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Trichloroethylene Removal from Groundwater in Flow-Through Columns Simulating a Permeable Reactive Barrier Constructed with Plant Mulch

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Groundwater contaminated with TCE is commonly treated with a permeable reactive barrier (PRB) constructed with zero-valence iron. The cost of iron has driven a search for less costly alternatives, and composted plant mulch has been used as an alternative at several sites. A column study was conducted that simulated conditions in a PRB at Altus Air Force Base, Oklahoma. The reactive matrix was 50% (v/v) shredded tree mulch, 10% cotton gin trash, and 40% sand. The mean residence time of groundwater in the columns was 17 days. The estimated retardation factor for TCE was 12. TCE was supplied at concentrations near 20 μM . Over 793 days of operation, concentrations of TCE in the column effluents varied from 0.1% to 2% of the column influents. Concentrations of *cis*-DCE, vinyl chloride, ethylene, ethane, and acetylene could account for 1% of the TCE that was removed; however, up to 56% of ^{13}C added as [1,2- ^{13}C] TCE in the column influents was recovered as ^{13}C in carbon dioxide. After 383 and 793 d of operation, approximately one-half of the TCE removal was associated with abiotic reactions with FeS that accumulated in the reactive matrix.

Introduction

There are hundreds of places in the United States where groundwater is contaminated with chlorinated solvents. Many plumes are treated with permeable reactive barriers constructed with zero-valence iron as the reactive medium. The high cost of zero-valence iron has driven a search for more cost competitive alternatives. In recent years permeable reactive barriers constructed with plant mulch have been used to treat chlorinated solvents in groundwater (1). These mulch-filled permeable reactive barriers are generally referred to as biowalls, because they are designed to enhance biotransformation of the chlorinated solvents under anaerobic conditions. In 2005, the U.S. Air Force installed more than 1000 meters of biowall along the southern perimeter of Altus Air Force Base in Oklahoma. The biowall was designed to treat TCE contamination in groundwater leaving the base.

Alcohols, fatty acids, and hydrogen are produced during the anaerobic degradation of plant mulch. These materials

can support microbial dechlorination of trichloroethylene (TCE) to *cis*-dichloroethylene (*cis*-DCE), then to vinyl chloride, and then to ethylene (2, 3). However, the residence time of groundwater in a biowall is short, on the order of days to weeks. As a consequence, TCE may not be completely dechlorinated in the biowall, resulting in the accumulation of *cis*-DCE and vinyl chloride.

If the groundwater contains sulfate, and the biowall matrix or the aquifer matrix contains iron minerals, then sulfide produced by biological sulfate reduction can react with the iron minerals to produce FeS. Poorly crystalline FeS can transform TCE to acetylene and to *cis*-DCE (4, 5). This nonbiological process may also play an important role in removing TCE in a biowall. At the Altus AFB, concentrations of sulfate in groundwater range from 10 to 20 mM. The sand that was mixed with the mulch to construct the biowall had 1800 mg/kg total iron, and the aquifer sediment has 31 000 mg/kg total iron.

Performance evaluations of permeable reactive barriers at field scale can be problematic. Monitoring wells installed within a biowall do not produce water that has completed the flow path across the reactive matrix. Monitoring wells installed down gradient can mix groundwater from the most highly contaminated flow path with groundwater that was less contaminated or never contaminated. It is also difficult to determine the actual residence time of groundwater in the reactive matrix at a full scale biowall. As a result, it is difficult to extract rate constants from field scale systems that can be used for rational design of biowalls at new sites.

The reactive matrix used to construct the field scale biowall at the SS-17 site at Altus AFB was a mixture of shredded tree mulch, cotton gin trash, and river sand. This laboratory study was conducted to determine the rate of TCE transformation and the potential for accumulation of *cis*-DCE and vinyl chloride in the reactive matrix used at the SS-17 site at Altus AFB. The retardation factor for TCE was determined to evaluate the contribution of sorption to TCE removal. A mass balance was calculated on sulfate removed and sulfide released from the columns to estimate the quantity of FeS that was precipitated in the columns. The pseudo first-order rate constant for removal of TCE was compared to the calculated accumulation of FeS to estimate the contribution of abiotic TCE degradation in the columns. To determine the ultimate fate of TCE that was removed in the mulch, [1,2- ^{13}C] TCE was added to the influent of the columns, and ^{13}C label was determined in methane and in dissolved organic carbon in the column effluents. To our knowledge, this is the first estimate of the overall rate of TCE removal by plant mulch, or the rate of abiotic TCE degradation by FeS produced by sulfate reduction in the presence of plant mulch.

