

Long-Term Performance of an In Situ "Iron Wall" for Remediation of VOCs

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Abstract

The use of granular iron for in situ degradation of dissolved chlorinated organic compounds is rapidly gaining acceptance as a cost-effective technology for ground water remediation. This paper describes the first field demonstration of the technology, and is of particular importance since it provides the longest available record of performance (five years). A mixture of 22% granular iron and 78% sand was installed as a permeable "wall" across the path of a contaminant plume at Canadian Forces Base, Borden, Ontario. The major contaminants were trichloroethene (TCE, 268 mg/L) and tetrachloroethene (PCE, 58 mg/L). Approximately 90% of the TCE and 86% of the PCE were removed by reductive dechlorination within the wall, with no measurable decrease in performance over the five year duration of the test. Though about 1% of the influent TCE and PCE appeared as dichloroethene isomers as a consequence of the dechlorination of TCE and PCE, these also degraded within the iron-sand mixture. Performance of the field installation was reasonably consistent with the results of laboratory column studies conducted to simulate the field behavior. However, if a more reactive iron material, or a higher percentage of iron had been used, complete removal of the chlorinated compounds might have been achieved. Changes in water chemistry indicated that calcium carbonate was precipitating within the reactive material; however, the trace amount of precipitate detected in core samples collected four years after installation of the wall suggest that the observed performance should persist for at least another five years. The study provides strong evidence that in situ use of granular iron could provide a long-term, low-maintenance cost solution for many ground water contamination problems.

Introduction

In 1994, the National Academy of Science (NAS 1994) reported that there are an estimated 300,000 to 400,000 hazardous waste sites in the United States and that over the next three decades, 750 billion dollars could be spent on ground water remediation at these sites. It was further indicated that the most common method of ground water remediation, pump-and-treat, has proven to be remarkably ineffective. As a consequence, there is great incentive for the development of alternative remediation technologies.

Of the 25 most commonly identified contaminants at hazardous waste sites, 10 are chlorinated organic compounds (NAS 1994), commonly originating as cleaning and degreasing solvents. These compounds generally have drinking water limits on the order of a few micrograms per liter, are highly recalcitrant in subsurface environments, have fluid densities greater than that of water and frequently occur as nonaqueous liquid phases in the subsurface.

Based on the results of laboratory tests, Gillham and O'Hannesin (1992) suggested the use of granular iron for the passive in situ remediation of ground water containing chlorinated organic compounds. Subsequent studies explored the range of compounds for which the technology could be applicable (Gillham and O'Hannesin 1994) and, based on studies of the degradation of

carbon tetrachloride in aqueous solution, Matheson and Tratnyek (1994) proposed possible mechanisms for the degradation process. Metal-enhanced degradation of chlorinated organic compounds has since become a major topic of environmental investigation. In summary, there is broad consensus that the process is an abiotic redox reaction involving reduction of the organic compound and oxidation of the metal. The reaction appears to be pseudo-first order with respect to the organic concentration and the products of the reaction are chloride (Cl^-), iron (Fe^{2+}) and non-chlorinated (or less chlorinated) hydrocarbons. In the case of chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE), dechlorination appears to be complete with ethene and ethane as the final carbon-containing compounds (Sivavec and Horney 1995; Orth and Gillham 1996), while for carbon tetrachloride, a portion of the parent compound persists as dichloromethane (Matheson and Tratnyek 1994).

In a parallel and independent reaction, iron is oxidized through the reduction of water, releasing additional Fe^{2+} to solution, as well as H^+ and OH^- . The H^+ forms hydrogen gas and the OH^- remaining in solution causes an increase in pH. Recent reviews of the topic are given in Gillham (1996) and Johnson et al. (1996).

The technology is currently being marketed, with long-term low operating and maintenance costs as a major advantage over conventional cleanup methods. However, in the absence of long-term monitoring data, the operational life of field installations remains an area of significant uncertainty. Pertinent questions concern the persistence of the iron, the activity of the iron surfaces, and passivation or pore clogging as a consequence of mineral precipitation in response to increasing pH.

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This paper reports the results of a field demonstration initiated in 1991 and terminated in 1996. Thus it provides a record of performance over a moderately long period of time. While providing the initial evidence that the reactions can proceed under natural hydrogeologic conditions, the results are of particular relevance to persistence and long-term efficacy of the technology. The field experiment was supplemented with laboratory tests to determine if such tests could be used to predict field performance, and thus serve as a useful method for determining design parameters for field installations.

