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Demonstration of Combined Zero-Valent Iron and Electrical Resistance Heating for In Situ Trichloroethene Remediation

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S Supporting Information

ABSTRACT: The effectiveness of in situ treatment using zero-valent iron (ZVI) for nonaqueous phase or significant sediment-associated contaminant mass can be limited by relatively low rates of mass transfer to bring contaminants in contact with the reactive media. For a field test in a trichloroethene (TCE) source area, combining moderate-temperature subsurface electrical resistance heating with in situ ZVI treatment was shown to accelerate TCE treatment by a factor of about 4 based on organic daughter products and a factor about 8 based on chloride concentrations. A mass-discharge-based analysis was used to evaluate reaction, dissolution, and volatilization processes at ambient groundwater temperature ($\sim 10^\circ\text{C}$) and as temperature was increased up to about 50°C . Increased reaction and contaminant dissolution were observed with increased temperature, but vapor- or aqueous-phase migration of TCE out of the treatment zone was minimal during the test because reactions maintained low aqueous-phase TCE concentrations.



INTRODUCTION

Zero-valent iron (ZVI) has been developed and applied for in situ remediation of chlorinated solvents where abiotic reductive elimination reactions^{1,2} are favored for treatment of chlorinated contaminants, such as trichloroethene (TCE), because no persistent hazardous degradation products are generated. ZVI reactions for TCE can also directly generate dichloroethene (DCE)^{1,3} and indirectly generate DCE⁴ and vinyl chloride (VC)⁵ through facilitation of biotic reductive dechlorination. The rate of ZVI-catalyzed TCE degradation is a function of temperature,³ TCE concentration,⁶ type of iron,^{3,7} and contaminants present including types and mixtures of chlorinated solvents and other organic and inorganic species.^{8–10} Reaction rates during ZVI treatment are diminished over time due to corrosion and mineral precipitation of the reactive iron surfaces, which is a function of groundwater chemistry.^{10,11} Hydrogen is produced by ZVI reactions with water¹² and may stimulate biotic reactions, including sulfate reduction, methane production, and TCE dechlorination. Thus, treatment occurs for dissolved contaminants in groundwater when contaminants are directly contacted by ZVI or contaminant-degrading microorganisms.

The effectiveness of ZVI and other in situ technologies for treating dense nonaqueous phase liquid (DNAPL) or significant

sediment-associated contaminant mass can be limited by the mass transfer of contaminants to the aqueous phase where they can be degraded. Increasing the degradation rate enhances mass transfer by increasing the concentration gradient between the DNAPL and water interface, which is the driving force for dissolution.^{13,14} Mass transfer of parent compounds can be enhanced by in situ degradation reactions which generate more soluble, less sorbing degradation daughter products and thereby increase the amount of contaminant mass that can be loaded in the aqueous phase.¹⁵ Environmental conditions can be manipulated to enhance mass transfer (e.g., dissolution) of contaminants to the aqueous phase using cosolvents,¹⁶ surfactants,¹⁷ and through dissolved organic matter partitioning.¹⁸ Combining subsurface heating with in situ treatment has the potential to further accelerate mass transfer and enhance remediation performance because higher temperatures can increase degradation rates, dissolution/desorption, and volatilization.

The rates of both biotic dechlorination and ZVI reactions are a function of temperature with biotic dechlorination reaching a

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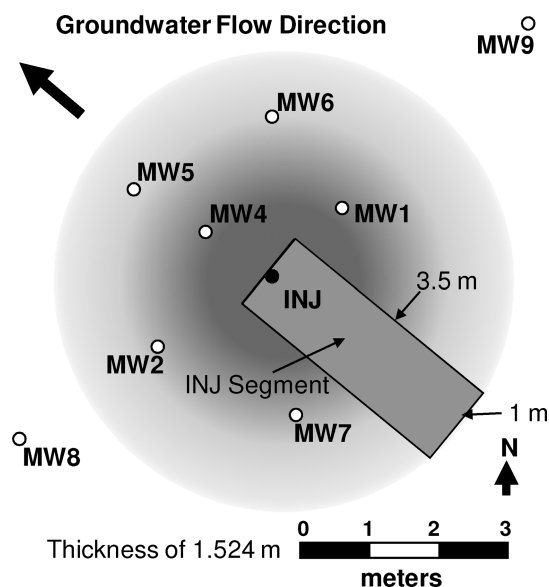