Materials and Methods

Design and Routine Operation of Laboratory Columns. Four continuous flow columns were constructed to simulate the biowall at the SS-17 site at Altus AFB, Oklahoma. The laboratory columns were constructed in glass columns 15 cm in diameter and 46 cm long. Two of the columns were filled with exactly the same materials used to construct the biowall at the Altus AFB SS-17 site. The fill material was 50% (v/v) shredded tree mulch, 10% (v/v) cotton gin trash, and 40% (v/v) sand (See Table 1 in the Supporting Information (SI) for the chemical composition of the mulch). The water-filled porosity of the first two columns was 0.43. These columns will be referred to as Mulch Column One and Mulch Column Two. A third column was constructed as described

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above, except for the addition of 36% (v/v) sand and 4% (v/v) granular hematite (Universal Minerals, Inc., Tucson, AZ, bulk density 2960–3360 g/m³). The water-filled porosity of the third column was 0.42. This third column will be referred to as the Column with Mulch and Hematite.

The rate of abiotic reaction of TCE with FeS increases with increasing pH (5). Fermentation of mulch components produces organic acids and carbon dioxide, which should lower the pH of the water and slow the abiotic degradation of TCE. A fourth column was constructed as described above, except for the addition of 32% (v/v) sand, 4% (v/v) granular hematite, and 4% (v/v) crushed limestone to buffer the pH. The water-filled porosity of the fourth column was 0.42. This fourth column will be referred to as the Column with Mulch and Hematite and Limestone.

The effluent from Mulch Column One and from Mulch Column Two was the influent of two columns that simulated the aquifer downgradient of the biowall. These columns were filled with sediment from the aquifer. These columns will be referred to as Sediment Column One and Sediment Column Two. The columns were 15 cm in diameter and 30 cm long. The water-filled porosity of the sediment columns was 0.33. The effluent of the two mulch columns with hematite was not delivered to a sediment column.

To create a dose solution for the columns, groundwater from Altus AFB was amended with TCE to a concentration near 15 μ M. The groundwater was stored in a Tedlar bag with minimal headspace. The groundwater was pumped from the Tedlar bag to each of the columns containing mulch at a flow rate of 0.2 L d⁻¹, resulting in a liquid residence time of approximately 17 d in the columns containing mulch and 10 d in the columns down stream containing aquifer sediment. The contents of the Tedlar bag were replaced with fresh dose solution every month.

Tracer Test and Sorption Study to Evaluate TCE Sorption in Columns. To evaluate the extent of TCE sorption to the plant mulch, a tracer test with bromide and TCE was conducted in one of columns that had been packed with plant mulch and sand. A 48 h sorption isotherm study and a long-term batch sorption study were also conducted. Details are presented in the SI.

Stable Isotope Test to Identify TCE Transformation Products. After routine operation of the columns for 353 d, the TCE in the dose solution was replaced with 15 μ M of [1,2-¹³C] TCE (99%, Cambridge Isotope Laboratories, Inc., Andover, MA). The columns were operated as before. To establish a baseline for comparisons, samples of groundwater and gas were collected for analysis of the ratio of stable carbon isotope in dissolved inorganic carbon (DIC) and methane. Then the TCE was replaced with [1,2-¹³C] TCE, and samples were collected after 23, 59, and 87 d of exposure to [1,2-¹³C] TCE.

Analytical Methods. TCE and [1,2-¹³C] TCE, along with *cis*-DCE, *trans*-DCE, 1,1-DCE, and vinyl chloride (VC) were analyzed using gas chromatography/mass spectrometry (GC/MS) according to a modification of the procedures established in EPA Method 5021A, "Volatile Organic Compound in Various Sample Matrices using Equilibrium Headpace Analysis," June 2003, in conjunction with EPA Method 8260C, "Volatile Organic Compound by Gas Chromatography/Mass Spectrometry (GC/MS)," August 2006. The method detection limit for each compound was 0.003 μ M.

Methane, ethylene, ethane, and acetylene were analyzed by injecting headspace gases into a HP Series P200H GC Chromatograph. The detection limit for each hydrocarbon was 0.5 μ g/L in the liquid phase.

Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in water was analyzed using a Dohrman DC-80 Carbon Analyzer. The method detection limit was 15 μ M. Sulfate was analyzed using a Waters capillary electrophoresis

system, while bromide was determined using a Lachat flow injection system (Lachat method 10-135.21-2-A in Quickchem 8000 Method Manual, Zellweger Analytics, Milwaukee, WI). The method detection limit was 1.8 μ M for sulfate and 3.1 μ M for bromide. Metals in the sand and aquifer solid materials were analyzed using an ICP after digestion with hot concentrated nitric acid. The detection limit for each element was below 0.0025%.

