ISOTOPIC FRACTIONATION OF CHLORINATED ETHENES DURING REDUCTIVE DEHALOGENATION BY ZERO VALENT IRON

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Isotopic Fractionation of Chlorinated Ethenes During Reductive Dehalogenation by Zero Valent Iron

by

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A thesis submitted to the
School of Graduate Studies
in partial fulfilment of the
requirements for the degree of
Master of Science

Environmental Science Programme
Memorial University of Newfoundland

June 1998

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Abstract

Many surface and groundwaters are contaminated by chlorinated ethenes as a result of their widespread use in different industries. One promising technique for the removal of these compounds is reductive dehalogenation using iron metal as the reducing agent. The method involves introducing an iron metal barrier into the flow of groundwater. Zero valent iron reacts with the chlorinated ethenes by either β-elimination or dehydrogenation, depending on the pH and Eh of the system. The purpose of this investigation was to determine the overall magnitude and direction of isotopic fractionation with respect to the stable isotopes of carbon (^{12}C, ^{13}C) during reductive dechlorination of selected chlorinated ethenes. By quantifying the fractionation of reductive dehalogenation as well as other reactions, the processes that may be dominant in the removal of the pollutants can be determined. Replicate experiments were done using low concentration solutions of trichloroethylene (TCE), perchloroethylene (PCE), 1,2-cis-dichloroethyelene (c-DCE) and 1,2-trans-dichloroethylene (t-DCE) and acid washed iron powder using compound specific isotopic analysis. The changes in the carbon isotope composition ($\delta^{13}C$) and the consumption of the ethenes were followed until they were no longer detectable by gas chromatography isotope ratio mass spectrometry (for 169, 345, 366 hours respectively). The presence of dissolved oxygen allowed for acidic conditions and the precipitation of ferric hydroxide. The consequence of this was the "natural" buffering of the system to pH between 5 and 6. The transition from β-elimination to dehydrogenation as the major reaction pathway also lies in this pH range. The pH also had an effect on the reaction rates. During the course of the reaction, enrichment in ^{13}C was observed in the isotopic composition of each of the compounds. Kinetic or Rayleigh processes can be used to explain this effect. Fractionation factors were calculated using the Rayleigh model and found to be 1.0146, 1.0036, 1.0087, and 1.026 for c-DCE, t-DCE, TCE and PCE respectively. Future studies should include changing parameters such as temperature, as well as using buffer solutions; these studies will be useful in order to obtain a more complete picture of processes in natural waters.

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List of Abbreviations Used in Text

atomic mass units	amu
Canadian Environmental Protection Act	CEPA
compound specific isotopic analysis	CSIA
Celsius	°C
change over	C/O
1,2-cis-dichloroethylene	c-DCE
dense non aqueous phase liquid	DNAPL
dichloroethylene	DCE
flame ionization detector	FID
gas chromatograph	GC
gas chromatography-combustion-isotope mass spectrometry	GC-C-IRMS
gas chromatography-mass spectrometry	GC-MS
lethal concentration required to observe mortality in 50% of a test population	LC$_{50}$
Molar Concentration in moles/l	M
methane-monooxygenase	MMO
parts per million	ppm
PeeDee Belemnite	PDB
perchloroethylene	PCE
per mil (parts per thousand)	$^{0}/_{00}$
personal communication	pers. comm.
polymethylsiloxane	PDMS
pounds per square inch	psi
solid phase microextraction	SPME
1,2-trans-dichloroethylene	t-DCE
trichloroethylene	TCE
vinyl chloride	VC
World Health Organization	WHO

Acknowledgments

I would like to take this opportunity to thank Dr. Jun Abrajano for giving me the opportunity to work in his lab. I also would like to thank Dr. Bob Helleur and Dr. Henry Longerich for being most patient with me during the first try at a Master's project.

I am also grateful to Linda Winsor and Jerry Pulchan at the Biogeochemistry Facility at MUN. Without them, there would probably be no results to speak of.

Thanks to Dr. Neil Sturchio and the group at Argonne Laboratory who did the BET analysis.

Thanks to Dr. Lynn Roberts for the one email that helped things progress during this project.

I would also like to thank Alden Woodward, who gave me a shoulder to cry on when things were looking pretty grim.

Thanks to Billie the cat who gives me unconditional love, and purrs.

Last and certainly not least, many thanks to Mom and Dad for always being there for me. This one's for you.

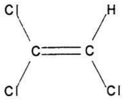
Chapter 1 - Introduction

The increased incidence of reported health problems and ecological damage associated with contaminated surface and ground waters has lead to a concerted effort, in scientific and engineering communities, to develop effective water quality characterisation and water treatment methods. Chlorinated ethenes are the focus of this type of research, since their presence has become ubiquitous in the environment with their extensive use in industry. These compounds are highly toxic to most organisms, and do not readily degrade naturally in the environment.

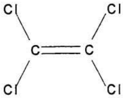
Reductive dehalogenation using zero valent iron is a new and promising technique for the treatment of water that is contaminated with chloroethenes. Current research focuses on the rates and mechanisms involved in this reaction and how the reductive dechlorination process can be engineered into contaminated sites.

The purpose of this study was to determine the magnitude and direction of the change in the carbon isotope signature of chlorinated ethenes during reductive dehalogenation. To date, very few studies of this type have been undertaken. Pollutants from different sources have unique isotopic compositions and these "fingerprints" can be used to trace pollutants to their sources (van Warmerdam *et al.*, 1995). This approach is premised on the assumption that no alteration of the isotopic composition occurs between the release and sampling of the contaminant. Just as compounds can have source isotopic "fingerprints", each chemical reaction involving the compound of interest could affect the isotopic composition in a predictable way. By understanding the extent of fractionation in reactions such as reductive dehalogenation, the type and extent of reaction of chlorinated ethenes can be understood in field situations.

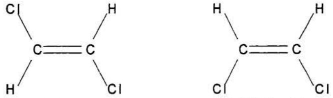
Bench scale experiments were conducted to model the carbon isotopic variations that would occur during reductive dehalogenation. Four chlorinated ethenes were selected: trichloroethylene (TCE), perchloroethylene (PCE), 1,2-*cis*-dichloroethylene (c-DCE) and 1,2-*trans*-dichloroethylene (t-DCE) (Figure 1). The environmental chemistry of these compounds is discussed in the following sections and a summary of their physical and chemical constants is given in Tables 1A and 1B.



Trichloroethylene



Perchloroethylene



1,2-*trans*-Dichloroethylene

1,2-*cis*-Dichloroethylene

Figure 1: Molecular Structures of the Chlorinated Ethenes Used in this Study.

Table 1A: Physical and Chemical Properties of TCE and PCE

Trichloroethylene (C_2Cl_3H)	
Property	Value
Physical State	colourless liquid
Molecular Weight	131.5 amu
Melting Point*	-87 °C
Boiling Point*	87 °C
Solubility in Water*	1100 mg/L
Density**	1.46 g/ml (20 °C)
Henry's Constant*	1.03×10^{-2} atm-m^3/mole

Perchloroethylene (C_2Cl_4)	
Property	Value
Physical State	colourless liquid
Molecular Weight*	165.8 amu
Melting Point*	-19 °C
Boiling Point*	121 °C
Solubility in Water*	1503 mg/L
Density**	1.62 g/ml (20 °C)
Henry's Constant*	1.49×10^{-2} atm-m^3/mole

* source: Howard, 1990

** source: Lide, 1995

Table 1B: Physical and Chemical Properties of c-DCE and t-DCE

1,2-*cis*-Dichloroethylene ($C_2Cl_2H_2$)	
Property	Value
Physical State	colourless liquid
Molecular Weight	96.9 amu
Melting Point*	-80.5 °C
Boiling Point*	60.3 °C
Solubility in Water*	3.5 g/L
Density**	1.24 g/ml (20 °C)
Henry's Constant*	0.00337 atm-m^3/mole

1,2-*trans*-Dichloroethylene ($C_2Cl_2H_2$)	
Property	Value
Physical State	colourless liquid
Molecular Weight	96.9 amu
Melting Point*	-50 °C
Boiling Point*	48 °C
Solubility in Water*	6.3 g/L
Density**	1.26 g/ml (20 °C)
Henry's Constant*	0.00672 atm-m^3/mole

* source: Howard, 1990

** source: Lide, 1995

1.1 Trichloroethylene

Trichloroethylene (TCE) is a colourless dense non aqueous phase liquid (DNAPL). It is moderately soluble in water, and has a higher density than water, forming "puddles" of solvent in natural waters. TCE has been placed on the Priority Substances List of the Canadian Environmental Protection Act (CEPA) (Moore *et al.*, 1991) because of its toxicity and stability in the environment.

Trichloroethylene is used in both industrial and household products (Government of Canada, 1993a, Moore *et al.*, 1991). Industrial uses for TCE include degreasing of fabricated metal parts and cleaning of electronic components. It is also used in the production of adhesive polymers, textile manufacturing and as an extractive solvent in foods. Paint coating removers and dry-cleaning fluids contain TCE as an active ingredient.

Several investigations have been undertaken in order to determine the toxicological effects of TCE. Effects include malignant tumours, changes in composition of lipids and proteins, and alteration of behaviour in mice and rats. Complete mortality of zooplankton required three days in test ponds (at 110 mg/L). Continuous exposure of TCE to fish also showed adverse effects on growth and survival rate at exposures to concentrations of 0.21 mg/L for 120 days (Government of Canada, 1993a).

Effects on humans have been identified in post mortem examination of adolescents who were addicted to inhaling the solvent in glue or cleansing fluid (Aviado *et al.*, 1976). Liver and brain damage were observed and in some cases death was caused by cardiac arrest. Kidney failure also occurred as a result of accidental poisoning.

The release of TCE to the environment is exclusively from anthropogenic sources as there are no known natural sources of this compound. The cycling of TCE in the environment is shown in Figure 2. Infiltration of TCE into soil and natural waters is usually a result of either spills, leakages of storage tanks, or leaching from landfills. It has been estimated that approximately 60% of the total world production of TCE is released to the environment (Moore *et al.*, 1991).

Surface spills of TCE will usually evaporate quickly into the atmosphere because of its high vapour pressure. Photochemical reactions in the atmosphere between TCE and hydroxyl radicals occur with half lives of approximately 3 days and 2 weeks in the summer and winter months, respectively (Government of Canada, 1993a). TCE that does not volatilize from surface water may be transported to groundwater. Natural removal of TCE from groundwater is through biodegradation with half lives of a few months to a few years (Government of Canada, 1993a).