Figure 1. ZVI test cell well layout with monitoring wells (MW) and an injection well (INJ). MW3 was screened within a till and not used for this analysis. Background gradient fill depicts the general pattern of ZVI concentration progressing from high to low moving away from the injection well (ref 25). This figure also shows an example of a “segment” that was applied for treatment performance analysis. The segment is the zone extending from the up-gradient edge of the ZVI injection to well INJ.

maximum rate near 35–40 °C and then declining,^{19,20} while ZVI reaction rates may continue to increase at least through 55 °C.³ In addition to increased reaction rates, contaminant dissolution and volatilization also generally increase with temperature.^{21–23} Imhoff et al.²⁴ empirically and predicatively demonstrated that moderate temperature applications of hot water flushing for chlorinated solvent treatment enhanced the mass transfer rate of residual DNAPL by a factor of 4–5 when temperatures were increased from 5 to 60 °C. High-temperature thermal treatment applications increase temperatures to near the boiling point and mobilize DNAPL through generation of vapors which are extracted and treated in above-ground treatment systems.

Subsurface heating to moderate temperatures coupled to in situ ZVI treatment could negate the requirement for vapor extraction and treatment, which is a large fraction of the cost of typical thermal applications that reach boiling temperatures. For this approach to be viable, however, increases in physical mass transfer rates (dissolution/desorption and volatilization) as temperature increases must be balanced by increased contaminant degradation rates or contaminant mass discharge from the source zone will increase and contaminants will migrate out of the treatment zone. To evaluate accelerated source treatment using moderate heating, a field test was conducted using electrical resistance heating and in situ ZVI treatment. The objectives of this effort were to evaluate the effect of temperature on in situ dechlorination rates and mass transfer processes for TCE remediation. A mass-discharge-based analysis was used to evaluate reaction, dissolution, and volatilization processes for each test condition.

MATERIALS AND METHODS

Test Site Description. Disposal of TCE as DNAPL at Joint Base Lewis–McChord (JBLM, formerly Fort Lewis) within Landfill 2

created a large groundwater contaminant plume. The project test cell was located within Landfill 2 in a region where TCE DNAPL had been disposed to surface trenches in quantities sufficient to migrate through the shallow vadose zone (2–3 m thick) and into the top portion of the aquifer. The aquifer is composed of interlayered outwash and till. Groundwater TCE concentration was initially 3800 $\mu\text{g L}^{-1}$ within the test cell and 49 $\mu\text{g L}^{-1}$ outside the test cell, indicating that the test was conducted within a TCE source zone. TCE is the dominant chlorinated contaminant in the groundwater with *cis*-1,2-dichloroethene present at about 20% of the TCE concentration. Additional details of the test site are described by Truex et al.²⁵

The layout of the test cell encompassed a targeted ZVI treatment volume (58 m³) with a 3.5 m radius and about 1.5 m thick (Figure 1). The test cell wells were nominally screened 2.5–4 m below ground surface within outwash material, although some till features were also present within this interval. Groundwater flow direction at the time of well installation was controlled by the nearby pump-and-treat system to an azimuth of about 233°. Prior to the test, however, several of the well pumps in this system failed, and the average groundwater flow direction during the test changed to an azimuth of 299°. As such, wells MW8 and MW9 were cross-gradient wells rather than the intended down-gradient and up-gradient wells, respectively.

Field Test Operation. The field test was conducted in two phases to quantify dechlorination reactions as a function of temperature. After ZVI injection (day 0), the first phase of treatment was conducted for 60 days at ambient temperature (~10 °C) conditions. During phase 2, electrical resistance heating increased the average temperature in the test cell to about 45 °C by day 100 using an average of 450 kW·h of power applied per day. An average of 170 kW·h of power was applied per day to maintain this elevated temperature at a relatively constant level through about day 200. After day 200, temperatures were more variable and declined because the heating system was shared with another test cell and was only applied sporadically to the ZVI test cell. The treatment was monitored approximately weekly through day 148 and then less frequently through the end of treatment (345 days).

Field ZVI Injection Methods. Details of ZVI injection are described by Truex et al.²⁵ The ZVI solution was injected at a rate of 22.7 gpm. The injection solution consisted of 0.02 wt % SlurryPro (SlurryPro CDP, KB International, Chattanooga, TN), 0.0008 wt % surfactant (Aerosol, Sigma Chemical, St. Louis, MO), 1.36 wt % S-3700 ZVI (Fe⁰ colloids with a diameter of $2 \pm 1 \mu\text{m}$, International Specialty Products, Wayne, NJ), and groundwater from the influent line of the Landfill 2 pump-and-treat system, which contained a nominal TCE concentration of 100 $\mu\text{g/L}$. The SlurryPro component of the injection solution was selected because its rheological properties as a shear-thinning fluid facilitate ZVI transport through porous media.²⁶ A total of 187 kg of ZVI was injected in 13 600 L of solution.