Stable isotope ratios for DIC and CH₄ in the effluents were analyzed by Isotech Laboratories, Inc. (Champaign, IL). The precision of the analyses was \pm 0.1‰.

Results and Discussion

Removal of TCE and Production of Transformation Products. The columns were supplied with groundwater from a well at Altus AFB that was expected to have high concentrations of TCE. When samples were acquired after 1 month of operation, it was discovered that the actual concentration of TCE in the influent was much lower than intended. Starting with day 65 of operation, the groundwater supplied to the columns was amended with TCE to a concentration near 15 μ M (Figure 1, Panel A). This concentration is more representative of the higher concentrations being treated by the full scale biowall at Altus AFB. Within 99 d of operation, the columns reached the maximum removal of TCE (Figure 1, Panel A). After the maximum removal of TCE was attained, the removal decreased steadily over time. After 793 d of operation, the concentration of TCE in the effluent of the Mulch Columns was 2% of the concentration in the influent; and the concentration of TCE in the effluent of the columns with mulch and hematite was 0.6% of the influent. There was further removal of TCE in Sediment Columns One and Two, and the removal increased over time. By 793 d of operation, the concentration of TCE in the effluent of the Sediment Columns was 3% and 1.4% of the concentration in the influent to the Sediment Columns.

The concentration of *cis*-DCE in the effluent of the mulch columns was greater than the concentration of *cis*-DCE in the influent (Figure 1, Panel B), indicating that the *cis*-DCE was produced by transformation of TCE. As was the case with TCE, there was additional removal of *cis*-DCE in the sediment columns, particularly after 578 d of operation.

In the Column with Mulch and Hematite, or the Column with Mulch and Hematite and Limestone, the removal of TCE was even greater (Figure 1, Panel C). The concentrations of *cis*-DCE were higher in the columns with hematite compared to the columns without hematite.

A pseudo first-order rate constant for removal of TCE across each column ($k_{overall}$) was calculated according to eq 1, where (C_{out}) is the concentration in the column effluent, (C_{in}) is the concentration in the column influent, and (τ) is the mean residence time of water in the column (17.5 d).

$$k_{overall} = -\ln(C_{out}/C_{in})/\tau \quad (1)$$

Table 1 compares the pseudo first-order rate constants in the columns after 383, 578, and 793 d of operation; 383 d represents the center of the period of operation, 578 d is the time with the greatest difference between TCE removal in the mulch columns without hematite and TCE removal in the mulch columns with hematite, and 793 d is the latest sample time available. Figure 1SM in the SI presents rate constants for all the sampling intervals. The rate constants varied from 0.20 to 0.55 d⁻¹.

If a zero-valence iron wall has a water filled porosity of 0.5, the rate of TCE degradation by Peerless Iron reported by Butler and Hayes (5) at pH 8.3 would produce a pseudo first-order rate constant of 4.1 d⁻¹. Rates extracted from the data reported by Wilkin and Puls (6) for core samples from an existing zero-valence iron wall correspond to a rate constant