In Canadian surface waters, the range in concentration of TCE was found to be from

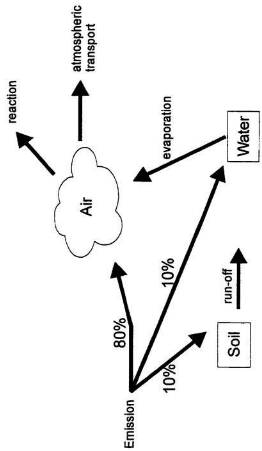


Figure 2: Cycling of TCE in the Environment (After Moore *et al.*, 1991). The above schematic shows that approximately 10% of the TCE released to the environment is found in surface and ground waters, however, this can differ from spill to spill.

below the limit of detection to as high as 0.09 mg/L. Groundwater near landfill sites had concentrations from 4.4-7.2 mg/L. The guidelines set by the Government of Canada were 0.02 mg/L for waters used for recreation and 0.05 mg/L for raw water for drinking supplies (Moore *et al.*, 1991). World Health Organization (WHO) guidelines for drinking water are set at 0.07 mg/L (WHO, 1993).

1.2 Perchloroethylene

The major use of perchloroethylene (PCE) in Canada is in the dry cleaning industry. Several other industries, such as textiles and ink manufacture also use PCE. It is also found in products such as water repellents, adhesives, paint removers and wood cleaners (Government of Canada, 1993b).

Adverse effects of PCE on kidney, reproductive and central nervous systems were observed in toxicological testing on rodents (Government of Canada, 1993b). LC_{50} (lethal concentration required to observe mortality in 50% of a test population) values for aquatic and marine biota were also investigated (Government of Canada, 1993b). The 24 hour exposure LC_{50} value for rainbow trout was approximately 5 mg/L. The 96 hour LC_{50} for fathead minnow larvae was between 13-24 mg/L.

Kidney and liver failure have been observed in accidental exposure of PCE on humans.

Indoor air pollution from PCE is common, and as a result, increased incidence of cancer to the liver and bladder have been observed. The risks of these effects are increased for individuals employed in the dry cleaning industry (Government of Canada, 1993b).

Anthropogenic activity is the only known source of PCE in the environment. Distillation vents, industrial liquid effluents and leaching from landfill sites are common sources to soil and groundwater.

PCE is more volatile than TCE, and will evaporate more quickly from surface water. In the atmosphere, PCE will react with hydroxyl radicals with half lives between 27-58 days in the summer months (Government of Canada, 1993b).

PCE has a higher density than water and will tend to sink to the bottom of bodies of water in which it is present. Larger spills will form "puddles" of solvent at the bottom of water bodies. These may break into smaller droplets which can be resuspended in the water column and eventually volatilize (Government of Canada, 1993b).

Concentration of PCE in surface water is generally quite low (between 0.01-0.02 mg /L) in Canadian waters. High concentrations have been found in groundwater near dry cleaning and land fill sites (0.06-200 mg/L). The WHO guideline for drinking water is 0.04 mg/L (WHO, 1993). The current guidelines for PCE in drinking water in Canada for

PCE is 0.03 mg/L (Government of Canada, 1996)

1.3 Dichloroethylene

1,2-*cis*-dichloroethylene (c-DCE) and 1,2-*trans*-dichloroethylene (t-DCE) are used as solvents in organic synthesis. They are also used in perfumes, and in the polymer industry in thermoplastics and rubber manufacturing (Verschueren, 1983).

Sources of DCE into the environment include air emissions or industrial liquid effluent (Howard *et al.* 1990). Isomers of DCE may also be present as degradation products of PCE and TCE.

DCE is highly volatile, and most surface water contamination can be expected to be lost through volatilization. Reactions in the atmosphere with hydroxyl radicals can occur with half lives of approximately eight days (Howard, 1990).

Toxicology studies in rats have shown that at low exposure levels (0.33 mmol/kg/day), some liver abnormalities were observed (McCauley *et al.*, 1995). Congenital heart defects were observed in rat fetuses whose mothers were exposed to DCE during pregnancy (Dawson *et al.*, 1993). These experiments were based on findings that in some areas in the United States, where drinking water was contaminated by TCE and DCE, cardiac defects were common in children. Leghorn chicks also develop heart defects following exposure to 5 µmol/L (approximately 0.052 µg/L) of DCE (Goldberg *et al.*, 1992). There is little data on the effects on aquatic biota, although rainbow trout responded (erratic movements and coughs) after one hour of exposure of 10 µg/L of c-DCE (Kaiser *et al.*, 1995).

Concentrations of DCE found in waters around the United States vary between 0.001-0.01 mg/L in surface waters. Concentrations in groundwater of 0.1 mg/L have been found. There are no guidelines for DCE available in Canada. WHO has set guidelines at 0.05 mg/L as a combined concentration of both cis and trans isomers (WHO, 1993).

1.4 Removal Processes

Current research into the environmental removal of these compounds, as well as other chlorinated solvents can be divided into biological and abiotic degradation processes. Biological degradation, or bioremediation involves the use of microbial or enzyme activity to degrade these compounds. Abiotic processes make use of chemicals such as Fe(0), $KMnO_4$, H_2O_2, as well as ultraviolet light (Committee on Ground Water Cleanup Alternatives, 1994). These methods may be applied *in situ,* where the reaction takes place within the aquifer; or *ex situ*, where water must be pumped to the surface for treatment.

Differences in site geology, hydrology and level of contamination demand certain requirements of contaminant removal methods. Information required about the geology of the contaminated site includes presence of fractures in the rock as well as permeability of the layers of the aquifer. Low permeability and the presence of fractures can confine contaminants to an area making treatment more difficult (Committee on Ground Water Cleanup Alternatives, 1994).

The solid media (e.g sands or clays) present in the aquifer must also be analysed to determine the retardation factor (Committee on Ground Water Cleanup Alternatives, 1994). This value quantifies the interaction between the solid media and the contaminant. When there is high organic content, organic solvents such as PCE, TCE and DCE will tend to adsorb to these particles. The mobility of the solvent through the aquifer also depends on the hydrophobicity which is quantified by K_{ow} (Octanol-Water equilibrium constant). The chlorinated solvents used in this study are moderately soluble in water and are therefore quite mobile.

A contaminant plume forms because of heterogeneites (such as pore size) within the aquifer, along with dispersion (lateral flow) and diffusion (gradient flow) processes. These processes are affected by the hydrology of the area (rate of flow of water through the aquifer). The longer the amount of time the contaminant has been present, the larger the area the plume may occupy.

The following sections are a brief description of current research in biological and abiotic reductive dehalogenation of chlorinated ethenes. Other removal methods are available and a description of these may be found in the book published by the Committee on Ground Water Cleanup Alternatives (1994).

1.4.1 *In Situ* Bioremediation

In situ bioremediation processes have been the focus of many laboratory and pilot scale experiments. The main advantage of this type of remediation, is that there is conversion of the contaminant to harmless products. Site geology and intrinsic microbial activity are important parameters to consider for bioremediation. As described in the previous section, the mobility of contaminants through an aquifer may limit the efficiency of removal. The presence of appropriate populations of microbes must also be assessed. Nutrients and sources of energy may need to be added to the subsurface in order to enhance microbial activity.

Several studies have shown that TCE, DCE and vinyl chloride (VC) can be degraded by methane-utilizing bacteria (methanotrophs) in a process known as cometabolism (Schaffner *et al.*, 1996; McCarty *et al.*, 1991). In cometabolism, bacteria expend energy to oxidize a substrate (in this case, chlorinated ethenes) with no added benefit to the microbes.

Barrio-Lage *et al.* (1986) and Moore *et al.* (1989) found that methanotrophs degrade DCE isomers. The former used anoxic conditions, and determined that processes other than reductive dehalogenation were involved in the breakdown of DCE. It was also determined that DCE was converted to VC only, a known carcinogen. When oxidizing conditions were used (Moore *et al.*, 1989), DCE isomers were mineralized to carbon dioxide. It was also observed that by the addition of methane, oxygen and other nutrients degradation rates were improved.

Methanotrophs are also able to oxidize TCE using methane-monooxygenase (MMO; an enzyme) (Anderson, 1993). MMO is inactivated following reaction with TCE, which is a drawback of this type of remediation. Methane, oxygen as well as nutrients must also be added in order to enhance microbial activity (Committee on Ground Water Cleanup Alternatives, 1994).

Biological reductive dehalogenation is typically the process by which more halogenated species are removed. For this process to be effective, it is important that the chlorinated hydrocarbons be the only electron donors present (Schaffner *et al.* 1996).

PCE was observed to undergo reductive dehalogenation to ethylene, a harmless product (also a plant hormone) by Freedman and Gossett (1989). Methanotrophs were believed to be the active microbes in the removal of PCE. In a study by Major *et al.* (1991), it was found that methanotrophs may not be the only microbes responsible for PCE removal. The low population of these microbes and high concentration of acetate demonstrated the possibility that acetogens (acetate-utilizing bacteria) may play an active role in PCE degradation.

Because the potential for reductive dehalogenation decreases with decreasing number of chlorine atoms, some investigators have focussed on the use of two stage reactors for the complete degradation of these chlorinated solvents (Fathepure and Vogel, 1991; Schaffner *et al.* 1996). The first stage uses anaerobic conditions to degrade PCE and TCE; the second stage uses aerobic conditions to enhance degradation of the less saturated chlorinated ethenes.

The half lives for these processes depend on conditions used. Fathepure and Vogel (1991) observed in their two stage reactor over 90% removal of TCE in less than two days (initial concentration of PCE was ~100 µg/L). Moore *et al.* (1989) conducted experiments in a simulated aquifer and found almost complete removal of t-DCE in approximately 100 hours (initial concentration of DCE was 1 mg/L). Fliermans *et al.*(1988) conducted experiments using a mixed culture (aerobic) over a period of 1-2 weeks, and observed 99% conversion of TCE to carbon dioxide.

There are several drawbacks with the use of bioremediation processes. Water quality of the aquifer may be affected by the addition of nutrients or the increased microbial activity (Committee on Ground Water Cleanup Alternatives, 1994). These factors may in turn dissolve metals from the surrounding bedrock. Bacterial metabolites may also affect the taste of drinking water. Finally, most contaminated sites usually have more than one type of contaminant. Palumbo *et al.* (1991) observed that the presence of DCE and methylene chloride in a contaminated aquifer affected the degradation rates of TCE.

1.4.2 *In-Situ* Chemical Remediation

Abiotic removal of chlorinated ethenes by hydrolysis or dehydrohalogenation has long half lives ($0.85\text{-}2.1\times10^{10}$ years for DCE, $0.49\text{-}1.3\times10^{6}$ years for TCE, and $3.8\text{-}9.8\times10^{8}$ years for PCE) (Barbee, 1994). These compounds are therefore quite stable in natural waters. Added chemicals, however, can react with the contaminants and convert them to harmless products. The advantage of chemical remediation is that unlike bioremediation processes, the oxidizing and reducing agents are non specific and can treat mixtures of contaminants (Committee on Ground Water Cleanup Alternatives, 1994). Chemical additives may also react with substances that cannot be biodegraded. The main drawback to using this method is that water quality (such as pH, dissolved metals, redox conditions) can be altered with the large amounts of reactant injected into the subsurface.

