

In Situ Dechlorination of TCE during Aquifer Heating

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Abstract

Laboratory and field efforts were undertaken to examine trichloroethene (TCE) dechlorination as a function of temperature as an aquifer is heated to temperatures approaching boiling. Experiments were conducted using sediment samples and during electrical resistance heating (ERH) treatment at the East Gate Disposal Yard (Fort Lewis, Washington), which contains nonaqueous phase TCE and hydrocarbon contamination. Laboratory microcosms with these sediments showed TCE dechlorination at 70°C with measured products of acetylene, ethene, and ethane, indicating an abiotic component of the degradation. In contrast, TCE was dechlorinated to *cis*-1,2-dichloroethene in experiments at 10°C, likely by biological reductive dechlorination. The observed products at 70°C suggest dechlorination catalyzed by reduced sediment iron. Indications of in situ dechlorination were observed in periodic ground water samples collected during field-scale ERH from an average ambient temperature of about 19°C to near boiling. Dechlorination indicators included an increase in chloride concentration at the onset of heating and observation of acetylene, ethene, and methane at elevated temperatures. The data collected in this study suggest that dechlorination can occur during ERH. The overall cost-effectiveness of ERH may be enhanced by fortuitous in situ dechlorination and, potentially, could be further enhanced by specifically designing and operating ERH to maximize in situ dechlorination.

Introduction

Subsurface conditions impact the type, rate, and extent of contaminant transformation/degradation reactions that occur. Oxidation/reduction conditions, presence of organic carbon as substrate for biological reactions, pH, presence of catalysts, and temperature can be key factors controlling subsurface reactions. Remediation of contaminant plume source areas containing dense nonaqueous phase liquid (DNAPL) may benefit from subsurface contaminant reactions if these reactions can significantly reduce the contaminant mass or mass flux to the plume. This study focuses on the reactions that may occur during aquifer heating via electrical resistance heating (ERH) between ambient ground water temperature and approximately 70°C as applied for thermal treatment of DNAPL and for initially reduced aquifer conditions. A temperature of approximately 70°C was selected as the approximate maximum temperature for the laboratory investigation portion of the study because above this temperature, TCE DNAPL in water boils and the rate of mass transfer to the vapor phase significantly increases such that extraction processes may dominate DNAPL treatment. As such, this study examines

one component of how subsurface reactions can be important to DNAPL remediation, though other types of reactions may be important under oxic conditions (Knauss et al. 1999), at higher temperatures with specific mineral phases present (Costanza et al. 2005), and after an aquifer is heated to boiling and then is cooling down (Friis et al. 2005).

Laboratory and field efforts were undertaken to examine trichloroethene (TCE) dechlorination as a function of temperature as an aquifer is heated to temperatures approaching boiling. ERH is a remediation technique that applies electrical energy to heat the subsurface and mobilize or volatilize contaminants for subsequent extraction. ERH passes an electrical current through the soil and ground water that requires treatment. The electrical current warms the soil and then boils a portion of the soil moisture into steam. Electrical energy is transformed to heat that evaporates the target contaminant and provides steam as a carrier gas to sweep the volatile organic compounds (VOCs) to the vapor recovery wells. After the steam is condensed and the extracted air is cooled to ambient conditions, the VOC vapors are treated using conventional methods. Heating of the subsurface may also create conditions conducive to in situ reactions that can transform or degrade contaminants. Enhanced biological or abiotic TCE dechlorination reactions are possible during heating from ambient aquifer

temperatures to near boiling temperatures. This study focuses on potential reaction processes under reducing conditions as an aquifer is heated to temperatures up to approximately 70°C.

Under anaerobic conditions, bacteria can transform chlorinated ethene compounds by hydrogenolysis, transferring electrons and replacing a chlorine atom with a hydrogen atom (e.g., DeBruin et al. 1992; Freedman and Gossett 1989). Biological transformation of TCE by hydrogenolysis produces dichloroethene (DCE) isomers, then vinyl chloride (VC) and ethene. In some instances, DCE and VC can accumulate as recalcitrant or persistent intermediate products of microbial reductive dechlorination.

Biological reaction rates increase with increasing temperature within a specific range of temperature. Microbial activity (e.g., metabolic reaction rates) is a function of temperature (Gaudy and Gaudy 1988; Atlas and Bartha 1987; Neidhardt et al. 1990; Stolp 1988). Mesophilic microorganisms typically have optimal metabolic rates at a temperature near 30°C to 40°C. The metabolic rates are lower at both lower and higher temperatures. For lower temperatures, the rates diminish by a factor of approximately 2 every 10°C (Atlas and Bartha 1987). This temperature relationship for mesophilic microorganisms has been demonstrated in many laboratory studies, including studies using ERH to vary the temperature (Heath and Truex 1994). For temperatures higher than approximately 35°C, the metabolic rate of mesophilic microorganisms typically decreases gradually up to a temperature between 40°C and 50°C. Typically at temperatures between 45°C and 60°C, mesophilic organisms become inactive and any microbial activity at these and higher temperatures is associated with microorganisms adapted to survive higher temperatures (i.e., thermophiles). The physiological tolerance to the effect of temperature is generally attributed to membrane lipid protein/enzyme structure and function (Neidhardt et al. 1990; Gaudy and Gaudy 1988). Thermophilic microorganisms may have an optimal metabolic rate somewhere between about 50°C and the boiling point of water. Thermophilic microorganisms have been isolated from a variety of high-temperature environments and can metabolize organic compounds at temperatures above 50°C (e.g., Atlas and Bartha 1987). Thermophilic organisms may also be present in soil that is normally at much lower temperatures (Stolp 1988). It has been demonstrated that there are soil microorganisms that survive steam treatment of soil (Dablow et al. 1995; Richardson et al. 2002) and that surviving microorganisms can degrade contaminants (Richardson et al. 2002).