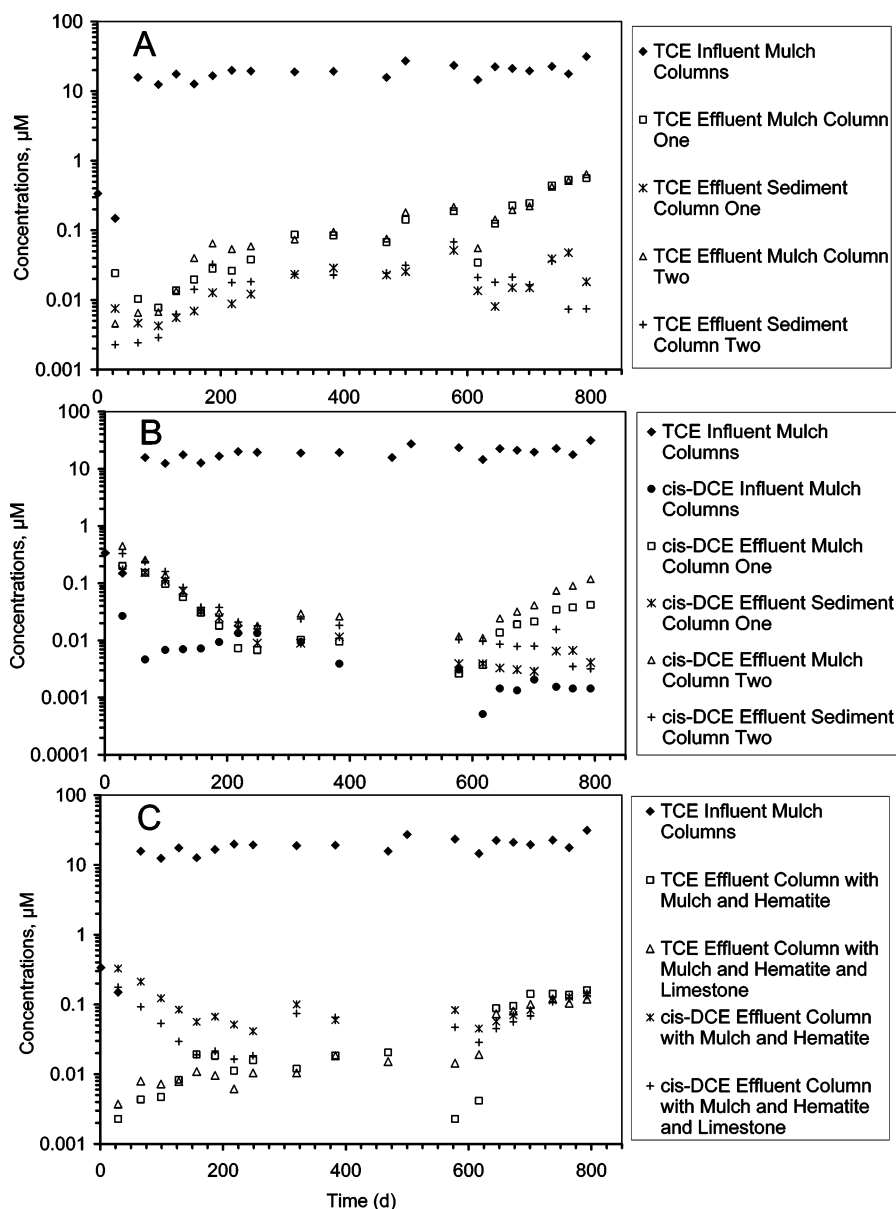


FIGURE 1. Behavior of TCE and *cis*-DCE in laboratory columns simulating a permeable reactive barrier constructed with plant mulch and in the aquifer downgradient of the PRB. Groundwater containing TCE was pumped through four columns packed with plant mulch. The effluent from Mulch Column One or Mulch Column Two was the influent to Sediment Column One or Sediment Column Two.

of 34 d⁻¹. The overall rates in the reactive matrix used to construct the SS-17 biowall at Altus AFB are approximately 10% to 1% of the rates attained with zero valence iron.

Low Concentrations of Biodegradation Products. In general, conditions were conducive for biological reductive dechlorination in the biowall columns (1, 2): DO was low, ORP was low, methane was being produced, and the pH was near neutral (See SI). However, there was little evidence of significant concentrations of reduction daughter products. As discussed above, less than 1% of TCE that was removed in the mulch columns can be accounted for as *cis*-DCE; and trans-DCE was not detected in any of the column effluents (data not shown). The maximum concentration of vinyl chloride determined in any of the column effluents was 0.03 μM (Figure 5SM), and the maximum concentration of 1,1-DCE was 0.04 μM (Figure 6SM). Ethylene and ethane were never detected above their method detection limits of 0.07 and 0.09 μM respectively. Acetylene was detected three times: twice in the feed solution at a concentration of 0.4 μM and once in the effluent of Mulch Column One at a concentration of 0.3 μM (the method detection limit for

acetylene was 0.1 μM and the lowest calibration standard was 0.4 μM).

TCE Adsorption. To determine whether sorption of TCE to the mulch could account for TCE removal in the columns, a tracer test was conducted with bromide and TCE to estimate the TCE retardation factor in the columns. The retardation factor was calculated as the volume of water required to recover one-half of the injected concentration of TCE, divided by the volume required to recover one-half of the injected concentration of bromide ion. Breakthrough of bromide at 50% of the injected concentration occurred after 60% of the water filled porosity in the columns had been displaced (Figure 7SM in the SI). Approximately 40% of the water in the column was stagnant. The water filled porosity was 0.42 and the effective porosity was 0.25. Breakthrough of TCE at 50% of the injected concentration occurred after 2.3 pore volumes, or 3.8 effective pore volumes, had been displaced. The TCE retardation factor was 3.8.

