Environ. Sci. Technol. **2002**, *36,* 5147−5154

Abiotic Reductive Dechlorination of Chlorinated Ethylenes by Iron-Bearing Soil Minerals. 1. Pyrite and Magnetite

WOOJIN LEE*,† AND BILL BATCHELOR‡

Environmental Science Research Center, School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405, and Department of Civil Engineering, Texas A&M University, College Station, Texas 77843

Abiotic reductive dechlorination of chlorinated ethylenes (tetrachloroethylene (PCE), trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE), and vinyl chloride (VC)) by pyrite and magnetite was characterized in a batch reactor system. Dechlorination kinetics was adequately described by a modified Langmuir−Hinshelwood model that includes the effect of a decreasing reductive capacity of soil mineral. The kinetic rate constant for the reductive dechlorination of target organics at reactive sites of soil minerals was in the range of 0.185 (±0.023) to 1.71 (±0.06) day^{-1}. The calculated specific reductive capacity of soil minerals for target organics was in the range of 0.33 (±0.02) to 2.26 (±0.06) μM/g and sorption coefficient was in the range of 0.187 (±0.006) to 0.7 (±0.022) mM^{-1}. Surface area-normalized pseudo-first-order initial rate constants for target organics by pyrite were found to be 23.5 to 40.3 times greater than those by magnetite. Target organics were mainly transformed to acetylene and small amount of chlorinated intermediates, which suggests that β-elimination was the main dechlorination pathway. The dechlorination of VC followed a hydrogenolysis pathway to produce ethylene and ethane. The addition of Fe(II) increased the dechlorination rate of *cis*-DCE and VC in magnetite suspension by nearly a factor of 10. The results obtained in this research provide basic knowledge to better predict the fate of chlorinated ethylenes and to understand the potential of abiotic processes in natural attenuation.

Introduction

Chlorinated ethylenes are widespread groundwater and soil contaminants in the United States (*1*−*5*). Their persistence in natural environments and toxicity to humans and animals have been well-known throughout the literature (*6*−*8*). Due to the prevalent occurrence of these contaminants in water and soil systems and the efforts to treat them, substantial research has been conducted to identify the mechanisms that describe their degradation and formation of products under various environmental conditions. Early research was mainly focused on the biotic reductive transformation of chlorinated organics, which generally includes dechlorination mechanisms such as halorespiration (*9*−*14*) and cometabolism (*15*, *16*). It has been shown that high contaminant concentrations and low temperatures limit the reactivity of microorganisms (*17*). Sequential transformation products (e.g., dichloroethylenes (DCEs) and VC (vinyl chloride)) accumulated by the microbial reductive dechlorination have been reported to be more toxic and persistent than mother compounds (*3*). Abiotic reductive dechlorination has attracted considerable attention in the past decade, due in part to the limitations of biotic processes.

Research has been conducted to characterize reductants that exist in natural environments that can dechlorinate. Sulfide compounds found in landfill leachate and estuary sediments have been reported to act as an electron donor in reductive dechlorination (*18*−*23*). NOM (*23*−*25*), macrocycles (*26*−*29*), and mineral surfaces (*17*, *30*−*33*) have been shown to significantly increase abiotic transformation rates of chlorinated organics by acting as electron mediators/carriers. The reactivity of iron-bearing soil minerals abundant in natural environments has been investigated as reductants. Abiotic transformation of carbon tetrachloride (CT), trichloroethane (TCA), trichloroethylene (TCE), and tetrachloroethylene (PCE) by iron sulfides has been investigated using pyrite (*32*, *34*), troilite (*35*), and mackinawite (*36*, *37*). The reactivity of sulfide minerals could be caused by Fe(II) or sulfide on surfaces of the minerals, depending on the experimental conditions employed (*34*, *35*). It has been shown that mixed iron oxides such as magnetite can reduce chlorinated organics. The reaction rate by magnetite has been reported to be much slower than that by other reactive iron-bearing soil minerals (*35*, *38*, *39*).

Extensive knowledge of the reductive dechlorination kinetics of target organics and distribution of transformation products under various environmental conditions is necessary for the successful application and operation of economical and effective remedial technologies as well as for the exact prediction of the fate of chlorinated organics in natural and engineered systems. The objective of this research was to systemically characterize the reductive dechlorination of chlorinated organics by iron-bearing sulfide and oxide minerals. A series of chlorinated ethylenes (PCE, TCE, *cis*-dichloroethylene (*cis*-DCE), and VC) was chosen as common environmental contaminants and iron-bearing polysulfide (pyrite) and oxide (magnetite) were used as representative soil minerals for the research.

Experimental Section

Anaerobic environments required for this research were maintained by following the procedures previously described (*40*) (see page S1, Supporting Information). Reagents and samples were prepared in an anaerobic chamber (Coy Laboratory Products Inc.), and aqueous solutions and chemicals sensitive to atmospheric oxidation were deoxygenated and kept in the anaerobic chamber.

Chemicals. The following chlorinated organics used to characterize dechlorination kinetics were ACS or higher grades: PCE (99.9%, Sigma), TCE (99.6%, Sigma), *cis*-DCE, (97.0%, Sigma), *trans*-dichloroethylene (*trans*-DCE, 98%, Sigma), 1,1-dichloroethylene (1,1-DCE, 99.0%, Sigma), and VC (20,000 mg/L, Sigma). C_2 hydrocarbons (ethane (99.0%), ethylene (1.0%), and acetylene (1,000 mg/L), Scott Specialty Gases) were used as standard gases for the measurement of non-chlorinated transformation products. Target organic stock solutions were prepared by diluting them in methanol (99.8%, HPLC grade, EM).

Deaerated deionized water (ddw) was prepared by deoxygenating deionized water with 99.99% nitrogen and

---

* Corresponding author phone: (812)855-8486; fax: (812)855-1881; e-mail: woojlee@indiana.edu.

† Indiana University

‡ Texas A&M University.

10.1021/es025836b CCC: $22.00

then by purging with mixed gases (5% hydrogen + 95% nitrogen) in the anaerobic chamber. Fe(II) stock solution was prepared by adding an exact amount of $FeSO_4 \cdot 7H_2SO_4$ (102.8%, Sigma) into ddw and kept in the anaerobic chamber for a maximum of 2 days. A 10 mM buffer solution was prepared by adding an exact amount of $NaHCO_3$ (100.3%, Sigma) to ddw. Acid and base solutions were prepared by diluting H_2SO_4 (95.7%, Sigma) and NaOH (97.0%, EM) with ddw.