Kengen et al. (1999) quantified reductive dechlorination of perchloroethylene by a thermophilic anaerobic enrichment culture, demonstrating that dechlorination is possible at high temperature. The temperature optimum for the enrichment culture in their study was 60°C to 65°C. Extracellular biomolecules of *Methanosarcina thermophila* have been shown to dechlorinate carbon tetrachloride (Baeseman and Novak 2001; Andrews and Novak 2001; Novak et al. 1998a, 1998b), and dechlorination occurs with increasing rates up to a temperature of about 65°C (Koons et al. 2001).

TCE can also be dechlorinated by reduced iron species in sediments. For TCE, the Fe(II)-catalyzed dechlorination pathway is a reductive elimination through chloroacetylene that is quickly transformed to acetylene and then ethene and ethane. Fe(II)-mediated dechlorination activity has been extensively studied and can be catalyzed by iron sulfide (Butler and Hayes 1999, 2000, 2001; Lee and Batchelor 2002a, 2003), green rust (Lee and Batchelor 2002b), magnetite (Lee and Batchelor 2002a, 2003), biotite (Lee and Batchelor 2003), clay minerals (Lee and Batchelor 2003; Cervini-Silva et al. 2003), or sorbed iron (II) (Amonette et al. 2000; Pecher et al. 2002). Additionally, sediment-associated iron reduced by dithionite has been shown to dechlorinate TCE (Vermeul et al. 2000). Biologically reduced iron can also catalyze dechlorination (McCormick et al. 2002; Gerlach et al. 2000; Amonette et al. 2000).

The degradation pathway of TCE and other chlorinated solvents by dithionite-reduced sediment has been investigated in bench-scale studies as well as in field-scale studies at Fort Lewis for the In Situ Redox Manipulation technology (Vermeul et al. 2000). Dithionite-reduced sediment transformed TCE to chloroacetylene via a reductive elimination reaction (Roberts et al. 1996), with subsequent reductive elimination to acetylene, then hydrogenolysis to ethylene and ethane (Szecsody et al. 2004). Reductive elimination has also been shown to be the major pathway in other studies using zero-valent and ferrous iron (Sivavec et al. 1996; Orth and Gillham 1996). TCE is abiotically degraded in dithionite-reduced sediment with a half-life of 3 to 50 h (25°C), depending on the mass of ferrous iron in the sediment (Vermeul et al. 2000).

The rates of transformation reactions catalyzed by Fe(II) have been shown to increase with increasing temperature. TCE dechlorination with reduced sediment was investigated from 2°C to 42°C and the reaction rates increased with increasing temperature (Szecsody et al. 2004). Subsequent studies suggested that adsorbed ferrous iron on clays or clay-sized particles dominated the reactivity (Szecsody et al. 2004). However, there are some studies that indicate temperatures associated with autoclaving (e.g., 120°C) of sediments can passivate heterogeneous reactions (Butler and Hayes 2001; Heijman et al. 1993; Wolfe et al. 1986). Additionally, the crystallization rate of amorphous iron oxides (e.g., ferrihydrite) increases with increasing temperature, and this crystallization may impact the rates of the oxidation-reduction reactions important to contaminant transformation. Heating ferrihydrite at neutral pH increases the rate of transformation of ferrihydrite to hematite (Payne et al. 1994). Hematite is the primary crystallization product of ferrihydrite at pH values between 6 and 9 with secondary amounts of goethite produced (Schwertmann and Murad 1983). At higher or lower pH values, goethite becomes the primary product (Schwertmann and Murad 1983). Rates of ferrihydrite crystallization at near neutral pH in laboratory experiments range from a half-life of about 200 d at 24°C (Schwertmann and Murad 1983) to a half-life of a few hours at 92°C (Johnston and Lewis 1983) and an estimated half-life on the order of weeks at 70°C (Payne et al. 1994). The impact on these crystallization rates of the iron oxide as part of a sediment

material rather than as a single phase in a laboratory test was not reported.

Chemical or biological processes can reduce sediment iron and maintain reduced conditions. Chemical reagents have been applied to reduce sediment iron with subsequent transformation of chlorinated solvents such as with the In Situ Redox Manipulation technology (Vermeul et al. 2000). Alternatively, a microbial substrate that supports biotic iron reduction may be used to reduce sediment iron and, potentially, to maintain the reduced conditions under higher temperatures. Studies have also shown that biological iron reduction occurs at high temperature (Zhang et al. 1996; Liu et al. 1997; Slobodkin and Wiegel 1997; Kieft et al. 1999; Kashefi and Lovley 2000; Roh et al. 2003).

