Reduction of PCE and TCE by Magnetite Revisited

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Abstract

Here we revisit whether the common mixed-valent Fe mineral, magnetite, is a viable reductant for the abiotic natural attenuation of perchloroethylene (PCE) and trichloroethylene (TCE) in anoxic groundwater plumes. We measured PCE and TCE reduction by stoichiometric magnetite as a function of pH and Fe(II) concentration. In the absence of added Fe(II), stoichiometric magnetite does not reduce PCE and TCE over a three month period. When Fe(II) is added to magnetite suspensions, PCE and TCE are reduced under Fe(II) and pH conditions that appear to be controlled by the solubility of ferrous hydroxide, $\text{Fe}(\text{OH})_2(\text{s})$. Reduction rates are slow with only 1 to 30% carbon products (primarily acetylene) accumulating over several months. We conducted a similar set of experiments with $\text{Fe}(\text{OH})_2(\text{s})$ alone and found that, compared to in the presence of magnetite, $\text{Fe}(\text{OH})_2(\text{s})$ reduces PCE and TCE only at Fe(II) concentrations that are too high (≥ 13 mM, 726 mg/L) to be representative of natural aquifer conditions. Our results suggest that magnetite present in aquifer sediments alone is unlikely to reduce PCE and TCE sufficiently fast to contribute to natural attenuation of PCE and TCE. The lack of compelling evidence for PCE and TCE reduction by magnetite raises important questions regarding the current application of using magnetic susceptibility as a potential indicator for abiotic natural attenuation. Dynamic conditions and high Fe(II) concentrations that favor active precipitation of minerals, such as $\text{Fe}(\text{OH})_2(\text{s})$ in the presence of magnetite (or other Fe minerals), however, may lead to PCE and TCE reduction that could help attenuate PCE and TCE plumes.

Environmental significance

We present evidence that suggests magnetite alone is unlikely to reduce PCE and TCE fast enough to significantly contribute to the natural attenuation of PCE and TCE in contaminated aquifer plumes. Under reducing conditions where high concentrations of ferrous iron may be present, however, active precipitation of metastable phases in the presence of magnetite (or other Fe minerals) may contribute to abiotic natural attenuation of PCE and TCE.

Submitted to *Environmental Science: Processes and Impacts*

Revised Manuscript

24 August 2018

Introduction

Perchloroethene (PCE) and trichloroethene (TCE) are chlorinated ethenes that were used at thousands of industrial and commercial facilities as cleaning and metal degreasing solvents.^{1,2} For decades, PCE and TCE have been, and continue to be, the most prevalent priority pollutants in groundwater at hundreds of sites and a major concern for the environment and human health.³⁻⁷ Despite extensive cleanup efforts costing billions of dollars, PCE and TCE are still detected at many groundwater sites at concentrations above regulatory limits.^{4,8,9} Recent concerns regarding energy consumption and carbon emissions have made it even more critical to assess whether it is feasible for site managers to rely on natural biological, chemical, and physical processes (i.e., natural attenuation) to remediate chlorinated ethene plumes.¹⁰

Biological natural attenuation of PCE and TCE via reductive dechlorination has been extensively studied. These investigations have resulted in several tools that can be used to provide lines of evidence for biological natural attenuation including methods for determining the numbers of *Dehalococcoides sp. (Dhc)* bacteria, vinyl chloride reductase gene copy numbers (*vcrA*),¹¹⁻¹⁴ and compound-specific isotope analysis of PCE and TCE.^{15,16} In addition, significant evidence has accumulated for biotic oxidation of chlorinated ethenes in aerobic plumes,^{17,18} and there are hints that anaerobic oxidation may also occur coupled to metal reduction.¹⁹ There still remains significant uncertainty, however, about how much abiotic reduction reactions, such as reduction by ferrous iron (Fe(II)) bearing minerals, natural organic matter, and reduced sulfur species contribute to natural attenuation.

Of the abiotic natural attenuation processes, reduction by Fe(II)-containing minerals has been discussed as a potentially promising degradation pathway for chlorinated solvents for over two decades.²⁰⁻²³ Abiotic PCE and TCE degradation remains of significant interest largely because abiotic reduction most often occurs by reductive elimination with acetylene observed as the primary end-product. Acetylene is a preferred end-product because it is benign and avoids the dichloroethene and vinyl chloride stall that commonly occurs with biotic reductive dechlorination pathways.²⁰⁻²⁴

Of the Fe(II)-containing minerals, magnetite (Fe₃O₄), a common mixed-valent Fe mineral, has been suggested to be responsible for chlorinated ethene attenuation at some field sites²⁴⁻²⁶ despite slow rates of reduction by magnetite observed in laboratory experiments.^{24,27-29} Indeed, the promise of magnetite as a reductant for chlorinated ethenes has recently led some to suggest that high magnetic susceptibility of aquifer sediments could be used as a potential indicator for abiotic natural attenuation at a site.²⁵ Such proxy methods are desirable due to the difficulty in measuring biologically labile products such as acetylene. We also note that more recent evidence alternatively implicates an oxidative abiotic pathway^{30,31} based on a Fenton-like process involving OH radical in chlorinated ethene degradation by pyrite (FeS₂) in the presence of oxygen.

Here we revisit whether the common mixed-valent Fe mineral, magnetite, is a viable reductant to contribute to abiotic natural attenuation of PCE and TCE in anoxic groundwater plumes. Our results suggest that magnetite present in aquifer sediments, alone, is unlikely to reduce PCE and TCE sufficiently fast to contribute to natural attenuation of PCE and TCE in anoxic plumes. Under dynamic conditions that result in active precipitation of minerals such as Fe(OH)₂(s), however, PCE and TCE may be reduced sufficiently fast to help attenuate PCE and TCE plumes.

Materials and Methods

Chemicals

Tetrachloroethylene (PCE, $\geq 99\%$) and trichloroethylene (TCE, $\geq 99\%$) were purchased from Sigma-Aldrich. Non-chlorinated C_2 gases were used from a certified mixture containing 2.0% ethane, 1.97% ethylene and 1.9% acetylene mixture in N_2 (Praxair). Hexanes and methanol (Fisher Scientific) were pesticide residue grade and ACS reagent grade $\geq 99.8\%$, respectively. PCE and TCE (24, 250 & 500) mM stock solutions were gravimetrically prepared in N_2 -sparged methanol, sealed with viton septa and stored in a glovebox.

All deionized water was deoxygenated by purging with N_2 and stored for 24 hours in an anoxic glovebox (93% N_2 /7% H_2) before being used in any experiments. Buffer solutions of 10 mM 3-(N-Morpholino)propanesulfonic acid (MOPS, RPI Corp.) buffer solution, or 10 mM Piperazine-N,N'-bis(3-propanesulfonic acid) (PIPPS, GFS Chemicals) with 10 mM sodium chloride (NaCl) background electrolyte were prepared. All pH adjustments were done with deoxygenated hydrochloric acid (HCl) or sodium hydroxide (NaOH).

Ferrous chloride stock solutions (~ 1.4 M $FeCl_2 \cdot 4H_2O$) were further purified by adjusting the pH to ~ 4.5 and filtering to remove any Fe(III) precipitates.