Chemical additives may be added to aquifers either by injection, or by installing reactive barriers (Committee on Ground Water Cleanup Alternatives, 1994). (Figure 3). The former involves injection of the reactants to the subsurface via pipes or wells. Reactive barrier technology is still in developmental stages. Funnel walls are built to direct the hydraulic flow in the aquifer to a permeable reactive barrier (sheet or slurry) made of a reactant of choice. This type of remediation may be more easy to design and maintain than other methods.

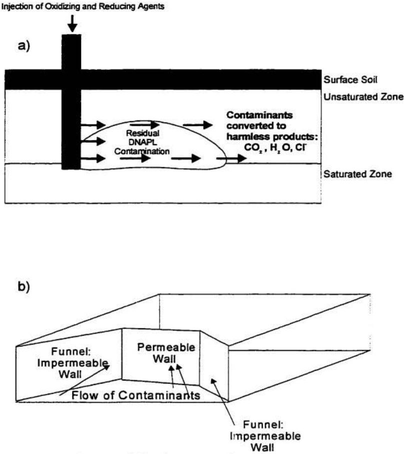


Figure 3: Application of Chemical Agents for Abiotic Remediation (after Committee on Ground Water Cleanup Alternatives, 1994). a) Injection of reactants to contaminated water. b) Reactive Barriers. Two impermeable walls act as funnels, to direct the flow of water towards the permeable reactive wall. On the other side of the wall, the contaminants are converted to harmless products.

1.4.3 Reductive Dehalogenation using Zero Valent Iron

Oxidizing (such as H_2O_2 or O_3) or reducing agents (such as Fe) are commonly used for the abiotic removal of chlorinated solvents (Committee on Ground Water Cleanup Alternatives, 1994). The discussion below will be limited to the use of zero valent iron for the reductive dehalogenation of chlorinated solvents.

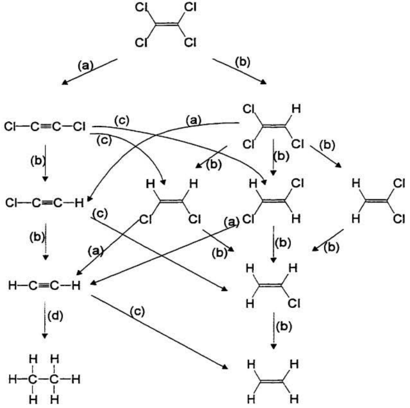
Iron can be applied in a number of ways to the contaminated site: by the use of reaction vessels with pump and treat technology; reactive barriers; or colloid injection. The advantage of using iron metal is that it is a low cost material. Industrial waste iron filings can be used to treat contaminated groundwater. Reductive dehalogenation with iron works well with saturated chlorinated hydrocarbons such as TCE or PCE, as well as other contaminants such as dyes, pesticides and heavy metals (Wilson, 1995; Tratnyek, 1996). Pumping is not required for this technology, allowing for relatively low operation and maintenance costs (Wilson, 1995). This method can also be used in combination with bioremediation.

The main disadvantage is that water quality must be carefully monitored or the reaction may not go to completion. Tratnyek (1996) found that the presence of oxides and carbonate ions on the surface of the iron may stop the reaction. As a result, toxic chlorinated products, such as vinyl chloride may accumulate.

The ability of iron to degrade organochlorine compounds was originally discovered in the seventies. These results were reconfirmed more recently by Reynolds *et al.* (1990) when galvanized and stainless steel groundwater monitoring equipment reacted with chlorinated solvents. The basis of these reactions is corrosion chemistry, and this simple concept sparked a great deal of interest and research. Many studies have investigated the kinetics of these reactions in order to minimize the reaction time, as well as to determine the extent to which these reactions go to completion.

There are two pathways for which reductive dehalogenation of chlorinated ethenes by iron can occur (Campbell, 1997). Reaction 1 shows the steps for hydrogenolysis. The last half reaction can be replaced by Reaction 2, β-elimination. Figure 4 is a schematic of the reaction pathways. Products from the reductive dehalogenation of chlorinated ethenes include: ethene, ethane and acetylene, as well as C_3 and C_4 hydrocarbons. In a study by Deng *et al.* (1997), it was found that a small percentage of carbides present in the iron may contribute to background concentration of aliphatic compounds.

$$\begin{array}{c} 2Fe^{0} \rightarrow 2Fe^{2+} + 4e^{-} \\ 3H_2O \rightarrow 3H^{+} + 3OH^{-} \\ 2H^{+} + 2e^{-} \rightarrow H_2 \\ X{-}Cl + H^{+} + 2e^{-} \rightarrow X{-}H + Cl^{-} \\ \hline 2Fe^{0} + 3H_2O + X{-}Cl \rightarrow 2Fe^{2+} + 3OH^{-} + H_2 + X{-}H + Cl^{-} \end{array} \tag{1}$$



(a) corresponds to reductive β-elimination:

$R(X)+R(X) + 2e^- \Rightarrow R{=}R + 2X^-$

(b) corresponds to hydrogenolysis

$RX + 2e^- + H^+ \Rightarrow RH + X^-$

(c) corresponds to reduction of a triple bond to a double bond

$R{\equiv}R + 2e^- + 2H^+ \Rightarrow R(H){=}R(H)$

(d) corresponds to reduction of triple bond to single

$R{\equiv}R + 4e^- + 4H^+ \Rightarrow R(H_2){-}R(H_2)$

Figure 4: Reaction Pathways for the Reductive Dehalogenation of Chlorinated Ethenes (after Campbell *et al.*, 1997). X in the reactions represents the halogen, in this case, Cl.

$$RCl{=}RCl + 2e^{-} \rightarrow R{\equiv}R + 2Cl^{-} \qquad \textbf{(2)}$$

There are three possibilities as to which species is involved in the dehalogenation: Fe(0), Fe^{2+}, or H_2. Gillham and O'Hannesin (1994) confirmed that the reaction was indeed taking place on the surface of the zero valent iron particles. Several studies have also shown that the rate of the reaction depends on the surface area of the iron available to the chlorinated species (Gillham and O'Hannesin, 1994; Orth and Gillham, 1996). Johnson *et al.* (1996) determined using previously published data, that the total surface area, as well as the reactive surface area were important parameters.

First order kinetics with respect to the hydrocarbons are involved in reductive dehalogenation. Johnson *et al.* (1996) also found that the reaction was first order with respect to the surface area of iron. Sorption processes also play a significant role in the disappearance of TCE and PCE in aqueous solutions (Burris *et al.*, 1995). Orth and Gillham (1996) hypothesized that TCE actually remains adsorbed to the iron particle until it is completely dehalogenated. The basis for this assumption was the fact that there was low concentration of chlorinated hydrocarbon products.

The reactions may be enhanced by doping iron with other metals such as nickel

(Appleton, 1996) or palladium (Muftikian, 1995). Pilot scale studies were done using nickel plated iron, with promising results. Thinner reactive barriers were required using the doped iron (10 inch thickness for iron alone as opposed to only 2 inches for the nickel plated iron), and the reaction proceeded ten times faster than for iron alone. Bench scale experiments were conducted by Muftikian et al. (1995) using palladium coated iron. Half lives were less that one hour for TCE.

1.5 Isotope Chemistry

Along with the treatment of contaminated waters, it is also important to trace the source of the pollutant, to prevent further contamination, or to charge those who fail to uphold environmental laws and guidelines. Organic pollutants will have specific stable isotopic signatures, depending on their source or mode of formation. Compound specific isotopic analysis (CSIA) can be commonly used to allocate sources using the stable isotopes of either carbon, hydrogen, oxygen, nitrogen, chlorine or sulfur. It has been found, for example, that chlorinated solvents from different sources have distinct carbon and chlorine isotopic signatures (van Warmerdam *et al.,* 1995). The variations in isotopic compositions of PCE and TCE from different manufacturers were presumed to have been caused by the processes used to manufacture the chlorinated solvents (van Warmerdam *et al.,* 1995). These variations apparently arise due to variations in synthesis substrates or during the manufacture of the solvents. In reductive dehalogenation, the C-Cl bond is broken and hence isotopic fractionation may be observed for isotopes of carbon and chlorine. For this study, the two stable and most abundant isotopes of carbon, ^{12}C and ^{13}C were of interest. Fractionation will be most evident between isotopes that are most abundant.

Reactions, such as photolysis, oxidation or reduction, that occur in the natural environment can change the isotopic composition of pollutants, presenting complications to simple tracing or apportioning of sources. Given that the isotopic consequence of biological and abiotic reactions can be studied, CSIA can also be used to study the mechanisms involved in biological or biotic transformations of compounds of interest. Transformation of pollutants in the environment can then be predicted, using the information on the direction and magnitude of the change in isotopic composition from experimental data.

There are two main processes that can cause isotopic fractionation: isotope exchange reactions and kinetic processes. The former involves the equilibrium isotopic distribution between different compounds, phases or molecules. The latter depends on reaction rates of isotopic molecules.

1.5.1 Isotope Exchange

A general form of isotopic exchange reaction can be represented by the following equilibrium:

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1 \tag{3}$$

where A and B are different species, and the subscripts represent 1 and 2 represent the lighter and heavier isotopes, respectively. A common example is the exchange of ^{18}O in the equilibrium between carbon dioxide and water:

$$C^{18}O^{16}O + H_2^{16}O \rightleftharpoons C^{16}O^{16}O + H_2^{18}O \tag{4}$$

The ratio of heavy to light isotope in a compound is represented as:

$$R_A = \frac{A_2}{A_1} \tag{5}$$

For the stable isotopes of carbon, the ratio would be $^{13}C/^{12}C$.

The fractionation factor α is defined relates the isotopic ratio of two compounds in equilibrium:

$$\alpha = \frac{R_A}{R_B} \tag{6}$$

where R_A and R_B are the isotopic ratios of two compounds defined in equation 3.

For reaction 4, α would be:

$$\frac{(^{18}O/^{16}O)_{CO_2}}{(^{18}O/^{16}O)_{H_2O}} \tag{7}$$

The value δ is defined as the isotopic composition of a compound:

$$\delta_A = (\frac{R_A}{R_{St}} - 1) \times 10^3 \tag{8}$$

where R_{st} is the isotopic ratio of a standard, and δ is expressed in per mil ($^0/_{00}$). The stable carbon isotope composition is represented as $\delta^{13}C$. The reference standard that is usually used for carbon isotopes is PeeDee Belemnite (PDB).

1.5.2 Kinetic Effects

Kinetic effects are observed in fast, incomplete or unidirectional reactions such as dissociation reactions. These effects are quite important, since they provide information about the mechanisms of chemical reactions (Hoefs, 1987).