Methods

Experiments were conducted using sediment samples and during ERH treatment at the East Gate Disposal Yard (EGDY), Fort Lewis, Washington. Wastes, including non-aqueous phase liquid hydrocarbons and TCE, were disposed at the EGDY between the 1940s and 1970s, resulting in a large TCE plume downgradient of the disposal area. TCE and *cis*-DCE are the dominant chlorinated solvents observed at the site, with only minor amounts of other chlorinated solvents present. The aquifer is generally oxic except within the EGDY, where significant hydrocarbon contamination is present and the pH is near neutral with a mean value of 6.5. Aquifer sediments are a glacial drift of intermingled till and outwash sequences with a well-graded mixture of silt, sand, and gravel components. Reducible iron content was determined in nearby wells as part of previous testing for the In Situ Redox Manipulation technology. In these tests, the dithionite-reducible iron content averaged approximately 0.25% by weight (Vermeul et al. 2000).

Source reduction was conducted at EGDY using the ERH technology applied to two approximately 1-acre zones determined to have high contents of non-aqueous phase liquid TCE. In the treatment zone selected for this study, nominally 35 feet of saturated sediments and 10 feet of unsaturated sediments were treated using ERH. Sediment samples were collected prior to ERH treatment and used in microcosm studies. During ERH treatment, ground water samples were collected and analyzed for constituents indicative of dechlorination reactions.

Laboratory Microcosm Studies

Prior to ERH application, sediment and ground water samples were retrieved from the zone targeted for treatment and used for laboratory tests examining the potential for high-temperature dechlorination reactions. TCE and dechlorination products were measured over time for treatments incubated at the ambient Fort Lewis ground water temperature (~10°C) and at 70°C. Chloride concentrations were not monitored in laboratory experiments because background chloride concentration in the ground water used for the experiments (~120 µM) was high compared to the expected increase in chloride concentration due to dechlorination reactions. Treatments were also included to examine the effect of added microbial substrate on TCE dechlorination.

Table 1 lists the specific experimental conditions that were evaluated in the tests. All treatments were conducted in duplicate with killed controls at the 70°C incubation temperature.

Sediment and ground water were collected prior to ERH treatment in a manner that minimized sample disturbance and exposure to nonindigenous microorganisms. Ground water was filter sterilized into presterilized polypropylene bottles. Sediment samples were processed in a field-portable glove box with an argon purge. Approximately 100 mL of filter-sterilized ground water were poured into presterilized mason jars for sediment collection. Individual sediment samples from the core material of a sonic drilling rig were transferred into the glove box. A sterile piece of aluminum foil was placed under the working area. The core liner was cut open and sediment from the liner was transferred into the mason jar using a sterile spatula. The mason jar was filled with sediment with a layer of ground water on top and the jar was sealed leaving no headspace. Sediment and ground water samples were stored at 4°C until used in the microcosm tests.

All microcosm bottles/vessels were prepared in an anaerobic glove box under a nitrogen gas atmosphere. Ground water samples were purged with anaerobic gas (nitrogen/carbon dioxide mixture) for approximately 16 h to remove any indigenous VOCs prior to construction of microcosms. Approximately 100 g of sediment were transferred into 500-mL serum bottles (working volume of 550 mL) for 10°C treatments. Approximately 200 g of sediment were transferred into 1-L stainless steel vessels

Table 1
Experimental Conditions for Microcosm Treatments

Treatment Number	Treatment	TCE and Other Amendments	Autoclaved	Incubation Temperature (°C)
1	Sediment only, high temperature	TCE	No	70
3	Added microbial substrate, high temperature	TCE, lactate (400 mg/L), and yeast extract (100 mg/L)	No	70
3	Sediment only, killed, high temperature	TCE	Yes	70
4	Added microbial substrate, low temperature	TCE, lactate (400 mg/L), and yeast extract (100 mg/L)	No	10

(Skeen et al. 1994) for treatments at 70°C. The vessels feature gastight stainless steel ball valves at all sampling ports to minimize losses through the sampling septa. The presence of stainless steel did not appear to cause iron-catalyzed dechlorination based on the minimal occurrence of dechlorination products in the control treatments. For low temperature treatments, 250 mL of ground water was added to each bottle and the bottles sealed with Teflon[®] lined, butyl rubber septa and aluminum crimp caps. For 70°C treatments, 500 mL of ground water was added to each vessel and the vessel sealed. The bottles/vessels were then transferred to a gassing station where the headspace was purged with anoxic gas containing 10% carbon dioxide and 90% nitrogen; thus, dissolved oxygen (DO) was not monitored in the microcosm test because it was assumed to be removed in the set up of the experiment. Killed controls were constructed using the same procedures as for the active microcosms except that after the vessels were constructed, sufficient sodium azide was added to achieve an aqueous concentration of 200 mg/L. The vessels were then autoclaved twice at 121°C for 1 h (Bradley and Chapelle 1999). After amendments were added, the bottles/vessels were mixed and incubated quiescently at the temperature indicated in Table 1. Serum vessels were inverted to minimize losses of volatile organics.

