

Dechlorination of Trichloroethene in Aqueous Solution Using Fe⁰

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Flow-through column tests were conducted to investigate the products of degradation of aqueous trichloroethene (TCE) in contact with granular iron metal. The results indicated the degradation process to be pseudo-first-order and the rate constant to be relatively insensitive to the initial concentration of TCE over the range from about 1.3 to 61 mg/L. The principal degradation product was ethene, followed by ethane with substantially smaller amounts of other C1–C4 hydrocarbons. About 3.0–3.5% of the initial TCE appeared as chlorinated degradation products, including the three dichloroethene isomers and vinyl chloride. Although the chloride mass balance was generally between 98 and 102%, a maximum of 73% of the carbon could be accounted for in the identified products. Based on the low concentrations of chlorinated degradation products in the solution phase, it is proposed that most of the TCE remains sorbed to the iron surface until complete dechlorination is achieved.

Introduction

The common occurrence of trichloroethene (TCE) in groundwater is largely due to its extensive use by industry and its resistance to both biotic and abiotic degradation under natural subsurface conditions. In addition to its wide spread occurrence, TCE has a drinking water limit of 0.005 mg/L (1) contributing further to the environmental concern for this compound. As a result, considerable research has been focused on the development of methods for removal of TCE as well as other chlorinated aliphatic compound, from groundwater.

Remediation schemes commonly involve pumping the contaminated groundwater to the surface and passing it through a treatment system, which either degrades the chlorinated compounds, as in the case of advanced oxidation systems, or transfers them to another medium, as in the case of air stripping and granular activated carbon. In principle, methods that degrade the contaminant are preferable to those that simply transfer it to another medium. With the exception of advanced oxidation methods, much of the research to date has been focused

on the biotic degradation pathways as these are often faster than abiotic processes (2), particularly under ambient groundwater conditions.

The carbon in compounds such as TCE is in an oxidized state due to the presence of the chlorine atoms. As a result, TCE is more likely to degrade biologically or abiotically under anaerobic (reducing) conditions (2, 3). Though there is considerable literature regarding abiotic transformations of chlorinated organic compounds (2), particularly in the presence of metal–organic complexes, studies of the use of zero-valent metals to enhance degradation in aqueous solution are relatively few and recent (4–10). Of 15 chlorinated aliphatic compounds investigated by Gillham and O'Hannesin (9), 14 were shown to degrade in the presence of zero-valent iron. When normalized to 1 m² of iron surface to 1 mL of solution, the *t*₅₀ values ranged from 0.013 to 20 h and were reported to be about 5–15 orders of magnitude faster than natural abiotic rates reported in the literature. Dichloromethane was the exception in that measurable rates of degradation were not observed. While these experiments showed that relatively rapid degradation can occur in the presence of granular iron, the occurrence of chlorinated breakdown products was not investigated in detail, and information concerning the mechanism of degradation was highly speculative.

Senzaki and co-workers in Japan (4–6) studied the degradation of 1,1,2,2-tetrachloroethane and TCE with electrolytic iron powder. The reaction of 1,1,2,2-tetrachloroethane (4) produced a gas phase consisting of at least 98% hydrogen, a small amount of nitrogen, and nonchlorinated hydrocarbons including methane, ethane, and propane. Ethane was the suspected end product of the reaction. In subsequent work (5), dehalogenation of trichloroethene (TCE) was shown to produce methane, ethane, ethene, and trace amounts of acetylene, with ethene and ethane as the primary products. In a further study (6), it was found that TCE degraded to ethene, ethane, and trace amounts of acetylene, although a mass balance on the carbon was not reported. The mass balance on chloride was 50% at low residence times and 100% at high residence times. The poorer mass balance at the shorter residence times was attributed to the formation of incompletely dechlorinated intermediate reaction products, though these were not identified or quantified.