Site Description and Implementation

The field demonstration was conducted at Canadian Forces Base, Borden, Ontario, in a surficial medium-fine sand aquifer, underlain by a thick clayey silt deposit at a depth of about 9 m below ground surface. The depth to the water table varied seasonally between about 2 and 3 m below ground surface, giving a saturated sand thickness of about 6 to 7 m. Detailed descriptions of the aquifer material are given in Mackay et al. (1986) and Ball et al. (1990). A previous study reported in Rivett et al. (1994) was undertaken to evaluate the dissolution characteristics of a mixed non-aqueous fluid. In that study, the source consisted of 0.75 m³ of native sand material that was brought to residual saturation with respect to a mixture of chloroform (TCM), trichloroethene (TCE) and tetrachloroethene (PCE). Gypsum (CaSO₄) was added to the source, such that dissolved sulphate would serve as a conservative tracer. The source, having a cross section normal to flow of 1.5 m wide × 1 m deep, was placed 1 m below the water table. Ground water passed through the source at a velocity of approximately 8.2 cm/day, creating a continuous downgradient plume of dissolved chlorinated organics. The plume was approximately 1 m thick and 1 m wide near the source, with peak TCE and PCE concentrations in the core of the plume of about 270 and 50 mg/L, respectively. At the time the present study was initiated, most of the TCM had been dissolved from the source, resulting in very low concentrations in the plume.

The reactive wall was installed 5.5 m downgradient from the emplaced source and was constructed to approximate the seasonal average direction of ground water flow (Figure 1A). In order to install the wall below the water table, sealable joint sheet piling (Starr et al. 1992) was used. Individual piles, 10 m long and 0.5 m wide were interlocked, creating an erect rectangular cell on the surface with dimensions of 5.5 × 1.6 × 10 m (l × w × h). The pilings were then driven to a depth of 9.7 m, using a seven ton (6350 kg) hydraulic vibratory driver (416 ICE), suspended by a 60 ton (54,432 kg) crane. The joints were then grouted with Benseal™, a bentonite-based sealant, and a dewatering well (5.1 cm I.D.) was used to lower the water table to below the anticipated depth of excavation.

The cell was excavated using a clam shell attached to the crane. The uncontaminated native material was removed and placed close to the excavation, while the contaminated soil from the vicinity of the plume was placed in a roll-off box and covered with tarpaulins. To prevent the sheet piling from collapsing, hydraulic braces were installed as the excavation proceeded to the desired depth (6 m).

The reactive material used to construct the wall consisted of 22% by weight (6100 kg) granular iron mixed with 78% by weight (21,500 kg) coarse sand, and had dimensions of 5.5 × 1.6 × 2.2 m (l × w × h), giving a volume of 19.6 m³. Coarse sand was used rather than the aquifer material to insure that the permeabil-

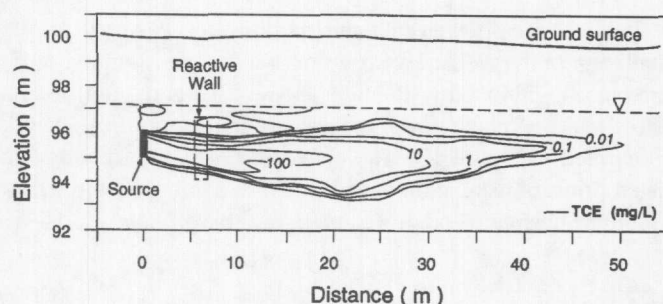


Figure 1a: Cross section of emplaced source, reactive wall and TCE plume.

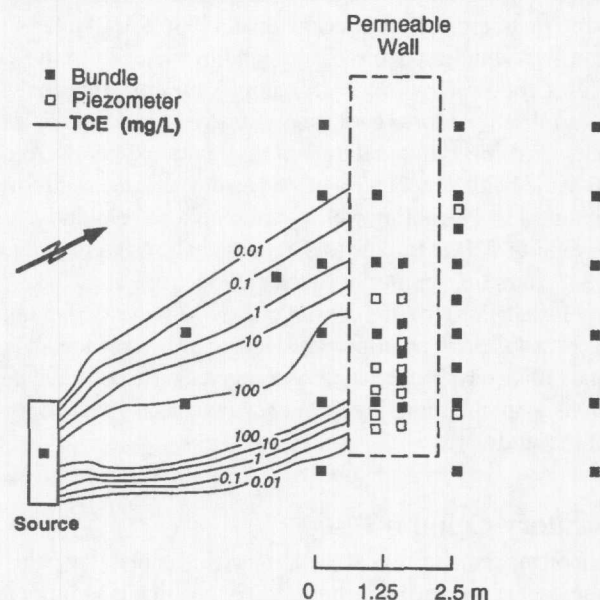


Figure 1b: A plan view of the test site, monitoring network and TCE plume. (TCE concentration contours adapted from Rivett et al. 1994).

ity of the wall would be at least as great as that of the surrounding aquifer. Permeameter measurements on samples of the native sand and the sand/iron mixture gave hydraulic conductivity values of 7.24×10^{-3} and 4.37×10^{-2} cm/sec, respectively. The granular iron (0.15 to 0.35 mm) was obtained as a waste product from a malleable iron foundry in the Kitchener-Waterloo area.

