arrow.
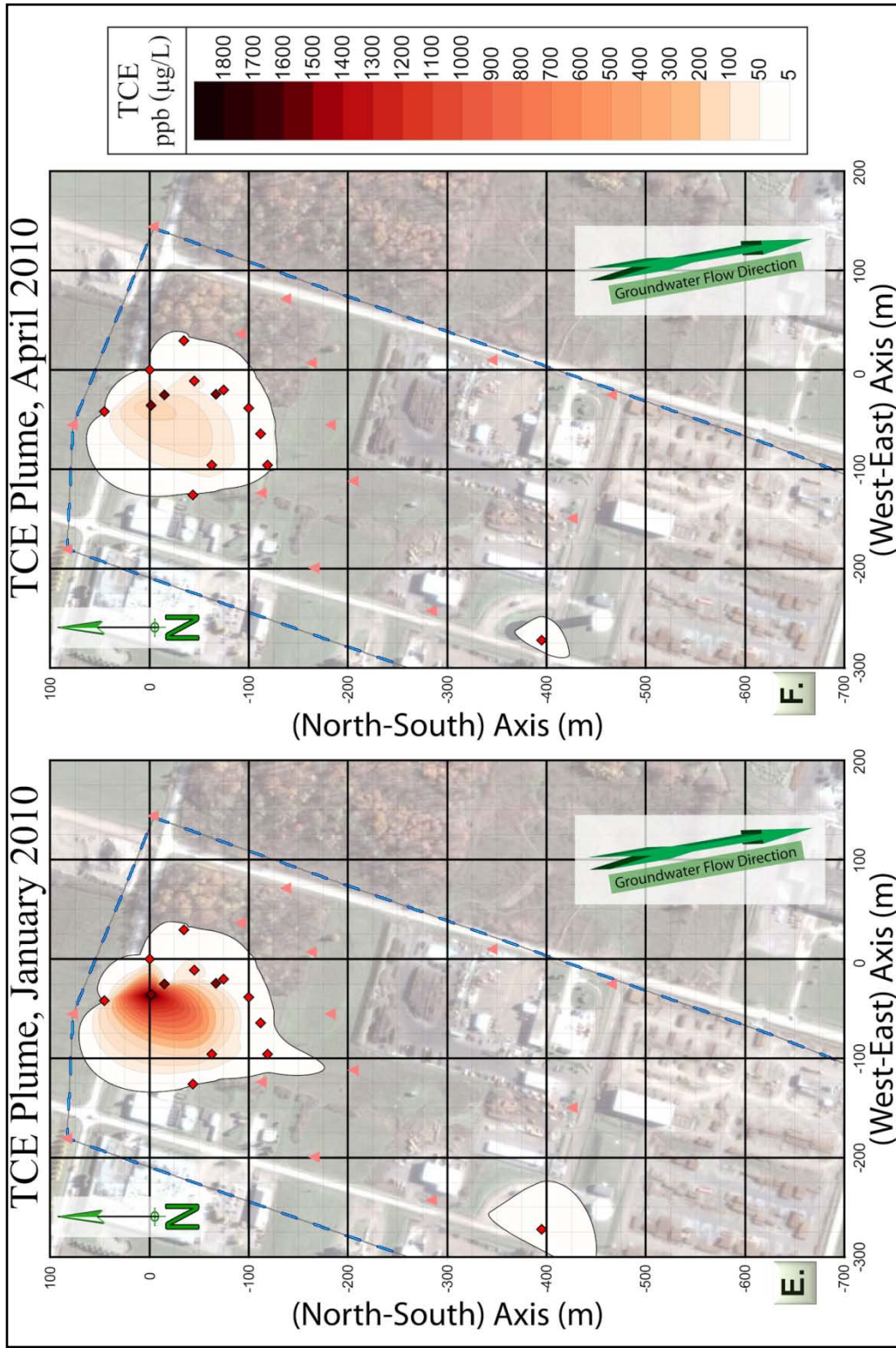
Figure 5.3, E & F. Contour map showing TCE concentrations in ppb (µg/L), January 2010 and April 2010. Sampled wells are shown as diamonds for the 14 wells primary to the study and triangles for other wells used to characterize the chemical concentrations. Groundwater flow direction is indicated by the green arrow.

Along with showing the TCE concentrations, corresponding DCE concentration contour maps for the six sampling times were also prepared. Before preparing these maps analyses of the isomers composing DCE were completed. It was found that only 78 samples analyzed had a total DCE concentration of greater than 1 ppb, all of which are after 2003. Of the samples with concentrations greater than 1 ppb (which is significantly larger than the limits of analytical error of .1 ppb) the average percentage of cDCE to total DCE (cDCE/DCE$_{total}$) is 95.9 % with a standard deviation of ~ 2%. This shows that, when DCE was well above detectable limits, transformation of TCE to DCE mostly forms cDCE. These figures (Figures 5.4 A-F) show the concentration of cDCE in parts per billion (micrograms per liter).

Comparing the two sets of figures (the TCE plume against the cDCE plume for a given sampling period) certain notable trends can be seen. The locations at which high cDCE concentrations were found are different than the locations at which high TCE concentrations were found. Additionally, the extent of cDCE contamination that is currently above 5.0 µg/L is much larger than the extent of TCE contamination above 5.0 µg/L. This is especially true for the data collected in December 2008.

The cDCE concentrations corresponding to well 3S8 are extremely low, given the high TCE concentrations observed in this well. The highest cDCE concentration observed, 540 ug/L, was collected during March of 2009 at well R7. This was the only sampling time from December 2008 until April 2010 in which highest concentrations observed in the field was not from well 17S9, which consistently had high concentrations of cDCE (about 350 to 400 ug/L). The concentrations of cDCE observed at wells R7 and 15S9 were also relatively high (generally between 100 and 250 ug/L) in this time period.

Other wells in the proximity of the source zone; wells R2, and R4-R7; were observed to consistently have cDCE concentrations well above 5 ppb. Well 34S12, which is over 400 meters away from the suspected release source zone, was found to have trace amounts of cDCE, with concentrations near 5 ug/L. In corresponding samples collected at the same time for TCE analyses, concentrations values are a bit higher (near 10 ppb).
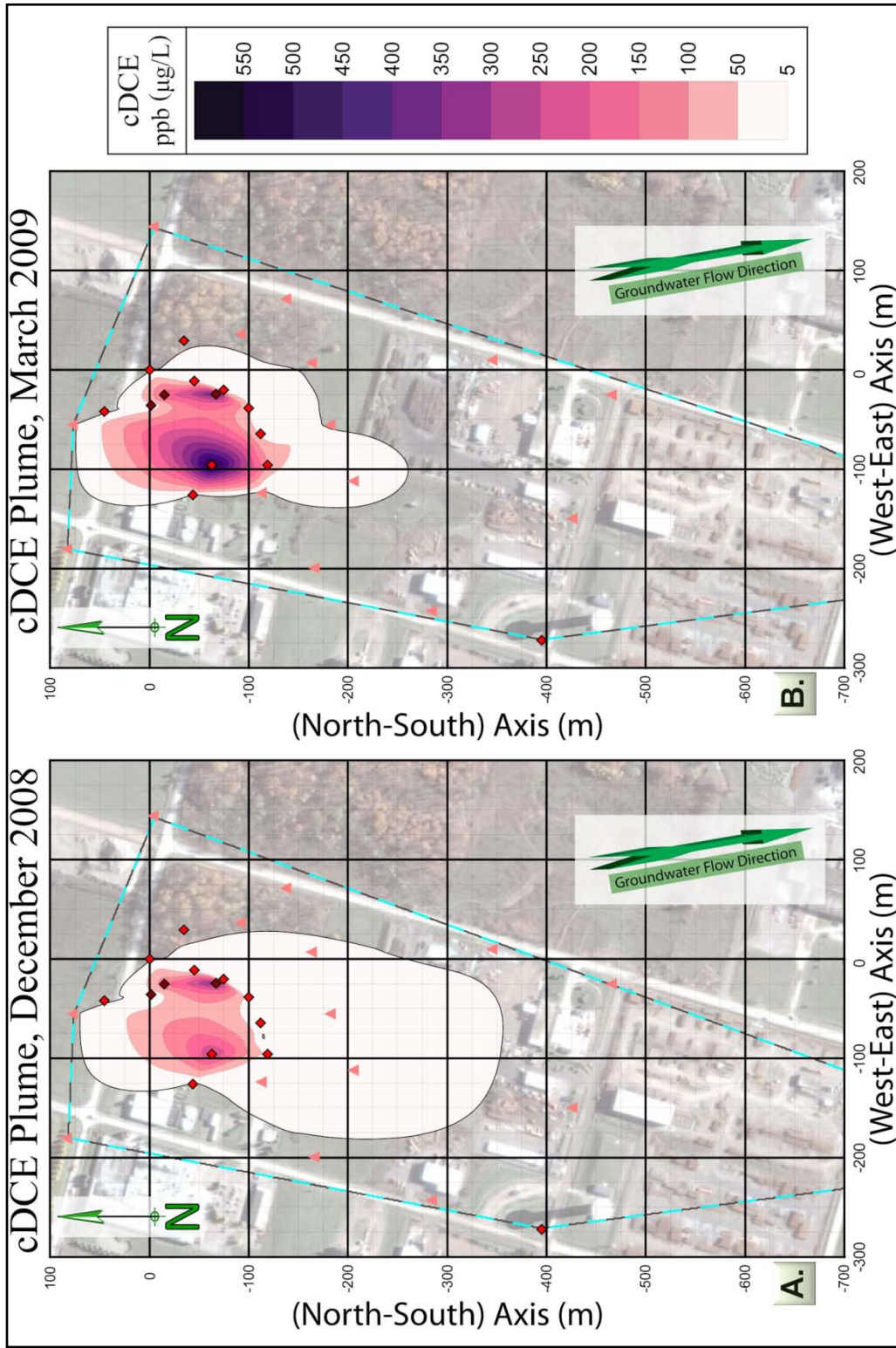
Figure 5.4, A & B. Contour map showing TCE concentrations in ppb (µg/L), December 2008 and March 2010. Sampled wells are shown as diamonds for the 14 wells primary to the study and triangles for other wells used to characterize the chemical concentrations. Groundwater flow direction is indicated by the green arrow.
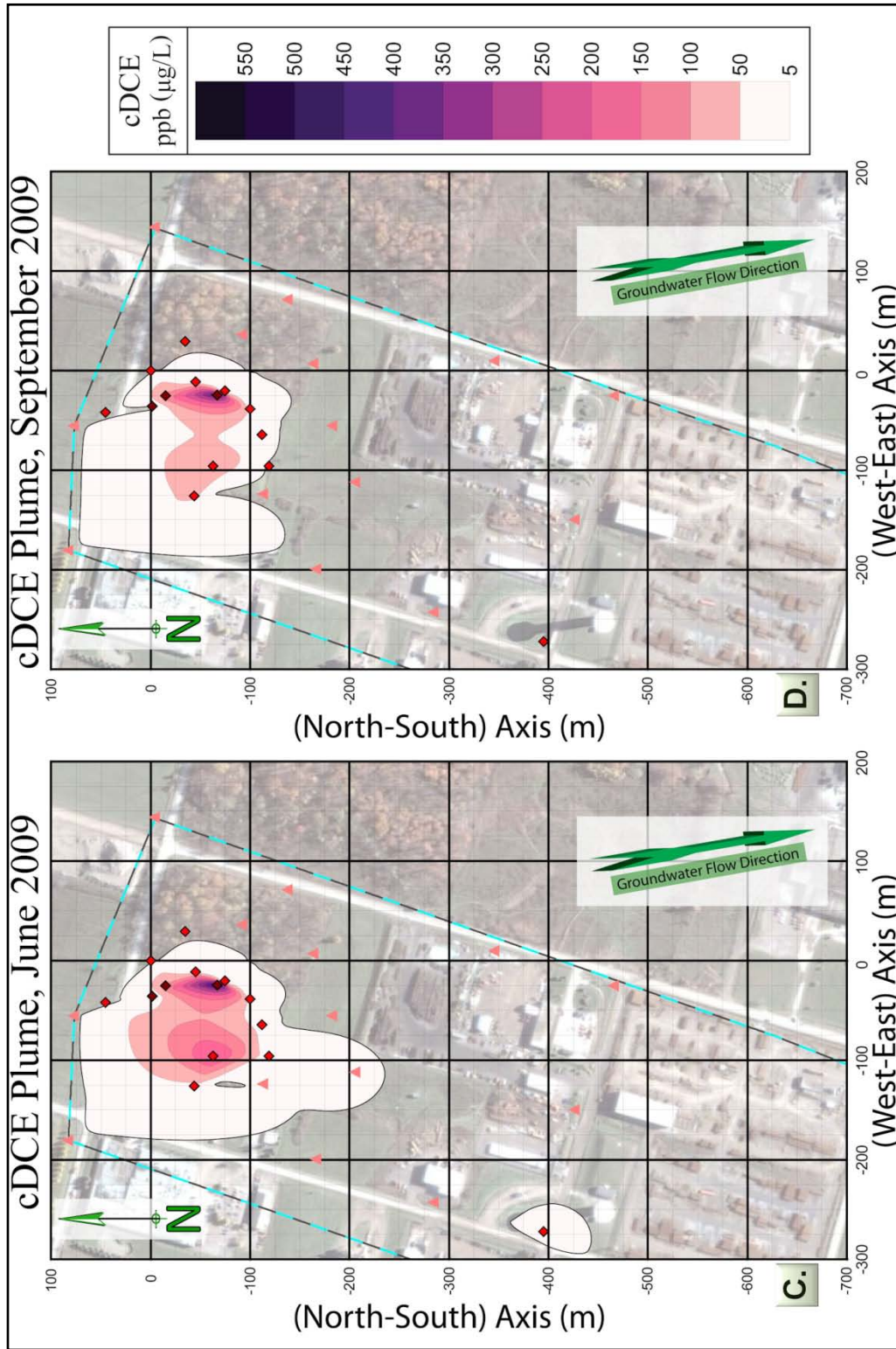
Figure 5.4, C & D. Contour map showing TCE concentrations in ppb (μg/L), June 2009 and September 2009. Sampled wells are shown as diamonds for the 14 wells primary to the study and triangles for other wells used to characterize the chemical concentrations. Groundwater flow direction is indicated by the green arrow.
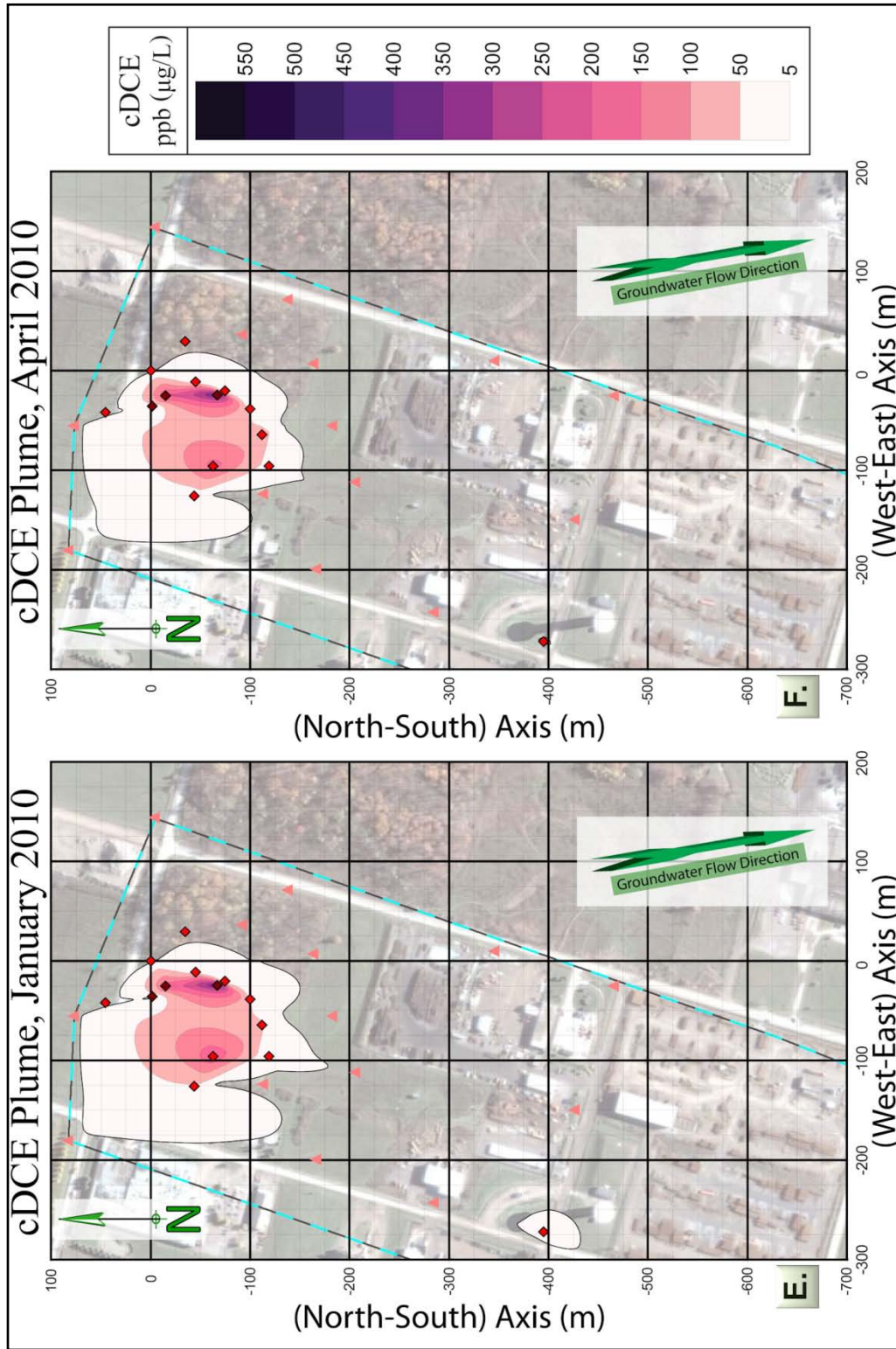
Figure 5.4, E& F. Contour map showing TCE concentrations in ppb (μg/L), January 2010 and April 2010. Sampled wells are shown as diamonds for the 14 wells primary to the study and triangles for other wells used to characterize the chemical concentrations. Groundwater flow direction is indicated by the green arrow.