More recently, Matheson and Tratnyek (10) reported the sequential dehalogenation of carbon tetrachloride to trichloromethane (chloroform) and subsequently to dichloromethane (methylene chloride) in the presence of 100-mesh iron powder. From observations made over a period of 1 month, it appeared that methylene chloride degraded very slowly, if at all. About 70% of the carbon tetrachloride that degraded appeared as chloroform, and about 50% of the chloroform that was lost appeared as methylene chloride. Though chloride and carbon balances were not reported, concentrations of chloromethane and methane were nondetectable; thus, the fate of the remaining carbon remains uncertain. TCE was also found to degrade in the presence of the iron powder, though products of degradation were not reported.

Should the dechlorination process involve step wise dechlorination, as suggested for carbon tetrachloride (10),

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the most probable chlorinated degradation products of TCE are the dichloroethene isomers and vinyl chloride. Drinking water limits for these, as established by the U.S. EPA (1) are as follows: 1,1-DCE 0.007 mg/L, *cis*-1,2 DCE 0.07 mg/L, *trans*-1,2-DCE 0.1 mg/L, and VC 0.002 mg/L. Should these compounds form during degradation of TCE, their persistence could represent a significant limitation to the use of zero-valent iron for remediation of TCE-contaminated groundwater.

The purpose of this study was to examine the sensitivity of the rate of degradation of TCE in the presence of iron powder to initial TCE concentration, to identify probable chlorinated products of degradation, and to perform a mass balance for carbon and chlorine. It was anticipated that careful mass balances would provide further evidence concerning the possible formation of toxic breakdown products and would shed further light on the degradation pathways.

Methods

Column Experiments. Simulated groundwater containing various concentrations of TCE was pumped through a column containing a mixture of silica sand and iron powder. Water samples were collected at points along the length of the column and analyzed for organic and inorganic parameters. The apparatus was similar to that described in Gillham and O'Hannesin (7), consisting of acrylic tubing, 50 cm long by 3.8 cm i.d. Sampling ports were located along the length of the column at distances of 2, 5, 10, 15, 20, 30, and 40 cm from the inlet. The ports were constructed of nylon Swage-Lok fittings (0.16 cm o.d.) tapped into the column, into which a 3.8 cm \times 16 gauge syringe needle was fastened. Teflon tubing (0.159 cm i.d.) was used for the influent and effluent lines to the column and a stainless steel "tee" was placed in the influent line to allow sampling of the source water.

The column packing consisted of 15% by weight Fisher 100-mesh electrolytic iron powder (>99% iron) mixed with sieved 35-mesh silica sand. The mixture was prepared in 100-g subsamples to ensure that the desired mixture was maintained during column packing and was packed to a porosity of about 0.4. BET analysis gave a specific surface area for the iron of 0.287 m²/g, resulting in an iron surface area to solution volume ratio in the column of 0.21 m²/mL.

Once packed, the column was flushed with CO₂ and then saturated with simulated groundwater (organic-free water with 40 mg/L CaCO₃), and at least 5 pore volumes of the simulated groundwater without TCE was passed through the column prior to commencing the experiments. Excluding the control columns, the experiments were conducted using the same simulated groundwater but with TCE concentrations of 1.27, 4.69, 10.2, and 61 mg/L. The water containing TCE was held in a 20-L collapsible Teflon bag to minimize losses due to volatilization as the source water was consumed. Source water was pumped from the collapsible bag to the column using an Ismatec variable speed, multi-channel peristaltic pump at a flow rate of approximately 0.1 mL/min. Actual flow rates, as determined by measuring the discharge, varied from 0.07 to 0.16 mL/min. Using a porosity of 0.4 and a flow rate of 0.1 mL/min, the residence time of water in the column (the time for one pore volume to pass through the column) would be 37.8 h. Viton tubing (0.2 cm i.d.) passed through the pump roller assembly; all other tubing used in the delivery system was Teflon.