The flow rate during the tracer test was more than 20 times faster than flow during regular operation of the columns. It is likely that mass transfer limitations prevented

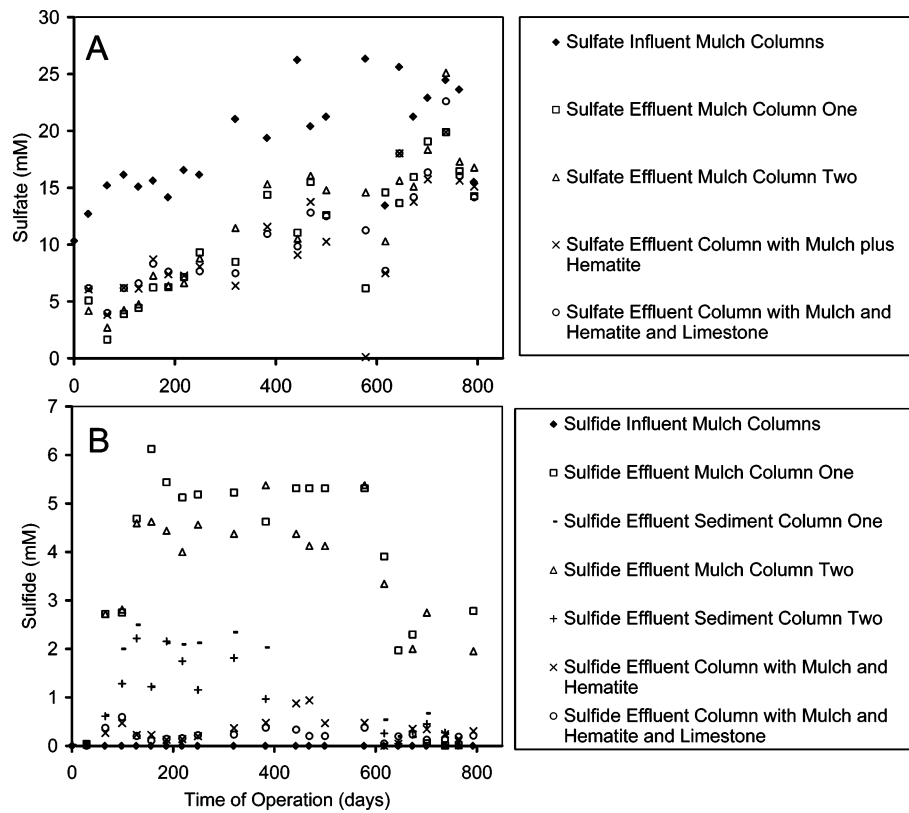


FIGURE 2. Behavior of sulfate and sulfide in laboratory columns simulating a permeable reactive barrier constructed with plant mulch and in the aquifer downgradient of the PRB.

TABLE 1. Pseudo First-Order Rate Constants for Removal of TCE in Laboratory Columns That Simulate a Permeable Reactive Barrier to Treat TCE in Groundwater

time of operation (d)	Mulch Column One	Mulch Column Two	relative difference ^a for mulch columns	Column with Mulch and Hematite	Column with Mulch and Hematite and Limestone	relative difference ^b for columns with mulch and hematite
$k_{overall}$, the overall rate constant (d^{-1})						
383	0.31	0.30	2.3%	0.40	0.40	0.2%
578	0.28	0.27	2.9%	0.53	0.42	22%
793	0.23	0.22	4.4%	0.30	0.32	5.5%
k_{FeS}, the rate constant associated with FeS (d^{-1})						
383	0.13	0.12	8.6%	0.22	0.24	7.2%
578	0.25	0.21	14%	0.53	0.34	37%
793	0.11	0.092	15%	0.15	0.22	37%
k_{nor}, the normalized rate constant associated with FeS ($d^{-1}M^{-1}$)						
383				1.6	1.8	14%
578				2.3	1.6	24%
793				0.53	0.90	52%

^a Relative Difference is the difference in the replicate values divided by the average of the values. ^b Relative Difference is the difference in the values for the Column with Mulch and Hematite and the Column with Mulch and Hematite and Limestone divided by the average of the values.

the system from coming to sorptive equilibrium. A sorption isotherm study incubated for 48 h indicated that the K_{oc} for TCE to the plant mulch was $21 \pm 2.3 \text{ L kg}^{-1}$ (Figure 8SM). This would result in a retardation factor in the columns of 12. A batch sorption study with times of incubation up to 25 d indicated that the K_{oc} for TCE to the plant mulch was near 14 L kg^{-1} after 18 d of incubation (Figure 9SM). This would result in a retardation factor in the columns of 8.4. See the SI for calculations and further discussion of sorption of TCE to the plant mulch.