Reaction 9 is an example of a rearrangement reaction studies by Bartholomew *et al* (1954). The rate determining step is the dissociation of the bond between C-Cl in *tert*-

butyl-chloride and it was found that ^{35}Cl reacted faster than ^{37}Cl.

$$C_4H_9Cl + C_2H_5OH \xrightarrow{silver\ nitrate} C_4H_9OC_2H_5 + H^{\cdot} \qquad (9)$$

The dissociation energies of molecules containing the heavy isotope are higher than those containing the lighter isotope (O'Neil, 1986). For example, bonds between ^{12}C-Cl are more easily broken then ^{13}C-Cl (Figure 5) This can be more easily understood by using the harmonic oscillator model for the vibrational frequency ν of a molecule:

$$\nu = \frac{1}{2\Pi} (\frac{k}{\mu})^{1/2} \qquad (10)$$

where, k is a force constant, and μ is the reduced mass for a diatomic molecule made up of masses m_1 and m_2 and is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (11)$$

If m_1 is the lighter isotope of the element of interest (for example, ^{12}C), it can easily be seen that if m_1 is replaced by the heavier isotope, μ will increase and the vibrational frequency will decrease (k does not change). Since ν is lower for the heavier isotope, the bond dissociation energy is greater than for the lighter isotope. Figure 5 is a schematic

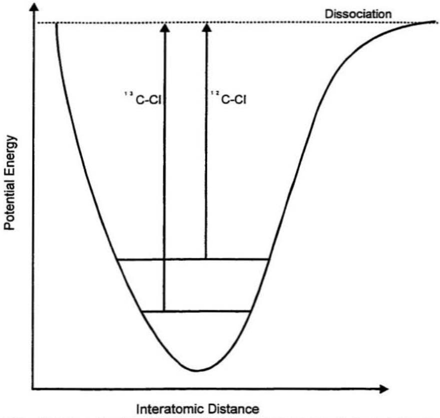


Figure 5: Schematic of the Difference in Dissociative Energies for Isotopic Species (after Hoefs, 1987). The ^{13}C-Cl bond is much more stable and has a higher dissociative energy than the ^{12}C-Cl bond.

representation of this. The implication is that a reactant will become isotopically heavier during the course of a reaction, as the molecules containing the lighter isotope are consumed first.

Kinetic isotopic effects have been found to depend on the activation energy for the reaction (Buist and Bender, 1958). For example, in Buist and Bender (1958) the ratio between reaction rate constants, k_{12}/k_{14} was determined for different reactions such as decomposition of substituted ureas and reaction of methyl iodide and substituted tertiary amines (where k_{12} represents the reaction rate constant where the bond with ^{12}C is broken, and similarly, k_{14} represents the reaction rate constant where the bond with ^{14}C is broken). These ratios were plotted with the activation energies of the different reactions. The higher the activation energy, the larger the isotopic effect observed (i.e k_{12}/k_{14} increased, indicating that the reaction with the lighter isotope was faster). This also showed that there is a strong dependence of the isotopic effect on temperature (since activation energies are temperature dependent).

Chapter 2 - Experimental Procedure

TCE (99.5%; Spectrophotometric Grade), PCE (99.9%; HPLC Grade), and DCE (98% mixture of c-DCE and t-DCE) were all purchased from Aldrich Chemical Company. Prior to use in the reactions, Nanopure water (17.5 MΩ) was boiled to remove any microbial activity. Electrolytic iron was purchased from Fisher Scientific Inc. The iron was cleaned with methanol for thirty minutes (Roberts, pers. comm.), then with 1 M HCl solution for 1 hour, rinsed with Nanopure water (17.5 MΩ) and dried under nitrogen. The cleaned iron was stored under nitrogen until use. The surface area of the iron was 4.17 m^2/g, determined by BET analysis.

For the reactions, 254 ml capacity bottles were used with Mininert valves. All glassware used in these experiments was washed with methanol and heated in a 100 °C oven until use.

Four replicates were prepared for each of TCE, PCE and DCE solutions in water. Volumes of 2 µl, 15 µl and 15 µl of TCE, PCE and DCE, respectively were measured using a 10 µl (±1%) syringe (Hamilton). The volume of water used was 245 ml, and the displacement of iron was 3 ml, allowing for 6 ml of headspace. Using the densities in Tables 1A and 1B, the concentrations calculated for TCE, PCE and DCE (combined isomers) were 12 ppm, 99 ppm and 76 ppm, respectively. Vapour pressures calculated from Henry's Constants are given in Table 2.

In three of the vessels, 20 g of iron was placed. The fourth vessel was a blank solution containing only the analyte of interest and water. A magnetic stir bar (displacement of 2-3 ml) was added to each blank to compensate for the displacement caused by iron. Each of the vessels were placed on a Burrel wrist action shaker. The temperature at which the reactions took place was 20 °C.

The headspace of the solutions was sampled using solid phase microextraction (SPME) using a polydimethylsiloxane (PDMS) fiber. The SPME assembly is made up of a coated fiber and a modified syringe (Figure 6). This simple extraction method was developed at the University of Waterloo (e.g. Chai *et al.*, 1993). The fiber is exposed to the headspace until the analytes equilibrate between the fiber and the sample matrix. For example, in the experiments for this study, 20 minutes was required for TCE, PCE and DCE in the headspace to equilibrate with a PDMS fiber (Hunt, 1996). No further preparation is required and the analytes are transferred directly into the injector of a gas chromatograph (GC) where they thermally desorb from the fiber at the injector temperature of (250 °C). At the injector, the desorbed compound is cryofocused (35 °C) onto the column for one minute prior to ramping the column temperature.

Table 2: Vapour Pressure for TCE, PCE and DCE Calculated from Henry's Constants

Property	TCE	PCE	t-DCE*	c-DCE*
volume (μl)	2.0	15.0	6.75	8.25
mass (g)	0.0029	0.024	0.0084	0.010
moles	0.000022	0.00015	0.000086	0.00011
concentration of solution (mol/m^3)	0.091	0.60	0.35	0.43
Pressure (atm)	0.00093	0.0089	0.0024	0.0014

* It was found from GC-C-IRMS, using the peak areas in the chromatograms, that the DCE solution is made up of approximately 55% c-DCE and 45% t-DCE.

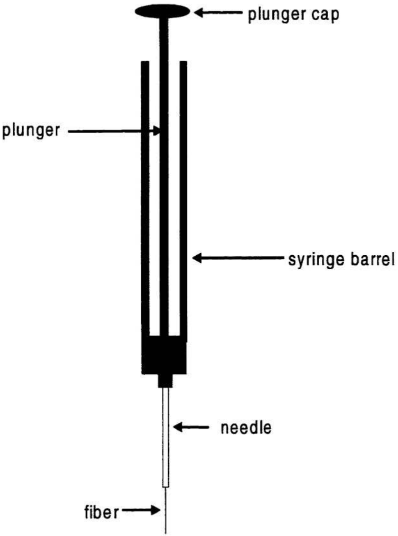


Figure 6: SPME Assembly (after Chai *et al.*, 1993). The plunger cap is pushed and the fiber is exposed to the sample.

Experiments in this study confirmed results from previous studies (Hunt, 1996; Dias and Freeman, 1997) that minimal carbon isotope ($<0.5^{0}/_{00}$) fractionation occurred during SPME fiber sampling. To determine if there was isotopic fractionation during the SPME sampling, each of the solvents were analyzed on a VG Optima mass spectrometer by dual inlet conventional analysis, to determine the isotopic composition of the bulk solution. This entailed reacting the solvent with precombusted CuO in evacuated sealed tubes, at 500 °C to produce CO_2 and CuCl. The CO_2 was cryogenically purified, using a vacuum line and then analyzed on the mass spectrometer for $\delta^{13}C$. The collected gas is analyzed directly on a mass spectrometer. The mass spectrometer has a reference and a sample bellows, or inlets. During a run, the bellows are alternated (opened and closed) so that each side is analyzed multiple times (for a more accurate isotopic composition measurement). When the CO_2 enters the mass spectrometer, it is ionized and a magnetic field is used to separate the different masses 44, 45, 46 amu, representing $^{12}CO_2$, $^{13}CO_2$ and $^{12}C^{16}O^{18}O$, respectively. The masses are separated because differences in momentum which causes a deflection in the magnetic field. The lighter ions (i.e mass 44 amu) are deflected the most. Three ion beams are created and each beam is "collected" by Faraday cups. When the ions strike the cups, a current is produced which is converted to isotopic compositions on by a computer. The ratio of masses 45:44 is used to calculated $\delta^{13}C$.

The results obtained from measurements of the headspace of the standard solutions using SPME were comparable to those from conventional analysis within the precision of gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) measurements (0.5 $^0/_{00}$).

Tests were also done in order to determine whether there was a difference in the stable carbon isotope composition between the vapour and the liquid phases in the reaction vessels. It was found that there was minimal difference (<0.5 $^0/_{00}$) between the headspace and the solvent solution in both the blank (without Fe^0) and reaction vessels. Sampling the headspace was preferred since the SPME fiber can be degraded by the iron powder suspended in the solutions.

Compound specific isotopic analysis (CSIA) was used to follow the stable carbon isotope composition ($\delta^{13}C$ with respect to PDB) of the solvent during the reaction, using gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) (Figure 7). The GC was a Hewlett Packard HP5890 Series IV, and the IR-MS was a VG Optima. The column used in the GC was a Restek RTX 502.2 100 m column (Chromatographic Specialties Inc.). The carrier gas was He at a column head pressure of 12 psi. The temperature program and all other parameters are summarized in Table 3. Identification of some of the products of the reductive dehalogenation of the chlorinated ethenes was done using a Varian Saturn 3 gas chromatograph-mass spectrometer (GC-MS), where a fused silica capillary column was used (30 m; DB 624; Chromatographic Specialties Inc).

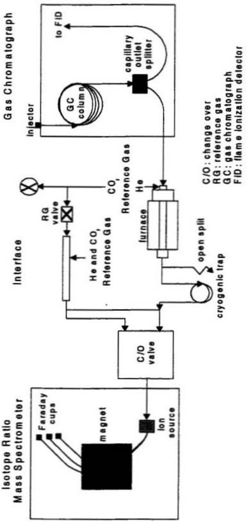


Figure 7: Schematic of GC-C-IRMS

Table 3: Temperature Program for TCE, PCE and DCE

TCE	
injector	250 °C
initial temperature	35 °C
hold	1 minute
rate	20 °C/minute
final temperature	250 °C
hold	10 minutes
total	21.75 minutes

PCE	
injector	250 °C
initial temperature	35 °C
hold	1 minute
rate	25 °C/minute
final temperature	250 °C
hold	13 minutes
total	22.6 minutes

DCE	
injector	200 °C
initial temperature	35 °C
hold	1 minute
rate	20 °C/minute
final temperature	250 °C
hold	7 minutes
total	18.75 minutes

The sample injected into the GC can be analyzed either by IRMS or by flame ionization detector (FID). For MS detection, the compounds are first separated on the column and then combusted at 800 °C in a furnace and converted to CO_2 by reaction with CuO. The gas is then cooled to -100 °C, to remove water. The change over (C/O) valve switches between reference CO_2 gas and the gas from the combusted sample (see Figure 7). During a run, sample (eluting from the column) or reference gas can be analyzed at pre-programmed intervals. The carbon dioxide gas is analyzed in the mass spectrometer as in dual inlet analysis (see above).