Groundwater Sampling and Analysis. Standard groundwater sampling procedures were used except that for sampling at groundwater temperatures above 30 °C, groundwater was passed through coiled tubing so that it cooled to below 30 °C before being discharged to the sample vial. Samples were analyzed by EPA method SW846 8260B (TCE, *cis*-dichloroethene, vinyl chloride), EPA 300 (chloride, bromide), and method RSK-175 (ethene, ethane, and acetylene).

Groundwater Flow Estimation. The average hydraulic gradient (0.04) and flow direction azimuth (299°) were estimated

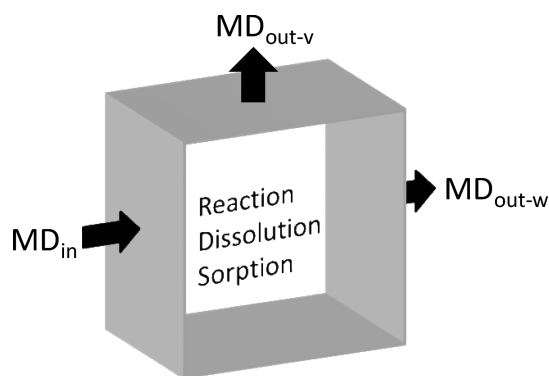


Figure 2. Mass-discharge analysis configuration, where MD_{in} is the influent mass discharge and MD_{out-w} and MD_{out-v} are the effluent mass discharge in the water and vapor phases, respectively.

from the triangulation of hydraulic head measurements at wells MW5, MW7, and MW9. Elution of tracer after ZVI injection using data from wells MW1 and MW4 was used to estimate the linear velocity of the groundwater flow (0.38 m day^{-1} , see the Supporting Information). Because the operations of the site pump-and-treat system remained relatively constant during the treatment period, it was assumed that the groundwater flow remained constant during the test. SlurryPro impacts groundwater flow through the test cell because it is viscous. SlurryPro viscosity, however, is not impacted by temperature up to 50°C (Supporting Information). If groundwater flow rate changed during the test, it would most likely have increased over time due to dissolution or degradation of the SlurryPro resulting in a decreased viscosity.

Mass-Discharge Analysis. A mass-discharge analysis was developed and applied to quantify the treatment zone processes using the data from monitoring wells and considering the rate of groundwater flow through the treatment zone segments ending at each monitoring well (e.g., Figure 1). The mass-discharge analysis computes rates of the multiple processes in the treatment zone by comparing the inflow and outflow discharge rates for a defined segment as shown in Figure 2. Because the treatment zone is a contaminant source area and up-gradient water is relatively uncontaminated, dissolution from DNAPL or sediment-associated TCE is the main mechanism adding contamination to groundwater. Treatment performance in terms of reducing the contaminant source is a function of the relative rates of (1) contaminant dissolution to the groundwater, (2) contaminant degradation, and (3) migration out of the treatment zone due to advection or volatilization. In the field, constituent concentrations from monitoring wells are the primary data available to quantify these processes. Additionally, a source area treatment analysis is unlike an analysis for a permeable reactive barrier where the primary goal is reduction of up-gradient contaminants as they flow through the treatment zone.

The first step of the analysis is to compute the influent and effluent discharges of the segments. For the analysis, mass is represented as moles so that stoichiometric relations of different groundwater constituents can be considered. The influent mass discharge of constituents to each segment was estimated from eq 1

$$MD_{in} [\text{mmol} \cdot \text{day}^{-1}] = C_{upgradient} Q \quad (1)$$

where $C_{upgradient}$ [mmol L^{-1}] is the concentration at well MW9. Data for well MW9 was assumed to represent conditions up-gradient

of the test cell because the ZVI injection did not reach this well.²⁵ A groundwater flow rate, Q , of 103 L day^{-1} was calculated from the estimated linear velocity, porosity (0.18), and cross-sectional area of the segments using Darcy's law and assumed to remain constant.

The effluent mass discharge in the water phase was estimated from eq 2

$$MD_{out-w} [\text{mmol} \cdot \text{day}^{-1}] = C_w Q \quad (2)$$

where C_w [mmol L^{-1}] is the concentration at the monitoring wells for the selected segments.