If the retardation factor were 12, sorption of TCE to the plant mulch would make a substantial contribution to the low concentrations of TCE in the effluent of the columns (Figure 1, Panel A). However, TCE would be expected to break

through at half the influent concentration after 216 d of operation in the absence of degradation of TCE in the columns, and it did not (Figure 1). We consider a K_{oc} of 21 L kg^{-1} and a retardation factor of 12 a conservative estimate of the contribution of sorption to removal of TCE by plant mulch in the columns.

Accumulation of Iron(II) Sulfide in the Columns. Significant reduction of sulfate was observed in all columns amended with the plant mulch (Figure 2, Panel A). Removal of sulfate in the effluent of the columns compared to the influent varied from no removal to 20 mM. The average removal was 8.8 mM. Sulfide was released from all four of the columns (Figure 2, Panel B). Starting at 157 d, the concentration of sulfide released from the Mulch Columns

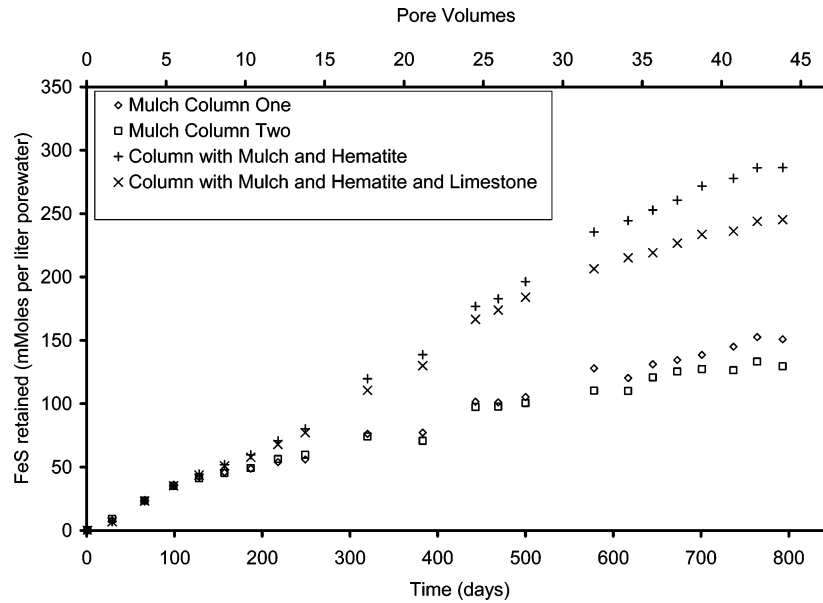
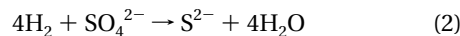


FIGURE 3. Calculations of the concentration of FeS retained in laboratory columns packed with plant mulch and sand to simulate a permeable reactive barrier to treat TCE in groundwater.

One and Two was similar to the concentration of sulfate removed in the columns (4–6 mM). After 157 d, almost all of the sulfide formed in the Mulch Columns One and Two was released from the columns. The concentration of sulfide released from the Column with Mulch and Hematite or the Column with Mulch and Hematite and Limestone was lower (0.6 mM or less), and accounted for no more than 7% of the sulfate removed from the columns. After 578 d of operation, the concentration of sulfide in effluent of Mulch Columns One and Two declined. By 793 d of operation, the concentration of sulfide in the column effluents was approximately one-half the maximum. The supplies of organic carbon that can support sulfate reduction may have been depleted.

A portion of the sulfide that was released by the Mulch Columns was removed in the downstream Sediment Columns (Figure 2, panel B). The concentrations of sulfide leaving the Sediment Columns were half or less of the concentrations leaving the Mulch Columns. The columns containing plant mulch and the dominant flow channels through the columns containing aquifer sediment quickly turned black, presumably through the precipitation of iron sulfide.

To estimate the quantity of iron sulfide formed in the columns, a mass balance was calculated on the concentration of sulfate removed as groundwater passed through each column, and on the concentration of sulfide released from the column. The differences between sulfate removed and sulfide released were assumed to be the concentration of sulfide that reacted with iron and was retained in the columns according to following stoichiometry:



To evaluate the capacity of other metals in the sand used to construct the columns to consume sulfide produced from sulfate reduction, the concentrations of lead, cadmium, copper, nickel, and zinc were also determined. Relative to iron, these metals were present at much lower concentrations (Table 2SM in the SI). The mass of sulfide consumed by these metals would be negligible (<0.6%) compared to that reacted with iron, and possible reactions of sulfide with other metals were excluded in the mass balance.