Before the experiments were initiated, several tests were done to ensure that the observed changes in peak area (in the chromatogram) and isotopic composition were in fact due to the reaction and not due to any other processes. Iron was tested both cleaned and uncleaned and solutions containing only water and iron were also prepared.

The headspaces of the reaction vessels were sampled during the course of the reaction. A typical run, consisted of sampling the headspace using SPME for twenty minutes, and then allowing the analytes to desorb in the injector for ten minutes. (It was found that this was sufficient time for desorption). Data collection was started with injection of the sample. During the analysis, reference CO_2 was used ($\delta^{13}C = -17.5\ ^0/_{00}$) to ensure that the instrument was performing properly. The software that accompanies the VG Optima calculated the isotopic composition of the major peaks in the chromatogram, relative to the PDB standard. The reaction was allowed to proceed until the reactant peak was no longer detectable by the MS (~1 week for TCE, ~2 weeks for PCE and DCE).

Chapter 3 - Results

3.1 pH

During the course of the reaction, changes in peak area and isotopic composition were recorded. Physical observations noted were gas production (H_2) and the formation of yellow-white precipitate (presumably, $Fe(OH)_3$). The reaction pH was not monitored during the individual experiments to avoid the possibility of reaction product loss or introduction of other experimental artifacts. However, (1) the beginning and final pH were measured in the PCE experiments, and (2) pH was monitored in "blank" (metal Fe and water only) experiments to identify the range of pH values likely encountered in all experiments. The latter was performed on the assumption that the reaction of water and metal Fe is the dominant influence on solution pH. The initial pH of the deionized water was 5.5, and the pH of the blank solutions remained constant at 4.5. The final pH of the PCE solution was 5.2. An alternate phase, $Fe(OH)_3$ was noted in most of the experiments (see Reaction 12). Vaillancourt *et al.* (1997) also observed the precipitation of $Fe(OH)_3$ during the reaction of metal Fe in water under similarly acidic conditions. No precautions were taken to ensure that the reactions would take place under an oxygen free atmosphere. Given the pH achieved in these experiments (pH of 4-6) and the presence of $Fe(OH)_3$, it is likely that oxygen was present either in dissolved form in the water, or as oxides of iron. (NOTE: Under completely reducing conditions, $Fe(OH)_2$ would precipitate; Gillham and O'Hannesin, 1994). The continued formation of Fe^{2+} and electrons from the iron, along with the precipitation of the ferric hydroxide (and dissolved oxygen) in the system, provided a "natural" buffer so that the pH did not drift.

$$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + e^- + 3H^+ \qquad (12)$$

3.2 Iron

In order to confirm that the observed changes and the reaction products were the result of the reductive dehalogenation reaction as opposed to the formation of organic compounds from residual carbides present in the iron (Deng *et al.*, 1997), tests were done on iron-water blanks (no solvent). No organic reaction products were detectable. Tests were also done using both cleaned and uncleaned iron and TCE. Organic reaction products could not be detected and there was no shift in the isotopic composition of TCE using the uncleaned iron. A thin organic coating appears to have been present on the Fe metal powder as suggested by the fact that organic solvent washing readily produced reactive Fe surfaces (Roberts, pers. comm.). Interestingly, the lack of reaction between the uncleaned Fe and the halogenated compounds, in spite of obvious presence of Fe^{2+} in these systems, supports suggestions made previously by others, that the surface of Fe metal powder is directly involved in the electron transfer step (i.e. heterogeneous reaction) (Burris *et al.*, 1995). The organic coating apparently had an inhibitory effect on the surface reactions involving the Fe metal powder.

3.3 Products

Identification of the organic reaction products was rather difficult. The mass spectra of the organic products from the GC-MS analysis could not be matched with library entries with high degree of confidence (Saturn GC-MS NIST92 Library). It appears that C_3, C_4 and C_5 hydrocarbons were among the products formed. It was confirmed however, that the three isomers of DCE were observed from the reductive dehalogenation of TCE and PCE (c-DCE and 1,1-dichloroethylene were present in approximately equal amounts, and trace amounts of t-DCE were also present). This result contrasts with previous zero valent Fe dehalogenation studies that showed both 1,1 DCE to be generally lacking and t-DCE at very low abundance (e.g. Campbell *et al.*, 1997). Ethene and acetylene were typical products observed in other studies (Gillham and O'Hannesin, 1994, Roberts *et al*, 1996). They were not detected in our experiments, although their presence cannot be completely ruled out. The conditions for the GC-MS analysis were not suitable for resolving acetylene and ethene. (These gases must be analyzed at subambient temperatures).

A mass balance is useful in accounting for all processes that are involved in the removal of chlorinated ethenes. It was not possible to perform isotopic mass balance calculations for the stable carbon isotopes from the GC-C-IRMS data, because the product peaks present for all the reactions were too small to be isotopically analyzed. For example, several of the isomers of DCE were resolved at single points in the TCE and PCE reactions, however an accurate isotopic composition could not be determined because the peak areas were too small. Future experiments should include increasing the concentration of the solvent, possibly focusing on the products as the reaction progressed.

3.4 Rate Constants

The reactions for TCE, PCE and DCE, were allowed to proceed for 169 hours, 345 hours, and 336 hours, respectively, until the compounds could no longer be analyzed by GC-C-IRMS. For DCE, the trans isomer was no longer detectable after 70 hours.

The plots of disappearance of each compound over time were fitted to first and second order reaction rate curves as shown in Figures 8-11. Curve fits for first order kinetics were calculated by Sigma Plot 4.00© using the following equation:

$$A = A_0 e^{-kt} \tag{13}$$

where A is peak area at time t, A_0 is the initial peak area, and k is the rate constant.

For PCE, TCE, t-DCE, c-DCE, correlation coefficients (R^2 values, where a perfect fit is $R^2 = 1$) of 0.80,0.99, 0.97 and 0.99 were obtained for the fit to the first order rate equation. For TCE, the initial four points were ignored for the fit since they have a great deal of variation, and are likely to represent slow approach to equilibrium between TCE, solid surfaces and headspace (c.f. Roberts *et al.*, 1996; Campbell *et al.*, 1997). Similarly, for the regression for PCE, the initial four points were ignored. The rate constants for the four compounds are shown in Tables 4A and 4B. Since three replicates were run for each reaction, the standard deviation plotted as error bars are also shown in Figures 8-11.

Also shown in Figures 8-11 are the plots of the blank solution analysis. The blanks remained relatively constant over time, and variations are caused by fluctuations in the performance of the GC-C-IRMS. Only one blank (control) was run for each ethene so no error bars could be calculated.

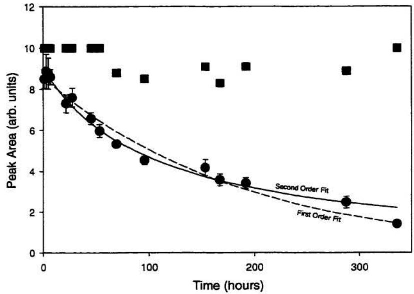


Figure 8: Consumption of c-DCE over Time. The circles represent the data from the reaction vessels, and the squares represent the c-DCE blank (solvent and water only).

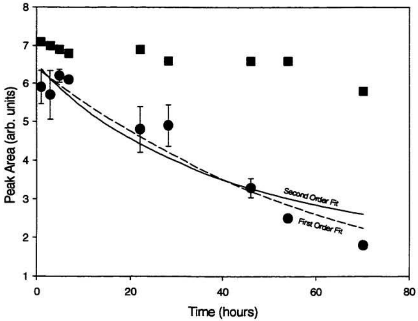


Figure 9: Consumption of t-DCE over Time. The circles represent the data from the reaction vessels, and the squares the t-DCE blank (solvent and water only).

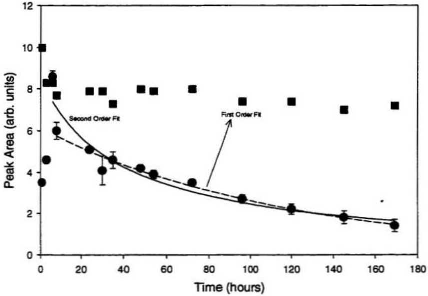


Figure 10: The Consumption of TCE over Time. The circles represent data from the reaction vessels, and the squares represent the TCE blank (solvent and water only).

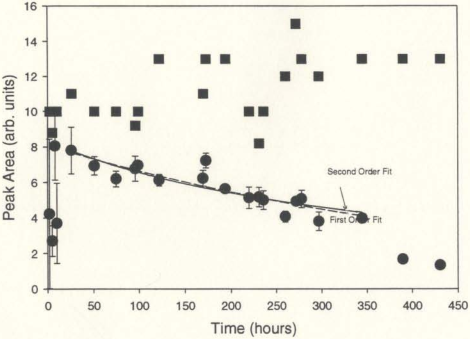


Figure 11: The Consumption of PCE over Time. The circles represent the data from the reaction vessels and the squares represent the PCE blank (solvent and water only).

Table 4A: First Order Rate Constants for Reductive Dehalogenation of Chlorinated Ethenes

Compound	Rate Constant (hr^{-1})	half life (hours)	half life (hours)[a]	half life (hours)[b]	half life (hours)[c]
PCE	0.00252	275.1	3.6	-	~300
TCE	0.0086	80.6	8.6	-	~26
t-DCE	0.015	46.21	252.0	~24	-
c-DCE	0.0053	130.78	82.0	~80	-

a as reported by Gillham and O'Hannesin (1994).
b as reported by Roberts *et al.*, (1996).
c as reported by Campbell *et al.* (1997).

Table 4B: Normalized Half lives of Reductive Dehalogenation of Chlorinated Ethenes*

Compound	half life ($hr\ m^2 ml^{-1}$)	half life ($hr\ m^2 ml^{-1}$)[a]
PCE	7665.9	0.28
TCE	2246.3	0.67
t-DCE	1287.8	19.7
c-DCE	3644.8	6.41

* Half lives were normalized to 1 m^2/ml surface area
a as reported by Gillham and O'Hannesin (1994).

The data were also fitted to the second order rate equation (Table 5):

$$A = \frac{1}{kt + \frac{1}{A_0}} \qquad \textbf{(14)}$$

where A is the peak area at time t, k is the rate constant and A_0 is the initial peak area. It is believed, that other processes were affecting the rates of the reductive dehalogenation of the chlorinated ethenes. These can include: the presence of hydrogen gas in the reaction vessel, the acidic conditions or the presence of chlorinated reaction products (such as DCE isomers) competing for iron surface area.