The chemical analysis of TCE and cDCE can be used to help determine whether degradation is occurring and the provided figures are useful in representing the extent of contamination by chlorinated ethenes. However, degradation can also produce other chemicals including VC, ethene and ethane. Studying these products of degradation and identifying where they are present may also help in characterizing chlorinated ethene degradation. Figure 5.3 A-D shows the concentrations of TCE, cDCE, VC, ethene and ethane at the four wells that are near the source area (wells 3S8, R7, 15S9 and 17S9) for all 6 sampling times between December 2008 and April 2010. Additional figures showing similar data for other wells in the source area (wells R4, R5 and R6) are shown in the Appendix A (Figures A 5 – A 7). Note that the concentration scales used for these figures can vary. For each of these wells, concentrations are presented in micromoles per liter (µmol/L), due to the fact that dechlorination reactions work on a molar basis (that is 1 µmol of TCE can completely degrade to form 1 µmol of other chlorinated ethenes).

Well 3S8, which is nearest to the source zone, often had the highest total concentration of chlorinated ethenes, out of the wells sampled (it was the largest concentration in June 2009, September 2009, and January 2010). This well was found to contain primarily TCE. Each time it was sampled the less chlorinated degradation products made up less than 5% of the total concentration of associated chemicals (chlorinated ethenes, ethene and ethane).

In well R7 a large percentage (about half) of the total mass of chlorinated ethenes, ethene and ethane is in the form of DCE. For this well nearly all of the remaining mass of the compounds tested was TCE. The concentrations of chlorinated ethenes observed in well 15S9 were found to have a very similar trend to those in R7. That is, TCE and cDCE make up the vast majority of the chlorinated ethene contamination and are found in nearly equal concentrations. In well 15S9, as in well R7, the concentrations of cDCE are consistently higher than the corresponding TCE concentration. In these two wells cDCE and VC are much more abundant than in 3S8, but TCE is still represents at least 15% of the total mass of the chlorinated ethene species, ethene, and ethane. In addition to this, the formation of VC, ethene and ethane is small in wells R7 and 15S9.
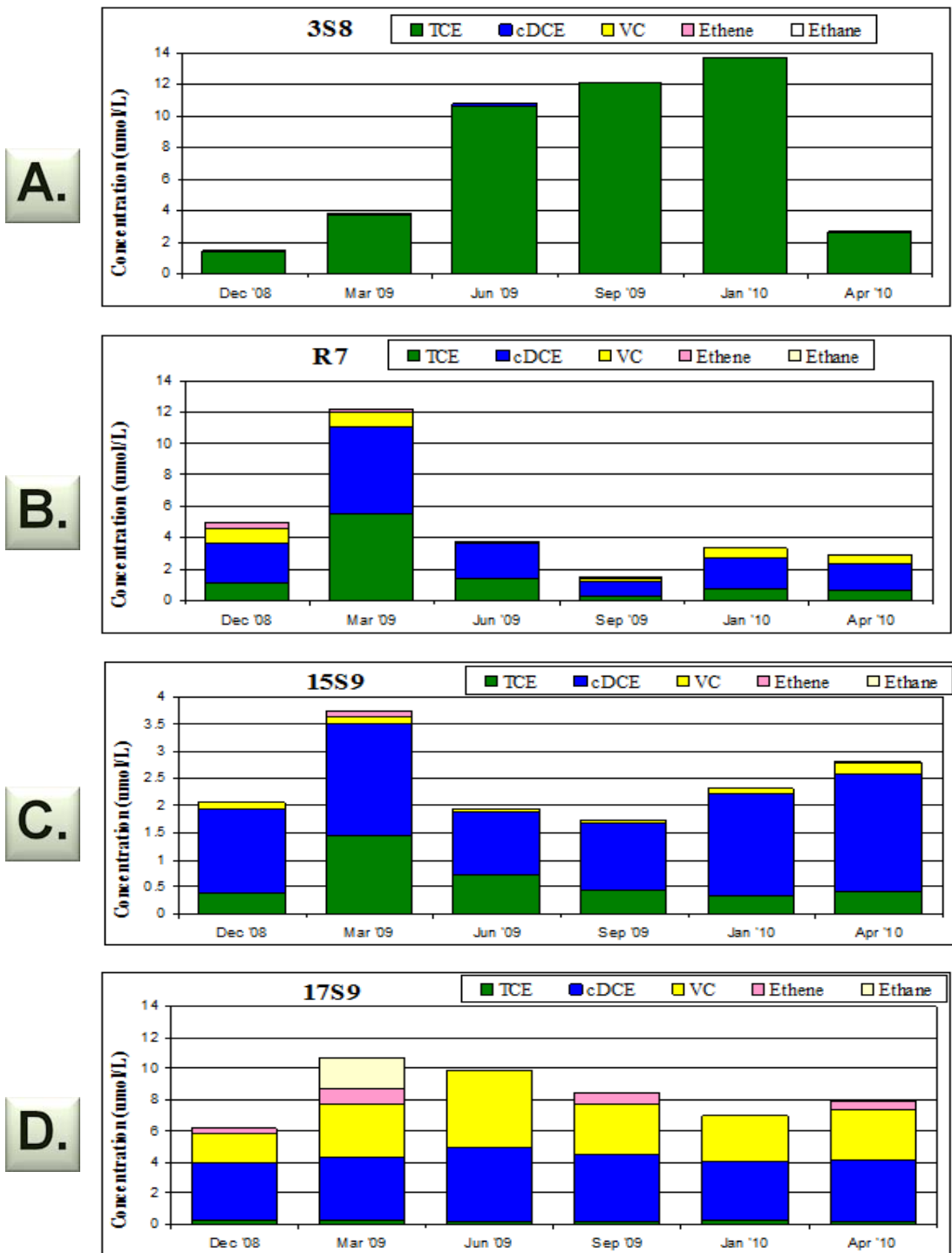
Figure 5.5 (A-D). Concentrations of chlorinated ethenes, ethene and ethane for select wells. All data presented in units of μmol/L.

The chemical data from well 17S9 shows an abundance of the more dechlorinated compounds formed during degradation (such as VC, ethene and ethane). This well is the only well sampled that consistently had detectible quantities of ethene and ethane. In addition to this, the mass of TCE detected is relatively low even though the total mass of chlorinated solvents is quite high.

5.3 Isotopic Results

Isotopic analyses have been developed for many years as a tool to assess degradation of chlorinated ethenes. In certain cases isotopes can vastly improve the understanding of the geochemistry of a given site. Though previous isotopic and biochemical experiments have not been conducted at this particular site, the former CWML site offers a location with significant chlorinated ethene sampling from many wells for many years. Furthermore, the physical characterization that is completed provides a more detailed site understanding than at many sites, and may lead to research modeling the transport and degradation of contaminants in the subsurface underlying the site.

For the purposes of this project, isotopic analyses are utilized to provide insight into the processes affecting degradation and the degree of degradation of TCE and DCE. Evidence provided by isotopic data compliments the chemical and physical data collected at the Smithville site. When chemical concentrations of TCE and cDCE were high enough for analyses to be possible, carbon and chlorine isotopic analyses were completed. This section of the thesis summarizes the results of isotopic analyses conducted on samples collected at the Smithville site. All of the isotopic data collected is presented in Appendix B (Table 7), with select data being shown in Figure 5.6, Figure 5.7 and Figure 5.8. The isotopic results presented below must be scrutinized alongside historical chemical and physical data to elucidate trends in degradation. Data collected from various reports on fractionation factors can be compared with the Smithville data to potentially determine the dominant processes that are affecting TCE degradation.

Different manufacturing methods can impart quite distinct isotopic ratios upon TCE due to differences in the manufacturing processes employed (Shouakar-Stash, 2003). If a company changes its manufacturing process, the isotopic signature of the compound created through this process would change accordingly. These distinct isotopic ratios can be used to indicate the manufacturing process responsible for generating the TCE and potentially determine the source of TCE contamination to a

given area (Van Warmerdam et al., 1995). Chlorine and carbon isotopic ratios of common TCE batches made by the top TCE manufacturers in the world are displayed in Figure 5.6. In this figure, the TCE manufacturer data is presented along with $\delta^{37}Cl_{TCE}$ vs $\delta^{13}C_{TCE}$ data (in low detail) for all samples analyzed at the Smithville site. The data presented may lead to identifying the manufacturer of the TCE or identifying the exact source of TCE from a particular spill. In addition to this, isotopic evolution as a result of degradation can be studied by measuring isotopic change along a flowpath (or within the same well throughtout time). Then identification of the source(s) of TCE to a given area can studied even with the occurrence of degradation.
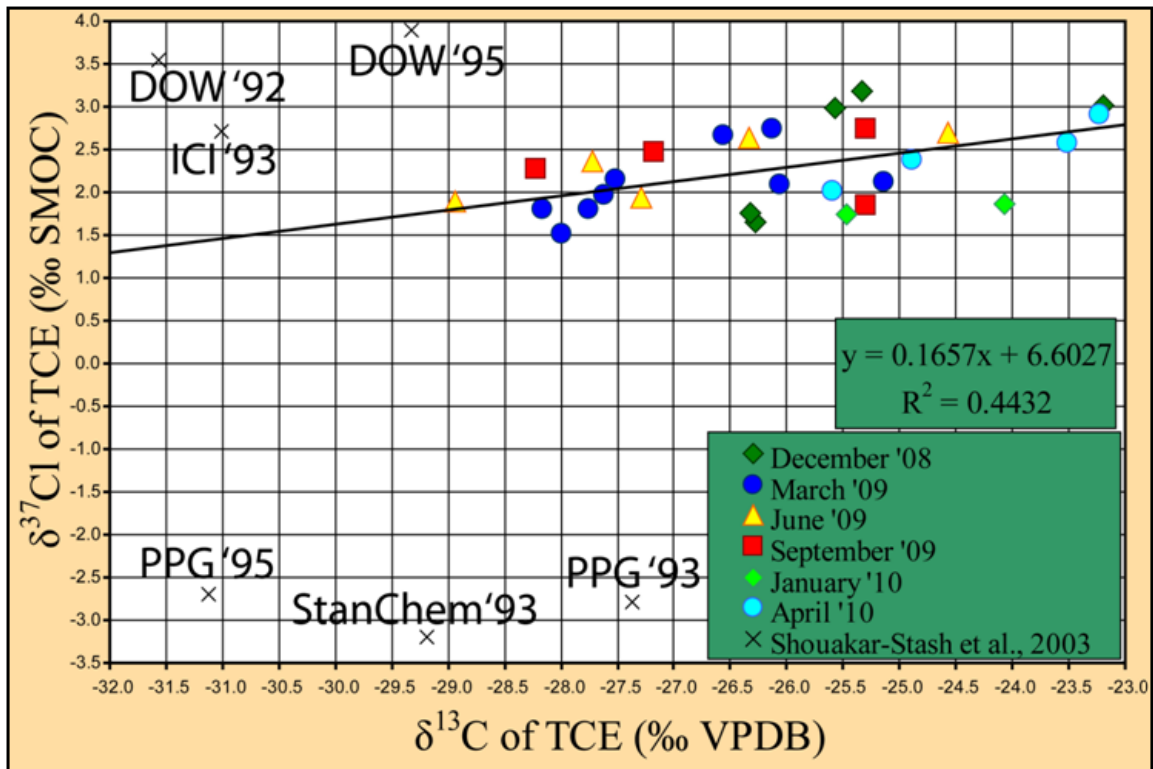
Figure 5.6. Graph showing $\delta^{37}Cl$ vs $\delta^{13}C$ (delta-delta plot) for TCE samples from common manufacturers (from Shouakar-Stash et al., 2003) and for TCE samples from the Smithville site. The line is an estimate of the slope of the all samples collected at the site.

Many samples collected contained concentrations of TCE that were too low for isotopic analyses to be performed on either the carbon or chlorine isotopes. Figure 5.7 is a delta-delta plot that shows a closer view of the variation of chlorine and carbon isotopes in TCE at the Smithville site, but only for

wells 3S8, R7, 15S9 and 17S9. The four wells emphasized here are the same wells for which extended redox and chemical data is presented in sections 5.1 and 5.2. This delta-delta plot only shows data from samples successfully analyzed for both the isotopic mass ratio of chlorine and carbon in TCE. The linear regression line - calculated from all of the data collected - is potentially a function of the carbon and chlorine isotopic fractionation factors for TCE degradation at the Smithville site. A trend in the slope shown may indicate the process affecting TCE degradation. However, the data does not fit the line well (as indicated by the low correlation coefficient).
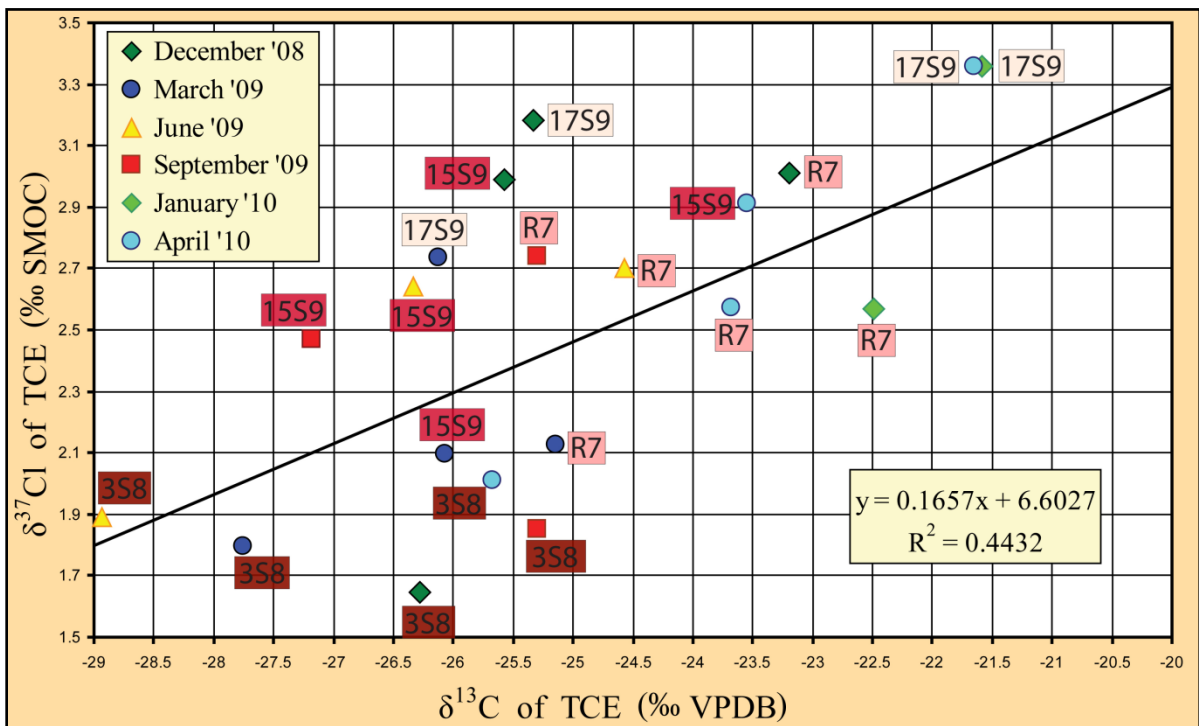
Figure 5.7. Graph showing δ^{37}Cl vs δ^{13}C (delta-delta plot) for TCE samples collected from the Smithville site. The line is an estimate of the slope of the all samples collected at the Smithville site.

Note that the data points from individual wells in Figure 5.7 seem to be in close proximity with one another or fall on a linear trend (with slope shown). Data from well 3S8 (the well closest to the source zone) all groups in the lower left corner of the plot shown for TCE isotopes. The chlorine isotopic ratio of TCE for samples collected from 3S8 is highly variable; whereas, the carbon isotopic ratios are very similar.