The effluent mass discharge in the vapor phase was estimated from eq 3.

$$MD_{out-v} [\text{mmol} \cdot \text{day}^{-1}] = D_{as} A_v \left(\frac{C_w H}{L_v} \right) \quad (3)$$

The diffusion coefficient for each compound in sediment, D_{as} , was calculated from the individual gas diffusion coefficients²⁷ ($T = 25^\circ\text{C}$) using the method of Millington and Quirk,²⁸ the measured porosity, and moisture content (14.5 vol %). The dimensionless Henry's law coefficient, H , corrected for temperature, was calculated for each compound from tabulated vapor pressure²¹ and solubility data^{27,29} as a function of temperature. The distance from the water table to the ground surface, L_v , was estimated as the average vadose zone thickness of 2.13 m. The surface area for diffusive mass transfer, A_v , was based on the distance from the up-gradient edge of the treatment zone to the monitoring well with a unit width of 1 m. Soil gas data were not used in the analysis because pretest vapor-phase TCE and DCE concentrations were an average of 69 and 15 times higher, respectively, in samples from the unsaturated sand pack of wells MW2 through 7 than vapor concentrations calculated based on the measured groundwater concentration and equilibrium partitioning by Henry's law. These data indicated the presence of significant vadose zone contamination that would interfere with directly measuring volatilization of TCE and DCE from the groundwater.

The next phase of the analysis relates the segment inflow and outflow of groundwater constituents, computed using eqs 1–3, to the rates of reactions and processes occurring in these segments. This approach enables estimation of the overall TCE dissolution and degradation rates, the amount of TCE released from the source but untreated, and the reaction rates producing specific reaction products as a function of the conditions within the test cell (e.g., temperature). These segment reaction rates define the treatment performance and, along with the ZVI amendment information, can be used for process scale-up and performance estimation. With respect to the processes shown in Figure 2, sorption of dechlorination products to sediments is low at the site³⁰ and was not included in the analysis. Initial sediment concentrations of DCE were 1–2 orders of magnitude lower than TCE sediment concentrations, and VC, ethene, and ethane were not detected. Thus, dissolution of TCE as a contamination source was the only dissolution process included in the analysis.

Dechlorination reaction rates, R (mmol day^{-1}), were estimated using eq 4.

$$R = (MD_{out-w} + MD_{out-v})_{products} - MD_{in-products} \quad (4)$$

When all organic dechlorination products were considered, the estimated reaction rate from eq 4 represents the overall rate of TCE transformation, R_t . An abiotic reaction rate, R_a (elimination reaction), was estimated using eq 4 by only considering transformation to ethene, ethane, and acetylene products.

A biotic reaction rate, R_b , was estimated using eq 4 by only considering transformation to DCE as the product, representing the combined effect of both biotic and direct ZVI hydrogenolysis reactions. Because negligible VC was observed during the test (3–4 orders of magnitude lower concentrations than DCE), it was assumed that biological dechlorination converted TCE to DCE only. One could consider R_a as representing the sum of reactions that produce nonhazardous products and R_b as DCE-producing reactions. The actual reactions occurring in the treatment zone are likely a mix of biotic and abiotic reactions. For instance, ZVI degrades DCE and VC, though at lower rates than TCE.⁷ Additionally, some biotic dechlorination beyond DCE is possible, though unlikely due to low observed VC concentrations. Molecular DNA data targeting *Dehalococcoides*, the bacteria that converts *cis*-DCE to ethene, remained at low levels during the test, generally below the threshold concentration of 10^6 gene copy L^{-1} to observe significant complete biotic dechlorination at JBLM groundwater,³¹ indicating biotic *cis*-DCE dechlorination was limited (Supporting Information).

The mass-discharge approach was also used to estimate the TCE net dissolution rate, N_d ($mmol\ day^{-1}$) using eq 5. This calculated value represents the net rate of TCE migrating out of the segment (e.g., released but untreated).

$$N_d = (MD_{out-w} + MD_{out-v})_{TCE} - MD_{in-TCE} \quad (5)$$

The overall rate of TCE dechlorination was also estimated using chloride data, R_{tc} ($mmol\ day^{-1}$), by inserting the results of eqs 1 and 2 in eq 6.

$$R_{tc} = MD_{out-w-chloride} - MD_{in-chloride} \quad (6)$$

To convert chloride data to the equivalent moles of TCE, the chloride stoichiometry can be assigned based on the relative molar amounts of DCE, ethene, and ethane products observed at each time point.