Preparation of Iron-Bearing Soil Minerals. Pyrite (Zacatecas, Mexico) was purchased from Ward's (Rochester, NY) and ground with ceramic mortar and pestle in the anaerobic chamber. It was then sieved and pretreated to remove oxidized soil mineral surfaces. Pyrite was washed with 1 M acid solution twice and rinsed with ddw several times until pH of the supernatant was greater than 6.7. It was then freeze-dried, dry-sieved, and stored in the anaerobic chamber. The 63 to 250 μm size fraction was used for this research. Magnetite was synthesized by modifying the method developed by Taylor et al. (*41*). The synthesized magnetite was freeze-dried, sieved, and stored under an anaerobic atmosphere. All soil minerals were used for experiments no later than 7 days after pretreatment and synthesis to preclude an aging effect (*42*). The characteristics of pyrite and magnetite used for this research were reported previously (see pages S1−S3, Supporting Information).

Experimental Procedures. Batch kinetic experiments were conducted to characterize dechlorination kinetics and to identify transformation products. These experiments were conducted in 20-mL (nominal volume) glass vials with three-layer seals (PTFE tape, lead foil, PTFE-lined rubber septum) (*43*). After equilibration with the anaerobic atmosphere for 2 days, exact amounts of soil minerals were transferred to the vials followed by a 10 mM $NaHCO_3$ solution (23.6 mL). Sodium azide (20 mg) was added to one set of soil mineral suspension to investigate potential microbial activity. A stock Fe(II) solution (0.5 M $FeSO_4$) was spiked to the magnetite suspension resulting in Fe(II) concentration of 42.6 mM in order to investigate the effect of Fe(II) addition on the dechlorination kinetics of *cis*-DCE and VC. The magnetite suspension was exposed to Fe(II) for 1 day in anaerobic chamber. pH values of soil mineral suspensions were adjusted to 8 (pyrite) and 7 (magnetite) by adding 1 M acid or base solutions before the start of experiments and kept constant during the experiments. The mass ratios of solid to water were 0.084 (pyrite) and 0.063 (magnetite) resulting in different surface area concentrations of pyrite (2340 m^2/L) and magnetite (3600 m^2/L). The average headspace volume of the vial was 0.6 mL, which would allow less than 1.5% of TCE partitioning to the headspace assuming a dimensionless Henry's law constant of 0.359 at 22 °C (*44*) and no sorption. Soil mineral suspensions were spiked with methanolic stock solutions (10−50 μL) to obtain initial concentrations of 0.19 mM PCE, 0.25 mM TCE, 0.41 mM *cis*-DCE, and 0.40 mM VC. The vials were rapidly and tightly capped, taken out of the anaerobic chamber, mounted on the tumbler, and then completely mixed at 7 rpm at room temperature (22 ± 0.5 °C). All soil mineral samples and controls (bicarbonate buffer + target organics) were prepared in duplicate. Target organics and their transformation products in aqueous solutions and on soil minerals were measured at each sampling time.

Analytical Procedures. Target organics and their chlorinated transformation products were analyzed by a Hewlett-Packard (HP) G1800A gas chromatography detector (GCD) system with a DB-VRX column (60 m × 0.25 mm i.d. × 1.8 μm film thickness, J&W Scientific) and a mass spectrometer detector (MS/EID). The oven temperature was isothermal at 80 °C for 8 min, increased to 160 °C at the rate of 20 °C/min, and then held for 2 min. To analyze target organics and chlorinated transformation products in aqueous solution, an aliquot of supernatant was rapidly withdrawn with a gastight syringe and transferred to an extraction vial with 2 mL of extractant (pentane with toluene as an internal standard). The target organics and chlorinated transformation products sorbed on soil minerals was extracted by adding 10 mL of the extractant to the solids that remained after removal of the supernatant. Extraction was conducted by shaking the extraction vials on an orbital shaker for 30 min at 250 rpm. A volume of extractant (1 μL) was injected into split/splitless injector at a split ratio of 30:1.

Non-chlorinated transformation products were analyzed by a HP 6890 gas chromatograph with a GS-Alumina column (30 m × 0.53 mm i.d., J&W Scientific) and a flame ionization detector. The temperature of oven was isothermal at 100 °C. Supernatant (10 mL) was rapidly transferred with 10-mL gastight syringe to a 20-mL amber vial. The vial was shaken for 1 h at 250 rpm and stood for 2 h at room temperature to equilibrate the aqueous and gas phases. The gas-phase sample (50 to 100 μL) was withdrawn from the headspace with a 100 μL gastight syringe (Hamilton) and introduced into the injector at a split ratio of 5:1. The concentrations of C_2 hydrocarbons in aqueous solution were calculated using dimensionless Henry's law constants at room temperature (20.4, ethane; 8.7, ethylene; 1.1, acetylene) (*45*, *46*).

Chloride was measured by an ion chromatograph (Dionex 500) equipped with AS9-HC column (250 mm × 4 mm i.d., Dionex) and conductivity detector. A 10 mM Na_2CO_3 solution was used as an eluent and flow rate was 1 mL/min. A sample (2.5 mL) of suspension or supernatant was filtered with 0.2 μm membrane filter, diluted if necessary, and injected into the column through a 10 μL sample loop.

Results and Discussion

Treatment of Kinetic Data (see pages S4−S5, Supporting Information). Chlorinated ethylenes in the soil mineral suspensions showed a rapid disappearance initially, followed by slower rates of removal or constant concentrations, depending on the reductive capacity of the soil minerals. This is different from the behavior of chlorinated organics in most other abiotic reductive transformations, where the kinetics are usually described by a pseudo-first-order or zero-order rate law (*22*, *32*, *34*−*37*, *45*, *47*). To describe dechlorination kinetics of target organics in the soil mineral suspensions, it is assumed that 1) target organics adsorb onto a finite number of reactive sites on the surfaces of soil minerals, 2) reductive dechlorination of the target organics occurs at these sites by a first-order reaction resulting in loss of activity of the sites, and 3) the reactive sites are the source of reductive capacity of soil minerals for target organic. Therefore, the decay rate of target organic (r_{decay}) would be proportional to the concentration of target organic adsorbed onto the reactive sites, which could be described by the Langmuir−Hinshelwood rate law