$\delta^{37}Cl_{TCE}$ and $\delta^{13}C_{TCE}$ values observed in well 17S9 tend to be much higher than they are for other samples. Wells 15S9 and R7 have intermediate carbon and chlorine isotopic ratios. The data collected from well R7 tends to be larger in isotopic mass ratios than 15S9, though the values in these wells are similar in isotopic character.

Figure 5.8 is another delta-delta plot with a line of best fit showing the isotopic variation of chlorine and carbon isotopes of cDCE at the Smithville site. The samples do match the best fit curve much more exactly as indicated by the significantly larger correlation coefficient. This is in part due to the fact that fewer wells had sufficiently high concentrations of cDCE for carbon isotopic analyses to be completed. Like other data collected on-site, this data is quite variable. However, the cDCE isotopic ratio data seems to group together relatively well for the individual locations. This may indicate a similar degradation mechanisms or relatively small variability in the degree of degradation in a given well.

The large degree of variation observed between the smallest and largest isotopic ratios, is also consistent with the results for TCE. However, the cDCE concentration in well 3S8 was so low that it could not be analyzed for carbon isotopic analyses. Thus, a larger degree of difference in values between isotopic sampling points would most likely be observed if analytical detection limits were improved.

The cDCE samples collected from well 17S9 are significantly more enriched in the heavier isotopes of chlorine and carbon than samples from other wells on site. It is also important to note that the difference between isotopic data for TCE collected from wells R7 and 17S7 is much less than the difference for cDCE isotopes. The $\delta^{37}Cl_{cDCE}$ and $\delta^{13}C_{cDCE}$ values are much higher than corresponding $\delta^{37}Cl_{TCE}$ and $\delta^{13}C_{TCE}$ values. As with TCE, the isotopic mass ratios in cDCE tend to be higher in well R7 than in well 15S9.
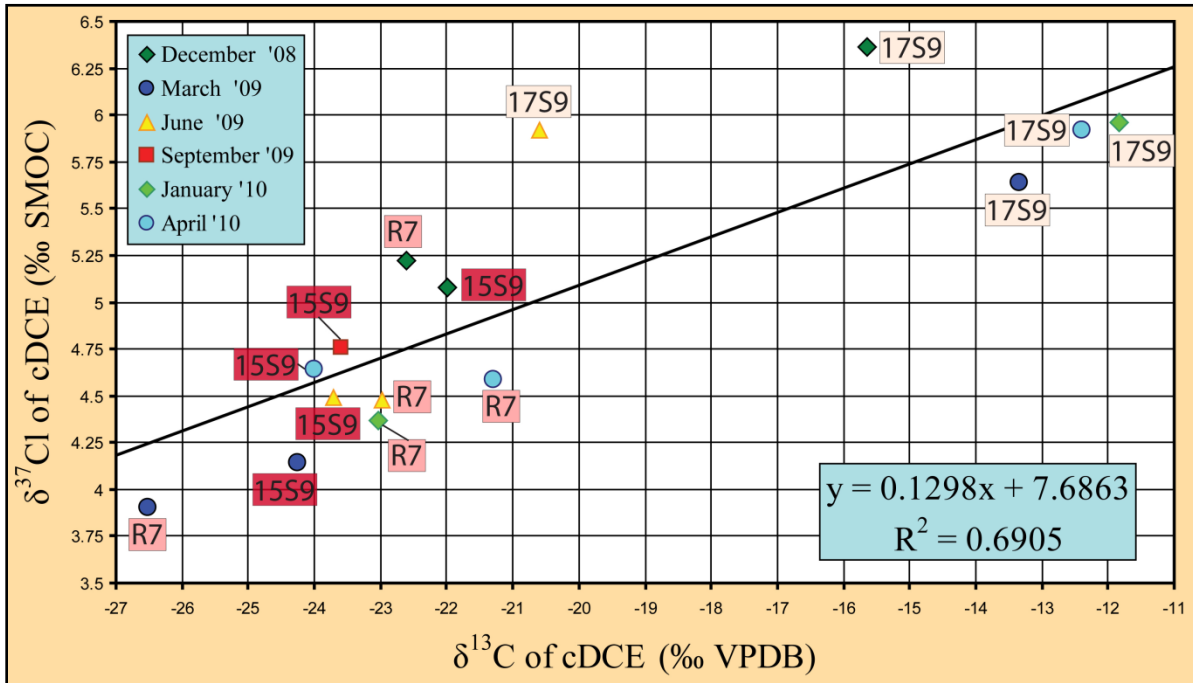
Figure 5.8. Graph showing δ³⁷Cl vs δ¹³C (delta-delta plot) for cDCE samples collected from the Smithville site. The line is an estimate of the slope of the all samples collected at the Smithville site.

5.4 Discussion of Results

The results presented in this chapter provide a few detailed representations of the geochemical setting at the former CWML site, for different dates sampled. Some additional tables and figures shown in Appendices A and B also present pertinent chemical data. This data, along with other data synthesized for this thesis but not presented, will be added to a database of information that has undergone QA/QC.

Nearly all of the results shown above for chemical and isotopic data have a large degree of variability. Fluid flow through fractured porous media is, by nature, complex. In fractured rocks, mixing due to vastly different groundwater head configurations can cause quite varied results. Much of the information on the contaminants spilled at this site was never documented, including the mass of contaminants lost to the subsurface, the exact chemical composition of fluids released, the exact location of releases and the dates of releases. In addition, increased mixing from infiltration and

pump-and-treat methods may also affect the results of chemical and isotopic analyses. These intricacies can lead to a complex distribution of groundwater head values and chemical concentrations in the subsurface. To understand what reactions affect TCE degradation, the relationships between the different datasets collected must be compared.

The redox conditions at a given sight can be quite useful in determining areas where a significant amount of degradation has occurred. This is due to the fact that in areas where redox reactions degrade contaminants released to the subsurface, the local groundwater electrochemical conditions will change accordingly. Knowledge of redox conditions cannot determine which reactions affect TCE degradation, but it does indicate which abiotic chemical reactions are thermodynamically feasible as well as which microbial communities may thrive.

The nitrate concentrations of the samples collected from the field are all below the detectable limits for the method used (only 1 ppm). In addition to this, methane data and E_h measurements indicate that all wells on-site are suboxic or reducing. The plumes of increased methane, reduced E_h, and increased sulfate agree well and areas where groundwater redox conditions are highly reducing have been identified. Determining H_2 concentration in groundwater might also have been useful to further track change in redox conditions and for future chemical modelling.

Wells sampled that are outside of the extent of contamination (such as wells 27S7 and 41S10) appear to be from more oxidizing areas. In these wells the low methane and relatively high E_h values indicate that the terminal electron accepting process in native groundwater in the Eramosa Member is sulfate reduction. Well 3S8 and 34S12 also were found to be less reducing than many of the other wells on-site. This is especially noteworthy for well 3S8 given its proximity to the source zone.

The results of analyses of redox parameters indicates that the an area of highly reducing groundwater is in proximity to wells 17S9 and 15S9 (near the source zone). In these wells methanogenesis is most likely the dominant terminal electron accepting process. Data collected from wells R6 and R7 is also indicative of more reducing electrochemical conditions. The results imply that significant chemical reduction of organic matter, most likely as a result of microbial mediation, is occurring near the identified source zone of contamination.

Redox data can eliminate potential mechanisms of degradation that are not thermodynamically favorable or biologically feasible. The electrochemical results indicate that oxidation reactions (that typically require respiration, of O_2, or denitrification as of nitrate) will not proceed. This is evidence

that direct aerobic oxidation and aerobic cometabolism can be eliminated from the reactions that may be affecting the transport of TCE in the subsurface. Microbial communities known to degrade chlorinated ethenes often require reducing environments to thrive. The results of redox analyses suggest that TCE underlying the Smithville site may be susceptible to biodegradation by known reductively dechlorinating microbial communities, especially in the proximity of wells 17S9 and 15S9. Electrochemical data can be used to constrain the potential mechanisms of biodegradation, by eliminating some of the potential degradation reactions. However, the redox data cannot determine conclusively which reactions affect TCE degradation.

Relevant chemical data can be scrutinized to further narrow down potential degradation mechanism and to independently verify conjectures based on redox data. Basic chemical data and physical characterization can give an indication of whether degradation of TCE is occurring. The only major compounds that have been consistently tested for, since 1996, that often play significant roles in TCE degradation are the chlorinated ethenes TCE, DCE and VC. The chemical concentrations of ethene and ethane were added to sampling from December 2008 until April 2010.

The contaminant plume geometry of the site and the concentration of chlorinated ethenes at a given location are highly variable with time. However, this may be expected in a fractured porous media with a complex release history and a pump-and-treat system. Results may be further biased by sorption and volatilization that can potentially remove and/or re-distribute subsurface contaminants, including TCE. A reduction in observed mass of TCE in multiple wells on site, even with increased pumping, can often indicative of degradation. Over the history of sampling at Smithville TCE concentrations have (generally) decreased in all wells on site (select results shown in Figures B 9 – A 15), though the exact concentrations have varied between sampling events. Highly variable chemical results, such as the ones observed in Smithville, can be hard to interpret which prevents observed decreases in chemical concentrations from being sufficient evidence for degradation of TCE.

Well 34S12 consistently has concentrations of TCE and cDCE above regulatory limits. This is strange due to the fact that this well is much farther from the source zone than many other wells that contain no detectable concentrations of TCE or cDCE. In addition to this, well 34S12 is not in the direction of groundwater flow that was determined by looking at the head data from the Eramosa Member. This may potentially be an example of contaminated water flowing through cracks, vugs and other fractures preferentially to well 34S12.

The area observed to have the highest TCE concentrations in the groundwater underlying the Smithville site is near wells 3S8 and R7, which are close to the original source zone. This implies that the center of the TCE plume is in the area between wells 3S8 and well R7. Each time it was sampled, well 3S8 was found to contain primarily TCE. The less chlorinated degradation products comprised under 5% of the total relative molar concentration of associated compounds. Degradation does not seem to be removing TCE at a significant rate in the proximity of this well. The chlorinated ethene concentrations observed in wells R1 and R3 further indicates that for some of the wells which are in close in proximity to the source zone degradation forming cDCE, VC, ethene and ethane has not been a significant removal process for TCE.

The results of the chlorinated ethene chemical analyses (and the analyses of ethene and ethane) indicates that TCE is degrading to form cDCE, VC, ethene and ethane at some contaminated areas of the Smithville site. The high relative and absolute concentrations of the more degraded contaminants (relative to the total mass of TCE, cDCE, VC, ethene and ethane) are useful evidence that reductive dechlorination may be a dominant degradation mechanism at this site. In addition to this, the formation of a large percent of cDCE (relative to the other DCE isomers) indicates that the reductive dechlorination is being mediated by microbial communities (i.e., halorespiration is occurring). However, conclusively determining specific details (such as characterizing reaction mechanisms or quantifying degradation) often cannot be accomplished by studying this data alone.

The mass of the sum of important contaminants is highest in wells 17S9 and 3S8, but still relatively high in wells 15S9 and R7. The chemical data collected from well 17S9 may be indicative of an area in which a significant destructive removal of TCE has occurred, though this data alone can be misleading in charterizing the degree of degradation.

The chemical analyses presented above are usually not to be used alone to determine the potential reaction mechanisms in the field, especially in such a complex subsurface environment. In April of 2010 propane analyses were completed for the 14 wells this thesis has focused on. None of the samples analyzed contained detectable concentrations of acetylene (results not shown). This may indicate that degradation processes affecting chlorinated ethenes that often form propane (such as cometabolic reactions) are not significant at the Smithville site. Additional analyses of Cl_2, acetic acid, CO_2, acetylene, chloroacetylene and dichloroacetylene may aid in further identifying potential mechanisms for TCE degradation. Even with such extended chemical data, determining the

mechanisms of degradation and the degree of degradation at a given site with chemical data alone is challenging.

A basic understanding of the electrochemical conditions and the concentrations of TCE and its degradation products in the Eramosa Member indicates that degradation is occurring. The important processes that may affect the mass and distribution of the TCE plume at the Smithville site are dilution (by means of diffusion and dispersion), removal through treatment methods, sorption, volatilization, and degradation. Dilution of organics does not change the isotopic ratio of TCE (Clark and Fritz, 1996; US EPA, 2008). Removal of TCE and other contaminants by pump-and-treat methods affects groundwater transport because of drawdown from pumping, thus it may affect the advection of contaminants. However, it does not impart fractionation upon the contaminants removed. Sorption and volatilization are processes that may be removing compounds from the aqueous phase. These two processes do not significantly fractionate carbon and chlorine isotopes, especially when compared with the degree of fractionation imparted by degradation. In the absence of significant fractionation from other processes, the fractionation observed at a field site can be attributed to chemical and biological degradation (the destructive processes).

The high range in the chlorine and carbon isotopic ratios of TCE indicate that some form of degradation is occurring at the Smithville site. The degree of fractionation observed is much larger than can be attributed to such processes as sorption, volatilization, and other process that do not degrade TCE. Based on Figure 5.6, the TCE contamination at the Smithville site most likely is a mix of TCE manufactured using multiple processes (i.e., made by different companies). This makes sense given that the contamination released by CWML was waste collected from multiple businesses in Ontario. Isotopic data collected from well 34S12 is in the same range as isotopic data collected from other wells on site (extended data in Figure B 8). This verifies that the source of chlorinated ethene contamination to this well is from the former CWML site. However, reducing conditions have not been observed at this location and biodegradation is most likely not occurring in the local vicinity of well 34S12.

The slope of the line shown in Figures 5.6 and 5.7 may indicate the dominant process that is affecting TCE degradation. Even with a more pronounced field-scale trend, identification of the specific process(es) controlling TCE degradation will be difficult due to a large range of potential slopes possible under Smithville site-specific geochemical conditions. Given the range of variability in isotopic field data, the accuracy of any conclusive assessment of the dominant degradation

mechanism by would be questionable. The slope shown is most likely a direct function of the carbon and chlorine isotopic fractionation imparted upon the original TCE by the process(es) affecting its degradation at the site. Furthermore, the slope is most likely a result of multiple degradation processes occurring in different zones of the plume, meaning that the specific process or processes (and thus the characteristic slope) may also vary from well to well. The data points from individual wells in Figure 5.7 tend to be in close proximity with one another or fall on a linear trend. This suggests that the dominant process of degradation (or the degree of degradation) for TCE is consistent for corresponding well data sampled from December 2008 until April 2010. Figure 5.8 may also be applied to determining the degree of further degradation past cDCE. The samples that group in the upper right are thought to have experienced a larger degree of isotopic fractionation due to continued degradation of cDCE.

The isotopic data suggests that TCE collected from well 3S8, which is the well closest to the source zone, has not undergone a large degree of degradation. This is consistent with data pertaining to the redox conditions and organic contaminant concentrations. The proximity of well 3S8 to the source zone may be the reason why significant degradation is not observed in this area. Other authors have documented that in areas with high concentrations of organic contaminants, such as TCE and TCA, microbes don't thrive (Wiedemeier et al., 1999). If the primary degradation mechanism is biodegradation this would decrease rates of degradation significantly.

The TCE isotopic ratios from wells 17S9 and R7 tend to be higher than the other samples collected, though well 15S9 has similar results to R7. The large departure of data from the lower left of this figure (where the assumed original source would plot) consistently observed in many wells may be due to a varying degrees of degradation, which is in agreement with the previously presented chemical and redox data.

Wells 15S9 and R7 are both relatively close to the source zone. Samples collected from these wells have many of the same characteristics. Looking at the redox conditions, the data from the two wells is electrochemically very similar. The two wells can be both classified as reducing, with sulfate reduction most likely being the dominant terminal electron accepting process. It is hard to determine the difference between these wells using redox data in conjunction with chemical data. However, isotopic data collected from the two wells is a bit more distinct. The $\delta^{37}Cl_{TCE}$ values and, even more so, the $\delta^{13}C_{TCE}$ values are greater in well R7 than in well 15S9. In addition to this, the $\delta^{13}C_{cDCE}$ are consistently higher in well R7, but chlorine isotopes of cDCE were a bit more variable. The isotopic

data suggests that the TCE sampled at well R7 has experienced a larger degree of degradation than samples from well 15S9.

Redox parameters and chemical concentration results suggest that degradation of TCE is a significant process occurring at well 17S9. Looking at the chemical data, it may be surmised that in the proximity of well 17S9 TCE appears to have been degraded significantly. Isotopic data from this well further indicates that TCE degradation is occurring. Isotopic data from well 17S9 also indicates that degradation of cDCE is also significant at this location, which can be corroborated with chemical data.

Applying isotopic methods to determining the mass of TCE removed can be much more difficult to implement at a given site. To solve for the degree of degradation at a given site, such as the Smithville site, it is necessary to apply the Rayleigh equation. However, application of this equation is questionable in extremely heterogeneous aquifers. This is because the assumptions made for the Rayleigh equation often cannot be applied to such complex contaminated field sites. Using isotopic methods to estimate the mass of TCE removed were not employed for this thesis, though future modelling and publication work may warrant such an attempt.