For each segment at the test site, the inflow concentrations remained essentially constant and use of the same time point for inflow and outflow data was considered acceptable. If the inflow concentration changed with time, then the time point for the inflow concentration may need to be different than for the outflow concentration to account for the residence time in the segment.

RESULTS AND DISCUSSION

Field Test Results: Overall Treatment. Conditions appropriate for anaerobic reactions, as measured by the oxidation–reduction potential (ORP), were maintained at all monitoring locations in the test cell for about 150 days after ZVI injection (Supporting Information). After this time, the ORP increased at most locations except at the injection well where ORP was maintained near -200 mV for over 200 days and below -80 mV for the full 345 day duration of the test. The pH, expected to increase due to ZVI reactions with water, increased from the initial value at all locations between 1 and 3 pH units, remained elevated for the full 345 day duration at well INJ, and declined at other wells after about 150–200 days (Supporting Information).

Overall, treatment during the ZVI test resulted in a decrease in groundwater TCE concentration (Table 1). Except for DCE, final groundwater concentrations of organic dechlorination products were 1–2 orders of magnitude higher at the end of treatment. To examine the overall temporal changes within the test cell during treatment, the aqueous mass of TCE and organic dechlorination

Table 1. Average Groundwater Concentration of TCE and Dechlorination Products ($\mu g\ L^{-1}$)^a

	TCE	DCE	VC	ethene	ethane
Test Cell Wells (INJ, MW1, MW2, MW4, MW5, MW6, MW7)					
start	3800	670	1	3	5
finish	93	600	32	170	180
Outside Test Cell (Well MW9)					
start	49	17	ND	ND	ND
finish	37	64	ND	ND	ND

^a ND = not detected.

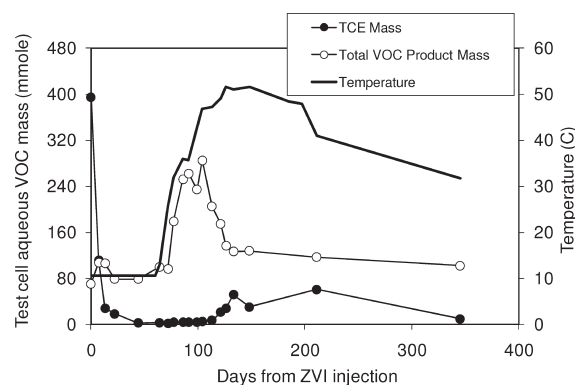


Figure 3. Estimated mass of VOCs (TCE, DCE, VC, ethene, ethane, and acetylene) in the groundwater within the test cell. Mass is estimated as the average of the monitoring well groundwater concentrations multiplied by the aqueous volume of the test cell. For comparison, the estimated TCE mass in the test cell would be 5 mmol if the concentration were uniformly equal to the concentration at well MW9. The average computed TCE mass for days 44–113 is 4.5 mmol.

products was estimated for each sampling time using the groundwater concentration data (Figure 3). This assessment does not consider the loss of compounds through volatilization and is not a direct measure of dechlorination rate but provides a snapshot of groundwater constituents at each sampling time. Initial high TCE mass declined during ambient temperature (~ 10 °C) treatment and remained low throughout the first 50 days of heating and then increased by a small amount but remained low compared to the initial value for the remainder of the test. Organic dechlorination products show a sharp increase during the first 50 days of heating and then begin to decline.

These data for the groundwater suggest that the ZVI created reducing conditions and reduced the mass of TCE in the test cell through dechlorination. Increases in dechlorination daughter products by a factor of about 3 without increases in TCE mass in the groundwater during initial heating suggest that heating enhanced dechlorination of sediment- or NAPL-associated TCE. The decline in daughter products after about 120 days and the subsequent rise in ORP by day 200 at most locations other than the injection well suggest that the reactivity of the injected ZVI had declined by this time. Because the increase in TCE groundwater mass after day 120 is small compared to the initial TCE mass, some of the decline in daughter product mass may also be due to decreased TCE mass available for dechlorination.