Magnetite synthesis

Magnetite was synthesized using iron chloride salts following the method used as previously described.^{32,33} Briefly, 0.1 M ferrous chloride ($FeCl_2 \cdot 4H_2O$) and 0.2 M ferric chloride ($FeCl_3 \cdot 6H_2O$) solutions were prepared in deoxygenated deionized water within the glovebox. Both solutions were combined. The mixture was vigorously stirred and titrated using 10 M NaOH to set the pH between 10.0 and 11.5. The magnetite suspension was sealed and left overnight before filtering. The minerals were removed from the glovebox in a sealed vessel and freeze-dried. Freeze dried minerals were ground with a mortar and pestle and sieved through a 150-micron sieve and stored in the glovebox. With this approach, the (~ 20 nm) magnetite particles have surface area values close to the previously reported 63 ± 7 m² g⁻¹ using N_2 -BET analysis.³³

Mineral characterization

Magnetite stoichiometries ($x = Fe^{2+}/Fe^{3+}$) were determined using previously established methods.³² The first approach was by acid dissolution (x_d) of the magnetite in 5 M HCl under glovebox atmosphere. Using the 1,10-phenanthroline method,^{32,34} we evaluated the Fe^{2+} and total Fe concentrations to determine the stoichiometric ratio. Powder X-ray diffraction (x_{xrd}) was the second approach using a Rigaku MiniFlex II system equipped with a Co source. Magnetite powders were mixed into two drops of glycerol to form a well-mixed paste in the glovebox to avoid oxidation of the mineral during analysis. The powder X-ray diffraction stoichiometries (x_{xrd}) were then derived from unit-cell dimension.³² Transmission Mössbauer spectroscopy was performed with a variable temperature He-cooled system with a ⁵⁷Co source. Unless otherwise noted, Mössbauer spectra were collected at 140 K. Spectra were fit using the Recoil software³⁵ and procedures outlined by Gorski and Scherer.³² To prepare samples and avoid oxidation, we sealed samples with Kapton tape in the glovebox. To characterize minerals after reaction, we shook the reactor and filtered a 5 mL aliquot. These post-reaction samples were sealed for XRD using a layer of Kapton tape over the sample to prevent rapid oxidation of $Fe(OH)_2$.

Reactor design

Reactors were 160 mL glass serum bottles sealed with Viton fluoroelastomer septas (20 mm x 8 mm depth, Wheaton) and contained 150 mL of liquid and 10 mL of headspace. All batch reactors were prepared in a N₂/H₂ filled glovebox with an oxygen content below 1 ppm. Each system was covered with foil, stored and mixed (~100 rpm) upside down to have the headspace in contact with glass rather than the septum. Mixing reactors upside down was important to minimize headspace gas loss through the septum. The desired mass of iron oxides was added to the buffer solution, then the reactor pH was adjusted (when needed) and the chlorinated solvent added via a spike from the stock solution. A PCE and TCE concentration of 50 µM (8,291 and 6,570 µg/L of PCE and TCE, respectively) was used for most experiments. Reactors contained either 10 mM MOPS (pH range of 7.5 to 8.0) and 10 mM NaCl or 10 mM PIPPS (pH > 8.0) and 10 mM NaCl as buffer and background electrolyte, respectively.

In magnetite reactors containing Fe(II), bottles containing buffer and background electrolyte were first spiked with Fe(II) from an 1.4 M FeCl₂ stock, and then the initial Fe(II) concentration was measured. In reactors containing magnetite, magnetite was added, and then the systems were titrated to the desired pH using 2.5 or 10 M NaOH. Because titration of Fe(II) solutions results in a pH plateau near pH 8.0, we took care to add the same volume of NaOH to reactors that were prepared as replicates. Once the pH was adjusted, a 500 µL sample was collected after filtration and the final Fe(II) concentration ([Fe(II)]_f) of the filtrate was determined. Reactors containing only Fe(II) were prepared as described above, but without the addition of magnetite.

Analytical Procedures

Analyses of parent and product analytes were performed using an Agilent 6890 gas chromatograph equipped with electron capture (ECD) and flame ionization (FID) detectors. PCE and TCE were quantified with GC-ECD after a liquid-liquid extraction of 0.25 to 1 mL of sample containing both the aqueous and solid phases added to 2 mL of hexanes. The daughter products ethane, ethylene, acetylene, the dichloroethenes, and vinyl chloride were detected using GC-FID. Further details on analytical methods are provided in the Supporting Information.

Results and Discussion

Reduction of PCE and TCE by Magnetite

To evaluate whether magnetite reduces PCE and TCE, we measured PCE and TCE reduction by stoichiometric magnetite ($x = \text{Fe}^{2+}/\text{Fe}^{3+} \approx 0.5$) over a range of pH values (7.0 – 8.0) and solids loading (5 – 20 g/L). In all experiments, we observed negligible loss of both PCE and TCE over 140 days (**Figure 1 and Table S1 in the Supporting Information**). Further, no carbon products were observed, and we were able to recover nearly all of the carbon initially present in the system (recoveries were TCE: $105 \pm 8\%$ for $n = 7$; PCE: $98 \pm 6\%$ for $n = 5$, details in **Table S1**). We originally anticipated that magnetite stoichiometry would affect the rate of PCE and TCE reduction by magnetite as we have previously observed that magnetite stoichiometry strongly influenced the rates and extent of uranium, mercury, and

nitroaromatic compound reduction.³⁶⁻³⁸ Here, however, we observed no measurable reduction of PCE and TCE by magnetite even with stoichiometric magnetite ($x \approx 0.5$) and therefore did not further explore reduction of PCE and TCE by non-stoichiometric magnetite.

The complete lack of PCE and TCE reduction by stoichiometric magnetite was unexpected as PCE and TCE reduction by magnetite has been previously reported.²⁶⁻²⁹ A close look at the data, however, reveals that prior evidence for reduction of PCE and TCE by magnetite is somewhat limited.

While an early study by Sivavec and Horney reported fast rates of TCE reduction by magnetite with a surface-area normalized rate coefficient (k_{SA}) of $4.5 \times 10^{-4} \text{ L m}^{-2} \text{ d}^{-1}$ (half-life of 19 days),²⁸ more recent studies²⁶⁻²⁹ reported about 100-fold slower rates ($k_{SA} \approx 10^{-6} \text{ L m}^{-2} \text{ d}^{-1}$) than those in Sivavec and Horney.²⁸ In addition, carbon reduction products were only reported in one study²⁹, and in that study the uncertainties on product measurements were quite large (30 – 200%). Based on the high uncertainties, the authors

appropriately chose not to quantify rates of reduction.²⁹ Of the other two studies, the anomalously high rate of reduction was based on TCE loss alone with no report of products²⁸ and the other study relied on chloride accumulation to indicate that reduction had occurred.²⁷ Given the rather limited observations of reduced carbon products and high uncertainties in the previously reported data, we suggest that our observation of negligible reduction of PCE and TCE by magnetite is not so surprising.