Three control columns were used to investigate the effects of various experimental factors on the results. The first was packed only with silica sand and received simulated groundwater with no TCE added. The second was packed with the 15% by weight iron powder and silica sand mixture, as in the reactive column, but received simulated groundwater without TCE. The third was similar to the first, packed only with silica sand, but received simulated groundwater with TCE. This column was used to determine if there was any loss and/or reaction of dissolved TCE with the silica sand and components of the column assembly. Based on the results of previous studies (9, 10), the degradation process was considered to be abiotic, and thus a poisoned control column was not included.

Sampling and Analyses. Samples for organic analyses were collected from the ports in the column and from the influent and effluent lines using a 2.0-mL glass syringe. Prior to sample collection, 0.25 mL was withdrawn to remove stagnant water from the port, and between samples, the sampling syringe was rinsed four times with methanol followed by four rinses with deionized water. Samples (1.5 mL) were collected and transferred to 2.0-mL vials with screw caps and Teflon-lined septa. The vials were then placed on an orbital shaker for 15 min to allow organic partitioning between the aqueous and gas phases.

Analyses for dissolved TCE and the DCE isomers were conducted using a Photovac Model 10S70 gas chromatograph equipped with a photoionization detector. The chromatograph contained an encapsulated fused silica capillary column (CPSil5CB) with an isothermal oven at 30 °C. The carrier gas was ultra-zero air, and flow through the column was approximately 5 mL/min. Samples of the headspace in the sample vials were injected manually using a syringe with a wetted barrel; injection volume ranged from 25 to 50 μ L. The method detection limits (MDL) for these compounds, as determined by the U.S. EPA method (11), were 0.005 mg/L for TCE, 0.005 mg/L for 1,1-DCE, 0.02 mg/L for *cis*-1,2-DCE, and 0.005 mg/L for *trans*-1,2-DCE.

Analyses for vinyl chloride were performed on a Photovac Model 10S50 gas chromatograph equipped with a photoionization detector. The chromatograph contained a 6.6% CSP-20M on Carboxen B column with a 15 \times 0.318 cm precolumn and a 122 \times 0.318 cm analytical column. The 10S50 had operating conditions similar to those described above for the 10S70. The MDL for vinyl chloride was 0.002 mg/L.

Analyses for hydrocarbon gases were performed on a Hewlett-Packard Model 5840 or 5790A gas chromatograph equipped with a flame ionization detector (FID) and a Megabore (GS-Q) capillary column. The carrier gas was ultra-zero air, and flow through the column was approximately 10 mL/min. Headspace samples were injected manually using a syringe with a wetted barrel, with an injection volume of 50 μ L. The gases that could be identified using this method included methane, ethene, ethane, propene, propane, 1-butene, and butane. Aqueous concentrations in samples were obtained by determining the volume of water and gas phases, determining the mass in the gas phase based on the gas concentration, the mass remaining in the water phase using Henry's law constants, and adding the two. The method detection limit for these gases was generally 0.002–0.01 mg/L. Henry's law constants were taken from Mackay and Shiu (12).

Chloride was analyzed using a Markson Model 95 meter, with a solid-state combination chloride electrode and a standard curve prepared using sodium chloride solutions. The detection limit for chloride was 0.1 mg/L. For lower chloride concentrations, a Dionex System 2000 ion chromatograph equipped with a Dionex AS3 anion-exchange column was used. The ion chromatograph had a detection limit for chloride of 0.01 mg/L.

Total Fe was analyzed using a Varian Model 1475 atomic absorption spectrophotometer with a detection limit of 0.05–0.25 mg/L. Samples were acidified to less than pH 2 prior to analysis.

Hydrogen gas was analyzed on a Hewlett Packard Model 5830 gas chromatograph with a 180 × 0.63 cm packed molecular sieve no. 5A column and a thermal conductivity detector. A 0.5-mL sample was injected onto the column, and helium was used as the carrier gas at a flow rate of 30 mL/min. The method detection limit was 0.01% H₂.

E_h measurements were made immediately after sample collection using a Markson Model 90 meter with a silver–silver chloride electrode. The same type of meter was used for pH measurements, in this case using a pH electrode. *E_h* and pH measurements were made of the influent solution and near the effluent end of the column; complete profiles were not measured.