The mixture was prepared using portable Mega Mix™ equipment. Appropriate amounts of iron and sand were dispensed, passed through a mixing auger and allowed to free-fall into the excavation. With the upper surface of the mixture located 3.8 m below ground surface, the remainder of the excavation was backfilled, first with a layer of coarse sand (8 cm), followed by the uncontaminated native soil previously removed. To complete the installation, the sealable sheet piling was removed using the hydraulic hammer (June 10, 1991).

A total of 10 PVC piezometers (1.3 cm I.D.) and nine bundle piezometers were installed within the reactive material. The bundle piezometers consisted of 14 Teflon® sampling tubes (3.2 × 1.6 mm) attached with nylon straps to a PVC centrestock. Each sampling tube was finished at the lower end with Nitex™ screen (70 mesh) held in place with stainless steel wire. The vertical sampling interval was 30 cm between adjacent sampling points. All centrestocks and piezometers were slotted at the lower end (10 cm) and covered with Nitex screen. The monitoring wells were installed by driving an outer casing to the desired depth using a vibrating hammer, placing the well inside the casing, then removing the casing.

To avoid changes in water chemistry, no water was used for the installation of the wells. Two rows or "fences" of sampling wells were placed within the wall, at distances of 0.5 and 1 m from the upstream face. A plan view of the test site and monitoring network is presented in Figure 1B. The network of sampling points that existed prior to installation of the wall was used to monitor concentrations upstream and downstream of the wall.

Monitoring

Ground water samples were collected periodically for organic and inorganic analyses from wells upgradient, downgradient, and within the wall. Samples were collected using a sampling manifold similar to that described in Mackay et al. (1986). A 50 ml volume of water was withdrawn to remove standing water from the sampling lines, followed by two 20 ml samples for inorganic analyses, and a 15 ml sample for organic analyses. Measurements of redox potential (Eh), pH, temperature and dissolved oxygen were conducted in the field. Water levels in the piezometers and centrestocks of the multi-level sampling wells were monitored regularly.

A total of 5200 samples for organic analyses were collected from 348 sampling points over the period from June 10, 1991 (time of installation) to April 29, 1996 (Day 1784, year 5). Samples were kept at 4°C during transport and storage, with a maximum holding time of five days before analysis. Samples were collected on 10 occasions, with the sampling frequency decreasing over the duration of the study.

Laboratory Column Tests

Laboratory column tests were designed to simulate the field test. The purpose was to determine the degree to which laboratory tests could represent field behavior, and thus serve as a means of deriving design parameters for field installations.

The column procedures were similar to those described in Gillham and O'Hannesin (1994). The columns were constructed of Plexiglas tubing, 50 cm long and 3.8 cm I.D. Seven sampling ports were positioned along the length of each column at distances of 2.5, 5, 10, 15, 20, 30 and 40 cm from the inlet end. Samples of influent and effluent solution could also be collected. Column tests were conducted at two temperatures, 23°C and 4°C.

The columns were packed with the same materials and in the same proportions as used in the field test. Detailed results are shown for only one column. In this column, the mass of iron to volume of solution ratio was 1.5 g : 1.0 ml and the specific surface area of the iron was 0.74 m²/g, determined by the BET method (Brunauer et al. 1938). The bulk density (ρ_b) of the iron-sand mixture was 1.76 g/cm³, with a porosity of 0.27. The total volume of void space in the column (the pore volume) was 151 ml.

The water used in the tests was organic free with 200 mg/L calcium sulphate (CaSO₄) added to represent the conservative tracer present in the source at the field site. Trichloroethene (TCE) was added to the background water, since it was the main organic compound present in the field test. Potential degradation products were also analyzed, including 1,1-dichloroethene (1,1-DCE), trans 1,2-dichloroethene (tDCE), cis 1,2-dichloroethene (cDCE) and vinyl chloride (VC) with method detection limits of 1.2, 0.8, 1.1 and 0.5 µg/L, respectively.

A peristaltic pump fed the simulated ground water from a collapsible Teflon bag to the influent end of the column at a flow velocity of 8.9 cm/day, similar to that of the field site. Profiles of

TCE concentration were measured at various times until steady state conditions were reached. Samples were also collected from the influent and effluent for organic and inorganic analyses. Details of the analytical procedures are given elsewhere (Gillham and O'Hannesin 1994; O'Hannesin 1993).