Despite the limited laboratory evidence for PCE and TCE reduction by magnetite, degradation rates extrapolated from fate and transport modelling of monitoring well concentrations in the field have sometimes been attributed to abiotic attenuation of chlorinated ethenes by magnetite.^{24-26,39} For example, aquifer degradation rate coefficients ($k_{aquifer}$) on the order of $\sim 1 \text{ yr}^{-1}$ were extrapolated from contaminated groundwater at Twin Cities Army Ammunition Plant (TCAAP) to describe chlorinated ethene plumes that were smaller than expected based on dilution.^{26,44,45} More extensive data was collected for cis and 1,1-DCE and the combination of plume attenuation beyond dilution, microcosm data showing similar degradation rates with sterile and autoclaved sediments, and the presence of magnetite in the sediments led the authors to conclude that the loss of DCE may be due to reaction with magnetite.²⁶ While this a reasonable conclusion to draw, it is not, as was noted by Ferrey et. al., the only potential explanation for their observations.²⁶

Fig. 1. PCE and TCE concentration versus time in the presence of stoichiometric magnetite ($x = \text{Fe}^{2+}/\text{Fe}^{3+} = 0.46 - 0.50$). Experimental conditions: 50 μM PCE/TCE, 10 mM MOPs/NaCl at pH 7.0, 7.5, and 8.0 for TCE reactors and pH 7.5 for PCE reactors, mass loading 5 - 20 g/L. Average carbon recoveries, TCE ($105 \pm 8\%$) for ($n = 7$), and PCE ($98 \pm 6\%$), for ($n = 5$). Error bars represent 1σ for a set of triplicate reactors (pH 8.0, 5 g/L, TCE)

Nevertheless, this work²⁶ is often cited as evidence for chlorinated ethene (PCE, TCE, and DCE) reduction by magnetite^{24-26,39} despite the data only being for DCEs, a need to use rate constants from batch reactors containing high Fe(II) concentrations, and the authors carefully stating that the loss of DCE *may be* due to reaction with magnetite and further research into the mechanisms of loss is needed. Collectively, the limited field and laboratory data for reduction of PCE and TCE by magnetite, and our observation of negligible reduction of PCE and TCE by magnetite, suggests that reduction by magnetite alone is unlikely responsible for field extrapolated degradation rates of PCE and TCE that have been previously attributed to magnetite. We note that there are some important differences between our experiments and aquifer plume conditions (e.g., buffers, magnetite crystallinity, flow environment, etc.). Taken together however, the existing literature and our findings provide no rigorous evidence that magnetite reduces PCE and TCE under anoxic conditions, and in fact, suggest that magnetite does not reduce PCE and TCE under a variety of conditions.

Reduction of PCE and TCE by Magnetite and Fe(II)

To investigate whether magnetite plus aqueous Fe(II) can abiotically degrade PCE and TCE, we measured the reduction of PCE and TCE by magnetite in the presence of Fe(II) over a range of Fe(II) concentrations and pH values (**Table S2 and S3**).

Consistent with previous chlorinated ethene work,^{27,40} we found that adding Fe(II) to magnetite suspensions did, in some cases, result in PCE and TCE reduction. For example, we observed measurable loss of PCE and TCE and

accumulation of 25% carbon products (primarily as acetylene) with 5 g/L magnetite and 9.3 mM Fe(II) or 33 mM Fe(II), for PCE and TCE, respectively (**Figure 2**). Our observation of acetylene as the primary product in all reactors suggests that reductive β -elimination of PCE and TCE was likely the primary mechanism for reduction.⁴¹ Carbon recovery was higher with TCE ($99 \pm 4.3\%$) than PCE (78%). In an attempt to better close the PCE mass balance, we measured for reductive dechlorination products, including dichloroethenes and vinyl chloride, but did not detect any. It is unclear if the mass balance loss of PCE is due to reduction to an unknown product or loss due to sorption or volatilization, however, we did observe up to 30% PCE and TCE loss in controls sampled more frequently than these reactors (**Table S1**), suggesting volatilization was likely the main contributor to loss.

To avoid including potential sorption and/or volatilization losses in estimated rates of PCE and TCE reduction, we quantified reduction rates based solely on accumulation of carbon reduction products (primarily acetylene). We modeled product accumulation over time using an exponential product in-growth equation (Equation 1), where $P(t)$ is the mass of

Fig. 2. Reduction of (A) PCE and (B) TCE over time with magnetite and aqueous Fe(II). Experimental conditions: (A) 54 μM PCE, 5 g/L Fe_3O_4 (s), 33 mM Fe(II), 10 mM MOPs/NaCl, pH 7.9, single reactor. (B) 50 μM TCE, 5 g/L Fe_3O_4 (s), 9.3 ± 0.6 mM Fe(II), 10 mM MOPs/NaCl, pH 8, for n from 3 to 12.

products (in $\mu\text{moles C}$) at time t , C_0 is the initial PCE or TCE amount (in $\mu\text{moles C}$), and k_{obs} is the first-order rate coefficient. Data for total products was linearized (Equation 2), and the slope of the linearized product accumulation versus time equation was used to determine k_{obs} .

$$P(t) = C_0(1 - e^{-k_{\text{obs}}t}) \quad (1)$$

$$\frac{\ln\left(1 - \frac{P(t)}{C_0}\right)}{t} = -k_{\text{obs}} \quad (2)$$

First-order rate coefficients for PCE and TCE reduction determined from product accumulation varied considerably depending on the Fe(II) concentration and pH and ranged from zero to $5.2 \times 10^{-8} \text{ s}^{-1}$ (**Table S2** and **S3**).

We plotted k_{obs} values versus initial Fe(II) concentration and pH to explore trends in reduction rate, as we anticipated reduction rates might increase with both pH and Fe(II) concentration (**Figure 3**). Although our data are concentrated around our most common condition ($\sim \text{pH } 8$ and $\sim 10 \text{ mM Fe(II)}$), there are still sufficient data to conclude that there is no clear trend with Fe(II) concentration. With pH, there is a pattern of higher pH reactors having measurable reduction ($k_{\text{obs}} > 0$), but no obvious trend of increasing rates at higher pH values. In addition, there was visual evidence from our reactors that experimental conditions had some influence on whether products were observed. More specifically, we observed a white precipitate forming in reactors in which products were observed (**Figure S1**). Given the pH and Fe(II) concentrations we used, we suspected that the white precipitate was ferrous hydroxide, $\text{Fe(OH)}_2(\text{s})$, which was confirmed by X-ray diffraction of the filtered reactor solids (**Figure S2**).

To quantitatively evaluate if $\text{Fe(OH)}_2(\text{s})$ precipitation was necessary for PCE and TCE reduction, we plotted k_{obs} values versus the saturation index (SI) for $\text{Fe(OH)}_2(\text{s})$ (**Figure 4**). We calculated the SI as $\log(\text{IAP}/K_{\text{sp}})$ using the initial Fe(II) concentration and an $\text{Fe(OH)}_2(\text{s})$ K_{sp} of 5×10^{-15} .⁴²⁻⁴⁴ A noticeable pattern emerges with PCE and TCE reduction corresponding to conditions where the initial SI > 0 . This pattern implies that PCE and TCE reduction only

Fig. 3. Plots of k_{obs} for PCE and TCE reduction as a function of $[\text{Fe(II)}]_0$ (initial Fe(II) concentration) (a) and pH (b).

Fig. 4. Plot of k_{obs} for PCE and TCE reduction vs. the $\text{Fe(OH)}_2(\text{s})$ initial saturation index (< 0 undersaturated, 0 at saturation, > 0 oversaturated).

occurs under experimental conditions that are saturated (or super-saturated) with respect to $\text{Fe}(\text{OH})_2(\text{s})$ based on the amount of $\text{Fe}(\text{II})$ added and the pH value the reactor was set at. We note that after precipitation of $\text{Fe}(\text{OH})_2$, the SI is likely closer to 0. For experiments that were saturated or super-saturated,

93% (27 of 29) had measurable reduction products form. Conversely, for experiments that were undersaturated only 18% (2 of 11) had measurable reduction products form.