$$r_{\text{decay}} = kC_{\equiv\text{SCE}} = \frac{kC_{\text{RC}}C_{\text{CE}}}{1/K + C_{\text{CE}}} \tag{1}$$

where k is the rate constant for the decay of target organic at the reactive sites (day^{-1}); $C_{\equiv\text{SCE}}$ is the concentration of target organic adsorbed on the reactive sites (mM); C_{CE} is the aqueous concentration of target organic (mM); K is the sorption coefficient of target organic on reactive sites (mM^{-1}); and C_{RC} is the concentration of reductive capacity of soil minerals for target organics (mM). The concentration of reductive capacity represents the total amount of target organic that the mineral can possibly reduce per unit volume of water and is proportional to the concentration of reactive sites. The reductive capacity of the soil minerals is expressed in terms of the target organic, because it is assumed that the reactive sites do not react with any transformation products. Therefore, the concentration of reductive capacity at any time can be calculated as the difference in the initial reductive capacity and the change in total concentration of target organic. The total concentration is obtained by multiplying the aqueous concentration by partitioning factor

$$C_{\mathrm{RC}} = C^0_{\mathrm{RC}} - (C^0_{\mathrm{CE,Total}} - C_{\mathrm{CE,Total}}) = C^0_{\mathrm{RC}} - p_{\mathrm{CE}}(C^0_{\mathrm{CE}} - C_{\mathrm{CE}}) \quad (2)$$

$$p_{\mathrm{CE}} = \left(1 + H_{\mathrm{CE}}\frac{V_g}{V_{\mathrm{aq}}} + k^s\right) \quad (3)$$

where C^0_{RC} is the initial concentration of reductive capacity of soil mineral for the target organic (mM); $C^0_{\mathrm{CE,Total}}$ is total concentration of target organic at time equal to zero (mM); $C_{\mathrm{CE,Total}}$ is the total concentration of target organic in all phases (mM); C^0_{CE} is the initial aqueous concentration of target organic (mM); p_{CE} is the dimensionless equilibrium partitioning factor that equals the ratio of the amount of target organic in all phases to that in the aqueous phase (*43*); H_{CE} is the dimensionless Henry's law constant for target compounds; V_g and V_{aq} are the volumes of gas and aqueous phases; and k^s is the dimensionless partition coefficient of chlorinated ethylenes to the solid phase of reactor system that are assumed to be nonreactive (see page S6, Supporting Information). The batch reactor used for this study had slightly different gas and aqueous phase volumes under various experimental conditions. The volumes of gas and aqueous phases were typically 0.6 ± 0.2 mL and 23.7 ± 0.2 mL. C_{RC} in eq 1 can be substituted by the right side of eq 2. The rate equation can then be described in terms of measured target organic concentrations as follows.

$$r_{\mathrm{decay}} = \frac{k\{C^0_{\mathrm{RC}} - p_{\mathrm{CE}}(C^0_{\mathrm{CE}} - C_{\mathrm{CE}})\}C_{\mathrm{CE}}}{1/K + C_{\mathrm{CE}}} \quad (4)$$

The material balance equation in the batch reactor can be combined with the rate equation to give the following relationship expressed in terms of aqueous concentrations.

$$\frac{\mathrm{d}C_{\mathrm{CE}}}{\mathrm{d}t} = -\frac{(k/p_{\mathrm{CE}})\{C^0_{\mathrm{RC}} - p_{\mathrm{CE}}(C^0_{\mathrm{CE}} - C_{\mathrm{CE}})\}C_{\mathrm{CE}}}{1/K + C_{\mathrm{CE}}} \quad (5)$$

The kinetic parameters (k, C^0_{RC}, and K) were obtained by an optimization procedure using MATLAB (MathWorks Inc.). This procedure solves eq 5 numerically by a fourth-order Runge−Kutta method, calculates the sum of squares for the parameters, and then minimizes it by adjusting values of the parameters with the Marquardt−Levenberg algorithm.

To compare the dechlorination kinetics reported here to those reported by others, corrected pseudo-first-order initial rate constants (k_1, day^{-1}) were calculated using eq 6, which was derived from equations 1 and 5.

$$k_1 = \frac{(k/p_{\mathrm{CE}})C^0_{\mathrm{RC}}}{1/K + C^0_{\mathrm{CE}}} \quad (6)$$

k_1 was then normalized by the surface area of the soil minerals (27.8 m^2/g (pyrite) and 57.2 m^2/g (magnetite)) (*40*) to give a surface area-normalized pseudo-first-order initial rate constant ($k_{1,\mathrm{sa}}$, Lm^{-2} day^{-1}).

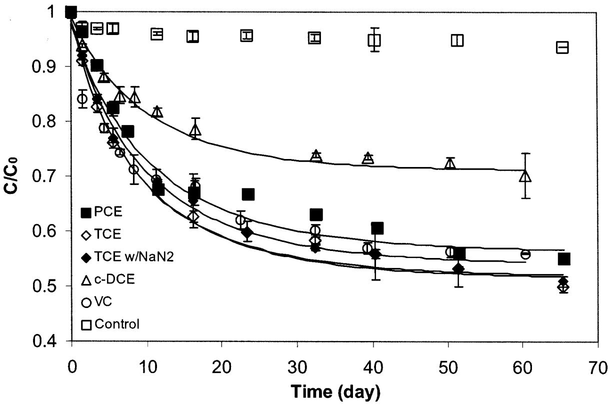

FIGURE 1. Reductive dechlorination of chlorinated ethylenes in 0.084 g/g pyrite suspensions. The error bars are 95% confidence intervals. Curves represent kinetic model fits. Control is the control sample for TCE.

Reductive Dechlorination of Chlorinated Ethylenes by Pyrite. Figure 1 shows the decay of target organics in controls and pyrite suspensions. TCE concentration in controls abruptly decreased at the start of the experiment due to sorption on the solid phases of the reactor system (Teflon septum liner + reactor wall). It reached approximately 97% of initial TCE concentration at 1.5 day and then gradually decreased over time reaching 94% of the initial value (65.3 days). The half-lives of TCE partitioning to the solid phases in controls (Teflon septum liner + reactor wall) and that to solid phases in pyrite suspensions (Teflon septum liner + reactor wall + pyrite) were less than 0.65 day. The rates of partitioning of TCE to the solid phases were much faster than rates of reductive dechlorination of TCE in pyrite suspension. Therefore, the assumption of instantaneous equilibrium for target organic partitioning to the solid phase is reasonable. The concentration of PCE in the control (not shown) also rapidly dropped and reached equilibrium at 1.5 day (approximately 94% of initial PCE). In cases of *cis*-DCE and VC controls (not shown), the concentrations of target organics were relatively constant (average > 98%), which indicates that partitioning of *cis*-DCE and VC to the solid phases of the reactor system was negligible.