Chapter 6:
Conclusion and Recommendations

This thesis attempts to determine the applicability of stable isotope geochemistry, used along with other chemical techniques, for assessment of the biodegradation and natural attenuation of a site underlain by a fractured dolostone bedrock. The location where applied research was implemented is a contaminated site formerly owned by a waste management company in Smithville, Ontario. A robust physical characterization and some historic chemical data aids in the study of this site. The heterogeneity and physical complexity of the groundwater flow regime at this site makes it a particularly hard location to study in terms of geochemistry. However, heterogeneity alone can account for only some of the complexity of the site geochemistry. Therefore, using multiple lines of evidence, including isotopic data, to study the site is the best way to elucidate the specific mechanisms of TCE degradation and/or natural attenuation. Significant conclusions are presented in this chapter along with some discussion of planned future work.

6.1 Conclusions

Samples collected in the field that were analyzed for chemical concentrations and isotopic mass ratios were found to be quite variable in both space and time. The redox conditions in the local area, but outside the extent of contamination, were studied in 1997 by Zanini, et. al. The study found highly variable redox conditions from well to well and even within a single well screened at multiple depths, with the majority of the upper part of the Eramosa Member at sulfate reducing conditions.

Classification of the current local groundwater redox conditions can help determine which mechanisms of degradation TCE might be undergoing, eliminating those degradation mechanisms that are not possible due to lack of biologic viability or thermodynamic feasibility. Documented changes in groundwater conditions to much more reducing environments indicate that degradation is occurring at the Smithville site, though the species being degraded cannot be determined by studying redox data alone. However, under field specific redox conditions, it can determined that aerobic oxidation and aerobic cometabolism can be eliminated as reaction mechanisms.

Wells R6, 15S9, R7 and 17S9 all are in the proximity of the source zone. Data collected from these wells indicates that water in the subsurface underlying this part of the site is highly reducing.

However, areas with less reduced groundwater conditions were observed very close in proximity to wells these wells. Redox data collected from well 3S8 shows that, even though organic concentrations are high, degradation of TCE is not a significant removal process. This is likely due to the fact that microbes generally do not thrive in extremely high TCE concentrations.

Combined chemical, redox and isotopic data shows that degradation seems to be a removal process for TCE at the Smithville site. Concentrations of chemicals created as a result of TCE degradation verify degradation, especially in wells 15S9, R7 and 17S9. Historically collected chemical data shows that the only samples in which concentrations above 1.0 ug/L of total DCE were observed were collected after 2003. In addition to this, DCE data shows that the percentage of DCE made up of cDCE is above 96%. This indicates that microbes most likely mediate the processes that formed DCE from TCE.

The isotopic data suggests that the source of TCE represents an average of different chemical processes used (i.e., it came from more than one source). Isotopic data also verifies that TCE contamination in well 34S12 is from the former CWML site, though biodegradation is most likely not occurring in the local vicinity of well 34S12.

The TCE samples collected from well 3S8, near the source zone, have been shown as not having undergone significant degradation. Redox data, organic chemistry data, and isotopic analyses corroborate this conjecture. The lack of degradation is most likely a result of chemical conditions in which the microbes capable of removing TCE from groundwater are not flourishing.

The linear regression of the delta-delta plot for TCE estimates a field-based parameter that is likely a direct function of the carbon and chlorine isotopic fractionation imparted upon the original TCE released. The slope found is consistent with data collected from other studies though cannot be applied to determining the process directly given the range of variability in isotopic field data.

6.2 Recommendations and Future Work

One goal of this project was to develop a dataset from a contaminated field site to be used in modeling of the site. Some additional tables and figures shown in Appendices A and B also present pertinent chemical data. This data, along with other data synthesized for this thesis but not presented,

will be added to a database of information that has undergone QA/QC. Though much of the data is not presented in this thesis it may prove useful in future modeling of the site. Currently a model is being developed that will incorporate the chemical data as well as previously collected physical data. Eventually the simulation model may be compared with chemical and isotopic data in an inverse model. This final inverse model, along with the results of primary models, chemical and isotopic data and laboratory experiments should give a good understanding of the physical and chemical nature of the TCE plume at the Smithville site in terms of its transport and degradation.

The current data from this site may help future scientist determine specific mechanisms of degradation at the Smithville site in other ways too, possibly by classifying the microbial species. The data collected and analyzed for this study also may guide other researchers seeking patterns indicative of degradation at natural field sites. Management of the Smithville site, which has been done by the Ontario MOE, may be aided by this thesis. The author suggests that additional sampling for ethene, ethane, and methane - which requires only one analysis - should be added to the list of analyses completed in samples collected in the field.

This research project is a single task in a larger study that attempt to simulate the heterogeneous nature of flow in the fractured networks (such as the one underlying the Smithville site). However, the research in this project and the larger study may also help to guide potential management scenarios of the Smithville site. As biodegradation mechanisms of TCE removal are better understood and modeled, the stimulation of specific processes may be possible. This may lead to increased rates of TCE removal and/or natural attenuation at the field site. The increased knowledge gained from a study as complex and multifaceted as this study may help to improve cleanup and control methods Smithville and at other sites.

Appendix A:

Additional Figures
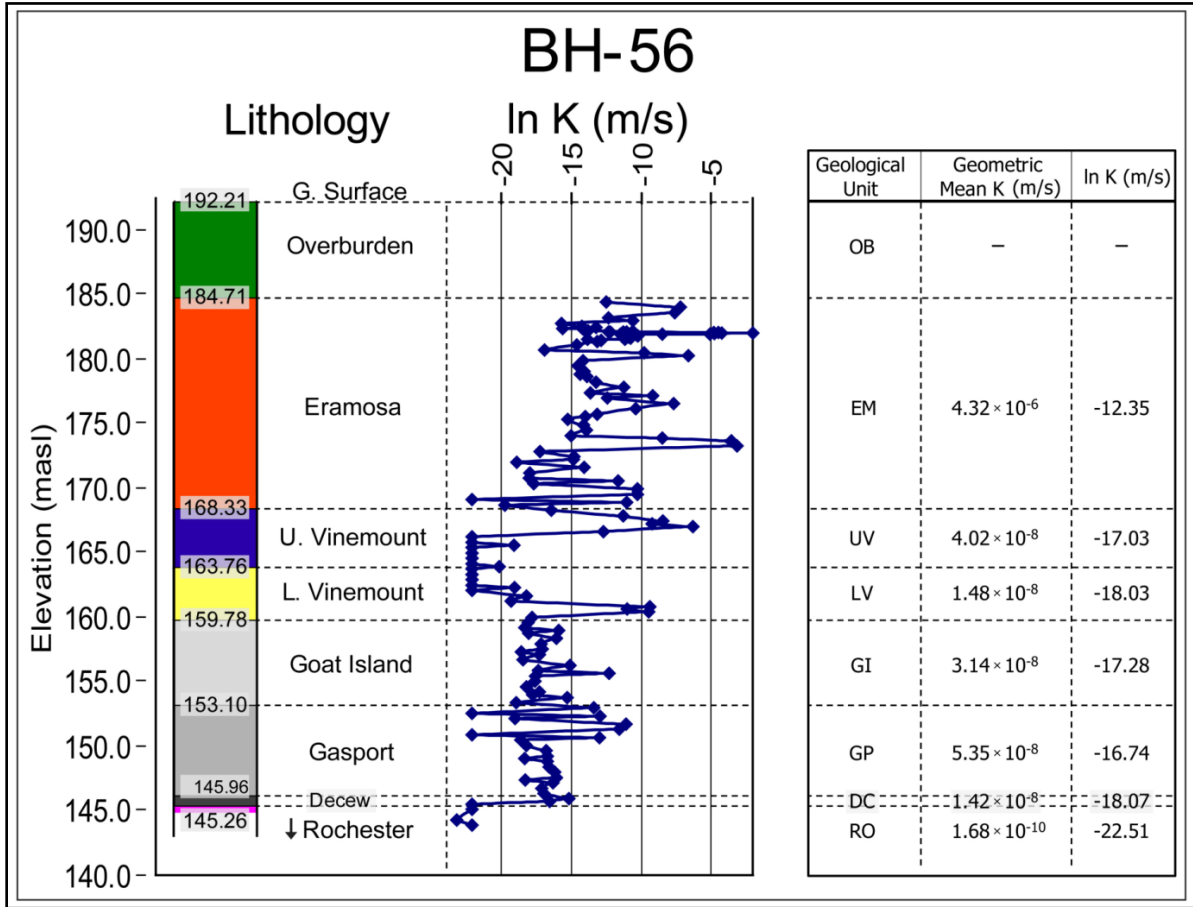
Figure A 1. Lithology and hydraulic conductivity (m/s) for borehole 56.
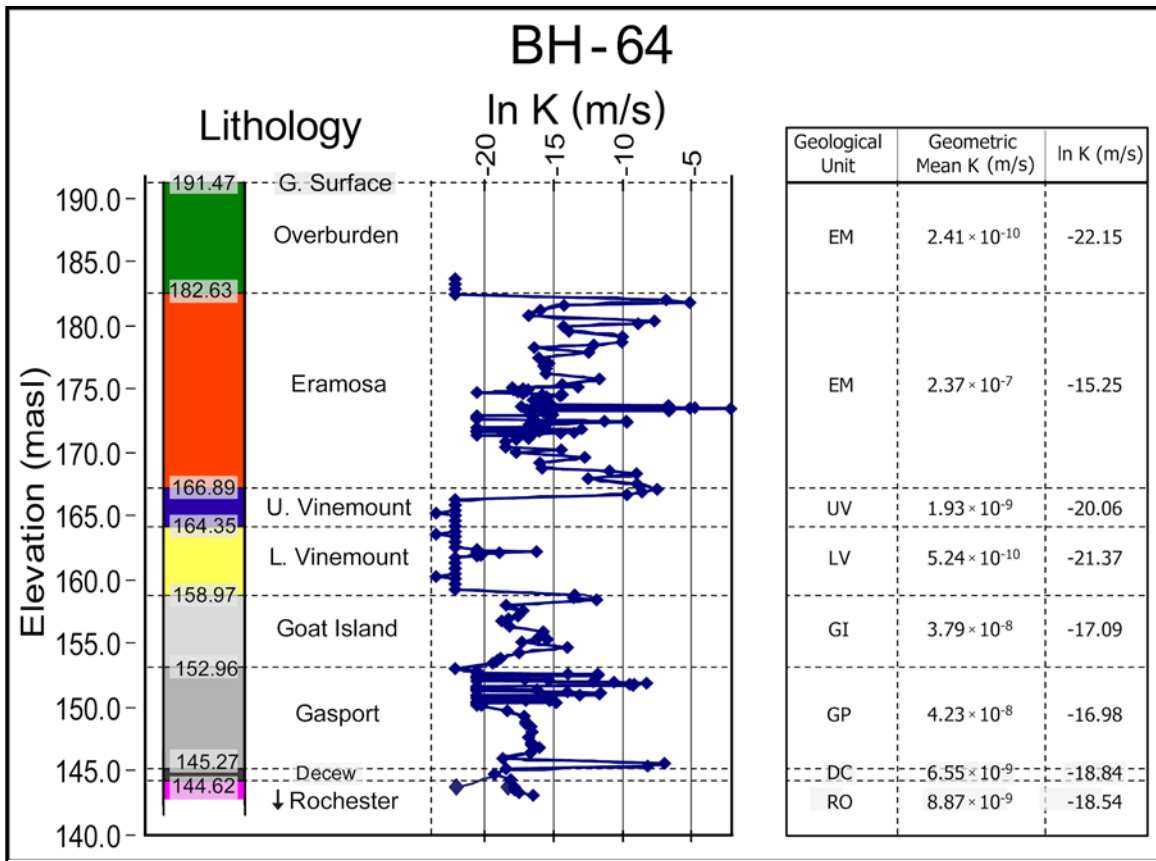
Figure A 2. Lithology and hydraulic conductivity (m/s) for borehole 64.
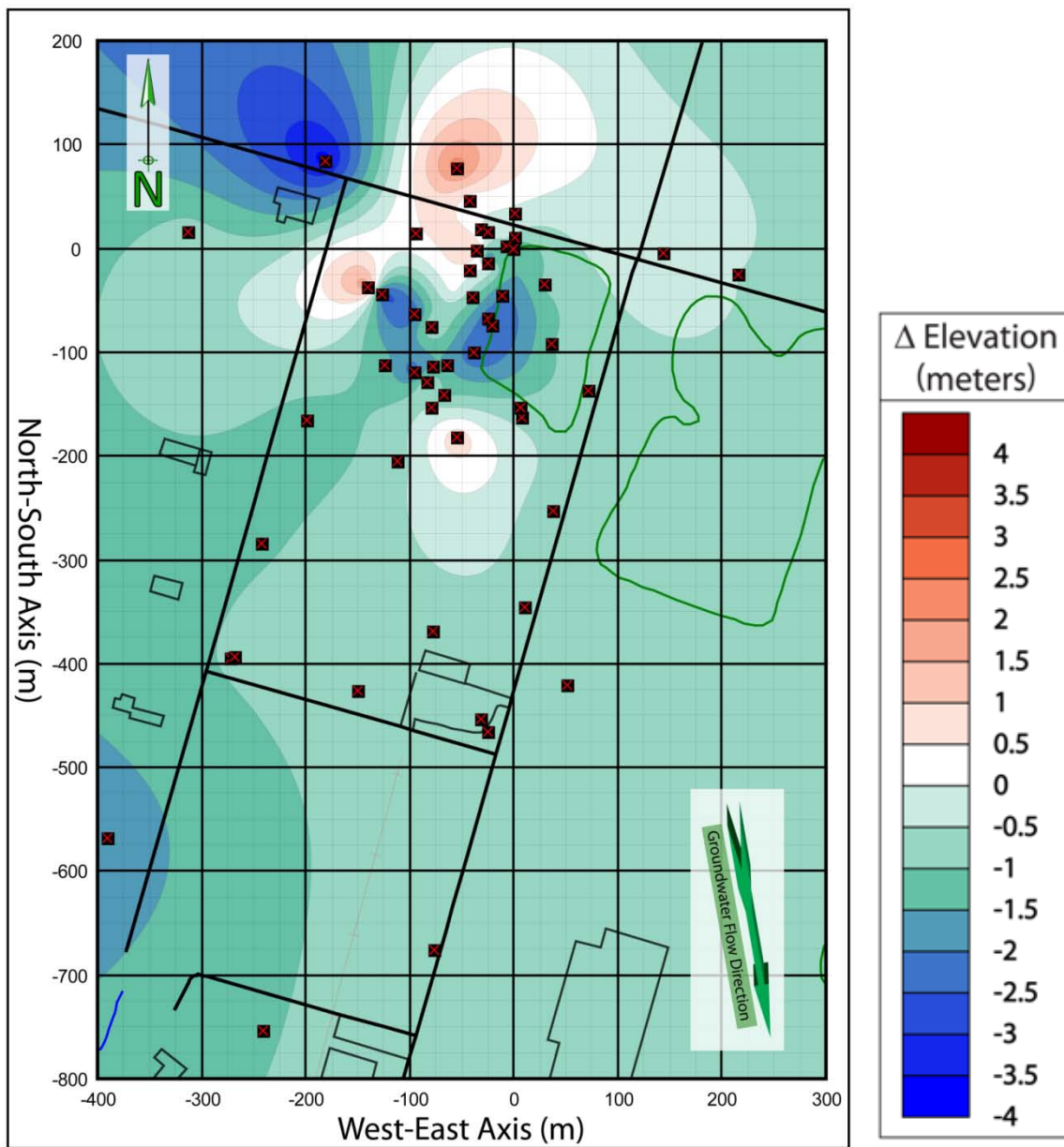
Figure A 3. Change in elevation of water table (from July 1989 to July 1999) +/- meters.
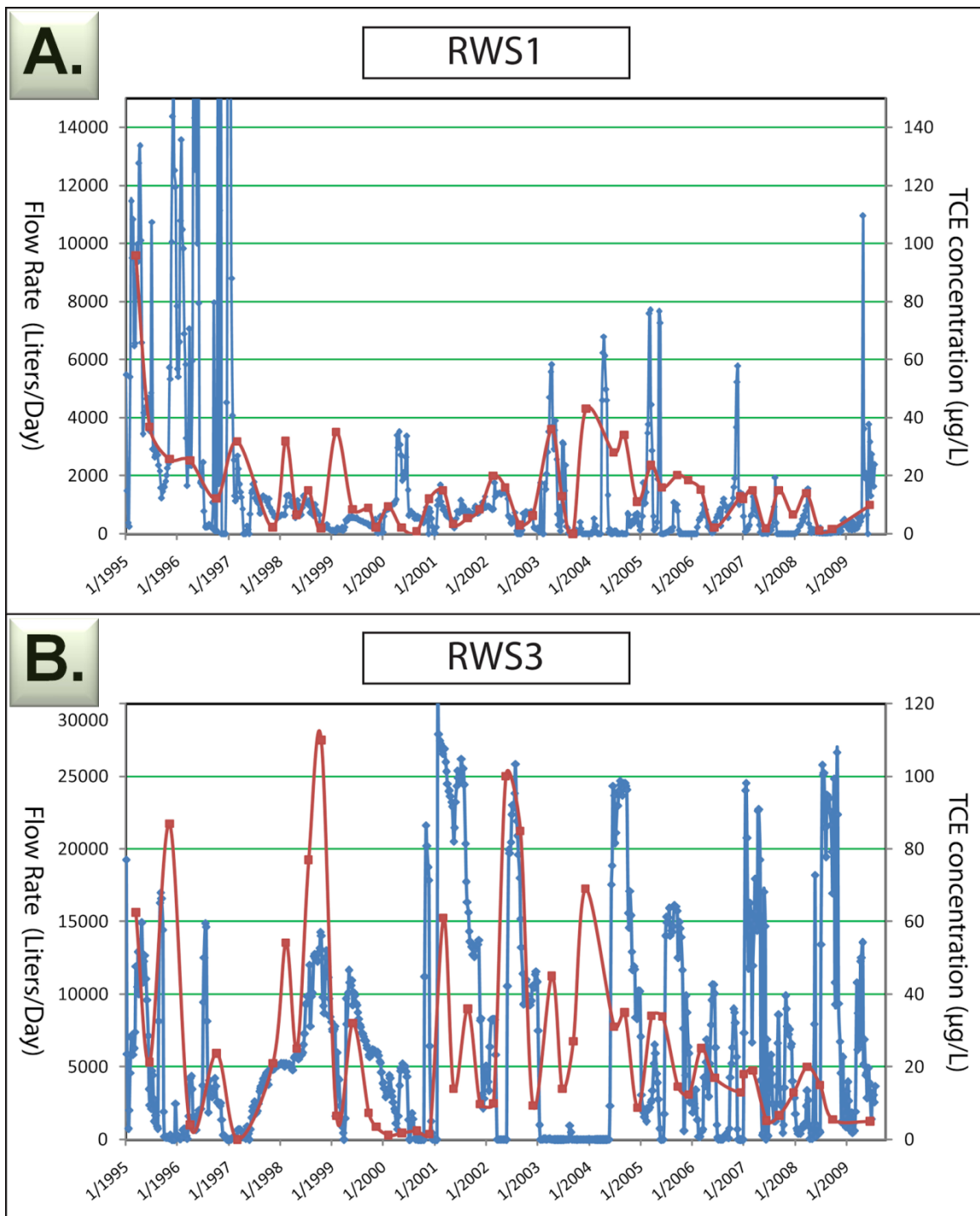
Figure A 4 (A & B). Rate of pumping and TCE concentration vs time for wells R1 and R3. Scale on left (blue diamond points) shows the pumping rate of well R3 in liters per day. Scale on right (red square points) shows the chemical concentration of TCE in micrograms per liter.
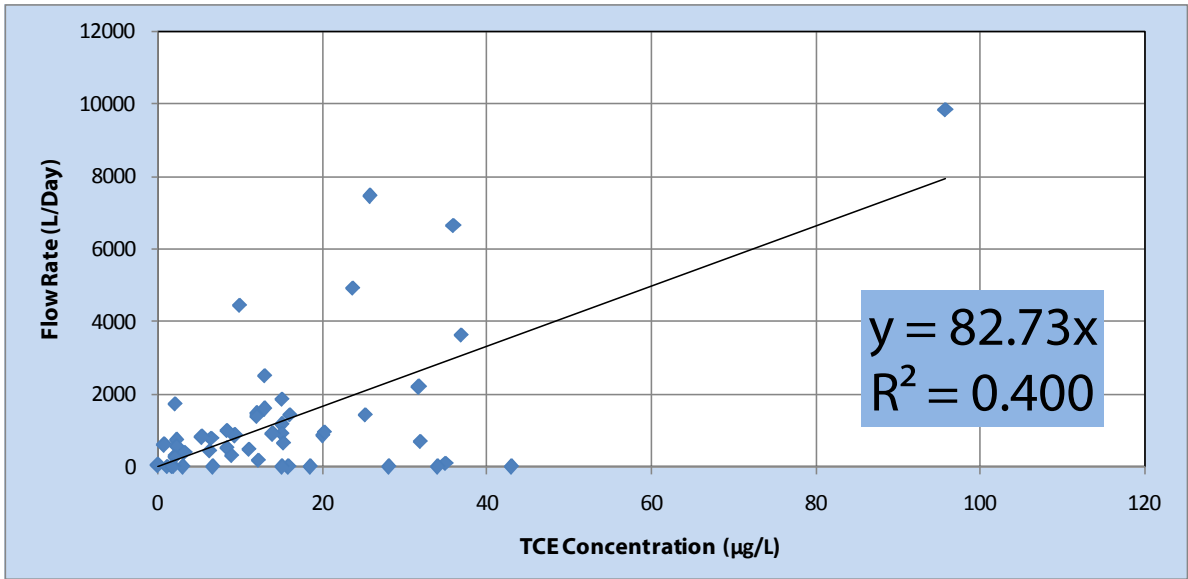
Figure A 5. Rate of pumping vs chemical concentration of TCE in µg/L (ppb) for well R1.
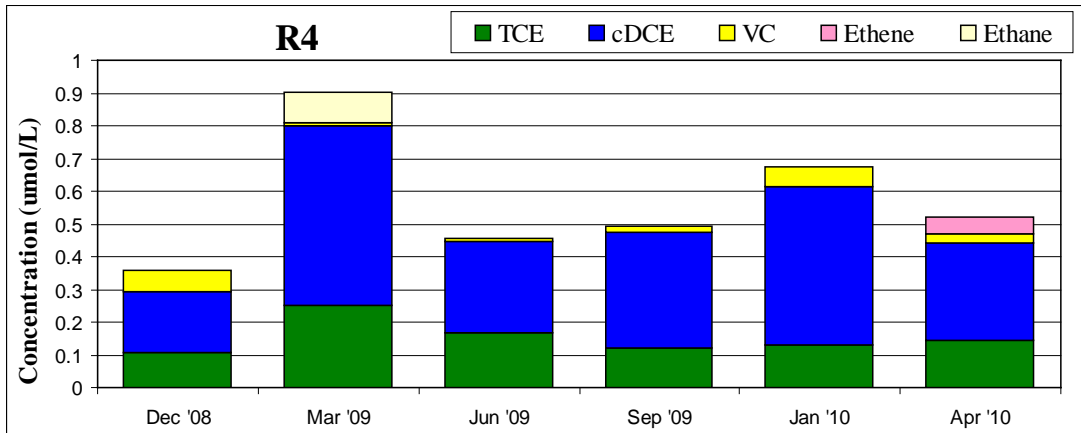
Figure A 6. Chemical concentration of TCE, cDCE, VC, ethene and ethane in micromoles per liter (µmol/L) for well R4.
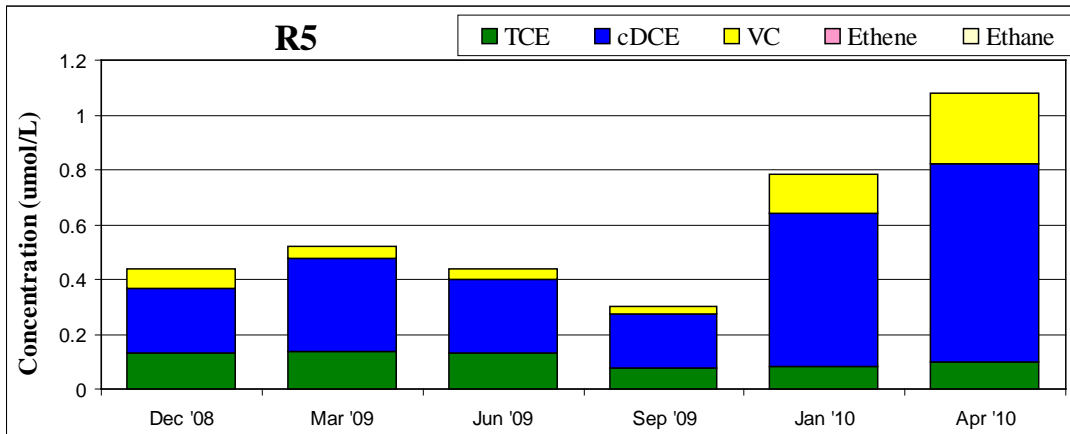
Figure A 7. Chemical concentration of TCE, cDCE, VC, ethene and ethane in micromoles per liter (µmol/L) for well R5.
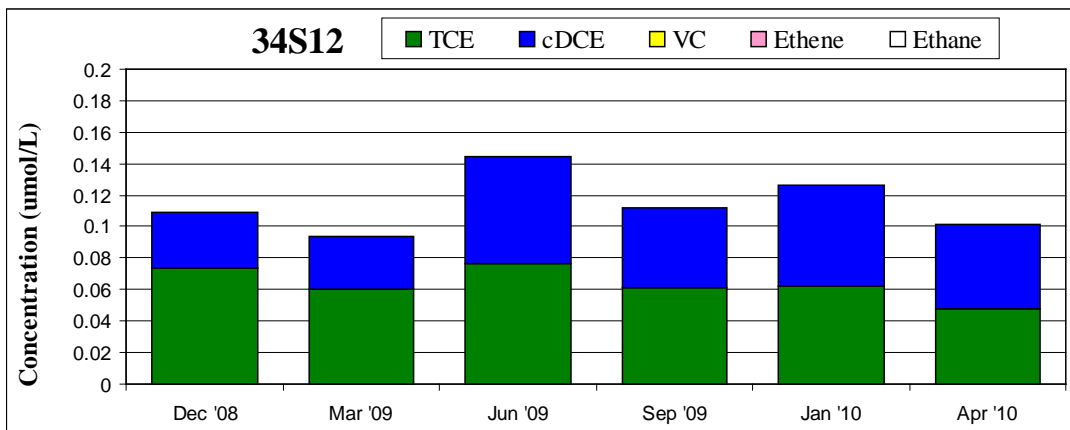
Figure A 8. Chemical concentration of TCE, cDCE, VC, ethene and ethane in micromoles per liter (µmol/L) for well 34S12.
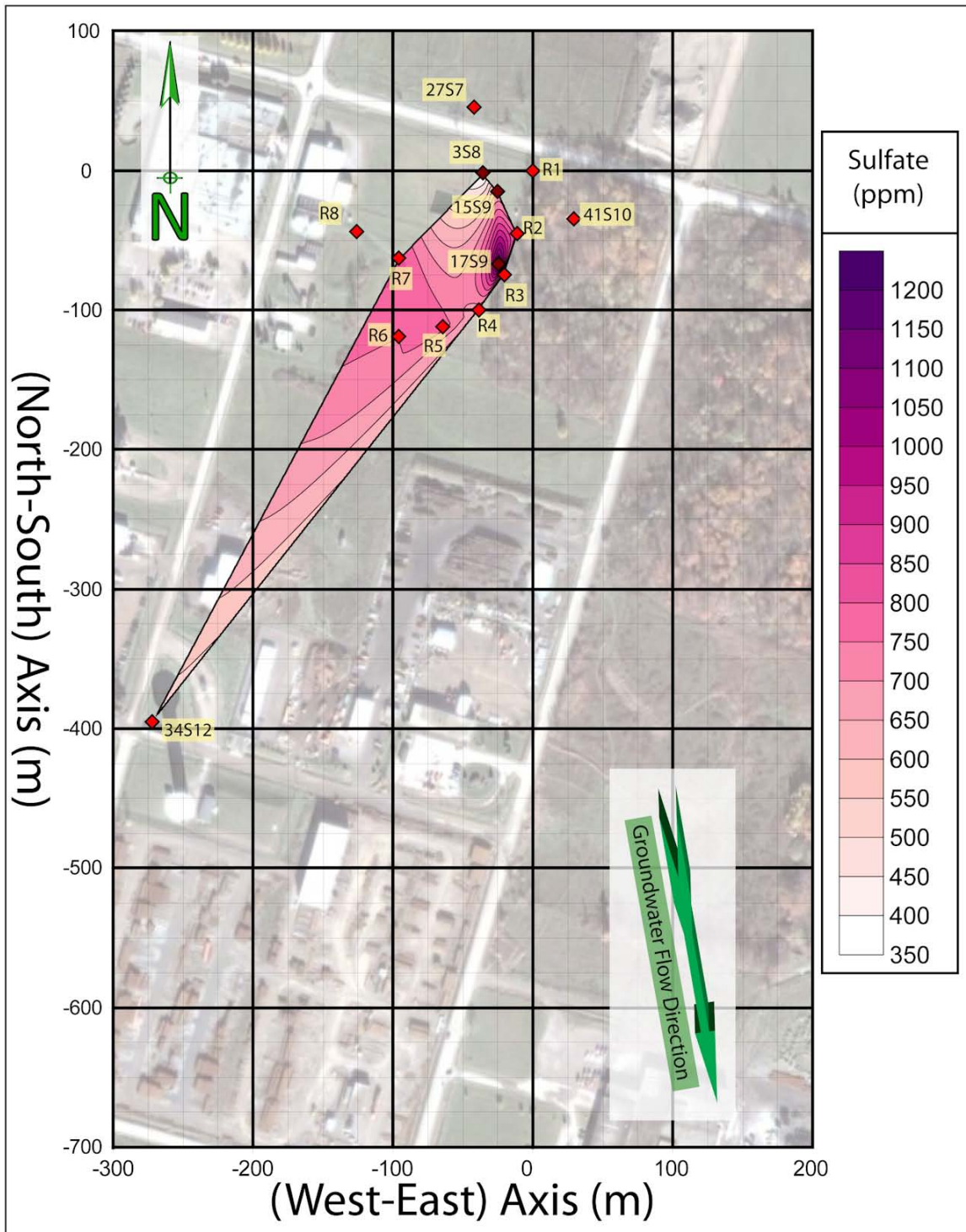
Figure A 9. The concentration of Sulfate (SO$_4^{2-}$) in ppb (ug/L) at the Smithville site. The samples indicating redox conditions were collected in April 2010.

Appendix B:

Additional Data

Table B 1. Well construction and elevation data for the 14 wells studied in detail.

Well	Casing Top	Ground Surface	Bottom Elevation	Bottom Depth	Screen Start	Screen Stop	Bedrock Surface	Borehole Diameter	screen type
units ->	[masl]	[masl]	[masl]	[mbgs]	[mbgs]	[mbgs]	[masl]	[cm]	-
RWS1	192.80	192.80	182.54	10.28	6.08	10.28	187.45	20.00	open hole
RWS2	192.79	192.79	181.65	11.14	6.84	11.14	186.49	20.00	open hole
RWS3	192.71	192.71	181.81	10.90	6.50	10.90	187.00	20.00	open hole
RWS4	192.94	192.94	181.97	10.97	6.55	10.97	187.23	20.00	open hole
RWS5	192.89	192.89	182.46	10.43	6.15	10.43	187.49	20.00	open hole
RWS6	193.00	193.00	181.83	11.17	6.45	11.17	187.36	20.00	open hole
RWS7	193.14	193.14	181.00	12.14	6.82	12.14	187.02	20.00	open hole
RWS8	193.66	193.66	181.91	11.75	6.59	11.75	187.90	20.00	open hole
34S12	193.44	192.49	180.02	12.47	8.00	12.47	185.28	4.20	4.2 cm steel riser pipe with screen, 9.6 cm diameter hole with sand pack
41S10	193.29	192.48		x	6.26	10.88	186.47	10.00	open hole
27S7	195.02	193.10	185.72	7.38	6.38	7.38	188.53	5.10	5.1 cm PVC well screen, 9.6 cm diameter hole with sand pack
17S9	193.80	192.66	183.39	9.27	7.76	9.27	187.88	3.20	3.2 cm PVC riser pipe with screen, 9.6 cm diameter hole with sand pack
15S9	194.03	192.95	183.42	9.53	5.50	9.53	188.02	9.60	open hole
3S8	193.49	193.03	184.53	8.50	4.74	8.50	188.14	x	open hole
18S9	193.96	192.99		x	6.50	9.30	187.12	10.00	5.1 cm PVC well screen, 9.6 cm diameter hole with sand pack
25S8	193.87	193.01		x	7.93	8.93	187.39	10.00	5.1 cm PVC well screen, 9.6 cm diameter hole with sand pack

Table B 2. Water level data from wells screened in the upper part of the Ermosa Member. Data from July 27, 1989.