To better visualize the influence of $\text{Fe}(\text{OH})_2(\text{s})$ precipitation on PCE and TCE reduction, we also plotted the initial pH and $\text{Fe}(\text{II})$ concentration of these magnetite plus $\text{Fe}(\text{II})$ experiments on an $\text{Fe}(\text{OH})_2(\text{s})$ solubility diagram (**Figure 5**). In Figure 5, solid, red markers indicate conditions where reduction products were observed, whereas open markers indicate conditions where no reduction products were observed. In addition, we scaled the size of the red markers to the relative amount of products formed.

A clear visual picture emerges highlighting that products were observed (i.e., red markers) only when $\text{Fe}(\text{II})$ concentration and pH values were such that $\text{Fe}(\text{OH})_2(\text{s})$ was expected (and visually observed) to precipitate. Of the forty experiments we conducted, thirty-six (90%) followed the trend of reduction occurring only when conditions were such that $\text{Fe}(\text{OH})_2(\text{s})$ was expected to precipitate. These results provide compelling evidence that, under our experimental conditions, precipitation of ferrous hydroxide is necessary for PCE and TCE reduction to be observed in the presence of magnetite. Note that in the presence of different buffers, such as carbonate, other minerals would likely precipitate (such as siderite or carbonate green rust).

Although adding $\text{Fe}(\text{II})$ to the magnetite suspensions resulted in reduction of PCE and TCE when $\text{Fe}(\text{OH})_2(\text{s})$ precipitated, the rates of reduction are still quite slow. Only 1 to 30% carbon products (primarily acetylene) accumulated over a three to five month time period.

Fig. 5. $\text{Fe}(\text{OH})_2(\text{s})$ solubility diagram with magnetite plus $\text{Fe}(\text{II})$ reactor conditions overlaid for (a) PCE and (b) TCE reactors. $\text{Fe}(\text{II})$ is plotted as the initial $\text{Fe}(\text{II})$ concentration – $[\text{Fe}(\text{II})]_0$. Red markers represent PCE and TCE reactors where carbon products were observed and the markers are scaled relative to the amount of products produced (ranging up to 46%). Black open markers represent reactors where no products were observed. The grey hatched area represents a range of ferrous hydroxide solubility product K_{sp} ($[\text{Fe}(\text{OH})_2(\text{s})] = [\text{Fe}^{2+}][\text{OH}^-]^2$) of $10^{-14.51}$ to $10^{-15.11}$. The grey hatched and shaded areas represent the region where $\text{Fe}(\text{OH})_2$ is expected to precipitate. Speciation diagrams were calculated with Visual MINTEQ for 10 mM Na^+ and 30 mM Cl^- to represent Cl^- added with a nominal $\text{Fe}(\text{II})$ spike of 10 mM.

Surface-area normalized first-order rate coefficients (k_{SA}) estimated from carbon product accumulation ranged from 3.7×10^{-7} to $1.5 \times 10^{-5} \text{ L m}^{-2} \text{ d}^{-1}$, corresponding to half-lives ($t_{1/2}$) ranging from 0.42 to 17 years (**Table S2 and S3**). These rates are much slower than those for TCE reported by Sivavec in experiments conducted at pH 6.0 and 200 mM Fe(II) with 217 g/L magnetite ($t_{1/2} \sim 3 \text{ d}$).⁴⁰ We attempted to reproduce the experimental conditions used in the Sivavec patent but observed no measurable TCE reduction (**Figure S3**). One possible explanation for the rapid TCE reduction observed by Sivavec is that the conditions may have led to formation of green rust, which has been shown to reduce PCE and TCE.⁴⁵ Note that our replication of Sivavec's conditions (marked by × in **Figure 5**) are well below ferrous hydroxide saturation and therefore consistent with our finding that no reduction by magnetite occurs under these conditions.

Reduction of PCE and TCE by Fe(II) and ferrous hydroxide

Our observation that $\text{Fe}(\text{OH})_2(\text{s})$ precipitation is necessary for PCE and TCE reduction to occur in the presence of magnetite led us to wonder whether $\text{Fe}(\text{OH})_2(\text{s})$ or even aqueous Fe(II) alone can reduce TCE. To evaluate whether $\text{Fe}(\text{OH})_2(\text{s})$ alone or aqueous Fe(II) alone could reduce TCE, we measured TCE reduction over a wide range of Fe(II) concentrations and pH values (in the absence of magnetite) and plotted the results on an $\text{Fe}(\text{OH})_2(\text{s})$ solubility diagram (**Figure 6**). As expected, no reduction of PCE and TCE was observed by aqueous Fe(II) (denoted by open markers). For most conditions, no PCE and TCE reduction were observed even when $\text{Fe}(\text{OH})_2(\text{s})$ had precipitated. However, at very high concentrations of initial Fe(II) (> 13 mM, 726 mg/L) some slow PCE and TCE reduction was observed with 0.3 to 13% products accumulating over a five to six month time period. First-order rate coefficients for PCE and TCE reduction determined from product accumulation for these high Fe(II) experiments (in absence of magnetite) ranged from $1.8 \times 10^{-10} \text{ s}^{-1}$ to $1.8 \times 10^{-8} \text{ s}^{-1}$ (**Table S4 and S5**). We thought the high Fe(II) concentrations might have resulted in precipitation of an additional phase possibly via secondary mineral transformation of the $\text{Fe}(\text{OH})_2(\text{s})$. However, XRD and Mössbauer spectroscopy of the solids after 150 days indicated no additional phases present other than $\text{Fe}(\text{OH})_2(\text{s})$ (**Figures S4 and S5**). While these results are interesting, we would like to emphasize that the high concentrations of Fe(II) (> 13 mM, 726 mg/L) make these conditions unlikely to be relevant in groundwater aquifers where Fe(II) concentrations rarely exceed 50 mg/L.⁴⁶⁻⁴⁹ Finally, we caution that we are using $\text{Fe}(\text{OH})_2$ saturation index and the plot in Figures 5 and 6 as a graphical aid to explain our data. The figures should not be used as a predictive tool because if $\text{Fe}(\text{OH})_2$ precipitates the saturation index will likely be near 0.

Fig. 6. $\text{Fe}(\text{OH})_2(\text{s})$ solubility diagram with aqueous Fe(II) reactors overlaid for PCE and TCE reactors. Fe(II) is plotted as the initial Fe(II) concentration – $[\text{Fe}(\text{II})]_0$. Red markers represent PCE and TCE reactors where products were observed and the markers are scaled relative to the amount of products produced (ranging up to 46%). Black open markers represent reactors where no products were observed. The grey hatched area represents a range of ferrous hydroxide solubility product K_{sp} ($[\text{Fe}(\text{OH})_2(\text{s})] = [\text{Fe}^{2+}][\text{OH}^-]^2$) of $10^{-14.51}$ to $10^{-15.11}$.⁴²⁻⁴⁴ The grey hatched and shaded areas therefore represent the region where $\text{Fe}(\text{OH})_2$ is expected to precipitate. Speciation diagrams were calculated with Visual MINTEQ for 10 mM Na^+ and 30 mM Cl^- to represent Cl^- added with a nominal Fe(II) spike of 10 mM.