Microcosms were periodically sampled for aqueous-phase chlorinated organics and headspace gases (methane, ethane, ethene, and VC). The initial sample was collected after 1 d of incubation. Before each sampling event, the headspace pressure for treatments was measured by puncturing the septa with a 22-gauge needle connected to a Tensimeter (SMS, Tucson, Arizona).

Aqueous-phase chlorinated ethenes were analyzed by removing 1 mL of aqueous sample with a 2.5-mL gastight glass syringe (Hamilton Co., Reno, Nevada) and extracting in 3 mL of hexane. After settling, the organic supernatant was transferred to a 2.0-mL gas chromatograph vial and sealed with a septa and aluminum crimp cap. The extracted aqueous-phase samples were analyzed for chlorinated organics using a modified version of the methods reported by Chen et al. (1996). Analysis was conducted with a 5890 Series II GC (Hewlett Packard Co., Wilmington, Delaware) equipped with an electron capture detector and a 75-m, 0.53-mm-inner diameter (ID), AT-624 column (Alltech Associates Inc., Deerfield, Illinois). Total amounts of each chlorinated ethene compounds were estimated in each bottle using the measured aqueous-phase concentration and an estimated Henry's law constant (Gossett 1987; Heron et al. 1998).

Selected headspace constituents were analyzed by collecting a 3-mL gas sample using a 5-mL gastight glass syringe (Dynatech, Baton Rouge, Louisiana). The headspace gas was then analyzed by direct injection into an HP model 5890 Series II GC (Hewlett Packard, Palo Alto, California) equipped with a flame ionization detector (FID) and a 7-m, 3.2-mm-ID, Hayesep D 100/120 column (Alltech Associates Inc., Deerfield, Illinois).

Aqueous samples for volatile organic acids, including acetate and propionate, were determined using an HP model 5890 Series II GC (Hewlett Packard) equipped with an FID and a 10-m Nukol column (Supelco, Bellefonte,

Pennsylvania). Lactate concentrations were determined using an enzymatic determination for lactate with Lactate Reagent (Sigma Diagnostics Inc., St. Louis, Missouri).

Field Test

The ERH treatment was applied through 157 electrodes placed in an array to distribute heat throughout the treatment zone. A total of 9181 mWh were applied to heat the zone (an average of 2202 kW). The heated zone and six monitoring locations for the study are shown in Figure 1. Throughout the heated zone, TCE contamination is commingled with petroleum contamination, whereby the petroleum can provide a substrate for microbial dechlorination reactions and maintaining reducing geochemical conditions. The aquifer solids also contain iron minerals, which have been shown to catalyze dechlorination at the solid surface when in a reduced chemical form (Vermeul et al. 2000).

The field test for in situ reactions was conducted by measuring the ground water concentrations of reactants, products, and geochemical indicators for potential TCE dechlorination reactions. Monitoring wells were sealed at the surface and included a Teflon sampling tube permanently installed for retrieving ground water from within the screened interval. Ground water was extracted for sampling using a peristaltic pump. At the surface, ground water passed through a stainless steel cooling coil to reduce ground water temperature to below 20°C before the pump inlet and prior to dispensing the ground water into the sample vials. The specific analytes included chlorinated ethenes by EPA 8260B; ethene, ethane, acetylene, and methane by RSKSOP-175 (Kampbell and Vandegrift 1998); chloride by EPA 300.0; sulfide by EPA 376.1; ferrous iron by Hach Method 8008 (Loveland, Colorado); and oxidation/reduction potential and DO using field instruments.

Laboratory Microcosm Results

Dechlorination of TCE was observed in all active treatments. The dechlorination products and rate of

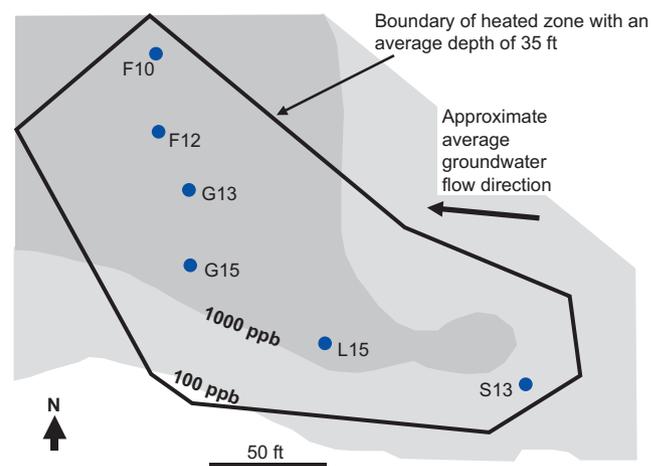


Figure 1. Location of monitoring wells (e.g., G15) within the ERH treatment zone. TCE contours based on peak TCE concentration in ground water during heating.