Results and Discussion

Field Test

The ground water flow direction varied seasonally by about 30 degrees. Furthermore, while the cross-sectional area of the plume was about 1 m × 1 m, the area of the high concentration central core of the plume was much smaller, possibly on the order of tens of centimeters by tens of centimeters. Thus, even with the dense array of sampling points, it was inevitable that on several occasions the maximum concentration at a particular sampling fence could not be detected. This is reflected in Figure 2, a longitudinal section through the site, showing concentration versus distance for the ten sampling times. There was no apparent trend over time, rather the apparent variability was a consequence of the small cross-sectional area of the plume and the changing flow direction. Each data point represents the maximum concentration observed for a par-

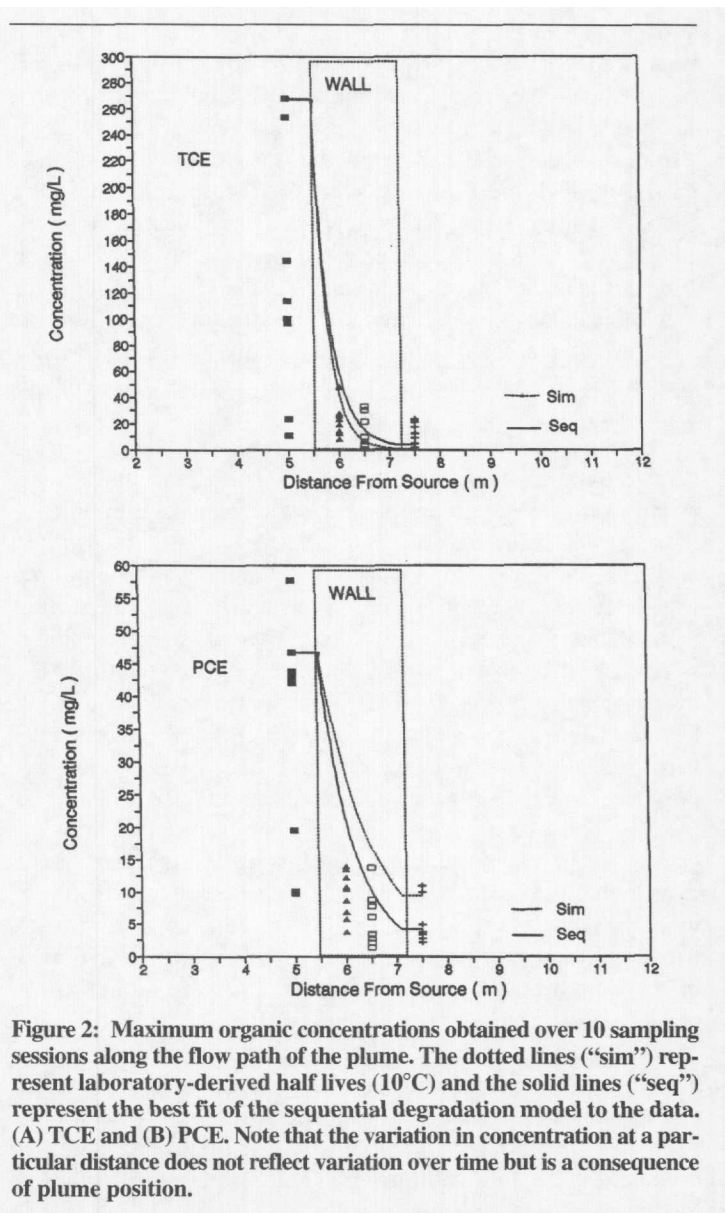


Figure 2: Maximum organic concentrations obtained over 10 sampling sessions along the flow path of the plume. The dotted lines ("sim") represent laboratory-derived half lives (10°C) and the solid lines ("seq") represent the best fit of the sequential degradation model to the data. (A) TCE and (B) PCE. Note that the variation in concentration at a particular distance does not reflect variation over time but is a consequence of plume position.

ticular sampling time at the respective sampling fences. For example, the apparent input concentration of TCE, as determined at the 5 m fence (0.5 m upgradient of the wall), varied from 10,500 to 268,000 $\mu\text{g/L}$ (Figure 2A), while that of PCE varied from 10,000 to 58,000 $\mu\text{g/L}$ (Figure 2B). Based on concentrations in the plume, as reported in Rivett et al. 1994, the highest measured concentration was considered to be representative of the input concentration in the core of the plume. Similarly, the highest concentrations recorded at the two fences located within the wall and the fence 0.5 m downgradient of the wall were considered to give the best measure of the degree to which the core of the plume was attenuated with passage through the reactive material.