Conclusions and Environmental Implications

Environmental Implications

Our results, combined with previous laboratory studies,^{27,29} suggest that magnetite in aquifer sediments is, on its own, unlikely to reduce PCE and TCE and contribute significantly to natural attenuation of PCE and TCE in anoxic plumes. We did, however, find that precipitation of ferrous hydroxide in the presence of aquifer minerals such as magnetite might provide a mechanism for abiotic attenuation of chlorinated ethenes. To evaluate whether PCE and TCE reduction by magnetite in the presence of ferrous hydroxide could be important in natural (or engineered) attenuation strategies at contaminated sites, we scaled our laboratory rate coefficients (k_{SA}) to reflect aquifer conditions (k_{field}) (example calculations in **Supporting Information**). Using a field magnetite content of 1 g kg^{-1} , we estimated field-scaled first-order rate coefficients (k_{field}) ranging from 0.070 to 2.8 yr^{-1} ($t_{1/2}$ from 0.25 to 9.9 years) (**Table S2**). These rates are comparable to both sediment microcosm rates and field rates that have been attributed to abiotic degradation.^{24,26} However, in nearly all of our experiments the amount of Fe(II) added exceeds typical concentrations of Fe(II) in groundwater (typically $< 50 \text{ mg/L}$ or 1 mM),⁴⁶⁻⁴⁹ making the precipitation of ferrous hydroxide unlikely to be relevant to field conditions. Furthermore, precipitation of ferrous hydroxide is unlikely in natural aquifers due the ubiquitous presence of carbonate, making siderite and ferrous hydroxy-carbonate species more likely candidates for Fe(II) precipitates. Our work does, however, highlight that active precipitation of reactive Fe(II) phases may be important in assessing abiotic natural attenuation.

The lack of compelling evidence for PCE and TCE reduction by magnetite raises important questions regarding whether magnetic susceptibility of aquifer sediments is a useful indicator for abiotic degradation of chlorinated ethenes by magnetite.²⁵ Recent work has suggested that *in situ* magnetic susceptibility measurements might be used along with chlorinated ethene concentration decreases in monitoring wells as a line of evidence for the occurrence of natural attenuation by sediment magnetite in an aquifer.²⁵ Our findings, however, suggest that magnetic susceptibility may not be a useful indicator for abiotic natural attenuation of chlorinated ethenes by reductive elimination. While magnetite and maghemite have magnetic susceptibilities of 2-3 orders of magnitude greater than the other Fe oxides, making magnetic susceptibility a reasonable proxy for sediment magnetite and/or maghemite content, the magnetic susceptibility of magnetite and fully-oxidized maghemite are within 20% of each other.⁵⁰ The similarity between maghemite and magnetite makes magnetic susceptibility measurements at the field level nearly insensitive to Fe redox speciation. Furthermore, the correlation shown in Weidemier et al.²⁵ between chlorinated ethene degradation and magnetic susceptibility is weak, with $r^2 = 0.18$ and a Spearman's rank-order correlation coefficient of 0.41 , making the correlation statistically non-significant at even a 90% confidence interval (critical $p = 0.49$).

Our work, together with the poor mechanistic and statistical correlation between magnetic susceptibility and abiotic chlorinated ethene reduction by magnetite suggests that further measurements are needed to link iron mineralogy to abiotic natural attenuation. Although our work suggests that magnetite is not likely to contribute significantly to abiotic degradation of PCE and TCE, there is substantial laboratory evidence that other Fe(II)-containing Fe minerals, such as mackinawite (FeS) and green rust, reduce chlorinated ethenes much faster (see reviews by He; Fan).^{24,51} The faster PCE and TCE reduction rates

for mackinawite and green rust suggest that reduction by these minerals may be an important degradation process in contaminated plumes. Indeed, sulfate amendments to induce biological formation of mackinawite in-situ has been demonstrated in the field and in the laboratory.⁵²⁻⁵⁶ Consistent with active precipitation of FeS being important for continued degradation of PCE and TCE in sulfate-reducing field sites,⁵⁴ it is possible that Fe(II) precipitation as Fe(OH)₂ and green rusts might occur in dynamic environments receiving a constant flux of Fe(II) from dissimilatory Fe reduction, or in zones where a change in pH occurs. We suggest that field screening methods for acid volatile sulfides targeting FeS⁵⁷ and citrate-bicarbonate (CB) extractable Fe targeting green rusts and labile Fe(II) phases^{58,59} might provide a measure of the potential for abiotic chlorinated ethene reduction by Fe(II) and sulfide minerals, although further study is needed. Zones of active Fe(II) precipitation in anoxic aquifer could result in PCE and TCE reduction that is sufficiently fast to help attenuate PCE and TCE plumes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research has been funded entirely with funds from the Strategic Environmental Research and Development Program – (SERDP) project ER-2532, and an NSF – GRFP to Johnathan Culpepper. The contents do not necessarily reflect the views and policies either of the sponsors nor does mention of trade names or commercial products that constitute endorsement or recommendation for use. The authors would like to thank Luiza Notini (University of Iowa) for designing the table of contents art.

Electronic Supplementary Information

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

References

1. Doherty, R. E., A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1, 1, 1-trichloroethane in the United States: Part 1--historical background; carbon tetrachloride and tetrachloroethylene. *Environmental forensics* **2000**, *1*, (2), 69-81.
2. Doherty, R. E., A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1, 1, 1-trichloroethane in the United States: part 2--trichloroethylene and 1, 1, 1-trichloroethane. *Environmental Forensics* **2000**, *1*, (2), 83-93.
3. Pankow, J. F.; Cherry, J. A., Dense chlorinated solvents and other DNAPLs in groundwater: History, behavior, and remediation. **1996**.
4. Kueper, B. H.; Stroo, H. F.; Vogel, C. M.; Ward, C. H., *Chlorinated solvent source zone remediation*. Springer: 2014.

- 500 5. Guyton, K. Z.; Hogan, K. A.; Scott, C. S.; Cooper, G. S.; Bale, A. S.; Kopylev, L.; Barone Jr, S.;
 501 Makris, S. L.; Glenn, B.; Subramaniam, R. P., Human health effects of tetrachloroethylene:
 502 key findings and scientific issues. *Environ. Health. Perspect.* **2014**, *122*, (4), 325.
- 503 6. Chiu, W. A.; Jinot, J.; Scott, C. S.; Makris, S. L.; Cooper, G. S.; Dzubow, R. C.; Bale, A. S.;
 504 Evans, M. V.; Guyton, K. Z.; Keshava, N., Human health effects of trichloroethylene: key
 505 findings and scientific issues. *Environ. Health. Perspect.* **2013**, *121*, (3), 303.
- 506 7. Lepom, P.; Brown, B.; Hanke, G.; Loos, R.; Quevauviller, P.; Wollgast, J., Needs for reliable
 507 analytical methods for monitoring chemical pollutants in surface water under the European
 508 Water Framework Directive. *J. Chromatogr. A* **2009**, *1216*, (3), 302-315.
- 509 8. Zogorski, J. S.; Carter, J. M.; Ivahnenko, T.; Lapham, W. W.; Moran, M. J.; Rowe, B. L.;
 510 Squillace, P. J.; Toccalino, P. L., Volatile organic compounds in the nation's ground water and
 511 drinking-water supply wells. *US Geological Survey Circular* **2006**, *1292*, 101.
- 512 9. Council, N. R., *Alternatives for managing the nation's complex contaminated*
 513 *groundwater sites*. National Academies Press: 2013.
- 514 10. Council, N. R., *Contaminants in the subsurface: Source zone assessment and*
 515 *remediation*. National Academies Press: 2005.
- 516 11. van der Zaan, B.; Hannes, F.; Hoekstra, N.; Rijnaarts, H.; de Vos, W. M.; Smidt, H.;
 517 Gerritse, J., Correlation of Dehalococcoides 16S rRNA and chloroethene-reductive
 518 dehalogenase genes with geochemical conditions in chloroethene-contaminated
 519 groundwater. *Appl. Environ. Microbiol.* **2010**, *76*, (3), 843-850.
- 520 12. Lee, P. K.; Macbeth, T. W.; Sorenson, K. S.; Deeb, R. A.; Alvarez-Cohen, L., Quantifying
 521 genes and transcripts to assess the in situ physiology of "Dehalococcoides" spp. in a
 522 trichloroethene-contaminated groundwater site. *Appl. Environ. Microbiol.* **2008**, *74*, (9),
 523 2728-2739.
- 524 13. Lu, X.; Wilson, J. T.; Kampbell, D. H., Relationship between Dehalococcoides DNA in
 525 ground water and rates of reductive dechlorination at field scale. *Water Res.* **2006**, *40*, (16),
 526 3131-3140.
- 527 14. Hendrickson, E. R.; Payne, J. A.; Young, R. M.; Starr, M. G.; Perry, M. P.; Fahnestock, S.;
 528 Ellis, D. E.; Ebersole, R. C., Molecular analysis of Dehalococcoides 16S ribosomal DNA from
 529 chloroethene-contaminated sites throughout North America and Europe. *Appl. Environ.*
 530 *Microbiol.* **2002**, *68*, (2), 485-495.
- 531 15. Damgaard, I.; Bjerg, P. L.; Bælum, J.; Scheutz, C.; Hunkeler, D.; Jacobsen, C. S.; Tuxen,
 532 N.; Broholm, M. M., Identification of chlorinated solvents degradation zones in clay till by
 533 high resolution chemical, microbial and compound specific isotope analysis. *J. Contam.*
 534 *Hydrol.* **2013**, *146*, 37-50.