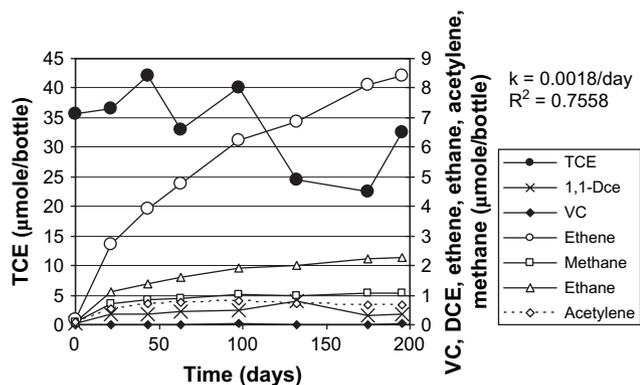


Figure 2. TCE, dechlorination products, and methane for an active unamended microcosm incubated at 70°C (treatment 1, Table 1, duplicate showed similar response). The k value is the first-order decay coefficient calculated based on the formation of observed dechlorination products.

transformation changed as a function of temperature (Figures 2 through 5). In treatments incubated at 70°C, the primary transformation products were acetylene, ethene, and ethane, suggesting an abiotic component of the degradation. A small amount of 1,1-dichloroethene was also observed as a potential transformation product. Only very small amounts of dechlorination products were observed in the killed control treatments. Transformation of TCE in the 10°C treatments followed the reductive dechlorination pathway and accumulated DCE over the duration of the incubation.

The TCE concentration data exhibited significant variability over the duration of the study for 70°C treatments. Though the cause of this variability is not directly known, it is likely due to sampling and extraction procedure variability. Initial concentrations of TCE are also variable due to difficulties with obtaining a consistent amendment from the TCE stock solution consisting of TCE in equilibrium with water. Data for the primary transformation products (acetylene, ethene, and ethane) for 70°C treatments have significantly less variability. These transformation products

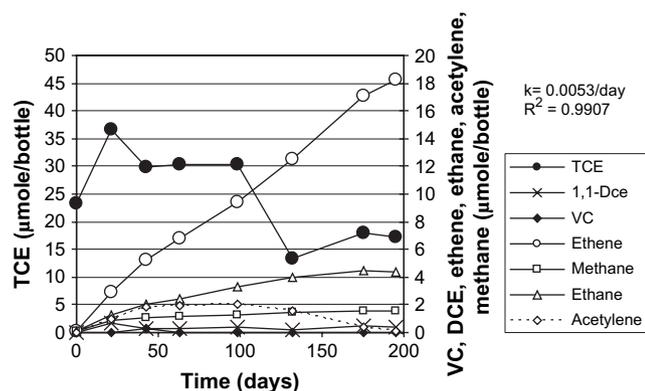


Figure 3. TCE, dechlorination products, and methane for an active amended microcosm incubated at 70°C (treatment 2, Table 1, duplicate showed similar response). The k value is the first-order decay coefficient calculated based on the formation of observed dechlorination products.

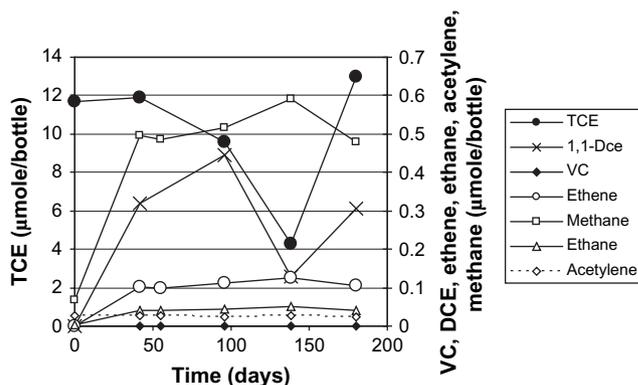


Figure 4. TCE, dechlorination products, and methane for a killed control microcosm (unamended) incubated at 70°C (treatment 3, Table 1, duplicate showed similar response).

were measured in the gas phase and directly injected to a gas chromatograph for analysis; thus, sampling variability was inherently lower than for the aqueous-phase TCE samples.

Because of the variability in TCE concentration data for the 70°C treatments, the amount of TCE transformed at each sampling interval was calculated using a mass balance of the transformation products. At each sampling time point, the concentration data for acetylene, ethene, ethane, and 1,1-dichloroethene (the only dechlorination products with concentrations over the detection limit) were used to calculate the number of moles for each species in each treatment based on the volume of the treatment vessel and the Henry's law constant (Gossett 1987; Heron et al. 1998). Sorption of species to sediment was not considered due to the low sediment/water ratio in the treatments. The moles of the transformation product species were then summed to estimate the total moles of TCE that had been transformed to produce these species at the specified time point. These calculated TCE transformation data were used for subsequent rate analysis where the first-order rate coefficient (1/d) was estimated by plotting $-\ln(C/C_0)$ vs. time and determining the slope of the linear regression of these data (Figures 2 and 3).

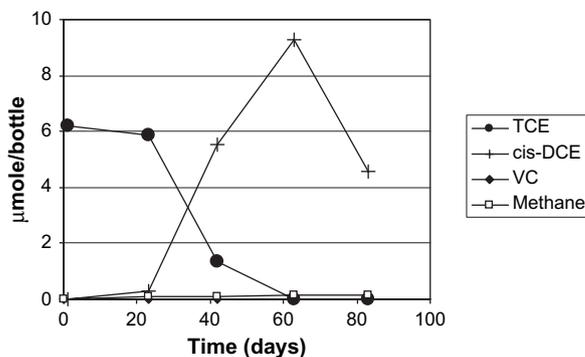


Figure 5. TCE, dechlorination products, and methane for an active amended microcosm incubated at 10°C (treatment 4, Table 1, duplicate showed similar response).