Results

The results obtained from the control columns are not shown but can be summarized as (1) detectable amounts of chlorinated organic compounds or hydrocarbon gases were not released from the column or packing materials; (2) there were no measurable losses of TCE to the column material or silica sand; (3) chloride concentration in the source water was approximately 1.0 mg/L and was unaffected by the column or packing material; (4) the pH and *E_h* in the control columns that did not contain iron remained constant at about 7.8 and 400 mV, respectively; and (5) in the column containing iron, the pH increased from 7.9 to 9.1 and the *E_h* decreased from 393 to –148 mV over the length of the column. Gas bubbles were observed to form on the interior wall of the control column containing iron, with occasional bubbles appearing in the effluent line. It should be noted that Hardy and Gillham (13) detected up to 10 hydrocarbons in batch and column tests containing water and granular iron. At the time the control columns of this study were run, hydrocarbon formation was not anticipated, and thus analyses for these compounds were not conducted.

Initially, in the reactive columns, TCE was observed to migrate along the column with the rate of migration decreasing with time. In all four reactive tests, after the passage of approximately 10 pore volumes of solution, there appeared to be no further migration of the TCE concentration front. At this point, the concentration profile was considered to be at steady state with the rate of degradation equal to the rate at which TCE was entering the column. From Figure 1a, the normalized concentration profile (C/C_0 = measured concentration/influent concentration) shows an exponential decline from the influent end of the column, and the concentration profiles for all four initial concentrations are similar. Some of the observed variation is a consequence of small variations in flow rate during the experiments. The results for the control columns containing only silica sand with the TCE solution are included in Figure 1a and show losses of TCE to be insignificant in the

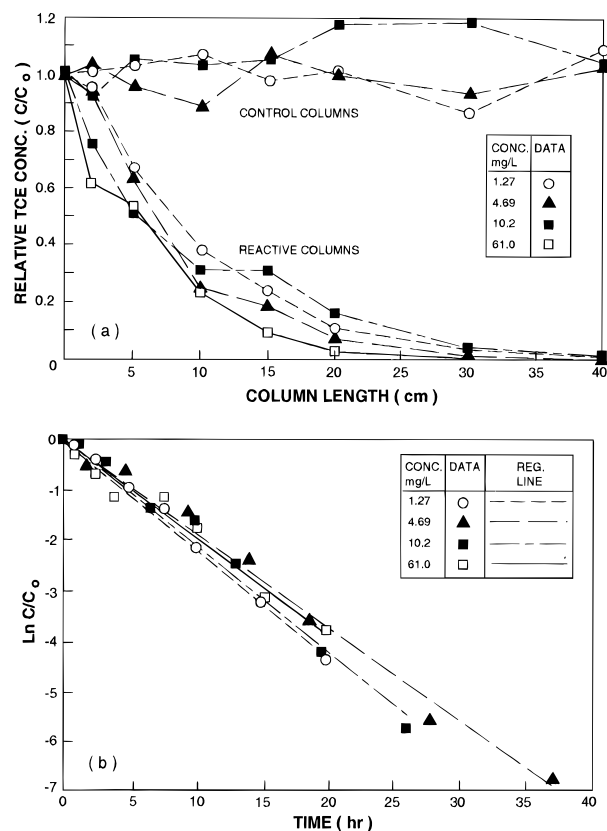


FIGURE 1. Steady-state concentration for TCE (a) relative concentration (C/C_0) versus distance along the column (b) natural log of the relative concentration versus residence time.

absence of iron. (A control column was not run for the 61 mg/L influent.) As in the control column containing iron, gas bubbles were observed to form on the walls of the reactive columns, and occasional bubbles were observed in the effluent line.