For both TCE (Figure 2A) and PCE (Figure 2B), there is a substantial decline in concentration of the core of the plume by the first sampling fence within the wall (50 cm into the wall), followed by a more gradual decrease with further distance through the wall. TCE declined from an influent value of 268,000 $\mu\text{g/L}$ to an effluent value, as determined at the 7.5 m fence (50 cm downgradient of the wall), of 23,350 $\mu\text{g/L}$. Similarly, PCE declined from 58,000 $\mu\text{g/L}$ to 10,970 $\mu\text{g/L}$. Thus, based on the maximum observed concentrations at each sampling fence, 91% of the TCE and 81% of the PCE was removed from solution with passage through the reactive material.

The data collected 299 days after the wall was constructed appeared to capture the core of the plume at all sampling fences and gave reasonably smooth concentration distributions at the respective fences. Considering a slice of the reactive material in the plane of a sampling fence to be 10 cm thick, assuming a porosity of 30%, and integrating the measured concentration over the face of the slice, the mass of TCE and PCE in solution at each sampling fence could be calculated. The computer code Surfer[™] (Golden Software 1990) was used to perform the integration. Surfer is a computer program routinely used for contouring data, and it also determined the mass of the respective contaminants at each fence. This procedure indicated mass losses of 90% and 86% for TCE and PCE, respectively. Because of the uncertainty in actual plume location, it is not possible to give quantitative estimates of uncertainty in the calculated mass loss values obtained from either method. However, the fact that the two methods are quite different but give very similar results, adds considerable confidence to the results. We believe it is reasonable to conclude that about 90% of the TCE and 85% of the PCE was removed from the ground water as it passed through the iron-sand mixture and that the uncertainty in these estimates is no greater than $\pm 5\%$.

Products of Dechlorination

In column studies of the dechlorination of TCE and PCE, maximum concentrations of less chlorinated hydrocarbons (DCE isomers and VC) equivalent to $< 5\%$ of the initial TCE or PCE have been reported (Orth and Gillham 1996; Sivavec et al. 1997). Figure 3 shows the concentrations of chlorinated degradation products through the iron-sand mixture. The major product was cDCE (2110 $\mu\text{g/L}$), with substantially lesser amounts of 1,1-DCE (453 $\mu\text{g/L}$) and tDCE (146 $\mu\text{g/L}$). The sum of these concentrations is equivalent to about 1% of the influent TCE. From Figure 3 it is clear that the DCE isomers also degraded within the iron-sand mixture. Concentrations of VC above the method detection limit were not detected.

Figure 3 includes the maximum chloride concentrations measured at the respective sampling fences. The increasing chloride concentration with distance through the wall indicates that the loss of

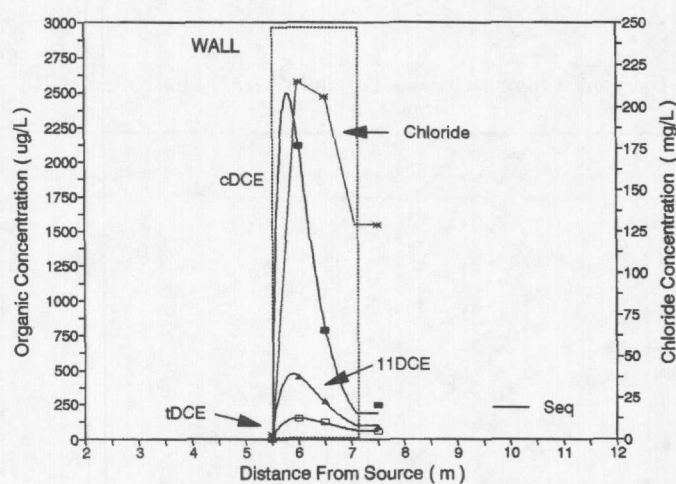


Figure 3. Degradation products versus distance from source. Symbols represent the data and the solid lines represent the best fit of the sequential degradation model.

TCE and PCE is indeed the result of dechlorination. The variability in chloride concentration over time was similar to that shown in Figure 2 for TCE and PCE. Using only the maximum chloride concentration (Figure 3), the increase in chloride concentration accounted for 91% of the chloride that would be expected if the decline in concentration of the chlorinated hydrocarbons was entirely the results of dechlorination. Because of the variability in concentration of both the chloride and chlorinated hydrocarbons, the chloride mass balance is considered to be reasonably good. In particular, it is not reasonable to assume that the negative chloride balance is evidence of the production of unidentified chlorinated hydrocarbons.