Table 1 shows the kinetic parameters, transformation products and their recoveries, and target organic remaining at the last sampling time. Recovery of transformation product and target organic remaining were calculated by dividing total concentrations of transformation product and target organic at the last sampling time by the initial concentration of target organic. This assumes that the initial target organic concentration is the maximum possible concentration of transformation products. The incompleteness of total recovery of target organics and transformation products may be caused by the formation of nondetectable products, inaccuracy in Henry's law constants, and volatilization loss during the sampling procedure.

Pyrite suspensions removed 29.8−50% of initial target organics, and the carbon mass balance stayed between 88.6 and 99% at the last sampling times. Target organics showed a pseudo-first-order decay during early reaction time, which is similar to that observed in the reductive dechlorination of chlorinated ethylenes by meta-stable iron sulfides and Zn(0) (*35*, *37*). However, the degradation rate by pyrite decreased as the reaction proceeded and the reductive capacity of pyrite was consumed. A similar trend on the degradation rate of TCE by pyrite was observed in Weerasooriya and Dharmasena's experiment (*32*). The rate constant for the reductive dechlorination of VC at the reactive surfaces of pyrite has the greatest value followed by those for TCE, PCE, and *cis*-DCE, although the constants are similar to each other differing by a factor of only 1.7. Over the 70-day sampling period, there were no significant differences observed for the kinetics of TCE removal between the samples with and without biocide (NaN$_3$), which shows that the reductive dechlorination process in these experiments was abiotic. Specific reductive capacities of pyrite for target organics were calculated by

TABLE 1. Kinetic Parameters, Transformation Products and Their Recoveries, and Target Organic[a] Remaining in Pyrite and Magnetite Suspensions[b] at the Last Sampling Time

soil minerals	target organics	specific reductive capacity (μM/g)[c]	K (mM^{-1})	k (day^{-1})	R^2 [d]	product recovery and target organic remaining (%)
pyrite	PCE	1.01 (±0.01)[g]	0.642 (±0.010)	1.01 (±0.02)	0.974	TCE: 6.7 C_2H_2: 32.0 C_2H_4: 6.0 PCE: 55 total[e]: 99.7
	TCE	1.48 (±0.03) 1.47 (±0.04)[h]	0.345 (±0.011) 0.346 (±0.010)[h]	1.59 (±0.02) 1.60 (±0.02)[h]	0.988 0.989[h]	*cis*-DCE: 3.3 C_2H_2: 43.0 C_2H_4: 2.2 TCE: 50 total[e]: 98.5
	cis-DCE	1.49 (±0.04)	0.300 (±0.005)	0.984 (±0.021)	0.983	C_2H_2: 13.2 C_2H_4: 5.2 *cis*-DCE: 70.2 total[e]: 88.6
	VC	2.26 (±0.06)	0.187 (±0.006)	1.71 (±0.06)	0.970	C_2H_4: 34 C_2H_6: 5.0 VC: 56 total[e]: 95
magnetite	PCE	0.33 (±0.02)	0.700 (±0.022)	0.202(±0.017)	0.910	chloride: 5.5 PCE: 90.1 total[f]: 95.6
	TCE	0.37 (±0.02)	0.503 (±0.014)	0.254 (±0.010)	0.961	chloride: 10.7 TCE: 86.3 total[f]: 97
	cis-DCE	0.54 (±0.06) 2.06 (±0.16)[i]	0.501 (±0.056) 0.344 (±0.018)[i]	0.185 (±0.023) 0.28 (±0.023)[i]	0.817 0.872[i]	chloride: 1.95/28.7[i] *cis*-DCE: 96.1/61.3[i] total[f]: 98.1/90[i]
	VC	0.73 (±0.07) 2.86 (±0.09)[i]	0.3 (±0.028) 0.2 (±0.010)[i]	0.193 (±0.021) 0.35 (±0.019)[i]	0.823 0.943[i]	chloride: 4.2/43.9[i] VC: 93.7/48.3[i] total[f]: 97.9/92.2[i]

[a] Initial concentrations of target organics were 0.19 (PCE), 0.25 (TCE), 0.41 (*cis*-DCE), and 0.40 mM (VC). pH of soil mineral suspension was constant at 8 (pyrite) and 7 (magnetite). [b] Mass ratios of solid to water were 0.084 (pyrite) and 0.063 (magnetite). [c] Specific reductive capacity was obtained by dividing C^0_{RC} by the solid concentration. [d] R^2 values of nonlinear regression for kinetic parameters. [e] Total is total carbon mass balance for pyrite. [f] Total is total chlorine mass balance for magnetite. [g] Uncertainties represent 95% confidence limits. [h] 20 mg NaN_3 was added. [i] Fe(II) was added. [Fe(II)] = 42.6 mM.

TABLE 2. Surface Area-Normalized Pseudo-First-Order Initial Rate Constants ($k_{1,sa}$)[a] for the Reductive Dechlorination of Chlorinated Ethylenes by a Variety of Reductants

reductants (surface area concn: m^2/L)	PCE	TCE	*cis*-DCE	VC	reference
pyrite[b] (2340)	1.97×10^{-5}	2.53×10^{-5}	1.32×10^{-5}	2.27×10^{-5}	this study
magnetite[b] (3600)	8.38×10^{-7}	7.21×10^{-7}	5.60×10^{-7} 5.74×10^{-6} [h]	5.64×10^{-7} 5.78×10^{-6} [h]	this study
magnetite[c] (81)		4.56×10^{-4}			(*35*)
Zn(0)[d] (5.47)	8.28	0.075×10^{-2}	8.45×10^{-5}	2.40×10^{-3}	(*45*)
mackinawite[e] (0.5)	2.74×10^{-2}	7.15×10^{-2}			(*37*)
troilite[f] (0.5)		5.52×10^{-2} [g]			(*35*)