Figure 1b shows the results plotted as $\ln C/C_0$ versus time, where time was calculated using the measured flow rates, the porosity of the reactive material, and the cross-sectional area of the column. By accounting explicitly for variations in flow rate, some of the variability evident in Figure 1a was removed. Linear regression of the first-order decay equation was performed for each data set (Figure 1b). The good fit of the linear model to the data ($R^2 > 0.98$ in all cases) provides strong evidence that the reaction is pseudo-first-order with respect to TCE concentration. The rate constants are the slopes of the regression lines, from which half-lives ($t_{1/2}$) were calculated. The values ranged from 2.91 to 3.67 h with an average of 3.25 h. Thus, considering the wide range in initial concentrations, the half-lives fall within a narrow range, and from Figure 1b, there is no apparent trend between the calculated half-lives and the initial TCE concentrations. It is therefore concluded that under the conditions of the tests, the reaction is pseudo-first-order with respect to TCE, and the rate constant (or half-life) is independent of the initial concentration. Previous work using similar compounds (9, 14) suggest that at moderately high iron surface area to solution volume ratios the rate of degradation is directly proportional to the surface area to volume ratio. Thus, normalizing results to 1 m² of iron surface area/mL of solution provides a convenient, though somewhat approximate basis for comparing results. In the present study, normalizing to 1 m²/mL gives a mean half-life of 0.68 h.

TABLE 1

Concentration of DCE Isomers and Vinyl Chloride along the Length of Column, Corresponding to Steady-State TCE Concentration Profiles

TCE source concn (mg/L)	distance from inlet (cm)	1,1-DCE (mg/L)	<i>trans</i> -1,2-DCE (mg/L)	<i>cis</i> -1,2-DCE (mg/L)	vinyl chloride (mg/L)	% of TCE degraded
4.7	2	0.022	<0.005	<0.02	0.006	3.5
	5	0.017	<0.005	<0.02	0.007	
	10	0.029	<0.005	0.051	0.009	
	15	0.029	<0.005	0.047	0.012	
	20	0.030	<0.005	0.051	0.010	
	30	0.030	<0.005	0.073	0.014	
10.2	40	0.027	<0.005	0.062	0.015	0.8
	2	<0.005	<0.005	<0.02	<0.002	
	5	<0.005	<0.005	<0.02	<0.002	
	10	<0.005	<0.005	<0.02	<0.002	
	15	<0.005	<0.005	<0.02	<0.002	
	20	0.031	<0.005	0.180	<0.002	
61.0	30	0.028	<0.005	0.095	<0.002	3.0
	40	0.017	<0.005	<0.02	<0.002	
	2	0.014	<0.005	0.222	0.022	
	5	0.118	0.009	0.410	0.033	
	10	0.049	0.012	0.690	0.057	
	15	0.053	0.012	0.690	0.045	
20	0.130	0.015	0.830	0.066		
30	0.034	0.016	0.020	0.072		
40	0.093	0.012	0.970	0.079		

This is remarkably similar to the value of 0.67 determined from batch tests as reported in Gillham and O'Hannesin (9). It should also be noted that all four tests were performed in the same column, with each test requiring the passage of at least 10 pore volumes of solution. Thus, with the passage of over 40 pore volumes of solution, there was no apparent change in the rate of degradation and thus in the reactivity of the iron material.

Concentrations of the DCE isomers and VC for three of the four tests are given in Table 1. For the test with an initial TCE concentration of 1.27 mg/L, the concentrations of the DCE isomers and VC were generally close to or below the detection limit and are therefore not included. Generally, the concentrations increased over the first 10–15 cm of the column, the region of greatest TCE loss. Though the data suggest a slight decline in DCE concentrations toward the effluent end of the column, concentrations beyond the first 10–15 cm remained relatively constant. From the half-lives of the DCE isomers and VC reported previously (9), at the residence time of the column tests reported here, there was insufficient time to observe significant declines in the concentrations of these compounds. The major chlorinated degradation product observed in the solution phase was *cis*-1,2-DCE followed by 1,1-DCE, VC, and *trans*-1,2-DCE. The trends in concentration over time in the solution phase are similar, suggesting that all are produced from the dechlorination of TCE rather than by sequential dechlorination. The final column of Table 1 shows the sum of the chlorinated degradation products at the final sampling port, expressed as percent of the TCE that was degraded. The intermediate TCE concentration (10.2 mg/L) gave the lowest concentrations of degradation products. Two subsequent tests, conducted with initial TCE concentrations of 43.7 and 4.5 mg/L, gave maximum chlorinated degradation products of 6.18 and 0.7% of the initial TCE, respectively. Variations in the percentage of the influent TCE that appeared as chlorinated degradation products did not appear to be related to the influent TCE concentration, and presently we have no reasonable explanation for the variation. The results are however