- 535 16. Hunkeler, D.; Aravena, R.; Butler, B., Monitoring microbial dechlorination of
536 tetrachloroethene (PCE) in groundwater using compound-specific stable carbon isotope
537 ratios: microcosm and field studies. *Environ. Sci. Technol.* **1999**, *33*, (16), 2733-2738.
- 538 17. Mattes, T. E.; Alexander, A. K.; Coleman, N. V., Aerobic biodegradation of the
539 chloroethenes: pathways, enzymes, ecology, and evolution. *FEMS Microbiol. Rev.* **2010**, *34*,
540 (4), 445-475.
- 541 18. Findlay, M.; Smoler, D. F.; Fogel, S.; Mattes, T. E., Aerobic Vinyl Chloride Metabolism in
542 Groundwater Microcosms by Methanotrophic and Etheneotrophic Bacteria. *Environ. Sci.*
543 *Technol.* **2016**, *50*, (7), 3617-3625.
- 544 19. Bradley, P. M.; Landmeyer, J. E.; Dinicola, R. S., Anaerobic oxidation of [1, 2-¹⁴C]
545 dichloroethene under Mn (IV)-reducing conditions. *Appl. Environ. Microbiol.* **1998**, *64*, (4),
546 1560-1562.
- 547 20. Haderlein, S. B.; Pecher, K., Mediation of organic pollutant reduction by iron oxides.
548 *Abstr. Pap. Am. Chem. Soc.* **1997**, *213*, 129-GEOC.
- 549 21. Cwiertny, D. M.; Scherer, M. M., Abiotic Processes Affecting the Remediation of
550 Chlorinated Solvents. In *In Situ Remediation of Chlorinated Solvent Plumes*, Stroo, H. F.;
551 Ward, C. H., Eds. Springer New York: New York, NY, 2010; pp 69-108.
- 552 22. Vogel, T. M.; Criddle, C. S.; McCarty, P. L., Transformations of halogenated aliphatic
553 compounds. *Environ. Sci. Technol.* **1987**, *21*, (8), 722-736.
- 554 23. Kriegman-King, M. R.; Reinhard, M., Reduction of hexachloroethane and carbon
555 tetrachloride at surfaces of biotite, vermiculite, pyrite, and marcasite. In *Organic Substances*
556 *and Sediments in Water*, Baker, R., Ed. Lewis: MI, 1991; Vol. 2, pp 349-364.
- 557 24. He, Y. T.; Wilson, J. T.; Su, C.; Wilkin, R. T., Review of Abiotic Degradation of
558 Chlorinated Solvents by Reactive Iron Minerals in Aquifers. *Groundwater Monitoring &*
559 *Remediation* **2015**, *35*, (3), 57-75.
- 560 25. Wiedemeier, T. H.; Wilson, B. H.; Ferrey, M. L.; Wilson, J. T., Efficacy of an In-Well
561 Sonde to Determine Magnetic Susceptibility of Aquifer Sediment. *Groundwater Monitoring*
562 *& Remediation* **2017**, *37*, (2), 25-34.
- 563 26. Ferrey, M.; Wilkin, R.; Ford, R.; Wilson, J., Nonbiological removal of cis-
564 dichloroethylene and 1,1-dichloroethylene in aquifer sediment containing magnetite.
565 *Environ. Sci. Technol.* **2004**, *38*, (6), 1746-1752.
- 566 27. Lee, W.; Batchelor, B., Abiotic reductive dechlorination of chlorinated ethylenes by
567 iron-bearing soil minerals. 1. Pyrite and Magnetite. *Environ. Sci. Technol.* **2002**, *36*, (23),
568 5147-5154.

- 569 28. Sivavec, T. M.; Horney, D. P. In *Reduction of chlorinated solvents by Fe(II) minerals*,
 570 213th National Meeting, San Francisco, CA, 1997; American Chemical Society: San Francisco,
 571 CA, 1997; pp 115-117.
- 572 29. Liang, X. M.; Philp, R. P.; Butler, E. C., Kinetic and isotope analyses of
 573 tetrachloroethylene and trichloroethylene degradation by model Fe(II)-bearing minerals.
 574 *Chemosphere* **2009**, 75, (1), 63-69.
- 575 30. Pham, H. T.; Suto, K.; Inoue, C., Trichloroethylene Transformation in Aerobic Pyrite
 576 Suspension: Pathways and Kinetic Modeling. *Environ. Sci. Technol.* **2009**, 43, (17), 6744-
 577 6749.
- 578 31. Pham, H. T.; Kitsuneduka, M.; Hara, J.; Suto, K.; Inoue, C., Trichloroethylene
 579 transformation by natural mineral pyrite: The deciding role of oxygen. *Environ. Sci. Technol.*
 580 **2008**, 42, (19), 7470-7475.
- 581 32. Gorski, C. A.; Scherer, M. M., Determination of nanoparticulate magnetite
 582 stoichiometry by Mössbauer spectroscopy, acidic dissolution, and powder X-ray diffraction:
 583 A critical review. *Am. Mineral.* **2010**, 95, (7), 1017-1026.
- 584 33. Gorski, C. A.; Nurmi, J. T.; Tratnyek, P. G.; Hofstetter, T. B.; Scherer, M. M., Redox
 585 behavior of magnetite: Implications for contaminant reduction. *Environ. Sci. Technol.* **2009**,
 586 44, (1), 55-60.
- 587 34. Tamura, H.; Goto, K.; Yotsuyan.T; Nagayama, M., Spectrophotometric determination
 588 of iron(II) with 1,10-phenanthroline in presence of large amounts of iron(III). *Talanta* **1974**,
 589 21, (4), 314-318.
- 590 35. Lagarec, K.; Rancourt, D. G. *Recoil-Mössbauer spectral analysis software for Windows*,
 591 University of Ottawa, Ottawa, ON: 1998.
- 592 36. Latta, D. E.; Gorski, C. A.; Boyanov, M. I.; O'Loughlin, E. J.; Kemner, K. M.; Scherer, M.
 593 M., Influence of magnetite stoichiometry on U^{VI} reduction. *Environ. Sci. Technol.* **2012**, 46,
 594 (2), 778-786.
- 595 37. Gorski, C. A.; Nurmi, J. T.; Tratnyek, P. G.; Hofstetter, T. B.; Scherer, M. M., Redox
 596 behavior of magnetite: Implications for contaminant reduction. *Environ. Sci. Technol.* **2010**,
 597 44, (1), 55-60.
- 598 38. Pasakarnis, T. S.; Boyanov, M. I.; Kemner, K. M.; Mishra, B.; O'Loughlin, E. J.; Parkin, G.;
 599 Scherer, M. M., Influence of Chloride and Fe(II) Content on the Reduction of Hg(II) by
 600 Magnetite. *Environ. Sci. Technol.* **2013**, 47, (13), 6987-6994.
- 601 39. Brown, R. A.; Wilson, J. T.; Ferrey, M., Monitored natural attenuation forum: The case
 602 for abiotic MNA. *Remediation Journal* **2007**, 17, (2), 127-137.
- 603 40. Sivavec, T. M. Composition and method for ground water remediation. U.S. Patent
 604 5,750,036, May 12, 1998.