Well	Elevation	Northing	Easting	Well	Elevation	Northing	Easting
units ->	[masl]	[m]	[m]	units ->	[masl]	[m]	[m]
10S9	184.80	619245.5	4773485.3	38S14	184.66	619254.1	4773130.1
11F	184.97	619421.7	4773679.4	39S13	184.77	619281.5	4773223.0
12E	184.35	619295.0	4773055.1	3S8	185.22	619208.2	4773473.6
13S9	184.76	619237.4	4773478.0	40S12	185.06	619315.0	4773338.0
14S9	185.88	619219.3	4773467.0	41S10	184.81	619273.5	4773440.8
15S9	184.57	619219.1	4773460.7	42S8	185.05	619189.0	4773293.3
16S9	186.23	619203.9	4773428.8	43S7	188.27	619146.2	4773476.6
17S7	186.21	619219.5	4773408.5	44S7	187.40	619104.2	4773438.0
18S9	184.87	619191.5	4773399.8	49S12	189.18	618931.5	4773490.6
19S9	185.02	619212.1	4773493.9	4S8	187.72	619149.7	4773490.0
1S10	184.26	619160.8	4773346.4	50S14	183.31	619044.0	4772531.6
20S9	185.00	619219.7	4773491.9	51S14	184.28	619167.9	4772800.1
21G	189.94	618939.1	4773515.5	52S14	184.60	618853.0	4772908.0
22S9	186.47	619201.3	4773454.0	5S11	184.94	619132.2	4773269.8
23S9	184.53	619224.2	4773453.4	6S11	184.44	619387.8	4773471.4
25S11	184.79	619165.9	4773361.1	7S13	185.40	619044.6	4773309.5
26S8	185.81	619164.7	4773399.4	8S7	188.92	619063.3	4773559.0
27S7	186.49	619201.7	4773520.7	9S8	186.42	619188.9	4773553.1
28S7	186.55	619245.2	4773508.4	LS9	187.03	619185.5	4773436.1
29S12	184.81	619120.3	4773362.8	RWS1	184.85	619244.0	4773475.5
2S9	186.75	619177.3	4773334.9	RWS2	184.77	619233.1	4773430.0
30S14	184.79	619001.6	4773191.6	RWS3	184.83	619223.5	4773400.9
31S12	184.81	619251.3	4773312.2	RWS4	184.83	619205.3	4773375.6
32S12	185.16	619280.7	4773384.1	RWS5	184.82	619179.3	4773363.2
33S12	185.12	619460.0	4773449.8	RWS6	184.81	619148.0	4773356.2
34S12	184.76	618972.0	4773080.5	RWS7	184.68	619148.2	4773412.4
36S12	184.73	619094.1	4773049.2	RWS8	185.52	619117.9	4773431.7
37S11	184.66	619218.8	4773010.1				

Table B 3. Water level data from wells screened in the upper part of the Ermosa Member. Data from July 10, 1999.

Well	Elevation	Northing	Easting	Well	Elevation	Northing	Easting
units ->	[masl]	[m]	[m]	units ->	[masl]	[m]	[m]
10S9	184.21	619245.5	4773485.3	41S10	183.92	619273.5	4773440.8
11F	184.04	619421.7	4773679.4	42S8	185.93	619189.0	4773293.3
12E	183.75	619295.0	4773055.1	44S7	189.27	619104.2	4773438.0
13S9	184.16	619237.4	4773478.0	49S12	188.40	618931.5	4773490.6
15S9	183.83	619219.1	4773460.7	4S8	188.14	619149.7	4773490.0
16S9	184.66	619203.9	4773428.8	50S14	182.51	619044.0	4772531.6
17S9	183.89	619219.5	4773408.5	51S14	183.63	619167.9	4772800.1
19S9	185.06	619212.1	4773493.9	52S14	182.83	618853.0	4772908.0
1S10	183.86	619160.8	4773346.4	53-1	184.19	619002.4	4772721.6
20S9	184.81	619219.7	4773491.9	5S11	184.28	619132.2	4773269.8
22S9	186.59	619201.3	4773454.0	6S11	184.20	619387.8	4773471.4
25S11	183.36	619165.9	4773361.1	7S13	185.22	619044.6	4773309.5
26S8	185.45	619164.7	4773399.4	8S7	188.74	619063.3	4773559.0
27S6	188.07	619201.7	4773520.7	9S8	187.19	619188.9	4773553.1
28S7	186.40	619245.2	4773508.4	RWS1	183.26	619244.0	4773475.5
29S12	183.57	619120.3	4773362.8	RWS2	182.67	619233.1	4773430.0
2S9	185.69	619177.3	4773334.9	RWS3	182.36	619223.5	4773400.9
30S14	183.75	619001.6	4773191.6	RWS4	182.34	619205.3	4773375.6
31S12	184.17	619251.3	4773312.2	RWS5	183.28	619179.3	4773363.2
32S12	184.15	619280.7	4773384.1	RWS6	182.50	619148.0	4773356.2
33S12	184.62	619460.0	4773449.8	RWS7	182.33	619148.2	4773412.4
34S12	183.82	618972.0	4773080.5	RWS8	182.83	619117.9	4773431.7
36S12	183.96	619094.1	4773049.2	64-1	183.34	619166.4	4773107.2
37S11	183.90	619218.8	4773010.1	37C-1	183.76	619212.7	4773022.1
38S14	184.08	619254.1	4773130.1	66-1	183.98	619250.7	4773322.4
39S13	183.93	619281.5	4773223.0	67-1	183.96	619164.9	4773322.2
3S8	186.32	619208.2	4773473.6	34C-1	183.75	618976.4	4773082.0
40S12	184.30	619315.0	4773338.0				

Table B 4. The estimated mass of selected contaminants removed from the Smithville site. Data based on the product of the volume of water removed from each well (recorded daily) and the chemical concentration of that well (collected quarterly).

	Totals	PCE	TCE	VC	DCE	PCB	TCB
RWS1	Total (g)	-	233.61	1.54	24.37	46.54	91.19
RWS2	Total (g)	2.73	1,606.67	59.41	414.81	10,557.31	2,030.90
RWS3	Total (g)	1.20	1,141.87	119.26	632.85	8,551.98	3,256.92
RWS4	Total (g)	0.00	890.75	62.27	286.53	9,890.13	1,717.76
RWS5	Total (g)	-	239.39	54.36	207.68	449.57	397.16
RWS6	Total (g)	-	981.14	157.26	760.80	938.03	1,906.04
RWS7	Total (g)	16.56	9,990.91	403.81	1,336.43	618,938.87	73,072.92
RWS8	Total (g)	-	161.04	9.33	51.79	2,562.92	450.04
(all)	Total (g)	20.48	15,245.38	867.26	3,715.25	651,935.35	82,922.95
(all)	Total (kg)	**0.02**	**15.25**	**0.87**	**3.72**	**651.94**	**82.92**
(all)	Density (kg/L)	1.62	1.46	0.90	1.27	1.40	1.46
(all)	Total Volume (L)	0.01	10.44	0.96	2.94	465.67	56.80

Estimate of total mass of chlorinated ethenes removed in kg (based on chemical concentration data)	19.85

Table B 5. Data pertaining to redox conditions. All analyses from wells sampled in April 2010.

Well ID	NO$_3$	NO$_2$	Ferrous Iron	Mn^{2+}	Sulphate	Sulphide	methane	Eh(field)
units -->	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L), SO$_4$	(mg/L), SO$_4$	(mg/L), SO$_4$	mV
34S12	< 0.1	< .01	0.85	0.09	520	< 0.02	8.6	84
RWS2	< 0.1	< .01	0.12	0.13	770	< 0.02	0	36
RWS3	< 0.1	< .01	0.08	0.13	680	< 0.02	0	30
RWS4	< 0.1	< .01	< 0.05	0.08	650	< 0.02	1.4	24
RWS5	< 0.1	< .01	0.12	0.08	780	< 0.02	0	37
RWS6	< 3.1	0.03	0.11	0.06	750	< 0.02	10.9	51
RWS7	< 4.1	< .01	0.15	0.09	820	< 0.02	2.6	58
17S7	< 0.1	< .01	0.34	0.13	1200	0.02	1322.4	26
15S9	< 2.1	< .01	0.09	0.06	650	< 0.02	418.7	63
3S8	< 1.1	0.04	< 0.05	0.02	370	0.12	4.3	86
RWS1	-	-	-	-	-	-	0	25
RWS8	-	-	-	-	-	-	5.4	67
27S7	-	-	-	-	-	-	5.6	356
41S10	-	-	-	-	-	-	0.4	125

Table B 6. Concentration data for chlorinated ethenes, ethene, and ethane. Data collected from 14 wells emphasized in this study.

well name	Date	TCE	cDCE	VC	Ethene	Ethane
units -->	-	[ug/L]	[ug/L]	[ug/L]	[ug/L]	[ug/L]
RWS1	2008-12	0.5	< 0.1	< 0.2	< 0.2	44
RWS2	2008-12	33	19	2.1	< 0.2	10.4
RWS3	2008-12	12	14	2.7	< 0.2	< 0.2
RWS4	2008-12	14	18	4.1	< 0.2	< 0.2
RWS5	2008-12	17	23	4.6	< 0.2	< 0.2
RWS6	2008-12	8.2	32	11	2.8	< 0.2
RWS7	2008-12	140	250	60	10.5	< 0.2
RWS8	2008-12	0.7	0.4	< 0.2	< 0.2	< 0.2
34S12	2008-12	9.7	3.4	< 0.2	< 0.2	< 0.2
27S7	2008-12	1.4	< 0.1	< 0.2	< 0.2	< 0.2
41S10	2008-12	0.6	< 0.1	< 0.2	< 0.2	< 0.2
17S7	2008-12	33	360	120	8.9	< 0.2
15S9	2008-12	52	150	7.0	< 0.2	< 0.2
3S8	2008-12	180	6	< 2	< 0.2	< 0.2
RWS1	2009-03	6.4	0.8	< 0.2	< 0.2	103
RWS2	2009-03	110	28	3.0	< 0.2	23.9
RWS3	2009-03	33	13	1.2	< 0.2	8.1
RWS4	2009-03	33	53	0.6	< 0.2	2.9
RWS5	2009-03	18	33	2.8	< 0.2	< 0.2
RWS6	2009-03	22	96	29	6.8	< 0.2
RWS7	2009-03	720	540	55	8.1	< 0.2
RWS8	2009-03	1.7	0.9	0.4	< 0.2	< 0.2
34S12	2009-03	7.9	3.3	< 0.2	< 0.2	< 0.2
27S7	2009-03	1.0	< 0.1	< 0.2	< 0.2	< 0.2
41S10	2009-03	14	0.6	< 0.2	< 0.2	< 0.2
17S7	2009-03	36	390	210	30.7	58.6
15S9	2009-03	190	200	8.0	2.8	< 0.2
3S8	2009-03	490	10	< 5	< 0.2	< 0.2
RWS1	2009-06	9.9	1.5	< 0.2	< 0.2	< 0.2
RWS2	2009-06	58	3.1	0.9	< 0.2	< 0.2
RWS3	2009-06	5.0	5.1	0.9	< 0.2	< 0.2
RWS4	2009-06	22	27	0.6	< 0.2	< 0.2
RWS5	2009-06	17	26	2.5	< 0.2	< 0.2
RWS6	2009-06	11	16	2.6	< 0.2	< 0.2
RWS7	2009-06	180	220	5.0	< 0.2	< 0.2
RWS8	2009-06	5.9	38	9.6	< 0.2	< 0.2
34S12	2009-06	10	6.6	< 0.2	< 0.2	< 0.2
27S7	2009-06	0.9	< 0.1	< 0.2	< 0.2	< 0.2
41S10	2009-06	6.1	0.4	< 0.2	< 0.2	< 0.2
17S7	2009-06	16	470	310	< 0.2	< 0.2
15S9	2009-06	97	110	5.0	< 0.2	< 0.2
3S8	2009-06	1400	13	< 20	< 0.2	< 0.2

well name	Date	TCE	cDCE	VC	Ethene	Ethane
units -->	-	[ug/L]	[ug/L]	[ug/L]	[ug/L]	[ug/L]
RWS1	2009-09	7.4	1	< 0.2	< 0.2	< 0.2
RWS2	2009-09	43	26	1.3	< 0.2	< 0.2
RWS3	2009-09	3.8	6.4	0.6	< 0.2	< 0.2
RWS4	2009-09	16	34	1.3	< 0.2	< 0.2
RWS5	2009-09	10	19	2	< 0.2	< 0.2
RWS6	2009-09	7.3	0.3	< 0.2	< 0.2	< 0.2
RWS7	2009-09	33	91	14	2.6	< 0.2
RWS8	2009-09	3.5	58	12	< 0.2	< 0.2
34S12	2009-09	8.1	4.9	< 0.2	< 0.2	< 0.2
27S7	2009-09	0.7	< 0.1	< 0.2	< 0.2	< 0.2
41S10	2009-09	2.1	0.1	< 0.2	< 0.2	< 0.2
17S7	2009-09	19	420	200	23	< 0.2
15S9	2009-09	57	120	4	< 0.2	< 0.2
3S8	2009-09	1600	< 10	< 20	< 0.2	< 0.2
RWS1	2010-01	6.5	3.1	0.4	< 0.2	< 0.2
RWS2	2010-01	71	26	1.6	< 0.2	< 0.2
RWS3	2010-01	13	11	0.8	< 0.2	< 0.2
RWS4	2010-01	17	47	3.8	< 0.2	< 0.2
RWS5	2010-01	11	54	8.9	< 0.2	< 0.2
RWS6	2010-01	8.2	9.4	2.1	< 0.2	< 0.2
RWS7	2010-01	100	190	37	0.5	< 0.2
RWS8	2010-01	5.1	45	9.7	< 0.2	< 0.2
34S12	2010-01	8.2	6.2	< 0.2	< 0.2	< 0.2
27S7	2010-01	0.6	< 0.1	< 0.2	< 0.2	< 0.2
41S10	2010-01	8.4	0.4	< 0.2	< 0.2	< 0.2
17S7	2010-01	32	370	180	< 0.2	< 0.2
15S9	2010-01	45	180	7.0	< 0.2	< 0.2
3S8	2010-01	1800	<10	< 20	< 0.2	< 0.2
RWS1	2010-04	4.9	3.4	0.2	< 0.2	< 0.2
RWS2	2010-04	68	25	1.7	< 0.2	< 0.2
RWS3	2010-04	10	10	1.0	< 0.2	< 0.2
RWS4	2010-04	19	29	1.7	1.4	< 0.2
RWS5	2010-04	13	70	16	< 0.2	< 0.2
RWS6	2010-04	6.1	27	10	1.0	< 0.2
RWS7	2010-04	83	170	32	1.1	< 0.2
RWS8	2010-04	1.6	23	5.6	0.2	< 0.2
34S12	2010-04	6.3	5.2	< 0.2	< 0.2	< 0.2
27S7	2010-04	< 0.1	< 0.1	< 0.2	< 0.2	< 0.2
41S10	2010-04	9.9	0.5	< 0.2	< 0.2	0.3
17S7	2010-04	29	380	200	17.6	< 0.2
15S9	2010-04	55	210	12	0.7	< 0.2
3S8	2010-04	340	7.0	< 5	< 0.2	< 0.2

Table B 7. Results of TCE and cDCE isotopic analyses. Analytical precision shown.

well name	Date	$\delta^{13}C_{TCE}$	Std. Dev.	$\delta^{37}Cl_{TCE}$	Std. Dev.	$\delta^{13}C_{cDCE}$	Std. Dev.	$\delta^{37}Cl_{cDCE}$	Std. Dev.
units -->	-	[‰, VPDB]	[‰, VPDB]	[‰, SMOC]	[‰, SMOC]	[‰, VPDB]	[‰, VPDB]	[‰, SMOC]	[‰, SMOC]
RWS1	2008-12	-	-	-	-	-	-	-	-
RWS2	2008-12	-26.3	0.5	1.65	0.06	-	-	4.94	0.07
RWS3	2008-12	-	-	2.56	0.05	-	-	6.39	0.07
RWS4	2008-12	-	-	2.53	0.03	-	-	6.22	0.07
RWS5	2008-12	-	-	2.50	0.07	-	-	6.16	0.08
RWS6	2008-12	-	-	2.70	0.05	-17.0	0.5	5.68	0.09
RWS7	2008-12	-23.2	0.5	3.01	0.02	-22.6	0.5	5.22	0.07
RWS8	2008-12	-	-	-	-	-	-	-	-
34S12	2008-12	-	-	1.94	0.09	-	-	5.22	0.1
27S7	2008-12	-	-	2.63	0.08	-	-	-	-
41S10	2008-12	-	-	-	-	-	-	-	-
17S7	2008-12	-25.3	0.5	3.18	0.02	-15.6	0.5	6.36	0.04
15S9	2008-12	-25.6	0.5	2.99	0.07	-22.0	0.5	5.08	0.05
3S8	2008-12	-26.3	0.5	1.76	0.09	-	-	4.38	0.12
RWS1	2009-03	-	-	1.80	0.09	-	-	-	-
RWS2	2009-03	-28.0	0.5	1.51	0.05	-	-	4.36	0.17
RWS3	2009-03	-28.2	0.5	1.80	0.00	-	-	4.47	0.09
RWS4	2009-03	-27.6	0.5	1.97	0.12	-22.7	0.5	4.70	0.15
RWS5	2009-03	-27.5	0.5	2.16	0.03	-21.3	0.5	5.20	0.07
RWS6	2009-03	-26.6	0.5	2.67	0.00	-20.4	0.5	4.79	0.18
RWS7	2009-03	-25.1	0.5	2.13	0.04	-26.5	0.5	3.90	0.03
RWS8	2009-03	-	-	-	-	-	-	-	-
34S12	2009-03	-	-	1.89	0.01	-	-	4.32	0.06
27S7	2009-03	-	-	-	-	-	-	-	-
41S10	2009-03	-	-	2.51	0.04	-	-	-	-
17S7	2009-03	-26.1	0.5	2.74	0.07	-13.3	0.5	5.64	0.1
15S9	2009-03	-26.1	0.5	2.10	0.01	-24.3	0.5	4.14	0.13
3S8	2009-03	-27.8	0.5	1.80	0.03	-	-	4.45	0.03
RWS1	2009-06	-	-	2.09	0.07	-	-	-	-
RWS2	2009-06	-27.3	0.5	1.94	0.11	-24.6	0.5	4.81	0.13
RWS3	2009-06	-	-	2.89	0.20	-	-	5.72	0.18
RWS4	2009-06	-27.7	0.5	2.36	0.10	-21.6	0.5	4.93	0.09
RWS5	2009-06	-	-	2.49	0.12	-21.8	0.5	5.10	0.07
RWS6	2009-06	-	-	2.28	0.16	-	-	5.49	0.09
RWS7	2009-06	-24.6	0.5	2.70	0.11	-23.0	0.5	4.48	0.07
RWS8	2009-06	-	-	4.18	0.02	-18.9	0.5	5.49	0.09
34S12	2009-06	-	-	2.12	0.07	-	-	4.19	0.1
27S7	2009-06	-	-	-	-	-	-	-	-
41S10	2009-06	-	-	3.30	0.10	-	-	-	-
17S7	2009-06	-	-	4.69	0.09	-20.6	0.5	5.92	0.08
15S9	2009-06	-26.3	0.5	2.64	0.14	-23.7	0.5	4.49	0.11
3S8	2009-06	-28.9	0.5	1.89	0.10	-	-	3.81	0.09