Inorganic Results

Though field pH and Eh were measured on five occasions, a complete set of samples for inorganic constituents was collected on only one occasion, Day 299. Results of the analyses are summarized in Table 1. The results listed as "background" are characteristic of the aquifer outside the influence of the wall and the contaminant plume; "downgradient aquifer" refers to areas downgradient of the wall but unaffected by the contaminant plume; and the three columns under "plume" reflect conditions upgradient of the wall, within the wall, and downgradient, as the contaminant plume passed through the wall.

The wall and the gypsum added to the source had relatively little effect on the concentrations of magnesium (Mg), sodium (Na), and potassium (K), and thus these parameters will not be discussed further. The pH of the aquifer was about 8, and increased to 8.7 in the wall as a consequence of the reduction of water. Downgradient, it appears to be returning to the background pH of the aquifer. The major features of the inorganic data are the elevated values of calcium (Ca^{2+}) and sulphate (SO_4^{2-}) in the plume upgradient of the wall, reflecting the presence of gypsum in the source, and the decline in concentration of Ca^{2+} , SO_4^{2-} , and alkalinity (HCO_3^-) as the plume passed through the wall. The geochemical model MINTEQA2 (U.S. EPA 1991) indicated that aragonite (a polymorph of CaCO_3) was supersaturated along the entire flow path, while siderite (FeCO_3) was supersaturated within the wall and downgradient from the wall. Thus there is strong evidence that both calcium carbonate and siderite were precipitating within the wall,

Table 1
Inorganic Characteristics of Ground Water In, and Adjacent To, the Reactive Wall

Compounds	Background Aquifer (mg/L)	Downgradient Aquifer (mg/L)	Upgradient	Plume (mg/L)	
				Wall	Downgradient
Total Fe	<0.5	<0.5	<0.5	5-10	1-7
Ca	55	62	278	92-112	78-91
Mg	4	5	3	2-5	4-9
Na	4	2	1	3	3
K	0.4	0.3	0.8	2	1
Cl	3	2	2	40	33
SO ₄	5-10	16	609	143	73
Alkalinity (as HCO ₃)	158	170	169	95	121
pH (unitless)	7.9	8.4	8.1	8.7	7.5
Eh (mV)	300	435	330	-350	90
DO	2.5-5	4.2	3.4	0-1.2	1.5

and possibly downgradient of the wall. The water was not super-saturated with respect to any solid phase containing sulphur and thus there is no immediate explanation for the decline in sulphate concentration. As indicated previously, the increase in Cl was undoubtedly the result of the dechlorination of the halogenated compounds.

Iron was oxidized both by water and by the chlorinated organic compounds. Concentrations in the plume entering the wall were < 0.5 mg/L, while within the reactive material they were generally within the range of 5 to 10 mg/L with an occasional value as high as 27 mg/L. Downgradient of the wall the highest concentration observed was 7 mg/L; however, most values were less than 0.5 mg/L. Though dissolved iron concentrations downgradient of the wall were commonly above the drinking water limit of 0.3 mg/L (aesthetic), the increasing downgradient Eh suggests that with further travel distance the iron would precipitate as iron oxyhydroxide. Background dissolved oxygen values ranged from 2.5 to 5 mg/L but were consistently zero, or very close to zero, within the iron-sand mixture. Corresponding Eh values ranged from +300 to +450 mV in the background water to strongly reducing values (-200 to -350 mV) within the treatment zone.

Angle-coring techniques were used on three occasions (one, two, and 3.8 years after installation) to obtain samples of the reactive material horizontally across the wall. After one year, there was no visual evidence of mineral precipitation or bacterial fouling, nor did the iron appear altered in any significant way. Biological studies conducted at the Oregon Graduate Institute after year one and two indicated very low levels of biological activity, suggesting low possibility for biofouling (Matheson 1994). Scanning electron microscopy techniques were applied to the cores taken two and 3.8 years after installation. After two years, there was no evidence of precipitation or cementation and after four years there was no cementation; however, traces of iron oxides, as well as calcium and iron carbonates (CaCO₃ and FeCO₃) were found within the first few millimeters of the wall at the upgradient interface between the aquifer sand and the wall.

Kinetics of Degradation

As indicated in the review articles of Gillham (1996) and Johnson et al. (1996), the kinetics of degradation are thought to be pseudo first-order with respect to the concentration of the organic compounds, with the rate constant increasing with increasing specific surface area of the iron (surface area of iron per volume of solution). The first order decay model was fitted to the concentration-distance data of Figures 2 and 3 using the maximum observed values at each distance (fitted curves not shown). The resulting half lives and coefficients of variation (r²) are included in Table 2. The r² values indicate the extent to which the first-order model represents the data. In principle, this procedure would only give the correct result for PCE, since PCE is not being produced from degradation of a more highly chlorinated compound. In practice, because the initial concentration of TCE is five times higher than that of PCE, conversion of a small amount of PCE to TCE would have little effect on the TCE concentrations and thus the calculated half lives. The model was fitted to the maximum observed concentrations of the DCE isomers; however, the fact that these compounds are being generated and degraded simultaneously causes considerable uncertainty in the accuracy of the calculated half lives.