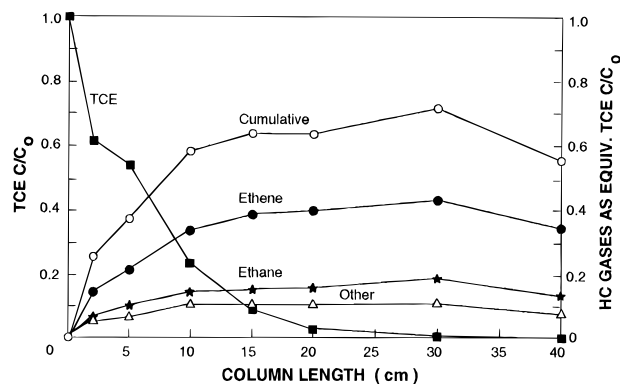


FIGURE 2. Concentration of non-chlorinated hydrocarbons, expressed as equivalent TCE, versus distance along the column. The increasing concentrations are in response to dechlorination of TCE at an initial concentration of 4.69 mg/L.

consistent with other studies (14) in which less than 10% of the influent TCE appeared as chlorinated degradation products.

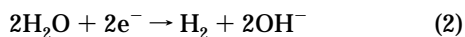
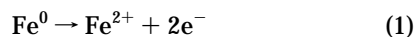
Concentrations of the C1–C4 hydrocarbons were measured along the length of the column for the experiments having TCE source concentrations of 4.69 and 61.0 mg/L. The dominant gases were ethene and ethane, with substantially lower concentrations of methane, propene, propane, 1-butene, and butane. The concentrations of the hydrocarbons were converted to equivalent TCE concentration and for the 4.69 mg/L TCE experiment are shown in Figure 2. The TCE concentrations along the column are included, and as shown, the increases in the hydrocarbon concentrations generally mirror the degradation of TCE, with the hydrocarbons accounting for about 70% of the degraded TCE. A similar profile for the 61.0 mg/L source accounted for about 35% of the TCE degraded. Including the chlorinated degradation products, the carbon mass balance is approximately 73 and 38% for initial TCE concentrations of 4.69 and 61 mg/L, respectively. As in the case of the chlorinated products, the hydrocarbons appeared to be produced simultaneously rather than se-

quentially. The chloride concentration increased over the length of the column, and accounting for the chlorinated hydrocarbons in the effluent gave effluent chloride mass balances between 98 and 102%.

The measured concentration of total dissolved iron in the effluent was generally below the detection limit. As discussed in the following section, the very low concentrations of iron undoubtedly reflect the precipitation of Fe^{2+} within the column. Typically, the pH increased by 1–1.5 pH units (from 7.5 to about 9), and the E_h decreased from 365 to –300 mV over the length of the column. There was insufficient pH and E_h data to evaluate detailed trends either in space or in time. Periodic analyses of the gas phase exiting the column with the effluent water indicated 64–78% H_2 .

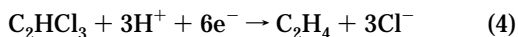
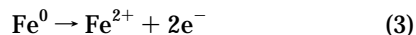
Discussion

The data are consistent with the simultaneous occurrence of two reactions, oxidation of iron by water and reductive dechlorination. The generation of hydrogen and the increase in pH in both the control column containing iron and the reactive column indicate that the oxidation of iron (and dissociation of water) proceed independently of the dechlorination reactions:



Using a commercial iron material of lower purity (Master Builders), Reardon (15) reported rates of hydrogen production of $0.7 \text{ mmol kg}^{-1} \text{ day}^{-1}$. Considering the greater purity of iron, higher rates could be anticipated in the present study; however, no attempt was made to quantify gas production.