For treatments 2 and 4, conversion of substrate to metabolites was observed based on a decrease in lactate concentration and an increase in acetate and methane concentrations. In all of these treatments, conversion of substrates to metabolites continued throughout the duration of the treatment. The extent of substrate metabolism varied with each treatment and was not correlated with the extent or rate of TCE dechlorination. Metabolites are consistent with fermentation processes and processes with iron, sulfate, and carbon dioxide as electron acceptors.

Field Test Results

Indicators of in situ dechlorination and biological reactions were observed at elevated temperatures during the field test. Chloride was the only conservative (nonvolatile, nonadsorbing) potential indicator of dechlorination during the field test. Other ground water constituents can be indicators of activity but can also be affected by other loss (or gain) mechanisms. Reductive dechlorination produces chloride, DCE, VC, ethene, and ethane. Iron-catalyzed dechlorination produces chloride, acetylene, ethene, and ethane. Biological activity associated with dechlorination under reducing conditions could result in formation of methane, ferrous iron, sulfide, and carbon dioxide.

Figures 6 through 8 show the molar concentrations of TCE, DCE, and chloride in conjunction with the temperature profile at selected monitoring wells. Monitoring wells were screened across an interval of approximately 30 feet and intersected a layered hydrologic system. As such, monitoring data reflect a composite of ground water recovered from these layers as a function of their transmissivity. In contrast to the laboratory experiments, the monitoring data from the field test do not represent a single aquifer condition and data are interpreted based on the overall trends observed in the data. Figures 6 through 8 are typical of locations with significant, moderate, and small increases in TCE concentration observed during heating, respectively. These data show that chloride concentrations increased

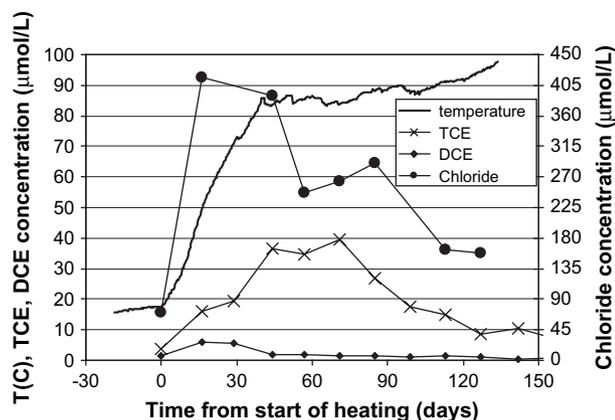


Figure 6. TCE, DCE, and chloride concentrations as a function of temperature at monitoring point G15. At this location, a significant increase in TCE concentration over a relatively long time period was observed during heating, likely indicating nearby presence of TCE DNAPL.

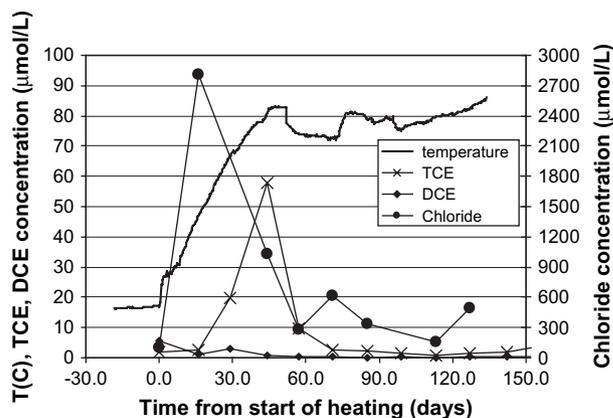


Figure 7. TCE, DCE, and chloride concentrations as a function of temperature at monitoring point G13. At this location, the increase in TCE concentration observed during heating occurred over a short time interval, likely indicating nearby presence of relatively smaller amounts of TCE DNAPL.

significantly at monitoring locations G13 and G15. The most significant increases in chloride were at monitoring location G13, even though it appears that there was more TCE DNAPL near location G15 based on the TCE concentration profile. Because the degradation reaction occurs in the aqueous phase and is influenced by the rate of dissolution, the overall extent of reaction would not necessarily be directly proportional to the amount of TCE DNAPL but may be more related to the availability of TCE for reaction at a given location and the subsurface oxidation-reduction conditions. At monitoring location S13, chloride concentration increases to a lesser extent and over a longer time-frame, potentially because there was not enough TCE DNAPL nearby to result in significant chloride production. The molar concentrations of VC were less than 0.3 $\mu\text{mol/L}$ at all monitoring points after heating was initiated. Potentially, chloride production in excess of the amount of DCE or VC that are formed from TCE reductive dechlorination