As an alternative method for determining half lives, an analytical sequential degradation model was fitted to the data

Table 2
Comparison of Half Lives Determined from the Field and Laboratory Data

Compounds	First Order Kinetics						
	Field (Maximum Concentration Values)					Laboratory	
	Linear Regression			Sequential Model		Linear Regression Generated at 10°C	
	t _{1/2} (hr)	r ²	t _{1/2N} (hr)	t _{1/2} (hr)	t _{1/2N} (hr)	t _{1/2} (hr)	t _{1/2N} (hr)
PCE	251	0.716	193	140	108	203	225
TCE	142	0.819	109	68 ^b	52	55	61
cDCE	104 ^a	0.999	80	46 ^b	35	NA	NA
1,1-DCE	133 ^a	0.972	103	93 ^b	72	NA	NA
tDCE	221 ^a	0.912	170	160 ^b	123	NA	NA

t_{1/2} = half life

t_{1/2N} = normalized half life to 1 m²/mL

r² = coefficient of variation

NA = not applicable

^aCalculated from the maximum concentration located at the 50 cm distance into the wall

^bUsing TCE as parent compound

(MicroMath Scientist 1995). This model adjusts the half lives of the parent compound and degradation products, as well as the mole percent conversion to the less chlorinated compound(s) to give a least squares best fit to the data. Because the influent concentration of TCE was dominant, all chlorinated degradation products were considered to be derived from the dechlorination of TCE. The half lives derived from application of the model to the data are included in Table 2, and the fit of the model to the data is shown by the solid lines of Figures 2 and 3. Because the highest measured concentration at each sampling fence was considered to be most representative of the concentration distribution through the wall, the model was applied to the highest concentrations. With the exception of the 6 m fence, the sequential model tended to give concentrations lower than the measured TCE and PCE values. Considering the uncertainty in the field data, the model represents the measured trends reasonably well. As shown in Figure 3, the model fits the measured chlorinated degradation products remarkably well and further suggests that the maximum concentrations occur upstream of the 6 m fence and are greater than the maximum measured values. Mass percent conversions from TCE that gave the best fit were 3.3% to cDCE, 0.4% to 1,1-DCE, and 0.1% to tDCE.

Laboratory Column Results

Figure 4 shows the steady-state concentration profile for the degradation of TCE at 23°C. A total of about 25 pore volumes of water had passed through the column at the time the profiles were determined, with one pore volume corresponding to a residence time of 5.6 days. A rapid decline in TCE concentration was observed from an initial value of 245,515 µg/L to an effluent concentration of 6 µg/L. Degradation products were detected, with peak concentrations for cDCE, 1,1-DCE, tDCE, and VC of 3474, 688, 296, and 22 µg/L respectively, observed at a travel distance of 15 cm. The peak concentrations were followed by a steady decline, giving effluent values of 430, 182, and 84 µg/L for cDCE, 1,1-DCE, and tDCE, respectively and no detectable VC. The sum of the maximum concentrations of breakdown products represented less than 1.8% of the original TCE. The concentration of chloride in the effluent varied between 88 and 110% of that expected on the basis of the apparent dechlorination reactions. Eh was slightly reducing, while the pH was close to neutral, ranging from 6.9 to 8.2. The TCE half life at 23°C for this test was 8.7 hours with a r^2 value of 0.968.

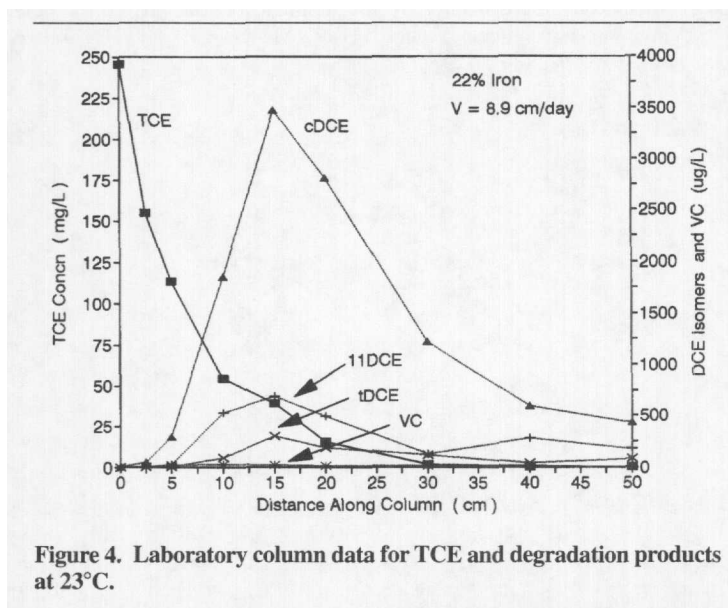


Figure 4. Laboratory column data for TCE and degradation products at 23°C.