Following Matheson and Tratnyek (10), it is proposed that the degradation process is a consequence of direct oxidative corrosion of the iron by TCE. The primary products of TCE degradation were ethene and ethane in the ratio of about 2:1 (Figure 2). Assuming ethene to be the primary product, the redox couple can be written as



Thus, the complete degradation of 1 mol of TCE would add 1 mol of ethene and 3 mol each of Cl^- and Fe^{2+} to the solution phase.

As a result of the simultaneous reactions (oxidation of iron by water and by TCE) with Fe^{2+} as a common product, as well as secondary reactions, stoichiometry is of limited value in confirming the applicability of the above equations. Furthermore, the dependence of the organic reduction reaction (eq 4) on the water reduction reaction (eq 2) is uncertain. Though reduction of water may provide the protons required for protonation of the organic molecule in eq 4, this has not been confirmed. The highest TCE concentration used, 61 mg/L (0.44 M/L) would result in 95 mg/L (1.32 M/L) iron in solution, and even higher concentrations could be expected as a result of the oxidation of iron by water (eqs 1 and 2). The measured total iron in the effluent was less than 0.05 mg/L. Clearly Fe^{2+} produced by oxidation of the iron was precipitating, possibly as siderite

(FeCO_3) and as $\text{Fe}(\text{OH})_2$. No attempt was made to identify the secondary solid phases formed during the reaction.

The most striking feature of the data is the very small proportion of chlorinated degradation products detected in the solution phase (<10% of the initial TCE). This suggests that at least at the spatial and temporal scales of sampling almost all of the TCE is completely dechlorinated in a single step. This differs considerably from previous studies of carbon tetrachloride degradation (10) in which stepwise dechlorination was reported. If we accept that the probability of an instantaneous six-electron transfer is exceedingly low, then the very low concentrations of intermediate products in solution suggests that the organic molecule must remain attached to the iron surface for a sufficient period of time for the six electrons to be transferred. Attachment to the metal surface may reflect the hydrophobic character of TCE, or as proposed for the degradation of pure-phase carbon tetrachloride in the presence of zinc (16), it may be a result of covalent bonding induced by the first electron transfer. Sivavec and Horney (14) suggest that strong chloroethene– Fe^0 π -bonding may prevent desorption until dechlorination is complete.

The small concentrations of the DCE isomers and VC observed in the solution phase are suggested to be a consequence of a probabilistic process by which some portion of the initial TCE is released from the iron surface before complete dechlorination has occurred. Though the controls on the process are not known, it was found that the relative solution-phase concentrations of the chlorinated breakdown products did not show trends with their respective reduction potentials or with hydrophobicity as reflected by the octanol–water partitioning coefficients.

Virtually all of the chlorine present in the influent TCE could be accounted for in the effluent as Cl^- or chlorine remaining on partially dechlorinated hydrocarbons. Thus, it is reasonable to conclude that the 27% of the carbon that was not accounted for in the carbon balance is not present as a chlorinated hydrocarbon. Indeed, there is reason to suspect that the discrepancy in the carbon balance is a consequence of experimental artifacts. It should be noted that the sampling procedure did not quantitatively include the gas phase, and because of the high Henry's constants for ethene and ethane (8.8 and 20.4, respectively), significant amounts of carbon may have been present (and unaccounted for) in the gas phase. Because the rate of gas production was not quantified, this hypothesis could not be evaluated. It is encouraging however that in tests of TCE degradation in which both the gas and liquid phases of the effluent were quantified, Sivavec and Horney (14) reported carbon mass balances generally greater than 90%.