Figure 3 compares the estimate of iron sulfide retained in the four columns that contained plant mulch, based on the mass balance of sulfate and sulfide, and the chemical stoichiometry in eqs 2 and 3. After 157 d of operation, the accumulation of FeS slowed in the columns that only contained plant mulch and river sand, while the accumulation of FeS in the columns with hematite continued at the previous rate. Because little sulfide escaped the columns with hematite, the rate of accumulation of FeS was controlled by the rate of sulfate reduction.

The concentration of total iron in the sand used to construct Mulch Columns One and Two was 1800 ± 130 mg/kg. Each liter of pore water would have been exposed to 61 mM of iron (See Supporting Information for calculations). At 157 d of operation, the columns retained 45 mM of FeS in contact with each liter of porewater (Figure 3). Retention of sulfide in the mulch columns slowed after approximately three-fourths of the iron available in the river sand had reacted to form FeS.

Rate of TCE Removal Associated with FeS. The removal of TCE was more extensive in the Column with Mulch and Hematite, and in the Column with Mulch and Hematite and Limestone. The two columns containing hematite accumulated greater quantities of FeS. If the extent of TCE transformation associated with FeS is proportional to the amount of FeS retained in the columns, and if the rate of biological transformation and the extent of sorption is the same in all the columns, it is possible to attribute a portion of the overall rate constant for removal of TCE (k_{overall}) to abiotic reactions with FeS (k_a).

We assume that the abiotic transformation rate of TCE follows a first-order reaction such that

$$-\frac{dC}{dt} \big|_{\text{abiotic}} = k_{na}[\text{FeS}][C] = k_a[C] \quad (4)$$

and

$$k_{na} = k_a/[\text{FeS}] \quad (5)$$

where k_{na} ($\text{M}^{-1} \text{d}^{-1}$) is the iron sulfide normalized rate constant, k_a (d^{-1}) is the pseudo first-order rate constant at a particular concentration of iron sulfide ($[\text{FeS}]$, M), and $[C]$ is the TCE concentration (M) at a particular time.

The value k_{na} for a particular column with hematite at a particular sampling time was calculated from values of $k_{overall}$ and the concentrations of FeS retained estimated at that same sampling time. First the values of $k_{overall}$ for Mulch Column One and Mulch Column Two were averaged and the values for the concentrations of FeS retained in Mulch Column One and Mulch Column Two were averaged. Then the average $k_{overall}$ for Mulch Columns One and Two was subtracted from the value of $k_{overall}$ for a column with hematite, and the average concentrations of FeS retained in Mulch Columns One and Two was subtracted from the concentration of FeS retained in the column with hematite. The value of k_{na} was calculated by dividing the difference in the values of $k_{overall}$ by the difference in the concentrations of FeS retained.

To estimate k_a for the Column with Mulch and Hematite or for the Column with Mulch and Hematite and Limestone, the value of k_{na} that was extracted by this procedure was multiplied by the total concentration of FeS in the column. To estimate k_a for Mulch Columns One and Two, the average of the values of k_{na} for the two columns with hematite was multiplied by the accumulated FeS in Mulch Column One or Mulch Column Two. Results of the rate calculations are presented in Table 1. Details of the calculations are presented in Table 3SM in the SI.

After 383 d of operation, on average, k_a was 49% of $k_{overall}$ (Table 1). This sampling date was approximately one-half of the total time period, and this was the first sampling date where there was a clear distinction between the extent of removal of TCE in the columns containing hematite and plant mulch compared to the columns that only contained plant mulch, and a clear distinction in the amount of FeS retained. After 578 d of operation, on average, k_a was 88% of $k_{overall}$. This was the sampling date with the greatest difference in removal of TCE in the columns containing hematite and plant mulch compared to the columns that only contained plant mulch. After 793 d of operation, on average, k_a was 52% of $k_{overall}$. This was the last sampling date available.