Table 5: Second Order Rate Constants for Reductive Dehalogenation of Chlorinated Ethenes

Compound	Rate Constant ($signal^{-1} \cdot hr^{-1}$)	half life (hours)	R^2
PCE	0.000324	474.2	0.78
TCE	0.00291	52.7	0.91
t-DCE	0.00329	46.6	0.89
c-DCE	0.00103	149.4	0.98

3.5 Isotopic Composition

Large shifts in the stable carbon isotope composition were observed during the reaction with each of the solvents. Plots of isotopic composition with time are shown in Figures 12-15. The $\delta^{13}C$ of PCE, TCE and c-DCE shifted by 24 $^{0}/_{00}$, 12 $^{0}/_{00}$ and 24 $^{0}/_{00}$, respectively. Each compound became enriched with ^{13}C. t-DCE was anomalous, since it became lighter first, before becoming isotopically heavier (after 25 hours). There was some difficulty in the measurement of the t-DCE isomer. The peak was not well resolved and therefore the integration and calculation of the isotopic composition may not have been very accurate. The same trend was observed for all replicates of this experiment, as well as during a preliminary set of experiments. The error bars shown represent the standard deviation of the isotopic composition in the three replicates for each time interval.

The analyses of the blank solutions are also plotted in Figures 12-15. The isotopic compositions of the blank solutions remained relatively constant over time ($\pm< 0.5$ $^{0}/_{00}$; note: this is also the uncertainty in any measurement on the GC-C-IRMS), indicating that degradation of the chloroethenes was caused by the presence of metallic iron. Only one control was run, so no standard deviation could be calculated.

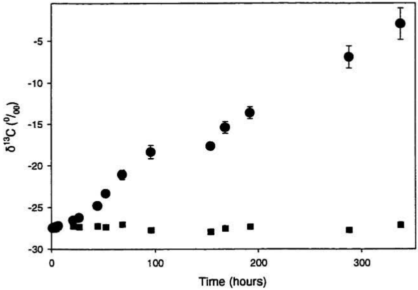


Figure 12: Isotopic Fractionation of c-DCE over Time. The circles represent data from the reaction vessels, and the squares represent the c-DCE blank (solvent and water only).

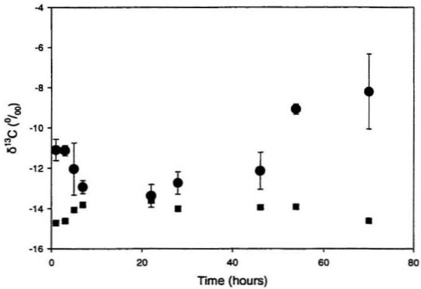


Figure 13: Isotopic Fractionation of t-DCE over Time. The circles represent data from the reaction vessels, and the squares represent the t-DCE blank (solvent and water only).

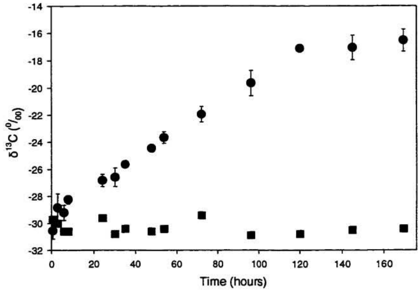


Figure 14: Isotopic Fractionation of TCE over Time. The circles represent data from the reaction vessels, and the squares represent the TCE blank (solvent and water only).

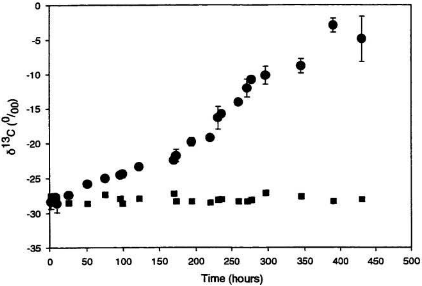


Figure 15: Isotopic Fractionation of PCE over Time. The circles represent data from the reaction vessels, and the squares represent the PCE blank (solvent and water only).

Chapter 4 - Discussion

4.1 Precision and Error

The experimental control samples (blanks) are used to determine the analytical precision (or reproducibility) of these measurements. The error in the isotopic composition (1σ deviation) of PCE, TCE, t-DCE and c-DCE controls were ±0.43 $^{0}/_{00}$, ±0.47 $^{0}/_{00}$, ±0.40 $^{0}/_{00}$ and ±0.25 $^{0}/_{00}$, respectively. The experimental error in the reaction vessels were PCE, TCE, t-DCE and c-DCE were ±0.76 $^{0}/_{00}$, ±0.50 $^{0}/_{00}$, ±0.55 $^{0}/_{00}$ and ±0.59 $^{0}/_{00}$, respectively Instrumental error with GC-C-IRMS is ±0.5 $^{0}/_{00}$. Since the peak areas were not calibrated, it could not be determined whether the 1σ deviation is acceptable error. The relative error for PCE, TCE, t-DCE, and c-DCE controls were: 15.8%, 9.24 %, 5.7 % and 6.8 %, respectively. The relative experiments error for the peak areas of PCE, TCE, t-DCE, and c-DCE reactions were: 11.9%, 8.6 %, 5.6 % and 6.7 %, respectively.

Potential sources of error in these experiments include variations of temperature in the laboratory, isotopic fractionation during sampling using SPME or between the vapour and liquid phases in the reaction vessels and instrumental error. Tests have shown that isotopic fractionation during sampling and between liquid and vapour phases is minimal. It is believed that the temperature variations may cause variation in the vapour pressure within the vessels and affect the concentrations measurements of each compound.

4.2 Reaction Rates

Previous studies (Gillham and O'Hannesin, 1994) found that under reducing conditions, the first order reaction rate decreased from PCE to DCE. The trends in measured rates of dehalogenation and half lives relative to the decreasing degree of halogenation from PCE, TCE, to DCE in our experiments are clearly opposite to the observations made by Gillham and O'Hannesin (1994). It is noteworthy that recent experiments performed by Campbell *et al.* (1997) also show TCE dehalogenation rates that are substantially faster than the corresponding rates for PCE, results that are consistent with our observations. The reverse trend observed in our experiments and Campbell *et al.* (1997) relative to those described by Gillham and O'Hannesin (1994) is quite interesting as they bear on the issue of efficacy of abiotic remediation of halogenated ethenes.

Comparison of the normalized half lives (normalized to 1 m^2/ml surface area) in our experiments, with those published by Gillham and O'Hannesin (1994) and Johnson *et al.* (1996), clearly shows the same trend as the un-normalized values. (The fastest rates were observed for PCE, whereas in our experiments, PCE had the slowest rate of reaction). It is interesting to note that despite the much smaller surface area of the iron metal used by Gillham and O'Hannesin (0.287 m^2/g), and the larger surface area of the iron used in our experiments (4.17 m^2/g), the rates of the reactions in our experiment were several orders of magnitude slower. This observation may be the result of a lower reactive surface area available for the dehalogenation of chloroethenes in our study, caused by the oxidation of the metallic iron surface. Johnson *et al.* (1996) proposed that the reactive surface area was more of a limiting factor than total surface area in reaction rates of reductive dehalogenation. The presence of oxygen in our reaction vessels may have oxidized the surface of the iron powder. The reaction between zero valent iron with the chlorinated ethenes was hindered, and as a result, the dehydrogenation reactions were slower than expected.

One key difference in the conditions used in Gillham and O'Hannesin (1994), Campbell *et al.* (1997) and our experiments is pH. The latter two were either buffered near neutral or drifted to slightly more acidic values (<6). In contrast, Gillham and O'Hannesin's (1994) experiments drifted to more basic values (>9). The difference in pH trends appears to be a result of the addition of $CaCO_3$ and the lack of headspace in Gillham and O'Hannesin's (1994) experiment. It is unclear how this difference in pH can potentially affect the reactivity of halogenated ethenes. The effect of pH deserves further investigation, and as will be discussed below, it may have a strong effect on the reaction rates of reductive dehalogenation. If a pH effect on reaction rates of the different chlorinated ethenes can be demonstrated in future experiments, it will have implications for the field application of zero-valent iron degradation for specific contaminant discharges.

One final aspect to consider is headspace. Although the headspace in our systems was very small (~2% of total volume), a zone where dehalogenation could not take place was provided for the chloroethenes. Chlorinated ethenes are very volatile and it is likely that they preferentially spend more time in the headspace than in the solution phase. The slower rates of dehalogenation may be a result of the presence of headspace in the reaction vessels, as was observed in our experiments. In contrast, Gillham and O'Hannesin conducted experiments with zero headspace. This may have resulted in the faster rates of dehalogenation observed in their experiments. Future studies should include zero headspace experiments to further elaborate the effect of headspace on reaction rates of reductive dehalogenation of chlorinated ethenes.

4.3 Isotope Effects

The enrichment of ^{13}C in the unreacted (residual) ethenes was not an unexpected result. Kinetic effects on isotopic fractionation, as described in O'Neil (1986), are well understood concepts. Bonds containing the heavier isotope are much more stable than those with the lighter isotope (Figure 5). It follows that during reductive dehalogenation, the ^{12}C-Cl bond is more prone to the two electron transfer steps (β-elimination or hydrogenolysis) shown in Figure 4. Similarly, it can be expected that the C-^{35}Cl bonds will also undergo this two electron transfer reaction preferentially to the C-^{37}C bonds. The latter was confirmed by Vaillancourt *et al.* (1997), who conducted similar experiments and measured the chlorine isotope variations. They found that the unreacted Cl of the chlorinated ethenes also became isotopically heavier with time (by about 15 $^0/_{00}$).

Buist and Bender (1958) showed that trends in kinetic isotopic effects mirror those in activation energies. Reaction rates will decrease with increasing activation energy and steric hindrance in the rate determining step, allowing for the full expression of isotopic effects. It follows that the selectivity for the lightest isotopes (i.e. ^{12}C-Cl) is greatest during slow reactions.

For reductive dehalogenation of the family of chlorinated ethenes, PCE with the largest number of Cl atoms would be the most sterically hindered, and have the highest activation energy (and slowest reaction rate). If kinetic isotope effects were the dominating factor controlling fractionation, the progression in reaction rates and isotopic fractionation should increase and decrease, respectively, from PCE to c-DCE (Buist and Bender, 1958). This prediction is inconsistent with the results obtained from our experiments with PCE, TCE and c-DCE. In our experiments, the reaction rates of PCE and c-DCE with zero valent iron were lower than for TCE. The isotopic fractionation of TCE was also lower than expected. This observation thus appears to be inconsistent with kinetic isotopic effects.

Alternatively, the changes in isotopic composition during reductive dehalogenation may be described using a Rayleigh model. A Rayleigh model is used to describe unidirectional processes such as evaporation, condensation and distillation, where it is postulated that isotopic equilibrium is instantaneously achieved during the progress of reaction (Hoefs, 1987) and that products are continuously removed from reactants. Several examples of this are well known, including the oxygen and hydrogen variations in atmospheric precipitation. The isotopic composition of the remaining liquid or vapour, according to the Rayleigh model, depends only on the initial isotopic composition of the vapour (or liquid), the temperature and the degree of evaporation or condensation. A corollary to the assumption of instantaneous equilibrium between reactant and product, is that the product becomes no longer available to the reactant for isotopic exchange. Such an assumption is reasonable for carbon isotope exchange between chlorinated ethenes and their breakdown products, because the only way carbon isotope exchange can occur in these systems is for the carbon-carbon bonds themselves to be broken.