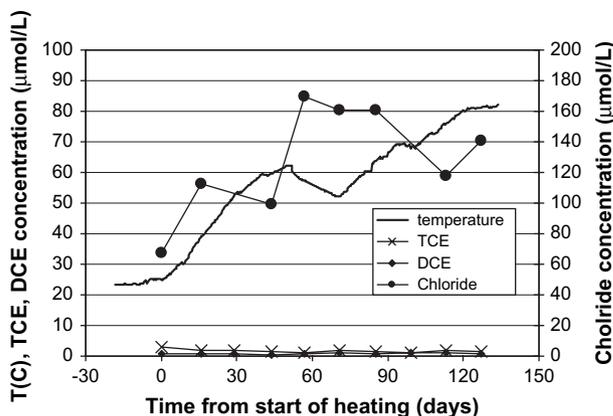


Figure 8. TCE, DCE, and chloride concentrations as a function of temperature at monitoring point S13. At this location, only a small increase in TCE concentration was observed during heating, likely indicating that there was not a significant amount of TCE DNAPL nearby.

may indicate that the TCE was dechlorinated via the iron-catalyzed pathway where DCE and VC are not produced as intermediates. Similar iron-catalyzed dechlorination was observed at elevated temperatures in the laboratory microcosm experiments. Alternatively, increased mineral dissolution at higher temperatures may have contributed to the high chloride concentration. However, greatest increases in chloride concentrations were observed by the first sampling time point at all wells except well S13. At the first sampling time point, ground water temperatures averaged 43°C compared to an average of 19°C before heating. Chloride concentrations had the potential to increase much more than is typically possible in laboratory microcosms where relatively low dissolved concentrations of TCE were used for initial conditions. In the field, the large mass of TCE present as DNAPL provides a source for significant increases in chloride concentration if there is a significant amount of dechlorination. The TCE concentration in the field is impacted by DNAPL dissolution and vapor extraction. Because the TCE concentration is significantly influenced by these phenomena, it is not a useful measure of in situ dechlorination reactions.

Dissolved methane and ethene were detected even at high temperatures (more than 60°C). For example, Figure 9 shows the VC, ethene, and methane concentrations as a function of temperature at well G15. Methane was consistently detected at all other wells with a median concentration of 1 µmol/L and a maximum of 22.5 µmol/L during the heating period. Ethene was detected in wells F10, F12, G15, L15, and S13 at temperatures above 50°C. Both methane and ethene have high Henry's law coefficients (26 and 8.49, respectively). Thus, detection of these compounds even at low concentrations at high temperatures may suggest that they were being continually produced at a significant enough rate/quantity that dissolved concentrations were measurable despite the elevated tendency for these compounds to volatilize at the high temperatures.

Acetylene was detected at wells F12, G15, L15, and S13 after heating started when temperatures were elevated. Acetylene is a transient intermediate compound in iron-catalyzed dechlorination that was also observed in the laboratory microcosm tests and is subsequently reduced to ethene.

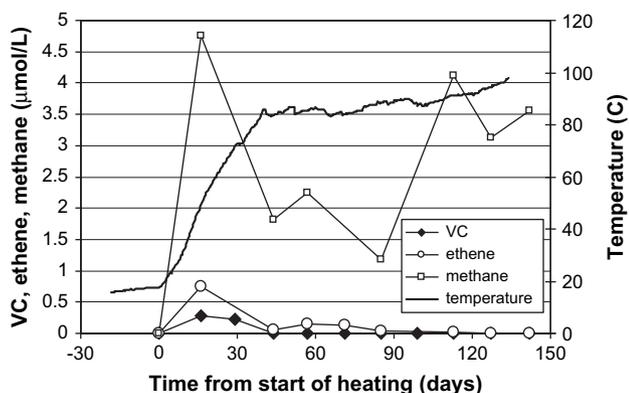


Figure 9. VC, ethene, and methane concentrations as a function of temperature at monitoring point G15.

Ferrous iron was only sporadically observed in any of the samples after heating started, though it was observed prior to heating. Other geochemical indicators suggest that the aquifer was anaerobic and ferrous iron would likely have been produced during the first approximately 44 d of heating. Sulfide was not observed at any time. Both ferrous iron and sulfide can be held at low concentrations in the ground water because they can combine to form a ferrous sulfide precipitate.

Oxidation-reduction potential (ORP) within the heated zone averaged -28 mV in the first 44 d of heating and +38 mV between 56 and 169 d of heating if data at well F10 are excluded. DO within the heated zone averaged 0.8 mg/L in the first 44 d of heating and 2.1 mg/L between 56 and 169 d of heating if data at well F10 are excluded. ORP and DO at well F10 were higher than at other wells throughout the test (well F10 is near an upgradient edge of the contaminated zone). At about day 44 of heating, temperatures in many wells had increased to near the boiling point of the TCE DNAPL and water mixture.