Field Test Results: Dechlorination as a Function of Temperature. A mass-discharge analysis was used to evaluate the performance

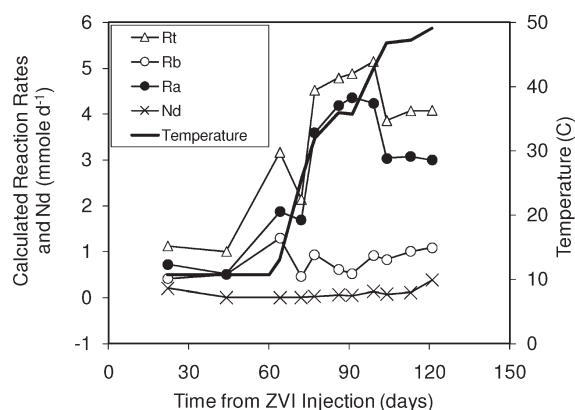


Figure 4. Calculated TCE reaction rates and Nd for the INJ segment.

of the treatment with respect to dechlorination as a function of temperature. Due to seasonal variation, the water level declined such that a portion of the screen was unsaturated starting at about day 121 reaching a minimum of 70% saturated thickness by day 184. Because of this large change in hydrologic conditions, the dechlorination rate analysis was constrained to data over the first 121 days of treatment.

Figure 4 shows the calculated TCE dechlorination rates and released but untreated TCE (Nd) over the first 121 days for the INJ segment. Flow paths through the test cell are uncertain. However, the INJ segment represents flow from up-gradient through the zone of highest ZVI concentration.

Abiotic reactions predominate in the INJ segment. Overall, abiotic reactions dominated in the up-gradient half of the test cell (MW1, MW2, MW7, and INJ) with biotic (hydrogenolysis) reactions becoming more prevalent toward the down-gradient portion (MW4, MW5, and MW6) (TCE reaction rates and Nd are presented for all wells in the Supporting Information). For the INJ segment, overall TCE transformation, R_t , was 3.6–4.8 times higher at temperatures above 30 °C compared to rates at the ambient temperature (~10 °C). This result is consistent with laboratory tests where the TCE degradation rate at 40 °C was 2.5–3 times greater than the rate at 20 °C in batch microcosms with ZVI, JBLM sediment, and groundwater (Supporting Information). The Nd remained near zero in the INJ segment through 121 days, suggesting that the overall in situ transformation rate was comparable to the gross TCE dissolution rate.

An objective of the combined process was to promote in situ dechlorination and minimize volatilization of TCE. The maximum calculated volatilization rate of TCE (MD_{out-v}) at INJ (eq 3) for the elevated temperature portion of the test (day 60–121) was about 1% of the R_t (eq 4) due to the low aqueous TCE concentrations. By integrating the mass discharge from the INJ segment over the 121 day analysis period and assuming dechlorination was for sediment-associated TCE, the ZVI treatment reduced the average sediment concentration by 9 mg/kg in these segments with about 85% of this reduction occurring during the 60 days of heating.

Chloride concentrations (Figure 5) were also used in a mass-discharge analysis to estimate the dechlorination rate as a function of temperature. The chloride data show an increase of about an order of magnitude in concentration coincident with the increase observed for organic dechlorination products during heating for wells INJ, MW4, and MW5. A 2–3 times increase in chloride was observed for wells MW1 and MW6 where moderate amounts of ZVI were delivered during injection²⁵ and moderate

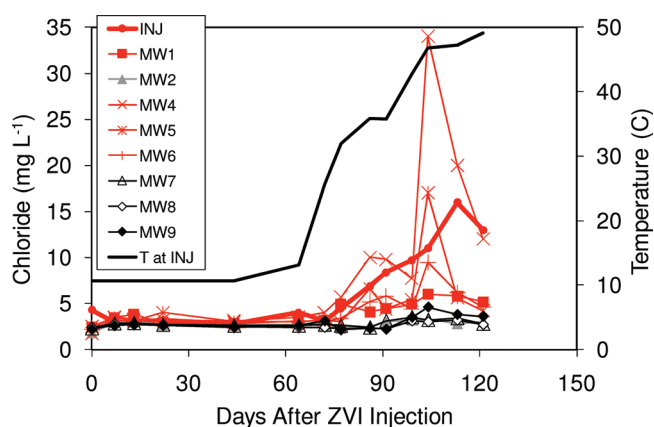


Figure 5. Chloride concentration over time in the test cell. Wells MW8 and MW9 are outside the injection zone, although a small amount of ZVI was distributed to MW8 during injection.

Table 2. Average Overall Rate of TCE Transformation Based on Organic Dechlorination Products (R_t) and Chloride Concentrations (R_{tc}) for the Injection Well Segment

	R_t [mmol TCE day ⁻¹]	R_{tc} [mmol TCE day ⁻¹]
(a) ambient temperature	1.1	1.2
(b) temperature > 30 °C	4.6	9.7
ratio (b/a)	4.4	8.3

dechlorination rates based on organic products were observed (Supporting Information). Chloride concentrations were generally declining by 120 days after ZVI injection, although chloride concentrations remain highest at wells INJ and MW4. Wells MW2 and MW7 show only small changes in chloride concentration during the test corresponding to the relatively small amount of ZVI delivered to these portions of the test cell²⁵ and low dechlorination rates based on organic products (Supporting Information).