well name	Date	$\delta^{13}C_{TCE}$	Std. Dev.	$\delta^{37}Cl_{TCE}$	Std. Dev.	$\delta^{13}C_{cDCE}$	Std. Dev.	$\delta^{37}Cl_{cDCE}$	Std. Dev.
units -->	-	[‰, VPDB]	[‰, VPDB]	[‰, SMOC]	[‰, SMOC]	[‰, VPDB]	[‰, VPDB]	[‰, SMOC]	[‰, SMOC]
RWS1	2009-09	-	-	-	-	-	-	-	-
RWS2	2009-09	-28.2	0.5	2.27	0.06	-	-	-	-
RWS3	2009-09	-	-	-	-	-	-	-	-
RWS4	2009-09	-	-	2.31	0.15	-22.2	0.5	4.76	0.11
RWS5	2009-09	-	-	2.25	0.09	-	-	-	-
RWS6	2009-09	-	-	-	-	-	-	-	-
RWS7	2009-09	-25.3	0.5	2.74	0.13	-19.7	0.5	4.73	0.09
RWS8	2009-09	-	-	-	-	-17.0	0.5	-	-
34S12	2009-09	-	-	2.14	0.12	-	-	-	-
27S7	2009-09	-	-	-	-	-	-	-	-
41S10	2009-09	-	-	-	-	-	-	-	-
17S7	2009-09	-	-	3.79	0.09	-	-	-	-
15S9	2009-09	-27.2	0.5	2.47	0.10	-23.6	0.5	4.76	0.12
3S8	2009-09	-25.3	0.5	1.85	0.07	-	-	3.57	0.21
RWS1	2010-01	-	-	1.74	0.17	-	-	5.13	0.27
RWS2	2010-01	-25.5	0.5	1.83	0.04	-24.5	0.5	4.47	0.10
RWS3	2010-01	-	-	1.86	0.03	-	-	4.93	0.10
RWS4	2010-01	-24.1	0.5	2.39	0.04	-20.7	0.5	4.85	0.00
RWS5	2010-01	-	-	2.32	0.14	-16.9	0.5	5.17	0.06
RWS6	2010-01	-	-	1.85	0.11	-	-	4.76	0.11
RWS7	2010-01	-22.5	0.5	2.57	0.12	-23.0	0.5	4.37	0.10
RWS8	2010-01	-	-	-	-	-17.6	0.5	-	-
34S12	2010-01	-	-	1.39	0.14	-	-	3.79	0.08
27S7	2010-01	-	-	-	-	-	-	-	-
41S10	2010-01	-	-	1.93	0.08	-	-	-	-
17S7	2010-01	-21.6	0.5	3.36	0.08	-11.8	0.5	5.96	0.15
15S9	2010-01	-20.6	0.5	2.91	0.12	-18.5	0.5	13.86	0.10
3S8	2010-01	-	-	2.01	0.06	-	-	4.48	0.11
RWS1	2010-04	-	-	1.74	0.17	-	-	5.89	0.16
RWS2	2010-04	-25.1	0.5	1.83	0.04	-24.0	0.5	4.57	0.11
RWS3	2010-04	-	-	1.86	0.03	-	-	5.24	0.07
RWS4	2010-04	-24.9	0.5	2.39	0.04	-20.9	0.5	4.68	0.05
RWS5	2010-04	-	-	2.32	0.14	-17.3	0.5	5.32	0.11
RWS6	2010-04	-	-	1.85	0.11	-17.7	0.5	5.57	0.03
RWS7	2010-04	-23.7	0.5	2.57	0.12	-21.3	0.5	4.58	0.10
RWS8	2010-04	-	-	-	-	-	-	5.35	0.03
34S12	2010-04	-	-	1.39	0.14	-	-	3.79	0.09
27S7	2010-04	-	-	-	-	-	-	-	-
41S10	2010-04	-	-	1.93	0.08	-	-	-	-
17S7	2010-04	-21.7	0.5	3.36	0.08	-12.4	0.5	5.92	0.15
15S9	2010-04	-23.5	0.5	2.91	0.12	-24.0	0.5	4.64	0.12
3S8	2010-04	-25.7	0.5	2.01	0.06	-	-	5.09	0.16

Table B 8. Concentrations of chlorinated ethene in well R1. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[µg/L]	[µg/L]	[µg/L]	units ->	[µg/L]	[µg/L]	[µg/L]
01-Jan-1900	62.3	-	-	31-Aug-2000	0.8	0.0	0.0
17-Apr-1990	124.9	-	-	28-Nov-2000	12.0	0.0	0.0
18-Jul-1990	274.0	-	-	07-Mar-2001	15.0	0.0	0.0
17-Oct-1990	-	-	-	17-May-2001	3.3	0.0	0.0
30-Jan-1991	-	-	-	27-Aug-2001	5.4	0.0	0.0
01-May-1991	183.0	-	-	22-Nov-2001	8.4	0.0	0.0
31-Jul-1991	-	-	-	25-Feb-2002	20.0	1.0	0.0
23-Oct-1991	21.0	-	-	23-May-2002	16.0	1.0	0.0
29-Jan-1992	47.1	-	-	03-Sep-2002	3.0	1.4	0.0
29-Apr-1992	55.3	-	-	03-Dec-2002	6.3	0.0	0.0
05-Aug-1992	40.0	-	-	14-Apr-2003	36.0	7.8	0.0
28-Oct-1992	11.2	-	-	30-Jun-2003	13.0	0.0	0.0
09-Mar-1993	46.0	-	-	15-Sep-2003	0.0	54.5	15.0
28-Jul-1993	27.6	0.0	-	18-Dec-2003	43.0	25.3	0.0
20-Oct-1993	8.8	0.0	-	30-Jun-2004	28.0	22.0	3.4
02-Feb-1994	14.9	-	-	14-Sep-2004	34.0	69.4	14.0
26-Apr-1994	54.7	-	-	15-Dec-2004	11.0	2.4	0.0
20-Jul-1994	24.6	-	-	22-Mar-2005	23.6	8.5	0.4
22-Nov-1994	15.7	-	-	09-Jun-2005	15.9	10.2	0.5
14-Mar-1995	95.8	4.1	-	26-Sep-2005	20.2	56.7	6.0
20-Jun-1995	36.8	1.7	-	12-Dec-2005	18.5	16.2	4.0
09-Nov-1995	25.8	-	-	13-Mar-2006	15.2	4.4	0.0
03-Apr-1996	25.2	1.3	0.0	16-Jun-2006	2.1	0.7	0.0
07-Oct-1996	12.2	0.8	0.0	18-Dec-2006	13.0	1.4	0.0
03-Mar-1997	31.8	0.0	0.0	14-Mar-2007	12.0	1.0	0.0
12-Nov-1997	2.2	0.0	0.0	19-Jun-2007	15.0	2.1	0.3
11-Feb-1998	31.9	1.3	0.0	17-Sep-2007	1.8	0.5	0.0
30-Apr-1998	6.5	0.0	0.0	27-Dec-2007	15.0	10.1	0.4
21-Jul-1998	15.0	1.0	0.0	01-Apr-2008	6.6	15.4	1.3
21-Oct-1998	2.0	1.6	0.0	21-Apr-2008	14.0	2.3	0.2
04-Feb-1999	35.0	1.7	0.0	02-Jul-2008	1.1	0.2	0.0
17-May-1999	8.4	0.0	0.0	14-Oct-2008	1.6	0.3	0.0
22-Sep-1999	8.9	0.0	0.0	24-Jun-2009	9.9	1.5	0.0
15-Nov-1999	2.2	0.0	0.0	26-Jan-2010	6.5	3.3	0.4
10-Feb-2000	9.4	0.0	0.0	15-Apr-2010	4.9	3.4	0.2
16-May-2000	2.1	0.0	0.0				

Table B 9. Concentrations of chlorinated ethene in well R2. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[μg/L]	[μg/L]	[μg/L]	units ->	[μg/L]	[μg/L]	[μg/L]
20-Oct-1989	466.0	-	-	28-Nov-2000	24.0	1.9	0.0
26-Jan-1990	609.0	-	-	07-Mar-2001	18.0	1.5	0.0
17-Apr-1990	142.3	-	-	10-Jul-2001	12.0	1.1	0.0
18-Jul-1990	887.0	-	-	27-Aug-2001	8.6	0.0	0.0
01-May-1991	46.2	-	-	22-Nov-2001	20.0	2.6	0.8
31-Jul-1991	52.3	-	-	25-Feb-2002	39.0	2.9	0.9
23-Oct-1991	198.0	-	-	23-May-2002	120.0	9.7	0.7
29-Jan-1992	146.5	-	-	03-Sep-2002	42.0	0.0	0.0
29-Apr-1992	70.2	-	-	03-Dec-2002	8.7	0.0	0.0
05-Aug-1992	189.0	-	-	14-Apr-2003	46.0	11.8	0.0
28-Oct-1992	7.8	-	-	30-Jun-2003	14.0	0.0	0.0
09-Mar-1993	68.5	-	-	15-Sep-2003	42.0	56.8	16.0
28-Jul-1993	66.9	-	-	10-Dec-2003	59.0	25.9	1.7
02-Feb-1994	82.2	-	-	30-Jun-2004	29.0	23.0	2.3
26-Apr-1994	52.5	-	-	14-Sep-2004	33.0	62.2	12.0
20-Jul-1994	77.8	-	-	15-Dec-2004	11.0	2.8	0.0
22-Nov-1994	187.0	-	-	22-Mar-2005	60.4	35.3	3.0
14-Mar-1995	35.1	0.9	-	09-Jun-2005	13.9	16.4	3.4
20-Jun-1995	42.2	0.9	-	26-Sep-2005	22.4	57.1	3.9
09-Nov-1995	152.0	-	-	12-Dec-2005	23.2	19.0	4.5
03-Apr-1996	102.0	2.3	0.0	13-Mar-2006	49.1	102.3	18.0
07-Oct-1996	247.0	2.9	0.0	16-Jun-2006	20.0	59.9	6.3
03-Mar-1997	175.0	0.0	0.0	18-Dec-2006	14.0	1.5	0.0
12-Nov-1997	41.6	2.2	0.0	08-Jan-2007	11.0	0.9	0.0
11-Feb-1998	109.0	4.7	0.0	14-Mar-2007	26.0	5.8	0.5
30-Apr-1998	39.0	0.0	0.0	19-Jun-2007	84.0	65.3	4.0
21-Jul-1998	17.0	0.9	0.0	17-Sep-2007	44.0	24.0	1.7
21-Oct-1998	11.0	0.0	0.0	27-Dec-2007	33.0	64.2	9.9
04-Feb-1999	130.0	5.1	0.0	01-Apr-2008	100.0	31.0	3.0
02-Jun-1999	20.0	0.0	0.0	02-Jul-2008	77.0	44.6	5.0
22-Sep-1999	48.0	0.0	0.0	01-Oct-2008	16.0	123.6	27.0
15-Nov-1999	27.0	1.7	0.0	24-Jun-2009	58.0	32.1	0.9
10-Feb-2000	52.0	5.8	0.0	26-Jan-2010	71.0	27.4	1.6
16-May-2000	15.0	1.3	0.0	15-Apr-2010	68.0	26.2	1.7
31-Aug-2000	37.0	2.7	0.8				

Table B 10. Concentrations of chlorinated ethene in well R3. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[μg/L]	[μg/L]	[μg/L]	units ->	[μg/L]	[μg/L]	[μg/L]
20-Oct-1989	1138.0	-	-	31-Aug-2000	2.4	1.0	0.0
26-Jan-1990	893.0	-	-	28-Nov-2000	1.5	0.0	0.0
17-Apr-1990	38.0	-	-	07-Mar-2001	61.0	6.0	2.2
18-Jul-1990	178.0	-	-	17-May-2001	14.0	1.5	0.0
01-May-1991	108.0	-	-	27-Aug-2001	36.0	6.2	2.1
31-Jul-1991	114.0	-	-	22-Nov-2001	9.8	2.4	0.0
23-Oct-1991	159.0	-	-	25-Feb-2002	10.0	1.3	0.7
29-Jan-1992	42.2	-	-	23-May-2002	100.0	15.6	2.1
29-Apr-1992	3.9	-	-	03-Sep-2002	85.0	28.4	7.5
05-Aug-1992	1.6	-	-	03-Dec-2002	9.3	1.9	0.0
28-Oct-1992	63.7	-	-	14-Apr-2003	45.0	10.7	0.0
09-Mar-1993	5.4	-	-	30-Jun-2003	14.0	0.0	0.0
28-Jul-1993	14.1	-	-	15-Sep-2003	27.0	42.4	12.0
20-Oct-1993	13.4	-	-	10-Dec-2003	69.0	28.3	2.7
02-Feb-1994	16.3	-	-	30-Jun-2004	31.0	24.0	3.4
26-Apr-1994	57.8	-	-	14-Sep-2004	35.0	66.5	13.0
20-Jul-1994	8.1	-	-	15-Dec-2004	8.7	2.6	0.2
22-Nov-1994	94.5	-	-	22-Mar-2005	34.0	15.5	0.5
14-Mar-1995	62.5	2.0	-	09-Jun-2005	33.8	29.8	2.4
20-Jun-1995	21.3	2.3	-	26-Sep-2005	14.6	90.9	16.0
09-Nov-1995	86.9	-	-	12-Dec-2005	12.4	11.8	3.1
03-Apr-1996	4.0	0.0	0.0	13-Mar-2006	25.1	66.6	10.0
07-Oct-1996	23.7	6.9	3.6	16-Jun-2006	17.0	50.9	10.0
03-Mar-1997	0.0	0.0	0.0	18-Dec-2006	13.0	3.4	0.0
12-Nov-1997	21.0	3.5	0.0	08-Jan-2007	18.0	1.7	0.0
11-Feb-1998	54.2	7.7	0.0	14-Mar-2007	19.0	17.8	2.1
30-Apr-1998	25.0	5.9	0.0	19-Jun-2007	5.2	22.4	1.7
21-Jul-1998	77.0	6.9	0.0	17-Sep-2007	6.6	8.0	1.7
21-Oct-1998	110.0	6.3	0.0	27-Dec-2007	13.0	123.6	26.0
04-Feb-1999	6.5	0.0	0.0	01-Apr-2008	20.0	8.2	1.1
02-Jun-1999	32.0	2.2	0.0	02-Jul-2008	15.0	17.7	3.1
22-Sep-1999	7.3	0.0	0.0	01-Oct-2008	5.5	27.0	8.0
15-Nov-1999	3.5	0.0	0.0	24-Jun-2009	5.0	5.1	0.9
10-Feb-2000	1.2	0.0	0.0	26-Jan-2010	13.0	11.4	0.8
16-May-2000	1.8	0.0	0.0	15-Apr-2010	10.0	10.3	1.0