For reductive dehalogenation, the following form of the Rayleigh model (note similarity to Rayleigh distillation) can be used to show the relationship between the isotope ratios of the remaining liquid (R), the initial liquid (R_0) and the fraction of liquid remaining (f):

$$\frac{R}{R_0} = f^{\frac{1}{\alpha}-1} \qquad \textbf{(15)}$$

where α is the fractionation factor which is constant throughout the reaction. 4. Reaction 15 can also be defined as:

$$\frac{\delta^{13}C + 1000}{\delta^{13}C_0 + 1000} = f^{\frac{1}{\alpha}-1} \tag{16}$$

where $\delta^{13}C$ is the isotopic composition at time t and $\delta^{13}C_0$ is the initial isotopic composition, relative to PDB.

In order to determine whether a Rayleigh process can describe the fractionation during reductive dehalogenation of chlorinated ethenes, R/R_0 was plotted against the fraction remaining (f) for each compound. The value for f was calculated by comparing the peak areas at specific points in the reaction with the maximum peak area. The curves were fitted to the following equation:

$$y = x^a \tag{17}$$

where a is $1/\alpha - 1$, y is R/R_0, and x is f. Table 6 has the R^2 (correlation coefficient) values for the fit, as well as the exponent and the calculated α for each compound. Figures 16-19 are the plots for each compound, containing the best curve fit, as well as a maximum and a minimum α to enclose most of the data points. The first two to three data points were ignored for these plots, since they appear to represent disequilibrium distribution possibly related to the dissolution of the chloroethenes in the water or sorption effects.

Table 6: Isotopic Fractionation Factors for Chlorinated Ethenes

α	exponent*	R^2
	c-DCE	
1.0146	-0.01435	0.98
	t-DCE	
1.0036	-0.0036	0.8
	TCE	
1.0087	-0.0086	0.93
	PCE	
1.026	-0.0258	0.86

* This is the value of the exponent in the equation for $y=x^a$

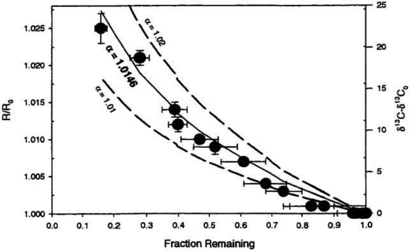


Figure 16: Plot of Isotopic Ratio Versus Fraction Remaining for c-DCE

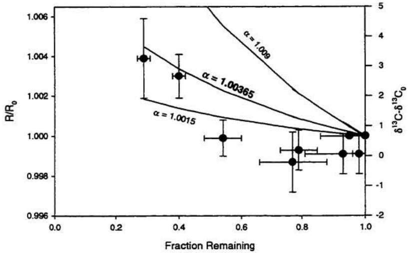


Figure 17: Plot of Isotopic Ratio Versus Fraction Remaining for t-DCE

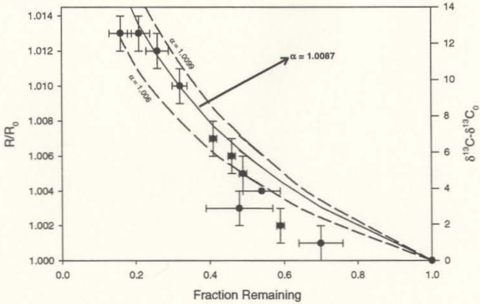


Figure 18: Plot of Isotopic Ratio Versus Fraction Remaining for TCE

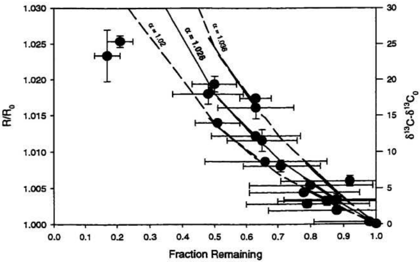


Figure 19: Plot of Isotopic Ratio Versus Fraction Remaining for PCE

It can be seen that the Rayleigh model can be used to describe reductive dehalogenation of chlorinated ethenes. The curve did not fit well for t-DCE, possibly as a result of the difficulties in resolving the peak in the chromatogram, and therefore, the isotopic compositions may have some error. The c-DCE had the best fit, followed by TCE and PCE. Given the calculated fractionation factors for each compound, the dehalogenation products will have an isotopic composition ($\delta^{13}C$) lighter than the reactant by 14.6 $^0/_{00}$, 8.7 $^0/_{00}$, 26 $^0/_{00}$ for c-DCE, TCE and PCE respectively. Slater *et al* (1997) estimated α for TCE and reaction with industrial iron filings to be 1.015. The impurities in the iron (such as Zn or Ni) or the presence of an oxidized surface coating on the iron filings, may have caused the differences between the reported α of Slater *et al.* (1997) and the results from our experiments.

There appears to be no real correlation between the number of Cl atoms and the value of α. (The α for TCE does not lie between those of PCE and c-DCE). It is noteworthy that TCE, which exhibited the smallest α, is unique in this chloroethene series, in that the Cl atoms are all energetically and sterically different. In contrast, each of the four Cl atoms in PCE and the two Cl atoms in DCE are energetically and sterically equivalent. Campbell *et al.* (1997) proposed that the formation of t-DCE from TCE was sterically hindered. When such a steric hindrance during reductive dehalogenation is present, it will overshadow the isotope induced fractionation effects. In symmetric compounds such as c-DCE and PCE, the equivalency of all Cl positions would allow for the full expression of isotope induced effects. In contrast, steric effects will mask isotope induced effects during dehalogenation of TCE, as is consistent with the low α factor observed.

Although kinetic isotopic effects and Rayleigh effects are mutually exclusive, solid conclusions could not be drawn from the experiments performed in our study as to which effect was dominant. Buist and Bender (1958) showed that for kinetic isotopic effects, the rate constant ratios (light isotope to heavy) were linearly dependent on the activation energies of reactions with ^{14}C labelled compounds. If such a linear correlation could be found between for reductive dehalogenation, then kinetic effects dominate the effects on isotopic composition. Future studies should include performing the experiments at different temperatures in order to determine the activation energies for reductive dehalogenation of the chlorinated ethenes.

The processes responsible for removal of chlorinated ethenes from natural waters can potentially be distinguished using α. For example, preliminary results from experiments done with TCE and microbial degradation in soil samples, have shown that isotopic fractionation during this process is not as extensive as for the abiotic process just described (Sturchio *et al.*, 1997).

Although a good fit to the Rayleigh model was obtained, it can be seen that there was a slight "step shift" in α for the first few points of TCE curve (the scatter in the PCE curve prevented this feature from being resolved). This step shift is statistically borne out by replicate experiment, hence deserves further consideration. There are a number of possible explanations for the occurrence of this step shift within the framework of the Rayleigh model. For example, the change in α implied by this step could indicate a change in reaction mechanism. As noted earlier, there are two potential pathways for the reductive dehalogenation to occur: dehydrogenation and β-elimination (Figure 4).

The phase diagram for Fe^{2+}, $Fe(OH)_2$, $Fe(OH)_3$ and the Eh-pH curves for reductive dehalogenation for each ethene are shown in Figures 20-24. (The Eh-pH curves for the reactions assumed a concentration for Cl^- of 10^{-3} M). It can be seen that for PCE and TCE, the intersection of the two curves for the different reaction pathways lies in the pH range of these experiments (pH 5-6). The shift in α may therefore correspond to drift in pH and the change in the predominant reaction: β-elimination at the beginning, dehydrogenation towards the end. Although no shift in pH was observed in the blank iron solutions, it is possible that in the presence of the chloroethenes as the sole electron acceptors, changes and pH and Eh occur. This can also explain the absence of acetylated products, and the presence of chlorinated products only; the acidic conditions favoured dehydrogenation. In experiments done under completely reducing conditions (Gillham and O'Hannesin, 1994), the higher pH is in the range for the predominance of the β-elimination reaction (and hence the presence of acetylated products).

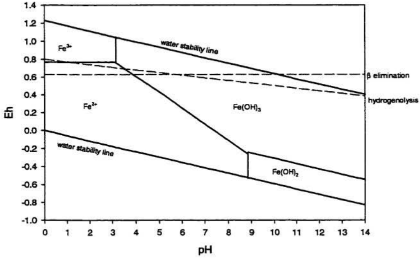


Figure 20: Phase Diagram for Iron Hydroxide Species and PCE Reductive Dehalogenation Reactions (after Brookins, 1988). Data for the dehalogenation was calculated from Roberts *et al.* (1996).

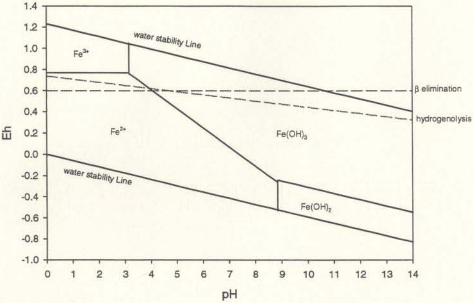


Figure 21: Phase Diagram for Iron Hydroxide Species and TCE Reductive Dehalogenation Reactions (after Brookins, 1988). The dehydrogenation product is cis-DCE. Data for the dehalogenation was calculated from Roberts *et al.* (1996).

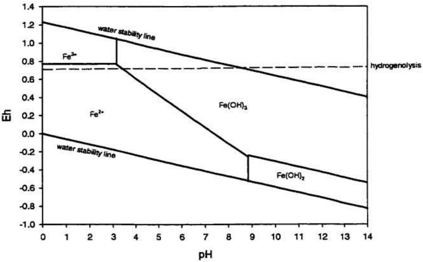


Figure 22: Phase Diagram for Iron Hydroxide Species and TCE Dehydrogenation (after Brookins, 1988). The dehydrogenation product is trans-DCE. Data for the dehalogenation was calculated from Roberts *et al.* (1996).

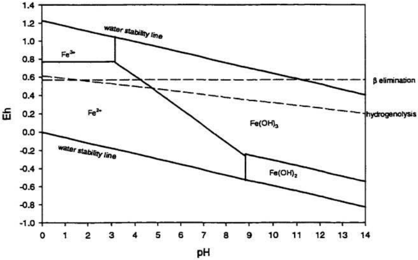


Figure 23: Phase Diagram for Iron Hydroxide Species and c-DCE Reductive Dehalogenation Reactions (after Brookins, 1988). Data for the dehalogenation was calculated from Roberts *et al.* (1996).

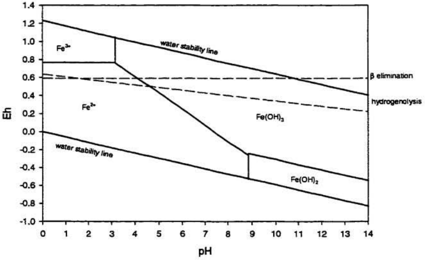


Figure 24: Phase Diagram for Iron Hydroxide Species and t-DCE Reductive Dehalogenation Reactions (after Brookins, 1988). Data for the dehalogenation was calculated from Roberts *et al.* (1996).