Average overall TCE transformation rates at the ambient temperature (~10 °C) and for data at temperatures above 30 °C through day 121 were calculated for the INJ segment using the organic dechlorination products (R_t) and chloride (R_{tc}) (Table 2). The two types of data show an increase in the reaction rate for temperatures above 30 °C compared to the rate at the ambient temperature (~10 °C). These and other field test data show that increasing temperature increases contaminant dissolution and degradation rates with minimal TCE volatilization and suggest that ZVI-based treatments can be enhanced with moderate heating. The mass-discharge analysis provides a means to quantify the different processes occurring during treatment using monitoring well data that is typically available for field applications.

■ ASSOCIATED CONTENT

Supporting Information. Data for hydraulic analysis, SlurryPro viscosity, geochemical parameters, a mass-discharge assessment for each test cell well, and laboratory dechlorination rates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Arnold, W. A.; Roberts, A. L. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environ. Sci. Technol.* **2000**, *34*, 1794–1805.
- (2) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. Reductive elimination of chlorinated ethylenes by zero-valent metals. *Environ. Sci. Technol.* **1996**, *30* (8), 2654–2659.
- (3) Su, C.; Puls, W. R. Kinetics of trichloroethene reduction by zerovalent iron and tin: Pretreatment effect, apparent activation energy, and intermediate products. *Environ. Sci. Technol.* **1999**, *33* (1), 163–168.
- (4) Hendrickson, E. R.; Payne, J. A.; Young, R. M.; Starr, M. G.; Perry, M. P.; Fahnestock, S.; Ellis, D. E.; Ebersole, R. C. Molecular analysis of Dehalococcoides 16S ribosomal DNA from chloroethene-contaminated sites throughout North America and Europe. *Appl. Environ. Microbiol.* **2002**, *68* (2), 485–495.
- (5) Maymo-Gatell, X.; Chien, Y.; Gossett, J. M.; Zinder, S. H. Isolation of a bacterium that reductively dechlorinates tetrachloroethene to ethene. *Science* **1997**, *276* (5318), 1568–1571.
- (6) Grant, G. P.; Kueper, B. H. The influence of high initial concentration aqueous-phase TCE on the performance of iron wall systems. *J. Contam. Hydrol.* **2004**, *74*, 299–312.
- (7) Ebert, M.; Kober, R.; Parbs, A.; Plagentz, V.; Schafer, D.; Dahmke, A. Assessing degradation rates of chlorinated ethylenes in column experiments with commercial iron materials used in permeable reactive barriers. *Environ. Sci. Technol.* **2006**, *40*, 2004–2010.
- (8) Dries, J.; Bastiaens, L.; Springael, D.; Agathos, S. N.; Diels, L. Competition for sorption and degradation of chlorinated ethenes in batch zero-valent iron systems. *Environ. Sci. Technol.* **2004**, *38*, 2879–2884.
- (9) Dries, J.; Bastiaens, L.; Springael, D.; Agathos, S. N.; Diels, L. Combined removal of chlorinated ethenes and heavy metals by zerovalent iron in batch and continuous flow column systems. *Environ. Sci. Technol.* **2005**, *39*, 8460–8465.
- (10) D'Andrea, P.; Lai, K.; Kjeldsen, P.; Lo, I. Effect of groundwater inorganics on the reductive dechlorination of TCE by zero-valent iron. *Water, Air, Soil Pollut.* **2005**, *162*, 401–420.
- (11) Farrell, J.; Kason, M.; Melitas, N.; Li, T. Investigation of the long-term performance of zero-valent iron for reductive dechlorination of trichloroethylene. *Environ. Sci. Technol.* **2000**, *34*, 514–521.
- (12) Reardon, E. J. Anaerobic corrosion of granular iron: Measurement and interpretation of hydrogen evolution rates. *Environ. Sci. Technol.* **1995**, *29*, 2936–2945.
- (13) Yang, Y.; McCarty, P. L. Biologically enhanced dissolution of tetrachloroethene DNAPL. *Environ. Sci. Technol.* **2000**, *34* (14), 2979–2984.