- 605 41. Arnold, W. A.; Roberts, A. L., Pathways and kinetics of chlorinated ethylene and
 606 chlorinated acetylene reaction with Fe(0) particles. *Environ. Sci. Technol.* **2000**, *34*, (9), 1794-
 607 1805.
- 608 42. Gustafsson, J. P. *Visual MINTEQ*, 3.0; 2011.
- 609 43. Bohnsack, G., Löslichkeit und thermodynamische Daten von Eisen(II)-Hydroxid durch
 610 analytische Bestimmung des Eisens und Leitfähigkeitsmessung im System Eisen-Wasser.
 611 *Berichte der Bunsengesellschaft für physikalische Chemie* **1988**, *92*, (7), 797-802.
- 612 44. Sawyer, C. N.; McCarty, P. L.; Parkin, G. F., Chemistry for environmental engineering
 613 and science. **2016**.
- 614 45. Lee, W.; Batchelor, B., Abiotic reductive dechlorination of chlorinated ethylenes by
 615 iron bearing soil minerals. 2. green rust. *Environ. Sci. Technol.* **2002**, *36*, (24), 5348-5354.
- 616 46. Litten, G. R., Quality of ground water used for selected municipal water supplies in
 617 Iowa, 1997-2002 water years: USGS Open File Report 2004-1048. In USGS, Ed. 2004; p 36.
- 618 47. Postma, D.; Boesen, C.; Kristiansen, H.; Larsen, F., Nitrate reduction in an unconfined
 619 sandy aquifer: water chemistry, reduction processes, and geochemical modeling. *Water*
 620 *Resour. Res.* **1991**, *27*, (8), 2027-2045.
- 621 48. Erickson, M. L.; Barnes, R. J., Glacial sediment causing regional-scale elevated arsenic
 622 in drinking water. *Groundwater* **2005**, *43*, (6), 796-805.
- 623 49. Anawar, H. M.; Akai, J.; Komaki, K.; Terao, H.; Yoshioka, T.; Ishizuka, T.; Safiullah, S.;
 624 Kato, K., Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and
 625 mobilization processes. *J. Geochem. Explor.* **2003**, *77*, (2-3), 109-131.
- 626 50. Mullins, C., Magnetic susceptibility of the soil and its significance in soil science—a
 627 review. *Eur. J. Soil Sci.* **1977**, *28*, (2), 223-246.
- 628 51. Fan, D.; Bradley, M. J.; Hinkle, A. W.; Johnson, R. L.; Tratnyek, P. G., Chemical
 629 Reactivity Probes for Assessing Abiotic Natural Attenuation by Reducing Iron Minerals.
 630 *Environ. Sci. Technol.* **2016**, *50*, (4), 1868-1876.
- 631 52. Kennedy, L. G.; Everett, J. W.; Gonzales, J., Assessment of biogeochemical natural
 632 attenuation and treatment of chlorinated solvents, Altus Air Force Base, Althus, Oklahoma.
 633 *J. Contam. Hydrol.* **2006**, *83*, 221-236.
- 634 53. Kennedy, L. G.; Everett, J. W.; Becvar, E.; DeFeo, D., Field-scale demonstration of
 635 induced biogeochemical reductive dechlorination at Dover Air Force Base, Dover, Delaware.
 636 *J. Contam. Hydrol.* **2006**, *88*, 119-136.
- 637 54. He, Y. T.; Wilson, J. T.; Wilkin, R. T., Transformation of reactive iron minerals in a
 638 permeable reactive barrier (biowall) used to treat TCE in groundwater. *Environ. Sci. Technol.*
 639 **2008**, *42*, (17), 6690-6696.

55. Whiting, K.; Evans, P. J.; Lebrón, C.; Henry, B.; Wilson, J. T.; Becvar, E., Factors controlling in situ biogeochemical transformation of trichloroethene: Field survey. *Groundwater Monitoring & Remediation* **2014**, *34*, (3), 79-94.
56. Evans, P. J.; Nguyen, D.; Chappell, R. W.; Whiting, K.; Gillette, J.; Bodour, A.; Wilson, J. T., Factors controlling in situ biogeochemical transformation of trichloroethene: Column study. *Groundwater Monitoring & Remediation* **2014**, *34*, (3), 65-78.
57. Simpson, S. L., A rapid screening method for acid-volatile sulfide in sediments. *Environ. Toxicol. Chem.* **2001**, *20*, (12), 2657-2661.
58. Trolard, F.; Bourrie, G.; Jeanroy, E.; Herbillon, A. J.; Martin, H., Trace-Metals in Natural Iron-Oxides from Laterites - a Study Using Selective Kinetic Extraction. *Geochim. Cosmochim. Acta* **1995**, *59*, (7), 1285-1297.
59. Latta, D. E.; Boyanov, M. I.; Kemner, K. M.; O'Loughlin, E. J.; Scherer, M. M., Abiotic reduction of uranium by Fe(II) in soil. *Appl. Geochem.* **2012**, *27*, (8), 1512-1524.

Table of Contents Artwork

Magnetite is unlikely to be as important as previously thought for abiotic reduction of PCE and TCE in groundwater plumes.

Supporting Information

Reduction of PCE and TCE by Magnetite Revisited

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Analytical methods for chlorinated ethenes and reduction products

PCE and TCE were quantified with GC-ECD after a liquid-liquid extraction of 0.25 to 1 mL of sample containing both the aqueous and solid phases added to 2 mL of hexanes. The ECD column was a Supelco Equity-5 (0.25 mm diameter x 30 m length, 0.5 μ m film thickness). The carrier gas was nitrogen at a constant total flow velocities of 1.0 mL/min and a 10:1 inlet split ratio. The detector make-up gas was 95% Argon: 5% methane with flow of 30 mL/min. The oven was programmed for an initial hold of 1 min at 45 °C, then 10 °C/min to 200 °C. The ECD method detection limits are 0.05 μ moles/L PCE and 0.02 μ moles/L TCE for ($n = 15$).