[a] Unit of surface area-normalized pseudo-first-order initial rate constant (Lm^{-2} day^{-1}). [b] Initial target organic concentration: 0.19 (PCE), 0.25 (TCE), 0.41 (*cis*-DCE), and 0.40 mM (VC), pH of soil mineral suspension: 7 (magnetite) and 8 (pyrite). [c] Experimental condition is not available. [d] Initial target organic concentration: 0.015 to 0.35 mM (PCE, TCE, and *cis*-DCE), 0.003 to 0.03 mM (VC), pH of Zn(0) suspension (50 mM Tris buffer): 7.2. [e] Initial target organic concentration: 0.013 (PCE) and 0.015 μM (TCE), pH of mackinawite suspension (50 mM Tris buffer): 8.3. [f] Initial concentration is not available, pH: 7.5 (influent) and 7.3 (effluent). [g] The surface area-normalized initial rate constant by troilite was calculated assuming surface area concentration of troilite is 0.5 m^2/L. [h] Fe(II) was added. [Fe(II)] = 42.6 mM.

dividing the initial concentration of reductive capacity by the concentration of pyrite. Except for the specific reductive capacity for VC, they were similar to those measured previously, differing at most by a factor of 1.5 (*40*). The 95% confidence intervals for the kinetic parameters are less than 4%, and the R^2 values for the nonlinear regressions are greater than 0.97. These results indicate that the model reasonably describes the dechlorination kinetics in pyrite suspensions.

The surface area-normalized pseudo-first-order initial rate constants are shown in Table 2. Rate constants for TCE were the highest, followed by those for VC, PCE, and *cis*-DCE. This result is interesting because the calculated reduction potentials for one (or two) electron reduction of PCE and *cis*-DCE are greater than those of TCE and VC, respectively (*45*, *47*), which indicates that PCE and *cis*-DCE should be more susceptible to reductive dechlorination. Similar results for relative rates have been reported for the reductive dechlorination of chlorinated ethylenes by mackinawite (*37*) and zerovalent metals (*45, 48*). *cis*-DCE has the smallest value, which agrees with previous research (*45*). The rate constants for pyrite are smaller than those reported for other reductants. They are approximately 2−5 orders of magnitude smaller than those reported for the reductive transformation of target organics by Zn(0) (*45*) and was 1390−2900 times smaller than those reported for mackinawite and troilite (*35, 37*). These results indicate that pyrite is less reactive than metastable iron sulfides and Zn(0) for the reductive dechlorination of chlorinated ethylenes in natural and engineered systems. A study in a model iron-reducing culture showed that abiotic reductive dechlorination of chlorinated organic at magnetite surfaces was 60−260 times faster than biotic reductive dechlorination using the produced total protein and mineral surface area during the growth in the system as a basis for comparison (*49*). This suggests that pyrite could be more important than microorganisms under some conditions (e.g., sulfate reducing condition) in affecting the fate of chlorinated ethylenes. The experimental efforts to further investigate the contribution of abiotic dechlorination process by iron sulfide minerals in natural reducing environments are needed to support the hypothesis.

The principal transformation product of VC in pyrite suspension was ethylene, which accounted for 77.3% of VC that was removed. Ethylene was further reduced to ethane in the suspension, accounting for 11.4% of the target organic removed. Acetylene was not observed throughout the experiment. A similar result was found in abiotic reductive transformation of VC by Zn(0), but no reduction to ethane was reported for Zn(0) (*45*). Based on these results, a sequential hydrogenolysis pathway can be hypothesized to explain the reductive transformation of VC in pyrite suspension (VC → ethylene → ethane).

The reductive dechlorination of *cis*-DCE in pyrite suspension produced acetylene and ethylene, which accounted for 44.3% and 17.5% of removed *cis*-DCE, respectively. Neither VC nor ethane was observed above the method detection limit (VC: 16 μM and ethane: 33.2 μM), while a trace amount of VC was detected as a transformation product of *cis*-DCE and *trans*-DCE by zerovalent Fe(0) and Zn(0) (*45, 47*). Based on the distribution of transformation products, the reductive elimination pathway is suggested to be a main pathway for the reductive dechlorination of *cis*-DCE by pyrite. Proposed pathways for reductive dechlorination of chlorinated ethylenes are shown in Figure 2.

The main transformation product for TCE dechlorination was acetylene, accounting for 86% of TCE that was removed. Minor products were *cis*-DCE (6.6% of removed TCE) and ethylene (4.4% of removed TCE). No 1,1-DCE was observed in these experiments, in contrast to those of Weerasooriya and Dharmasena's (*32*). Similar product distributions have been found during reductive dechlorination of TCE by mackinawite and troilite, where approximately 70 to 80% of removed TCE was transformed to acetylene, 7% was transformed to *cis*-DCE, and 15 to 20% was transformed to ethylene, ethane, and other C_2 to C_6 hydrocarbon (*35, 37*). Because acetylene was the main transformation product, a reductive elimination pathway would appear to be the primary one. Acetylene could also be produced by first converting TCE to *cis*-DCE. If this were an important pathway, the yield of acetylene relative to *cis*-DCE would increase over time. However, this yield was observed to be almost constant, so this pathway is probably not important. Removal of TCE without observing stoichiometric production of a chlorinated intermediate suggests that the acetylene formed during the TCE dechlorination is produced via an unstable intermediate (chloroacetylene) that quickly decays. One possible reaction pathway, TCE → chloroacetylene → VC → ethylene, has been proposed for dechlorination of TCE by Zn(0) (*45*). However, this reaction does not seem to apply to the transformation of TCE in pyrite suspension because of the absence of VC. Therefore, TCE → chloroacetylene → acetylene → ethylene would be a reasonable main transformation pathway (see Figure S-2, Supporting Information).

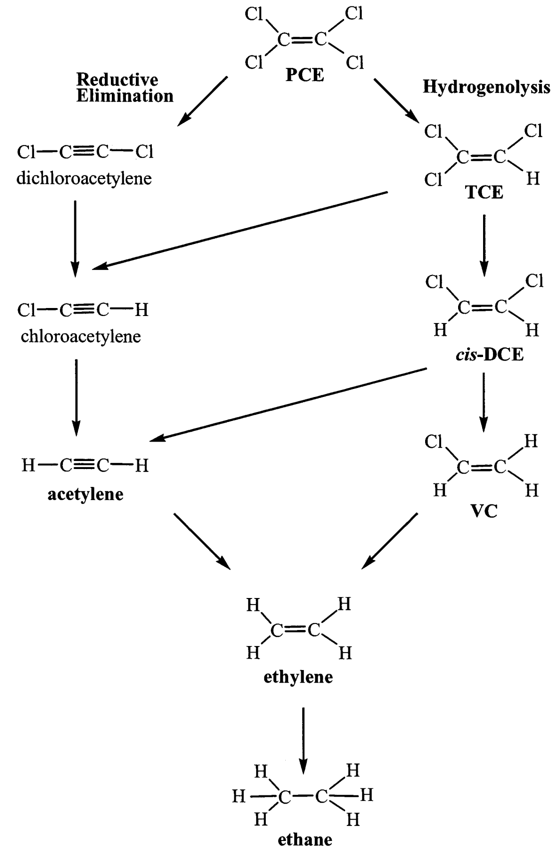

FIGURE 2. Possible pathways for the reductive dechlorination of chlorinated ethylenes by pyrite. Chemical compounds in bold characters were detected in the experiments (see Figure S-2, Supporting Information).