Table B 11. Concentrations of chlorinated ethene in well R4. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[μg/L]	[μg/L]	[μg/L]	units ->	[μg/L]	[μg/L]	[μg/L]
20-Oct-1989	940.9	-	-	28-Nov-2000	81.0	15.6	6.0
26-Jan-1990	812.0	-	-	07-Mar-2001	11.0	3.8	1.8
17-Apr-1990	647.3	-	-	17-May-2001	49.0	10.0	0.0
18-Jul-1990	81.0	-	-	27-Aug-2001	38.0	6.2	1.0
01-May-1991	103.0	-	-	22-Nov-2001	38.0	27.6	9.4
31-Jul-1991	311.0	-	-	25-Feb-2002	140.0	17.3	3.5
23-Oct-1991	161.0	-	-	23-May-2002	28.0	4.1	0.0
29-Jan-1992	146.5	-	-	03-Sep-2002	52.0	18.6	4.6
29-Apr-1992	144.0	-	-	05-Dec-2002	14.0	13.6	4.0
05-Aug-1992	29.8	-	-	14-Apr-2003	46.0	10.7	0.0
28-Oct-1992	82.7	-	-	30-Jun-2003	95.0	37.2	12.0
09-Mar-1993	23.5	-	-	15-Sep-2003	41.0	68.0	22.0
28-Jul-1993	17.8	-	-	10-Dec-2003	70.0	26.8	1.9
20-Oct-1993	20.9	-	-	30-Jun-2004	32.0	26.3	2.7
02-Feb-1994	46.3	-	-	14-Sep-2004	35.0	65.2	12.0
26-Apr-1994	47.5	-	-	15-Dec-2004	9.5	3.2	0.0
20-Jul-1994	35.1	-	-	22-Mar-2005	34.5	15.5	0.5
22-Nov-1994	20.5	-	-	09-Jun-2005	37.3	36.8	3.2
14-Mar-1995	51.5	5.9	-	26-Sep-2005	14.4	32.6	7.6
20-Jun-1995	37.4	4.3	-	12-Dec-2005	14.7	28.5	5.8
09-Nov-1995	46.2	-	-	13-Mar-2006	34.1	31.0	1.2
07-Oct-1996	35.5	3.1	0.0	16-Jun-2006	21.0	57.4	8.5
03-Mar-1997	46.5	0.0	0.0	18-Dec-2006	12.0	2.0	0.0
12-Nov-1997	26.0	0.0	0.0	08-Jan-2007	18.0	23.8	0.0
11-Feb-1998	111.0	6.0	0.0	14-Mar-2007	31.0	84.8	11.0
30-Apr-1998	125.0	0.0	0.0	19-Jun-2007	10.0	41.1	9.6
21-Jul-1998	130.0	15.5	5.9	17-Sep-2007	7.0	9.7	1.5
21-Oct-1998	30.0	3.3	0.0	27-Dec-2007	10.0	43.3	8.1
04-Feb-1999	110.0	13.0	0.0	01-Apr-2008	30.0	20.5	1.6
02-Jun-1999	63.0	9.6	2.2	02-Jul-2008	13.0	9.4	0.8
22-Sep-1999	60.0	9.0	0.0	01-Oct-2008	14.0	32.0	6.1
15-Nov-1999	89.0	14.9	5.1	24-Jun-2009	22.0	28.0	0.6
10-Feb-2000	51.0	10.8	6.0	26-Jan-2010	17.0	48.4	3.8
16-May-2000	30.0	6.9	3.9	15-Apr-2010	19.0	29.9	1.7
31-Aug-2000	51.0	12.5	3.8				

Table B 12. Concentrations of chlorinated ethene in well R5. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[µg/L]	[µg/L]	[µg/L]	units ->	[µg/L]	[µg/L]	[µg/L]
20-Oct-1989	197.5	-	-	31-Aug-2000	18.0	1.8	0.0
26-Jan-1990	143.5	-	-	28-Nov-2000	32.0	5.1	1.2
17-Apr-1990	402.2	-	-	07-Mar-2001	11.0	1.6	0.0
18-Jul-1990	53.0	-	-	10-May-2001	11.0	2.2	0.0
01-May-1991	40.0	-	-	27-Aug-2001	4.2	0.0	0.0
31-Jul-1991	25.5	-	-	22-Nov-2001	3.9	0.0	0.0
23-Oct-1991	32.4	-	-	25-Feb-2002	2.0	0.0	0.0
29-Jan-1992	27.2	-	-	23-May-2002	31.0	5.2	0.4
29-Apr-1992	33.5	-	-	03-Sep-2002	80.0	27.3	4.8
05-Aug-1992	39.9	-	-	03-Dec-2002	9.8	10.1	2.0
28-Oct-1992	20.0	-	-	14-Apr-2003	40.0	10.7	0.0
09-Mar-1993	8.5	-	-	30-Jun-2003	76.0	30.4	9.5
28-Jul-1993	4.2	-	-	15-Sep-2003	33.0	50.0	11.0
20-Oct-1993	9.8	-	-	10-Dec-2003	55.0	23.0	0.0
02-Feb-1994	7.9	-	-	30-Jun-2004	26.0	23.1	3.3
26-Apr-1994	9.6	-	-	14-Sep-2004	32.0	59.1	10.0
20-Jul-1994	17.7	-	-	15-Dec-2004	6.7	2.2	0.0
22-Nov-1994	7.3	-	-	22-Mar-2005	32.3	20.7	2.0
14-Mar-1995	7.2	0.5	-	09-Jun-2005	36.7	34.7	2.7
20-Jun-1995	5.2	0.0	-	26-Sep-2005	5.1	1.9	0.3
09-Nov-1995	9.1	-	-	12-Dec-2005	18.4	47.2	10.9
03-Apr-1996	20.9	5.3	11.6	13-Mar-2006	22.4	31.8	5.3
07-Oct-1996	31.1	5.8	0.0	16-Jun-2006	12.0	35.3	5.9
03-Mar-1997	65.5	0.0	0.0	18-Dec-2006	14.0	10.3	0.3
12-Nov-1997	8.5	0.5	0.0	08-Jan-2007	3.7	1.8	0.0
11-Feb-1998	2.2	0.0	0.0	14-Mar-2007	3.7	3.8	0.2
30-Apr-1998	6.3	0.5	0.0	19-Jun-2007	15.0	45.2	11.0
21-Jul-1998	11.0	0.5	0.0	17-Sep-2007	10.0	10.5	0.4
21-Oct-1998	5.9	0.0	0.0	27-Dec-2007	8.1	31.2	8.0
04-Feb-1999	9.1	0.7	0.0	01-Apr-2008	27.0	31.5	3.9
17-Jun-1999	0.0	0.0	12.0	02-Jul-2008	14.0	10.6	1.0
22-Sep-1999	9.2	0.0	0.0	01-Oct-2008	2.6	1.6	0.3
15-Nov-1999	8.3	0.0	0.0	24-Jun-2009	17.0	27.0	2.5
10-Feb-2000	6.8	0.0	0.0	26-Jan-2010	11.0	56.2	8.9
16-May-2000	5.0	0.0	0.0	15-Apr-2010	13.0	72.7	16.0

Table B 13. Concentrations of chlorinated ethene in well R6. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[μg/L]	[μg/L]	[μg/L]	units ->	[μg/L]	[μg/L]	[μg/L]
20-Oct-1989	143.5	-	-	31-Aug-2000	3.0	0.0	0.0
26-Jan-1990	4.8	-	-	28-Nov-2000	8.4	0.0	0.0
17-Apr-1990	124.9	-	-	07-Mar-2001	7.4	0.0	0.0
18-Jul-1990	95.8	-	-	10-May-2001	7.9	0.0	0.0
01-May-1991	57.9	-	-	27-Aug-2001	9.2	0.0	0.0
31-Jul-1991	29.3	-	-	22-Nov-2001	6.9	0.0	0.0
23-Oct-1991	64.4	-	-	25-Feb-2002	6.3	0.0	0.0
29-Jan-1992	49.2	-	-	23-May-2002	25.0	9.9	3.2
29-Apr-1992	54.3	-	-	03-Sep-2002	6.4	0.0	0.0
05-Aug-1992	36.1	-	-	03-Dec-2002	5.7	0.0	0.0
28-Oct-1992	39.1	-	-	14-Apr-2003	35.0	10.5	0.0
09-Mar-1993	31.6	-	-	30-Jun-2003	5.6	0.0	0.0
28-Jul-1993	32.4	-	-	15-Sep-2003	6.0	0.0	0.0
20-Oct-1993	24.5	-	-	10-Dec-2003	6.3	0.0	0.0
02-Feb-1994	32.9	-	-	30-Jun-2004	6.2	0.0	0.0
26-Apr-1994	24.1	-	-	14-Sep-2004	7.5	0.0	0.0
20-Jul-1994	30.1	-	-	15-Dec-2004	7.7	0.0	0.0
22-Nov-1994	21.3	-	-	22-Mar-2005	7.5	1.3	0.3
14-Mar-1995	22.2	0.0	-	09-Jun-2005	6.8	6.8	1.5
20-Jun-1995	24.8	0.5	-	26-Sep-2005	7.7	0.3	0.0
09-Nov-1995	23.0	-	-	12-Dec-2005	6.6	1.0	0.0
03-Apr-1996	23.8	0.0	0.0	13-Mar-2006	18.0	31.4	5.3
07-Oct-1996	16.1	0.0	0.0	16-Jun-2006	7.0	0.5	0.0
03-Mar-1997	13.6	0.0	0.0	18-Dec-2006	38.0	66.6	12.0
12-Nov-1997	13.9	0.0	0.0	08-Jan-2007	52.0	86.3	16.0
11-Feb-1998	5.0	0.5	0.0	14-Mar-2007	71.0	73.6	12.0
30-Apr-1998	4.2	0.0	0.0	19-Jun-2007	28.0	45.2	9.2
21-Jul-1998	16.0	0.7	0.0	17-Sep-2007	14.0	33.4	5.2
21-Oct-1998	17.0	0.0	0.0	27-Dec-2007	11.0	22.9	6.1
04-Feb-1999	13.0	0.0	0.0	01-Apr-2008	23.0	63.5	16.0
02-Jun-1999	10.0	0.0	0.0	02-Jul-2008	12.0	44.7	13.0
22-Sep-1999	10.0	0.0	0.0	01-Oct-2008	5.4	0.6	0.0
15-Nov-1999	9.5	0.0	0.0	24-Jun-2009	11.0	16.7	2.6
10-Feb-2000	11.0	0.0	0.0	26-Jan-2010	8.2	10.0	2.1
16-May-2000	9.6	0.0	0.0	19-Apr-2010	6.1	27.9	10.0

Table B 14. Concentrations of chlorinated ethene in well R7. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[μg/L]	[μg/L]	[μg/L]	units ->	[μg/L]	[μg/L]	[μg/L]
20-Oct-1989	4.8	-	-	31-Aug-2000	1.7	0.0	0.0
26-Jan-1990	49.4	-	-	28-Nov-2000	190.0	123.0	30.0
17-Apr-1990	360.4	-	-	07-Mar-2001	63.0	21.3	5.6
18-Jul-1990	9.6	-	-	10-May-2001	190.0	31.2	5.1
01-May-1991	32.4	-	-	27-Aug-2001	310.0	92.4	27.0
31-Jul-1991	37.1	-	-	22-Nov-2001	410.0	133.1	35.0
23-Oct-1991	620.0	-	-	25-Feb-2002	390.0	99.8	36.0
29-Jan-1992	1080.0	-	-	23-May-2002	250.0	117.7	14.0
29-Apr-1992	624.0	-	-	03-Sep-2002	7.4	0.0	0.0
05-Aug-1992	694.0	-	-	03-Dec-2002	130.0	112.2	23.0
28-Oct-1992	426.9	-	-	14-Apr-2003	31.0	8.4	0.0
09-Mar-1993	957.0	-	-	30-Jun-2003	32.0	11.0	3.0
28-Jul-1993	452.5	-	-	15-Sep-2003	6.6	0.0	0.0
20-Oct-1993	752.4	-	-	10-Dec-2003	7.5	1.8	0.0
02-Feb-1994	438.8	-	-	30-Jun-2004	11.0	9.4	0.0
26-Apr-1994	425.4	-	-	14-Sep-2004	11.0	14.9	1.1
20-Jul-1994	502.5	-	-	15-Dec-2004	14.0	8.0	0.4
22-Nov-1994	102.0	-	-	22-Mar-2005	14.1	13.8	1.7
14-Mar-1995	312.0	6.8	-	09-Jun-2005	138.0	305.6	60.2
20-Jun-1995	316.0	5.6	-	26-Sep-2005	25.8	88.6	30.0
09-Nov-1995	494.0	-	-	12-Dec-2005	155.0	60.4	4.0
03-Apr-1996	445.0	18.2	38.8	13-Mar-2006	1070.0	458.0	1.0
07-Oct-1996	511.0	18.8	0.0	16-Jun-2006	1200.0	488.4	1.3
03-Mar-1997	323.0	0.0	0.0	18-Dec-2006	1500.0	593.0	19.0
12-Nov-1997	237.0	10.5	0.0	08-Jan-2007	1800.0	614.8	29.0
11-Feb-1998	226.0	11.0	0.0	14-Mar-2007	1300.0	463.0	1.0
30-Apr-1998	121.0	0.0	0.0	19-Jun-2007	750.0	431.0	1.0
21-Jul-1998	140.0	52.7	7.2	17-Sep-2007	48.0	16.1	0.0
21-Oct-1998	44.0	11.5	0.0	27-Dec-2007	55.0	38.7	0.6
11-Feb-1999	96.0	34.0	0.0	01-Apr-2008	23.0	63.6	17.0
02-Jun-1999	250.0	40.9	4.9	02-Jul-2008	800.0	660.0	1.0
22-Sep-1999	420.0	74.0	14.0	01-Oct-2008	260.0	232.0	3.0
15-Nov-1999	420.0	94.0	17.0	24-Jun-2009	180.0	229.0	5.0
10-Feb-2000	450.0	112.0	23.0	26-Jan-2010	100.0	199.0	37.0
16-May-2000	480.0	84.2	14.0	19-Apr-2010	83.0	178.3	32.0

Table B 15. Concentrations of chlorinated ethene in well R8. Data presented in ug/L.

Date	TCE	cDCE	VC	Date	TCE	cDCE	VC
units ->	[μg/L]	[μg/L]	[μg/L]	units ->	[μg/L]	[μg/L]	[μg/L]
20-Oct-1989	0.0	-	-	31-Aug-2000	19.0	4.1	0.8
26-Jan-1990	0.2	-	-	28-Nov-2000	4.2	1.2	0.0
17-Apr-1990	0.0	-	-	08-Mar-2001	2.1	0.0	0.0
18-Jul-1990	2.6	-	-	10-May-2001	1.5	0.0	0.0
01-May-1991	2.5	-	-	27-Aug-2001	0.8	0.0	0.0
31-Jul-1991	0.0	-	-	22-Nov-2001	0.9	0.0	0.0
23-Oct-1991	1.3	-	-	25-Feb-2002	3.6	1.4	0.6
29-Jan-1992	0.0	-	-	23-May-2002	92.0	43.4	9.8
29-Apr-1992	0.0	-	-	03-Sep-2002	6.9	0.0	0.0
05-Aug-1992	0.0	-	-	03-Dec-2002	56.0	49.2	11.0
28-Oct-1992	0.0	-	-	14-Apr-2003	7.9	2.1	0.0
09-Mar-1993	0.0	-	-	30-Jun-2003	28.0	8.4	3.0
28-Jul-1993	3.2	-	-	15-Sep-2003	6.2	0.0	0.0
20-Oct-1993	1.3	-	-	10-Dec-2003	47.0	76.1	11.0
02-Feb-1994	0.0	-	-	30-Jun-2004	0.8	0.0	0.0
26-Apr-1994	1.1	-	-	14-Sep-2004	2.8	0.0	0.0
20-Jul-1994	1.3	-	-	15-Dec-2004	1.8	0.0	0.0
22-Nov-1994	2.3	-	-	22-Mar-2005	24.3	20.4	0.4
14-Mar-1995	7.9	0.0	-	09-Jun-2005	5.2	5.1	0.9
20-Jun-1995	1.3	0.0	-	26-Sep-2005	1.2	0.8	0.0
09-Nov-1995	0.9	-	-	12-Dec-2005	1.6	1.9	0.3
03-Apr-1996	6.7	0.0	0.0	13-Mar-2006	2.9	2.9	0.5
07-Oct-1996	5.9	0.0	0.0	16-Jun-2006	1.6	0.5	0.0
03-Mar-1997	0.0	0.0	0.0	18-Dec-2006	1.7	0.5	0.0
12-Nov-1997	40.8	3.7	0.0	08-Jan-2007	2.2	0.8	0.0
11-Feb-1998	87.0	9.0	0.0	14-Mar-2007	0.8	0.2	0.0
30-Apr-1998	113.0	0.0	0.0	19-Jun-2007	0.5	0.7	0.0
21-Jul-1998	0.0	0.0	0.0	17-Sep-2007	1.3	0.3	0.0
21-Oct-1998	0.0	0.0	0.0	27-Dec-2007	0.7	0.2	0.0
04-Feb-1999	9.2	1.0	0.0	01-Apr-2008	1.2	0.4	0.0
17-Jun-1999	0.0	0.0	0.0	02-Jul-2008	1.8	2.1	0.5
22-Sep-1999	3.3	0.0	0.0	01-Oct-2008	1.1	0.9	0.2
15-Nov-1999	2.9	0.0	0.0	24-Jun-2009	5.9	39.5	9.6
10-Feb-2000	2.1	0.0	0.0	26-Jan-2010	5.1	47.1	9.7
16-May-2000	1.5	0.0	0.0	19-Apr-2010	1.6	24.1	5.6

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