It may be expected that the larger the difference in reduction potentials for half reactions, the larger the driving force for the overall reaction (and the smaller the α). Based on this, Vogel *et al.* (1987) demonstrated that at pH of 7, dichloroelimination is more favourable than hydrogenolysis. As can be seen in the phase diagrams and Tables 7A and 7B, this situation changes under more acidic and oxidizing conditions (at pH=5, both reactions can occur, and at pH=4, hydrogenolysis becomes more favourable for PCE and TCE). For c-DCE and t-DCE, β-elimination is the dominant pathway until pH of about 1.5. Future studies should include pH controlled experiments at low (e.g. pH=3-4), neutral (pH=7), and high (pH=8-9) values of pH to reveal the pH dependence of reaction mechanisms.

Based on our experiments, the isotopic composition of the acetylated products (from β-elimination) will be heavier than the olefins (from dehydrogenation). This difference will be determined by the fractionation factor. For TCE, the first few points fit to α of 1.006 and the remaining points to α of 1.009. If the change of the proposed mechanism is correct, the difference in the calculated α for hydrogenolysis and the β-elimination reflects the α between the acetylated and the olefin products. From the step shift in the TCE Rayleigh curve this α value is about 1.003 or an approximate ^{13}C difference of 3.1 $^0/_{00}$.

Table 7A: Standard Reduction Potentials for Dehydrogenation of Chlorinated Ethenes

Compound	E° (V)	$E_{pH=7}$ (V)*	$E_{pH=5}$ (V)*	$E_{pH=4}$ (V)*
PCE → TCE	0.7104	0.592	0.651	0.681
TCE → c-DCE	0.648	0.530	0.589	0.619
TCE → t-DCE	0.627	0.513	0.719	0.717
c-DCE → VC	0.525	0.407	0.467	0.496
t-DCE → VC	0.546	0.428	0.487	0.517

* assumes concentration of Cl^- of 10^{-3} M.

Table 7B: Standard Reduction Potentials for β-Elimination of Chlorinated Ethenes

Compound	E° (V)*	product
PCE	0.631	dichloroaceteylene
TCE	0.599	chloroacetylene
c-DCE	0.568	acetylene
t-DCE	0.589	acetylene

* Eh for β-elimination does not depend on pH.

Our results have potential implications for various facets of site characterization and remediation. We have shown, for example, that reaction mechanisms and rates can potentially be affected by solution pH, an effect that is only poorly appreciated in existing literature. It appears that β-elimination is the dominant pathway at high pH regimes, whereas the systems that are more acidic tend to be dominated by hydrogenolysis. It also appears that the relative susceptibility of different chlorinated ethenes to dehalogenation (as expressed in estimated reaction rates) significantly depend on solution pH. Given these findings, groundwater pH conditions may be a critical factor in the engineering design of zero valent iron dehalogenaion. Nevertheless, it is possible to adjust groundwater pH as part of the remediation design.

The fact that these large changes in isotopic composition can occur during reductive dehalogenation has enormous implications for monitoring the progress of zero valent iron remediation. Chlorinated ethenes from contaminated sites can be analyzed for carbon isotope composition at any given point of the remediation program, and the efficacy of remediation can be assessed quantitatively even if contaminant dispersion and dilution were to occur (i.e. unlike raw compound concentrations, the carbon isotope compositions of chlorinated ethenes will be not compromised by these processes).

The flow of groundwater through a plume can cause spatial variation in the concentration of pollutants. A low measurement down stream from a source may lead to the conclusion that the compound is degrading naturally in the environment. Isotopic compositions along with α of the various processes will provide a complete picture of both the movement and reactivity of the pollutants in the water. However, studies of isotope exchange systematics, such as that done in this work, will be needed before other degradative, migration and retardation can be similarly evaluated. Isotopic data can be combined with hydraulic flow data through an aquifer to determine the potential size and age of a plume.

Future direction for this study should include monitoring and changing pH (by adding buffers). Repeating the experiments at different temperatures can further elucidate the mechanisms involved for each reaction pathway. Using higher concentrations of the chlorinated ethenes to produce larger concentration of dehalogenated products will be useful in identification of the products, as well as following the isotopic composition of the products during the course of the reaction.

Chapter 5 - Summary and Conclusions

Chlorinated ethenes and their chlorinated degradation products are prevalent soil and groundwater contaminants that are closely regulated by various state, provincial and federal agencies. Trichloroethylene, perchloroethylene, the isomers of dichloroethylene, and vinyl chloride are considered priority pollutants because of their known toxicity and carcinogenity. Anthropogenic sources are the only known sources of these compounds to the natural environment.

Several methods exist for the remediation of these contaminants from surface waters including biological and chemical remediation methods. Both types of remediation methods can adversely affect water quality (dissolved oxygen, pH, metals) when applied *in situ*.

The use of reductive dehalogenation with zero valent iron is proving to be an effective method for the removal of chlorinated hydrocarbons in contaminated waters. This method was discovered in the 1970's, but it was not until the possibility of *in situ* treatment using permeable reaction walls was suggested (Gillham and O'Hannesin, 1994), that interest in this process was revitalized. Current research activities are motivated by interest in maximizing the effectiveness of the removal of the chlorinated hydrocarbons, as well as in determining the practical limits of this method.

The purpose of our experiments was to determine the magnitude and direction of isotopic fractionation during reductive dehalogenation of chlorinated ethenes by zero valent iron. The results of this study have implications for pollutant source allocation, as well as monitoring the progress of remediation efforts. To the extent that abiotic reductive dehalogenation could occur naturally in groundwater systems (with other electron donors), the present study could also have implications for monitoring the effectiveness of natural attenuation reactions.

Three replicate experiments for each compound (PCE, TCE, t-DCE, c-DCE) were conducted, as well as a corresponding blank (which contained only water and solvent, but no iron). The blank was useful in establishing that the reactions observed in the other experiments were occurring only in the presence of iron. All compound specific carbon isotope measurements were done using GC-C-IRMS. Identification of reaction products was attempted by GC-MS, and the products positively identified include the chlorinated products of PCE and TCE and C_3, C_4 and C_5 hydrocarbons.

The rate of the reactions was slower (and the half lives were longer) than previously published data. The trend from PCE to c-DCE was also the opposite than previously reported results (e.g. Gillham and O'Hannesin, 1994). In our experiments, half lives for PCE were much greater than for TCE or c-DCE. In Gillham and O'Hannesin's experiments, the opposite trend was reported, with the fastest rates observed for PCE and the slowest for DCE. Reactive surface area appears to have been more important than total surface area, as suggested by Johnson *et al* (1996). The rates for reductive dehalogenation of chlorinated ethenes were much slower in our experiments than previously published (e.g. Gillham and O'Hannesin, 1994). The surface area of the iron metal used in our experiments was about 15 times greater than the surface area of the iron metal used by Gillham and O'Hannesin (1994). The oxidation of the surface of the metallic iron in our experiments may have resulted in slower reaction rates.

The prevalent difference between our experiments and those by Gillham and O'Hannesin was the drift in pH. In the latter experiments, pH had drifted to more basic values, whereas in our experiments they drifted to acidic values (pH=4-6). Campbell *et al.* (1997) also found that rates for TCE were faster than for PCE under neutral pH (pH=7). It still remains unclear how pH can affect the reaction rates of the different chlorinated ethenes. The Eh-pH diagrams clearly show, however, that pH can affect the dehalogenation pathways.

The reaction may be modeled using first or second order kinetics. Reactive surface area of zero valent iron was previously found to be an important parameter in the efficacy of reductive dehalogenation (Johnson *et al.*, 1996). It was also found in our experiments that headspace was another limiting factor on reaction rate. The headspace provided a reaction-free zone for the chloroethenes. The second order fits obtained in our study imply that the above parameters may have a stronger effect on the reductive dehalogenation reaction rates than had previously been anticipated.

It was found that the stable carbon isotope composition ($\delta^{13}C$) of the chlorinated ethenes changed by 24 $^{0}/_{00}$, 12 $^{0}/_{00}$ and 24 $^{0}/_{00}$ for PCE, TCE, and c-DCE, respectively. The fractionation may be explained by kinetic effects, or modeled to Rayleigh processes. The former is the result of the differences in bond strengths, whereby, ^{13}C-Cl bonds are preferentially retained in the unreacted residue. Based on the expected trend in reaction rates and activation energies, the trend in kinetic isotopic effects was not as expected. From c-DCE to PCE steric hindrance increases causing an increase in activation energy and isotopic fractionation. This was not observed in our experiments because in PCE and c-DCE the Cl atoms are sterically equivalent and in TCE the Cl atoms are sterically different. The energetic differences in the Cl atoms of TCE increased its reactivity with zero valent iron. The increase in reactivity, decreased the selectivity for ^{12}C and the isotopic fractionation of TCE during reductive dehalogenation.

Rayleigh processes are typically used in describing unidirectional reactions such as distillation and condensation. The fits to the Rayleigh equation were quite good for the PCE, TCE and especially the c-DCE data. The fit for the t-DCE data may have been adversely affected by the difficulty in resolving the peak in the chromatogram. Future experiments should focus on improving the resolution of t-DCE. No correlation between the degree of halogenation and magnitude of fractionation factors was observed. Whereas this observation may be taken to support the importance of kinetic effects in controlling carbon isotope fractionation in these systems, the possibility of differing reaction mechanisms (shift from β-elimination to hydrogenolysis) must continue to be investigated. Future experiments conducted in pH regimes that are clearly dominated by either β-elimination or hydrogenolysis will help resolve these possibilities; examination of reaction products (acetylene or chloroacetylene vs. DCE) will further clarify the significance of the calculated α values. The distinct possibility that steric effects due to the non equivalency of the three Cl atoms in the TCE molecule, swamped either a kinetic effect or equilibrium fractionation needs to be examined. Future experiments should also include a determination of activation energies for each reductive dehalogenation of the chlorinated ethenes in order to conclude which of the above isotopic effects is dominant.

The results of this experiment may have implications for contaminant source apportionment. The determination of the source of a pollutant is premised on the assumption that each source has an isotopic fingerprint that is either retained or altered predictably through a range of geochemical pathways. Our data clearly indicate that only the latter can be expected. This implies that fractionation factors corresponding to a range of other processes including microbial transformation and other abiotic reactions must be ascertained before any form of source apportionment can be attempted.

Further investigation into the kinetics and type of fractionation of chlorinated ethenes is needed. Increasing the concentrations of the chlorinated solvents, as well as the amount of iron may help in identification of the reaction products. These types of experiments may also help elucidate the mechanisms that are involved in these reactions. The reactions may also be done at other temperatures in order to determine their effects on isotopic fractionation. These experiments may be especially useful in distinguishing kinetic and equilibrium isotope effects. Using lower temperature may also provide a more useful picture as to what is occurring in northern natural waters. Finally, understanding the isotopic fractionation of chlorine isotopes (work in progress) may further provide useful information about the fundamental mechanisms involved in the reductive dehalogenation of chlorinated ethenes.

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