The main transformation product of PCE dechlorination by pyrite was acetylene, which accounted for 71.1% of removed PCE. Minor products were ethylene (13.3% of removed PCE) and TCE (14.9% of removed PCE). Neither *cis*-DCE nor VC was observed above the method detection limit (*cis*-DCE: 2.06 μM and VC: 16 μM). PCE could be transformed to TCE, followed by the parallel transformation to acetylene and *cis*-DCE. Because *cis*-DCE was not detected during the transformation of PCE, the reaction pathways, PCE → TCE → *cis*-DCE → acetylene and PCE → TCE → *cis*-DCE → VC, are not supported by observations. If TCE were a main intermediate for the transformation of PCE to acetylene, the yield of acetylene relative to TCE would increase over time. However the yield was almost constant, suggesting that other parallel transformation pathways with highly reactive intermediates (dichloroacetylene and chloroacetylene) exist for the transformation of PCE to acetylene. Because no DCEs were observed during the reaction, the reductive transformation of PCE to acetylene seems to follow the pathway of PCE → dichloroacetylene → chloroacetylene → acetylene rather than the pathway of PCE → dichloroacetylene → *cis*-DCE or *trans*-DCE → acetylene.

Reductive Dechlorination of Chlorinated Ethylenes by Magnetite. Figure 3 shows the decay of target organics in controls and magnetite suspension with and without addition of 42.6 mM Fe(II). Concentrations are shown as total chlorine concentration (organic chlorine and chloride) relative to the

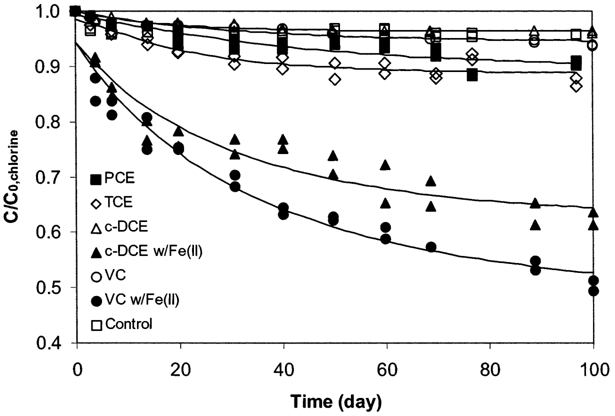

FIGURE 3. Reductive dechlorination of chlorinated ethylenes in magnetite suspension (0.063 g/g) with and without 42.6 mM Fe(II) addition. Curves represent kinetic model fits. Control is the control sample for PCE.

initial total chlorine concentration. The concentration of PCE in controls rapidly dropped due to the partitioning to the solid phases of the reactor system and reached equilibrium concentration (approximately 96% of initial PCE concentration) in 3 days. The concentrations of controls for TCE, *cis*-DCE, and VC (not shown) also decreased rapidly and reached equilibrium (96.5, 97.7, and 98%, respectively) in 3 days. The rates of target organics partitioning to solid phases in controls and magnetite suspensions were also much faster than the dechlorination rates of target organics by magnetite. The amount of sorption of each target compound in magnetite suspension was greater than that in pyrite suspension. The surface area of magnetite is 2.1 times greater than that of pyrite, which may cause higher sorption capacity of magnetite for target organics.

The trends in decay of target organics observed in magnetite suspension with and without Fe(II) were similar to those observed in pyrite suspensions. Approximately, 3.9 to 13.7% of the initial target organics were removed in magnetite suspension and 1.95 to 10.7% were dechlorinated in 100 days. The relative total chlorine concentration of target organics (chlorine balance) in magnetite suspension was 95.6 to 98.1% at the last sampling time. The rate constant for the reductive dechlorination of TCE at the reactive magnetite surfaces is the greatest, followed by those for PCE, VC, and *cis*-DCE (Table 1). The specific reductive capacity of magnetite for target organics shown in Table 1 was 2.8 to 4 times smaller than that of pyrite, which is very similar to the measured results previously reported by Lee (*40*). The sorption coefficients of target organics in magnetite suspension were slightly greater than those in pyrite suspension by a factor of 1.1 to 1.7. The $k_{1,sa}$ for the reductive dechlorination of PCE by magnetite (Table 2) has the greatest value followed by those for TCE, VC, and *cis*-DCE, in contrast to the results for pyrite suspensions in which TCE dechlorination was most rapid. The surface area-normalized rate constants for the dechlorination of different target organics by pyrite and magnetite are similar for each soil mineral, differing by a factor of less than 2. This result provides evidence that an electron transfer may not be the rate-limiting step in these reactions. However, no efforts were made to identify another type of controlling reaction mechanisms in this research. The reductive dechlorination of target organics by magnetite is much slower than dechlorination by other reductants. For example, values of $k_{1,sa}$ for magnetite were approximately 23.5 to 40.3 times smaller than those for pyrite and 2−7 orders of magnitude smaller than those for Zn(0) (*45*). The $k_{1,sa}$ for reductive dechlorination of TCE by magnetite observed in this study was 630 times smaller than that reported by Sivavec et al. (*35*, *50*). The greater rate constant reported by Sivavec et al. could be caused by the lower initial concentration of TCE used in their experiments if saturation kinetics apply rather than first-order kinetics.