The values of k_{an} varied from 0.53 to 2.3 d⁻¹ M⁻¹. These rate constants are rapid compared to rates available from the literature. Butler and Hayes reported first-order rates of transformation of TCE in contact with 10 g/L FeS (4, 5). At pH 7.3 the rate was $5.0 \pm 1.7 \times 10^{-4} \text{ h}^{-1}$. This rate is equivalent to a k_{na} of 0.067 d⁻¹ when exposed to 1.0 M of FeS in contact with 1.0 L of pore water (d⁻¹ M⁻¹). From 383 to 793 d of operation, the pH in the effluent of the mulch columns varied from 7.0 to 7.5 (Figure 3SM). The normalized rates of abiotic reaction associated with FeS in the biowall columns were approximately 8–34 times faster than rates produced by FeS in the form of poorly crystalline mackinawite as determined by Butler and Hayes (4, 5).

Abiotic transformation of TCE associated with FeS provided a major contribution to the removal of TCE from the groundwater from Altus AFB. This was possible because the groundwater had high concentrations of sulfate. At sites with lower concentrations of sulfate, it may be possible to supplement the biowall matrix with gypsum or some other source of sulfate, as was done in a field demonstration at Dover AFB, DE (7). The rates of abiotic degradation of TCE that were attained in this study would provide significant removal of TCE in groundwater flow systems with less FeS, but much longer residence time. Sulfate reduction is common in many chlorinated solvent plumes. Abiotic degradation associated with FeS may have an important role in many natural attenuation remedies.

Recovery of ¹³C from [1,2-¹³C]-TCE in Methane and Carbon Dioxide. Starting on day 353, the TCE in the feed solution delivered to the columns was replaced with [1,2-¹³C] TCE. The isotopic ratio of ¹³C to ¹²C in dissolved methane

and in dissolved inorganic carbon (DIC) was determined in the column effluents 37 d prior to addition of the [1,2-¹³C] TCE and again 23, 59, and 87 d after addition of the [1,2-¹³C] TCE. The recovery of the added ¹³C in methane or carbon dioxide was calculated by subtracting the isotopic ratio 37 d prior to the addition of the [1,2-¹³C] TCE from the ratio after addition of [1,2-¹³C] TCE, then multiplying the difference by the molar concentration of DIC or methane in the column effluent. The initial concentration of [1,2-¹³C] TCE was 13 μM, equivalent to 6.5 μM ¹³C. The measured isotopic ratios in DIC and methane are presented in Figure 12SM in the SI. Table 5SM summarizes the recovery of the ¹³C added as [1,2-¹³C] TCE. The recovery of ¹³C as methane was trivial, never greater than 0.6%. The recovery of ¹³C as carbon dioxide increased with time in each of the biowall columns. The recovery averaged across all four columns was $11 \pm 5.1\%$ after 23 d, $34 \pm 14\%$ after 59 d, and $53 \pm 18\%$ after 87 d.

There are two pathways for abiotic degradation of TCE by FeS (5). The major pathway, which accounts for 80–90% of the TCE degraded at pH 7.3, produces acetylene. Acetylene is readily fermented to ethanol and acetate (8), which in turn would be readily oxidized to carbon dioxide by sulfate reducing bacteria or iron(III) reducing bacteria. Ethanol and acetate can also be fermented to produce methane. The other abiotic pathway produces *cis*-DCE, as does biological reductive dechlorination. It is likely that *cis*-DCE also reacts with FeS to produce acetylene, and *cis*-DCE can undergo anaerobic biological oxidation to carbon dioxide (9).

Acetylene or *cis*-DCE would be produced at low concentrations. If ¹³C in these materials are largely incorporated into biomass during their metabolism by sulfate reducing bacteria or iron reducing bacteria, then released back to the water as carbon dioxide as the biomass is turned over, the concentration of ¹³C label in the column effluents would be expected to increase over time. The data in Table 1 strongly indicate that sulfate-reducing and iron-reducing bacteria dominated, and that biodegradation to carbon dioxide is the ultimate fate of most of the TCE degraded in the mulch.

Acknowledgments

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Supporting Information Available

Composition of the plant mulch; changes in rate constants ($k_{overall}$) over time; the geochemistry of the water in the column effluents; concentrations of DOC, methane, vinyl chloride, 1,1-DCE and pH of column effluents; breakthrough of bromide and TCE in a tracer test; details on the estimation of the extent of sorption of TCE to plant mulch; 48 h sorption isotherm for TCE to plant mulch; K_{oc} for long term sorption of TCE to plant mulch; the amount of iron available to react to form FeS; methods to characterize the plant mulch; metal composition of the sand; calculations of rate constants; mass balance of carbon lost as DOC, carbon consumed by methane production, carbon consumed by sulfate reduction and carbon available from the mulch; and recovery of ¹³C from [1,2-¹³C] TCE in methane and DOC in column effluents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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