The ground water temperature at the field site was 10°C (Rivett et al. 1994). To adjust the half lives measured at 23°C to 10°C, column tests were conducted at 4°C (the only available cold room) and the Arrhenius equation was used to interpolate to 10°C. A TCE half life of 135 hours was obtained at 4°C. Using the Arrhenius plot of $\ln(k)$ versus $1/T$, the half life for 10°C was calculated to be 55 hours. Additional column tests conducted for PCE at temperatures of 23 and 4°C gave half lives of 71 and 339 hours respectively, resulting in a half life of 203 hours at 10°C. Simulated curves of concentration versus distance, using the laboratory derived half lives, are included in Figure 2. Both the fitted curves and those constructed on the basis of the laboratory half lives provide reasonable representations of the field data. As one would expect, the longer half life determined for PCE in the laboratory relative to that obtained by fitting the model results in higher predicted effluent concentrations, though still within the range of the measured values. The lower half life determined for TCE results in a lower predicted effluent concentration. In the case of TCE, both the fitted and predicted curves significantly underestimate the maximum effluent concentration. The relatively low r^2 values obtained by fitting the first order decay model to the field results obtained for PCE and TCE (Table 2), as well as the divergence of the simulated curves from the data with progressive distance through the wall, suggest that the behavior is not first order. Considering the weight of evidence in the literature indicating that the reaction is pseudo-first order with respect to the organic concentration, it is suggested that the reaction rate declines with travel distance through the wall. Though we have no defensible explanation at this time, factors such as variations in the iron-sand mixture or changes in the inorganic water chemistry could account for the apparent decline in reaction rate with distance.

Though differences between laboratory and field performance were evident, the parameter values determined in the laboratory provided reasonably good representations of the field data. It is therefore concluded that laboratory tests can be a useful tool in the design of field installations. When normalized to 1 m² of iron surface per milliliter of solution, iron materials that are now commercially available typically give half lives that range from 1.1 to 4.6 hours for TCE and 2.1 to 10.8 hours for PCE (Gillham 1996). The normalized half lives of Table 2 are about two orders of magnitude greater, indicating that the iron available at the time this test was initiated was much less reactive than the materials that are now in use. This is supported by hydrogen evolution tests. Using the methods presented in Reardon (1995), the rate of hydrogen evolution from the iron used in this study, was approximately 50% lower than from commercial materials presently available. The reason for the lower activity is not clear, but may be the result of differing metallic composition, contamination of the surface, or the fact that it was not heat treated, as are the materials now available.

Conclusions

This study provides the earliest field evidence that granular iron could serve as an effective medium for the in situ destruction of chlorinated organic compounds dissolved in ground water. High rates of mass removal were observed for both TCE and PCE. The formation of DCE isomers as products of the dechlorination of TCE and PCE, and their subsequent degradation within the reactive material, were consistent with the results of laboratory tests. Finally, the increase in chloride across the wall provides strong evidence that the decline in concentration of TCE and PCE was indeed the result of dechlorination processes. Though chlorinated compounds exited

the wall at concentrations far in excess of common drinking water standards, it is reasonable to expect that the quality of the effluent would have met drinking water standards had a higher percentage of iron been used in the iron-sand mixture, or had a more reactive iron material been used.

Considering the uncertainty typical of field data, the kinetics of degradation were reasonably consistent with the first-order decay model. Furthermore, half lives determined in the laboratory reasonably matched the observed field data, suggesting that laboratory measurements can be a useful means of determining the parameters necessary for the design of field treatment systems.

Of particular importance, the five year record of performance is the longest available for an in situ iron treatment wall. Though analyses of both the water and the solids indicated that calcium carbonate was precipitating, particularly near the upstream interface between the treatment zone and the natural aquifer material, there was no evidence of a decline in performance over the five year duration of the study. Furthermore, from the small amount of precipitate that could be identified, there is no reason to believe that the performance would not continue for at least another five years. Though this result can not be directly extrapolated to other sites with other types of ground water, it provides great encouragement regarding the long-term efficacy of the technology.

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