Ferrous iron was added to investigate the effect of additional Fe(II) on the dechlorination kinetics of *cis*-DCE and VC. Such additional Fe(II) could be produced by the microbial reduction of Fe(III) to Fe(II), which would provide a continuous source of reducing power in natural environments. No significant difference was observed on the decay of *cis*-DCE and VC between the controls with and without Fe(II) addition (see Figure S-3, Supporting Information) indicating that the reductive dechlorination of target organics by dissolved Fe(II) is not important. No obvious precipitates were observed in the controls with Fe(II), although a very thin layer of precipitate was occasionally observed in the controls (after 60 days) after centrifugation. No analytical effort was made to identify the precipitates, and no significant difference was observed on the dechlorination kinetics between the controls with and without the precipitate. This indicates that the precipitate (presumably, siderite ($FeCO_3$)) did not play a significant role in the dechlorination of target organics. The addition of Fe(II) to magnetite suspensions increased the dechlorination rates of *cis*-DCE and VC by a factor of 10 and increased the specific reductive capacity of magnetite for *cis*-DCE and VC by a factor of approximately 4. The increased reactivity of magnetite caused by Fe(II) addition may be due mainly to the formation of reactive surface-bound Fe(II) species. The reactive surface-bound Fe(II) species responsible for the increased decay rate would be surface precipitates or surface clusters rather than isolated surface complexes of Fe(II) such as $\equiv FeOFe^+$ or $\equiv FeOFeOH^0$ because the high Fe(II) concentration and sufficient Fe(II) contact time employed in this experiment could allow for the rearrangement of the surface complexes to more reactive surface precipitate or cluster forms (*51*). The enhanced reactivity of magnetite due to Fe(II) addition indirectly shows the potential link between biotic and abiotic processes in the reductive dechlorination of *cis*-DCE and VC in contaminated plumes. Microorganisms (e.g., *Geobacter metallireducens*) can reduce hydrous ferric oxide to magnetite (*39*, *49*) and/or to Fe(II) surface species bound to the magnetite under Fe(III) reducing conditions. These biogenic magnetite and Fe(II) surface species could be regenerated by Fe(II) produced by microorganisms after their oxidation by chlorinated organics. The effect of Fe(II) addition to the magnetite suspension, therefore, may be due to the reductive regeneration of magnetite by Fe(II) or by the activity of Fe(II) surface species bound to magnetite or its oxidation products (*38*, *52*).

The results obtained in these laboratory studies can be extrapolated to estimate behavior in saturated soils and aquifers using eq 6. These calculations are presented to demonstrate the potential for abiotic processes to impact the fate of chlorinated organics, not to predict actual behavior. The initial reductive capacity concentration (C^0_{RC}) in the field can be calculated by assuming that it is proportional to the concentration of iron. The concentration of iron (mass Fe/volume water) in the field is calculated as 91 g/L by assuming an iron content of 2.6%, bulk density of 1.4 kg/L, and porosity of 0.40. The concentration in the laboratory experiments was calculated as 18.1 and 45.5 g/L for pyrite and magnetite suspensions, respectively, using their solid/liquid mass ratios (0.084 and 0.063, respectively) and their measured iron contents (0.215 g/g and 0.722 g/g, respectively). A partitioning factor (p_{CE}) for PCE in the field of 4.6 can be calculated by further assuming a soil organic fraction of 0.005 and an organic carbon partition coefficient of 206 L/kg. Kinetic coefficients for assumed field conditions were calculated by applying results from Table 1 and are shown in Table 3. The

TABLE 3. Extrapolated Kinetic Parameters for PCE Degradation under Field Conditions

reductants	$C^0_{RC,F}$ (mM/L)[a]	k_1 (day^{-1})	$t_{1/2}$ (days)[b]
pyrite	0.428	0.054	13
magnetite	0.042	1.1×10^{-3}	608

[a] Initial reductive capacity concentration in the field. [b] Degradation half-life.

half-life for PCE degradation by pyrite under field conditions is smaller than often observed in the field, which indicates that abiotic degradation by pyrite could be an important factor. The half-life for PCE degradation by magnetite is much larger but could be reduced if Fe(II) were formed biologically. These results indicate that abiotic reductive dechlorination may be an important factor in determining fate of chlorinated organics during natural attenuation.

Acknowledgments

This research has been funded entirely with funds from the State of Texas as part of the program of the Texas Hazardous Waste Research Center. The contents do not necessarily reflect the views and policies of the sponsor nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Supporting Information Available