The large number of hydrocarbons detected in the solution phase could be viewed as evidence of multiple degradation pathways. There are however alternate hypotheses. Ethene and ethane in a ratio of about 2:1 constitute well in excess of 80% of the mass (expressed in terms of equivalent TCE) of the hydrocarbons that were identified. There is considerable evidence (17) for example that in the gas phase the transformation of ethene to ethane can be catalyzed by metal surfaces. This reaction appears to be slow in the presence of water however (18, 19). Thus, while it is reasonable to expect that ethene is a direct product of dechlorination, it is unclear if ethane represents an alternated degradation mechanism or is a product of catalytic transformation of ethene on the iron surface.

Through analogy with Fischer–Tropsch synthesis and using evidence from aqueous electrochemistry studies (20), Hardy and Gillham (13) present evidence that hydrocarbons can be produced on the iron surface through reduction of aqueous CO₂ and that hydrocarbon chains, up to C₅ or greater, can be produced on the surfaces. Thus, the range of hydrocarbons that was detected does not necessarily imply multiple degradation pathways.

Conclusions

Under the conditions of this study, the mean half-life for degradation of trichloroethene was 3.25 h, and if normalized to 1 m²/mL the half-life was 0.68 h. Thus, the rates of degradation are remarkably fast compared to natural rates of abiotic degradation reported in the literature (1.1 × 10¹⁰ h, Jeffers et al. (21)). Although the degradation process is generally considered to be pseudo-first-order with respect to the substrate (9, 10, 14), it is also considered to be a surface process, and thus one would anticipate that at some upper limit in concentration the reactive sites would be saturated, and thus at higher concentrations the reaction would not appear to be first order. In this study, the reaction was shown to be pseudo-first-order over the initial concentration range of 1.3–61 mg/L TCE. The upper limit exceeds the concentration normally found in groundwater contamination plumes, and thus the first-order model appears to be appropriate for the design of field-scale remediation systems.

Chlorinated products of degradation included *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE, and VC. The sum of these products represented only about 3–3.5% of the TCE that was degraded. This is reasonably consistent with previous work (14) reporting <10% conversion to chlorinated degradation products. In addition to the low concentrations of these chlorinated products, they all degrade in the presence of iron (9), though at rates that are lower than for TCE. Thus, no persistent toxic products of TCE degradation were identified. The major nonchlorinated hydrocarbons identified were ethene and ethane, though detectable concentrations of methane, propene, propane, 1-butene and butane were also noted. While it is reasonable to expect that ethene was a direct product of dechlorination, it is uncertain if ethane is a direct product or is a product of catalytic conversion of ethene on the iron surface. The additional C₁–C₄ hydrocarbons are not believed to be indicative of multiple pathways, but are a result of catalytic processes, including CO₂ reduction, on the iron surface.

The favorable chloride mass balance is strong evidence that unidentified chlorinated hydrocarbons were not present in the effluent. As discussed and as supported by the literature (14), the 27% of the carbon that could not be accounted for is probably an artifact of the sampling procedure.

While the mechanism remains uncertain, the results are consistent with reductive dechlorination, with the TCE serving as an oxidant of the iron. Although electron transfer and dechlorination mechanistically may proceed sequentially on the iron surface, phenomenologically, the small proportion of chlorinated intermediates and their simultaneous appearance in the solution phase argues against sequential dechlorination.

The low half-life and the small proportion of the initial TCE that appeared as chlorinated products of degradation provide considerable promise for the use of granular metallic iron in the remediation of TCE-contaminated groundwater. In particular, the fact that energy and

additives are not required suggests that granular iron could be appropriate for long-term passive in situ treatment. This study provided evidence that iron was precipitating within the column. From the increase in pH, precipitation of other solid phases, depending upon the inorganic chemistry of the natural groundwater, can also be anticipated. Reduced activity as a result of precipitate coatings and clogging of pores by precipitates are potential problems in long-term remediation schemes. In this study, in excess of 40 pore volumes of solution passed through the column, with no measurable deterioration in performance. Further investigation of the inorganic consequences of the degradation process are clearly required.

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