DCE concentrations were relatively high compared to TCE concentrations at some locations prior to heating, suggesting that microbially catalyzed reductive dechlorination was occurring before ERH treatment. In general, during ERH treatment, the DCE concentration decreased compared to pretreatment concentrations. Interpretation of DCE data during heating is complicated by its presence prior to heating. The amount of DCE that would have been produced from transformation of TCE to DCE during heating was calculated at each time point based on the measured molar chloride concentrations. In general, the amount of DCE calculated from the chloride data is orders of magnitude more than the measured DCE concentrations. Thus, it appears that during heating, DCE was not a persistent intermediate associated with the dechlorination activity estimated based on chloride concentrations unless it rapidly volatilized. With the initially high DCE concentrations prior to heating, the initial molar ratio of DCE to TCE in the ERH vapor extraction system was 0.95. By day 8 of heating, the molar DCE/TCE ratio had dropped to 0.39 and then averaged 0.18 with a standard deviation of 0.08 for the remainder of the heating period. The associated DCE concentrations over this time period were 91 mg/m³ initially, 57 mg/m³ by day 8, and an average of 20 mg/m³ with a decreasing trend for the remainder of the heating period. It is not possible to conduct a mass balance to relate potential DCE production to the amount retrieved in the vapor extraction system. However, the data do not show any spike in DCE concentrations associated with the time periods when chloride concentrations were highest.

Discussion

Laboratory and field data associated with ERH treatment at the EGDY site suggest that in situ dechlorination reactions can occur during heating of the subsurface. Laboratory data suggest that TCE dechlorination at elevated temperatures can occur through iron-catalyzed reactions. The sediments at Fort Lewis contain a substantial amount of iron and reducing conditions that were prevalent in the

treatment zone prior to and during initial heating, likely due to the presence of hydrocarbon co-contaminants. Thus, conditions in the field were initially appropriate to support iron-catalyzed dechlorination in addition to reductive dechlorination. Data from the field and laboratory indicate that at lower temperatures, reductive dechlorination is the predominant reaction occurring and produces DCE as a significant intermediate product.

The field test was an open system, and the presence of a downgradient temperature plume and measurement of the hydraulic gradient indicate that there was ground water flow through the heated area during treatment. Thus, data collected during heating are indicators of microbial activity and dechlorination but not quantitative measures for the amount of dechlorination. Some of the compounds observed, such as acetylene and ethene, are unique to dechlorination processes. At the Cape Canaveral field demonstration of ERH, steam heating, and chemical oxidation, the concentration of chloride increased dramatically in the ERH test but not in the steam or chemical oxidation tests (Battelle 2003). These researchers suggested that thermally induced vertical currents may have caused higher salinity water from below the test zone to move upward and increase the chloride concentration. Alternatively, the researchers suggested that some of the observed chloride could have been from dechlorination reactions or dissolution of minerals. At the Fort Lewis study site, none of the adjacent ground water contains high levels of chloride. Thus, increases in chloride concentration would be due to either dechlorination reactions or dissolution. Fort Lewis data indicate that the greatest increases in chloride (by a factor of 10 or more in three of six wells) were observed during initial heating except at well S13. The average temperature at this sample point was about double the preheating temperature. Though the form of chloride minerals at Fort Lewis and, therefore, the solubility and mass transfer kinetics that control the dissolution rate are not known, enhanced dissolution may have had less impact on ground water concentrations at these lower temperatures than later in the heating period when higher temperatures were maintained for a relatively long timeframe.

The subsurface conditions appeared to change during the course of heating with a transition to more oxidizing conditions. Thus, dechlorination via the reductive processes described in this study was likely more prevalent up through about day 44 of the heating and in the zones with reducing conditions within the aquifer. After day 44, reductive processes may have still been active within portions of the aquifer that remained under reducing conditions, but the overall conditions after day 44 would be more conducive to other oxidative reaction processes if they occurred. The impact of potentially more reducing conditions near the electrodes or stainless steel monitoring wells used for subsurface heating conditions is uncertain but may contribute to the reductive reactions in the subsurface. However, the overall contribution of these potential catalysts for reductive dechlorination would be a function of the surface area and contact with the contaminants. By day 44, temperatures were rapidly approaching 70°C where volatilization processes are greatly increased due to

boiling of TCE DNAPL in water, and the extraction component of the treatment may become the most important TCE removal mechanism at these temperatures. Additionally, after day 44, rates of reaction may decrease because higher temperatures may change the catalytic nature of the subsurface iron minerals due to crystallization of the iron minerals as discussed in the introduction.

The ERH treatment at EGDY was not specifically operated to induce or sustain in situ dechlorination reactions. The data collected in this study, however, suggest that dechlorination can occur during ERH. The overall cost-effectiveness of ERH may be enhanced by fortuitous in situ dechlorination and, potentially, could be further enhanced by specifically designing and operating ERH to maximize in situ dechlorination.

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Biographical Sketches

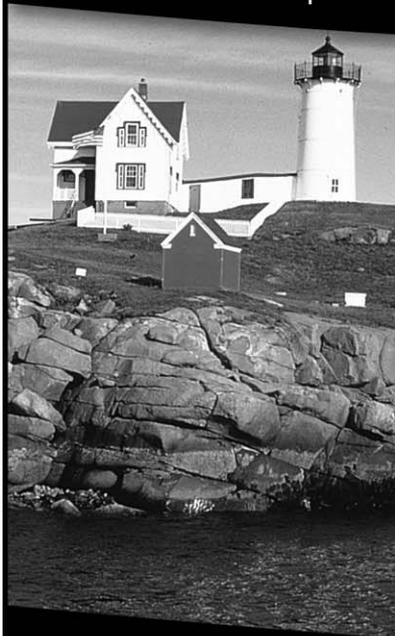
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