Anaerobic environments, preparation of soil minerals, characterization of soil minerals, derivation of kinetic equations, and solid phase partition coefficients for chlorinated ethylenes, X-ray diffraction patterns of pyrite and magnetite used in this research (Figure S-1), reductive transformation of 0.25 mM TCE in 0.084 g/g pyrite suspension (Figure S-2), reductive dechlorination of 0.4 mM VC by magnetite (0.063 g/g) with and without 42.6 mM Fe(II) addition (Figure S-3), characteristics of soil minerals (Table S-1), and solid phase partitioning coefficients (k^s) and partitioning factors (p_{CE}) of chlorinated ethylenes in pyrite and magnetite suspensions (Table S-2). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) McCarty, P. L.; Semprini, L. *Handbook of Bioremediation*; Lewis Publishers: Boca Raton, FL, 1994; pp 87−116.
(2) Bouwer, E. J. *Handbook of Bioremediation*; Lewis Publishers: Boca Raton, FL, 1994; pp 149−175.
(3) Weaver, J. W.; Wilson, J. T.; Kampbell, D. H. Case Study of Natural Attenuation of Trichloroethene at St. Joseph, Michigan. Ward, C. H., Ed.; In *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*; EPA: Dallas, TX, 1996; pp 69−73.
(4) EPA U.S. *Common Chemicals Found at Superfund Sites*; EPA 540/R-94/044; Office of Emergency and Remedial Response: Washington, DC, 1994.
(5) Leisinger, T. In *Biotechnology*; Rehm, H. J., Reed, G., Eds.; VCH Verlagsgesellschaft: Weinheim, 1986; Vol. 8, pp 475−513.
(6) Hutzinger, O.; Veerkamp, W. In *Microbial Degradation of Xenobiotic and Recalcitrant Compounds*; Leisinger, T., Ed.; Academic Press: London, 1981.
(7) Hileman, B. *Chem. Eng. News* **1993**, *19*, 11−20.
(8) Ukrainczyk, L.; Chibwe, M.; Pinnavaia, T. J.; Boyd, S. A. *Environ. Sci. Technol.* **1995**, *29*, 439−445.
(9) Bagley, D. M.; Gossett, J. M. *Appl. Environ. Microbiol.* **1990**, *56*, 2511−2516.
(10) Freedman, D. L.; Gossett, J. M. *Appl. Environ. Microbiol.* **1989**, *55*, 2144−2151.
(11) Fathepure, B. Z.; Nengu, J. P.; Boyd, S. A. *Appl. Environ. Microbiol.* **1987**, *53*, 2671−2674.
(12) Fathepure, B. Z.; Boyd, S. A. *Appl. Environ. Microbiol.* **1988**, *54*, 2976−2980.
(13) Holliger, C.; Schraa, G.; Stams, A. J. M.; Zehnder, A. J. B. *Appl. Environ. Microbiol.* **1993**, *59*, 2991−2997.
(14) Holliger, C.; Schumacher, W. *Antonie Van Leeuwenhoek* **1994**, *66*, 239−246.
(15) Gossett, J. M. Microbiological Aspects Relevant to Natural Attenuation of Chlorinated Ethenes. Ward, C. H., Ed.; In *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*; EPA: Dallas, TX, 1996; pp 10−13.
(16) McCarty, P. L. Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water. Ward, C. H., Ed.; In *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*; EPA: Dallas, TX, 1996; pp 5−9.
(17) Butler, E. C. Ph.D. Dissertation, University of Michigan: Ann Arbor, MI, 1998.
(18) Roberts, A. L.; Sanborn, P. N.; Gschwend, P. M. *Environ. Sci. Technol.* **1992**, *26*, 2263−2274.
(19) Schwarzenbach, R. P.; Giger, W.; Schaffner, C.; Wanner, O. *Environ. Sci. Technol.* **1985**, *19*, 322−327.
(20) Hagg, W. R.; Mill, T. *Environ. Toxicol. Chem.* **1988**, *7*, 917−924.
(21) Barbash, J. E. Ph.D. Dissertation, Stanford University: Stanford, CA, 1993.
(22) Kriegman-King, M. R.; Reinhard, M. *Environ. Sci. Technol.* **1992**, *26*, 2198−2206.
(23) Curtis, G. P.; Reinhard, M. *Environ. Sci. Technol.* **1994**, *28*, 2393−2401.
(24) Dunnivant, F. M.; Schwarzenbach, R. P.; Macalady, D. L. *Environ. Sci. Technol.* **1992**, *26*, 2133-2141.
(25) Schwarzenbach, R. P.; Stierli, R.; Lanz, K.; Zeyer, J. *Environ. Sci. Technol.* **1990**, *24*, 1566−1574.
(26) Burris, D. R.; Delcomyn, C. A.; Smith, M. H.; Roberts, A. L. *Environ. Sci. Technol.* **1996**, *30*, 3047−3052.
(27) Assaf-anid, N.; Hayes, K. F.; Vogel, T. M. *Environ. Sci. Technol.* **1994**, *28*, 246−252.
(28) Chiu, P.; Reinhard, M. *Environ. Sci. Technol.* **1995**, *29*, 595−603.
(29) Chiu, P.; Reinhard, M. *Environ. Sci. Technol.* **1996**, *30*, 1882−1889.
(30) Schreier, C. G. M.S. Thesis, Stanford University: Stanford, CA, 1990.
(31) Kriegman-King, M. R.; Reinhard, M. Chapter 16: Reduction of Hexachloroethane and Carbon Tetrachloride at Surface of Biotite, Vermiculite, Pyrite, and Marcasite. In *Organic Substances and Sediments in Water*; Baker, R. A., Ed.; Lewis Publishers Inc.: Chelsea, MI, 1991.
(32) Weerasooriya, R.; Dharmasena, B. *Chemosphere* **2001**, *42*, 389−396.
(33) Klausen, J.; Tröber, S. P.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, *29*, 2396−2404.
(34) Kriegman-King, M. R. *Environ. Sci. Technol.* **1994**, *28*, 692−700.
(35) Sivavec, T. M.; Horney, D. P. Reduction of Chlorinated Solvents by Fe(II) Minerals. 213th ACS National Meeting; ACS, 1997; pp 115−117.
(36) Butler, E. C.; Hayes, K. F. *Environ. Sci. Technol.* **1998**, *32*, 1276−1284.
(37) Butler, E. C.; Hayes, K. F. *Environ. Sci. Technol.* **1999**, *33*, 2021−2027.
(38) Lee, W.; Batchelor, B. Abiotic Reductive Dechlorination of Chlorinated Ethylenes by Iron-bearing Soil Minerals and Potential Interactions with Biotic Processes. In *Chemical-Biological Interactions in Contaminant Fate*; Tratnyek, P. G., Adriaens, P., Roden, E. E., Eds.; 220th ACS National Meeting; American Chemical Society: Washington, DC, 2000; pp 338−340.
(39) McCormick, M. L.; Kim, H. S.; Adriaens, P. Transformation of Tetrachloromethane in a Defined Iron Reducing Culture: Relative Contributions of Cell and Mineral Mediated Reactions. In *Specialty Chemicals in the Environment*; Stone, A. T., Ed.; 219th ACS National Meeting; American Chemical Society: San Francisco, CA, 2000; pp 138−141.
(40) Lee, W. Ph.D. Dissertation, Texas A&M University: College Station, TX, 2001.
(41) Taylor, R. M.; Maher, B. A.; Self, P. G. *Clay Miner.* **1987**, *22*, 411−422.
(42) Kriegman-King, M. R. Ph.D. Dissertation, Stanford University: Stanford, CA, 1993.
(43) Hwang, I.; Batchelor, B. *Environ. Sci. Technol.* **2000**, *34*, 5017−5022.
(44) Gossett, J. M. *Environ. Sci. Technol.* **1987**, *21*, 202−208.
(45) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*, 3017−3025.
(46) Mackay, D.; Shiu, W. Y. *J. Phys. Chem. Ref. Data* **1981**, *10*, 1175−1199.

(47) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654−2659.

(48) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958−967.

(49) McCormick, M. L.; Bouwer, E. J.; Adriaens, P. *Environ. Sci. Technol.* **2002**, *36*, 403−410.

(50) Sivavec, T. M.; Park, C. Inventors; General Electric Company, Assignee; Composition and Method for Ground water Remediation. USA patent 5750036. May, 1998.

(51) Pecher, K.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **2002**, *36*, 1734−1741.

(52) Heijman, C. G.; Grieder, E.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, *29*, 775−783.

Received for review May 30, 2002. Revised manuscript received September 13, 2002. Accepted September 25, 2002.

ES025836B