- (14) Cope, N.; Hughes, J. B. Biologically-enhanced removal of PCE from NAPL source zones. *Environ. Sci. Technol.* **2001**, *35* (10), 2014–2021.
- (15) Carr, C. S.; Garg, S.; Hughes, J. B. Effect of dechlorinating bacteria on the longevity and composition of PCE-containing nonaqueous phase liquids under equilibrium dissolution conditions. *Environ. Sci. Technol.* **2000**, *34* (6), 1088–1094.
- (16) Imhoff, P. T.; Gleyzer, S. N.; McBride, J. F.; Vancho, L. A.; Okuda, I.; Miller, C. T. Cosolvent-enhanced remediation of residual dense nonaqueous phase liquids: Experimental investigation. *Environ. Sci. Technol.* **1995**, *29* (8), 1966–1976.
- (17) Johnson, J. C.; Sun, S.; Jaffe, P. R. Surfactant enhanced perchloroethylene dissolution in porous media: The effect on mass transfer rate coefficients. *Environ. Sci. Technol.* **1999**, *33* (8), 1286–1292.
- (18) Macbeth, T. W.; Harris, K. S.; Rothermel, J. S.; Wymore, R.; Sorenson, K. S.; Nelson, L. Evaluation of whey for bioremediation of trichloroethene source zones. *Biorem. J.* **2006**, *10* (3), 115–128.
- (19) Kohring, G. W.; Rogers, J. E.; Wiegel, J. Anaerobic biodegradation of 2,4-dichlorophenol in freshwater lake sediments at different temperatures. *Appl. Environ. Microbiol.* **1989**, *55*, 348–353.
- (20) Holliger, C.; Schraa, G.; Stams, A. J.; Zehnder, A. J. A highly purified enrichment culture couples the reductive dechlorination of tetrachloroethene to growth. *Appl. Environ. Microbiol.* **1993**, *59*, 2991–2997.
- (21) Yaws, C. L.; Narasimhan, P. K.; Gabbula, C. *Yaws' Handbook of Antoine Coefficients for Vapor Pressure*, 2nd ed. [Online]; Knovel, 2009. http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1183 (accessed June 18, 2010).
- (22) Sleep, B. E.; Ma, Y. Thermal variation of organic fluid properties and impact on thermal remediation feasibility. *J. Soil Contam.* **1997**, *6* (3), 281–306.
- (23) Horvath, A. R. *Halogenated Hydrocarbons: Solubility—Miscibility with Water*; Marcel Dekker: New York, 1982.
- (24) Imhoff, P. T.; Frizzell, A.; Miller, C. T. An evaluation of thermal effects on the dissolution of a nonaqueous phase liquid in porous media. *Environ. Sci. Technol.* **1997**, *31* (6), 1615–1622.
- (25) Truex, M. J.; Vermeul, V. R.; Mendoza, D. P.; Fritz, B. G.; Mackley, R. D.; Oostrom, M.; Wietsma, T. W.; Macbeth, T. W. Injection of zero-valent iron into an unconfined aquifer using shear-thinning fluids. *Ground Water Monit. Rem.* **2010**, *31* (1), 50–58. DOI: 10.1111/j1745-6592.2010.001319.x.
- (26) Oostrom, M.; Wietsma, T. W.; Covert, M. A.; Vermeul, V. R. Zero-valent iron emplacement in permeable porous media using polymer additions. *Ground Water Monit. Rem.* **2007**, *27*, 122–130.
- (27) Yaws, C. L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; Knovel, 2003. http://www.knovel.com/web/portal/basic_search/display?_EXT_KNOVEL_DISPLAY_bookid=667 (accessed June 18, 2010).
- (28) Millington, R. J.; Quirk, J. P. Permeability of porous solids. *Trans. Faraday Soc.* **1961**, *57* (7), 1200–1207.
- (29) Mackay, D.; Shiu, W. Y.; Ma, K.; Lee, S. C. *Handbook of Physical—Chemical Properties and Environmental Fate for Organic Chemicals*, 2nd ed.; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2006; Chapter 5, Halogenated Aliphatic Hydrocarbons.
- (30) Truex, M. J.; Johnson, C. D.; Cole, C. R. Numerical Flow and Transport Model for the Fort Lewis Logistics Center; DSERTS NO. FTLE-33; Fort Lewis Public Works: Building 2102, Fort Lewis, WA, 2006.
- (31) Macbeth, T. W.; Sorenson, K. S. ESTCP Final Cost and Performance Report ER-0318: Applying Diagnostic Tools for Performance Evaluation of In Situ Bioremediation of a Chlorinated Solvent Source Area, in press. Available at <http://www.serdp-estcp.org>.