The daughter products ethane, ethylene, acetylene, the dichloroethenes, and vinyl chloride were detected using a GC-FID. The column used was an Agilent GS-GasPro column (0.320 mm diameter x 30 m length). The carrier gas was nitrogen at a constant total flow of 1.4 mL/min and 7.5:1 inlet split ratio. The detector air flow was 450 mL/min, hydrogen flow 40 mL/min, and make-up gas type was nitrogen and a combined flow rate of 35 mL/min. The oven was set for an isothermal run of 4.5 min at 70 °C. The C₂ gas analysis was done with 100 μ L headspace injections into the column. The detection limits for the FID method are 1.35 μ moles/L ethane, 1.36 μ moles/L ethylene and 1.34 μ moles/L acetylene for ($n = 10$). Products with carbon number >C₂ were not analyzed in this study. We used Henry's law and the specific dimensionless coefficient H^{cc} to calculate dissolved C₂ gases and headspace PCE and TCE.¹ The averaged values for the H^{cc} are as follows: PCE = 1.54, TCE = 2.447, Ethane = 0.0471, and Ethylene = 0.146 and Acetylene = 1.016.¹

Calculation of k_{field} and $t_{1/2-field}$

In order to estimate field rates for PCE and TCE reduction, we have calculated a k_{field} value (in yr⁻¹) following a scheme used in Wiedemeier et al.² In that study, the authors used magnetic susceptibility data to calculate the amount of magnetite in their field samples. They used a value for the magnetic susceptibility of their field sediments of 4×10^{-8} m³/kg. They then used this value to derive the amount of magnetite per kg of aquifer material based on the magnetic susceptibility of magnetite (1.117×10^{-3} m³/kg), the density of magnetite (5,170 kg/m³), and the bulk density of an aquifer sediment (1,700 kg/m³). Based on this calculation, estimated magnetite concentrations were ~0.1 g magnetite/kg sediment. The maximum magnetic susceptibility that they report in their paper is $\sim 1 \times 10^{-6}$ m³/kg. Based on their magnetic susceptibility data, one could expect masses of magnetite from 0.1 g to 10 g/kg.

Using this value, we calculated the in-aquifer 1st order decay constant ($k_{aquifer}$) based on our rate constant for PCE and TCE degradation:

For example, the average k_{SA} for our pH ~8.0, 5 g/L magnetite, ~10 mM Fe(II) experiments is:
 $k_{SA} = k_{obs}/SA = 1.9 \times 10^{-8} \text{ s}^{-1}/(5 \text{ g/L} \cdot 60 \text{ m}^2/\text{g}) \cdot 3.1536 \times 10^7 \text{ s/year} = 2.0 \times 10^{-3} \text{ L m}^{-2} \text{ yr}^{-1}$

Assuming $\rho_{bulk} = 1700 \text{ kg/m}^3$, effective porosity: $\eta_e = 0.2$, that the aquifer magnetite specific surface area is consistent with that used in our study (SSA ~ 60 m²/g), and 1 g magnetite/kg sediment (m_{mag}):

$$k_{field} = \frac{m_{mag} \cdot \rho_{bulk} \cdot SSA_{mag} \cdot k_{SA}}{\eta_e} \times \frac{1m^3}{1000 L}$$

$$k_{field} = 1 \frac{\text{g magnetite}}{\text{kg sediment}} \times 1,700 \frac{\text{kg sediment}}{\text{m}^3} \times 60 \frac{\text{m}^2}{\text{g}} \times \frac{1}{0.2} \frac{\text{m}^3 \text{ sediment}}{\text{m}^3 \text{ groundwater}} \times 2.0 \times 10^{-3} \frac{\text{L}}{\text{m}^2 \cdot \text{yr}} \times \frac{1m^3}{1000 L} = 1.0 \text{ yr}^{-1}$$

We estimate $k_{field} = 1.0 \text{ yr}^{-1}$. Which gives a half-life of $\ln(2)/1 = 0.69$ year.

Table S1. PCE/TCE with Magnetite alone

[C] _o (μM) ^a	pH	Mass loading (g/L)	Stoichiometry			% loss ^b	% Products ^b	% C recovery ^b	Duration (days) ^b
			<i>x</i> _{ms}	<i>x</i> _d	<i>x</i> _{XRD}				
PCE									
~50 ^c	7.5	5	0.50	0.55 ± 0.02	0.53	7.0	0	88	139
~50 ^c	7.5	5	0.50	0.55 ± 0.02	0.53	7.0	0	97	139
~50 ^c	7.5	5	0.50	0.55 ± 0.02	0.53	6.9	0	101	105
~50 ^c	7.5	5	0.50	0.55 ± 0.02	0.53	6.87	0	96	105
~50 ^c	7.5	5	0.50	0.55 ± 0.02	0.53	6.87	0	106	105
TCE									
48	7.0	10	0.46	0.5 ± 0.02	n.d. ^d	-10.7	0	111	91
52	7.5	5	0.50	0.55 ± 0.02	0.53	9.9	0	93	56
45	7.5	20	0.46	0.5 ± 0.02	n.d.	-6.3	0	106	140
49	8.0	10	0.45	0.5 ± 0.02	n.d.	-7.8	0	111	91
56 ^e	8.0	5	0.50	n.d. ^d	0.52	-2.3 ^e	0	102 ^e	142 ^e
PCE Control ^e									
55	7.5	0	-	-	-	30	0	70	172
TCE Control ^e									
55	7.5	0	-	-	-	29	0	71	135

^a [C]_o is the initial concentration of the analyte spiked within reactor.

^b % products, % analyte loss, and % C recovery are evaluated at the final reported time point.

^c ~50 is the nominal concentration of PCE or TCE added. Calculations in ^b are based on nominal concentrations.

^d n.d. measurement not determined.

^e Averages of triplicate reactors.

TABLE S2. PCE/TCE Magnetite + aqueous Fe(II) reactors with products.

[CE] ₀ ^a μM	pH	Solids loading (g/L)	[Fe(II)] ₀ mM ^b	Saturation Index ^c	[Fe(II)] _f mM ^b	Stoichiometry		% loss ^f	% products ^f	% C recovery ^f	Duration (days)	<i>k</i> _{obs} <i>s</i> ⁻¹	<i>k</i> _{SA} <i>L m</i> ⁻² <i>d</i> ⁻¹	<i>k</i> _{field} ^h <i>yr</i> ⁻¹	<i>t</i> _{1/2 field} <i>years</i>
						<i>x</i> _d ^d	<i>x</i> _{xrd} ^e								
PCE															
53.7	7.9	5	32.9	0.66	29.7	0.52 ± 0.03	0.50	28	6	78	125	6.1 × 10 ⁻⁹	1.8 × 10 ⁻⁶	0.33	2.1
54.0	8.0	5	0.93	-0.72	n.d. ^g	0.54 ± 0.03	0.51	18	3	85	140	2.9 × 10 ⁻⁹	8.4 × 10 ⁻⁷	0.16	4.5
50.1	8.5	5	32.0	1.81	3.60	0.52 ± 0.03	0.50	40	16	76	125	1.7 × 10 ⁻⁸	4.9 × 10 ⁻⁶	0.91	0.76
55.3	8.6	5	7.58	1.30	1.61	0.52 ± 0.03	0.50	41	13	72	125	1.3 × 10 ⁻⁸	3.7 × 10 ⁻⁶	0.70	0.99
53.1	9.0	5	0.86	1.24	n.d.	0.54 ± 0.03	0.51	32	12	80	140	1.0 × 10 ⁻⁸	2.9 × 10 ⁻⁶	0.54	1.3
53.3	9.3	5	7.71	2.71	0.71	0.52 ± 0.03	0.50	32	10	77	125	9.6 × 10 ⁻⁹	2.8 × 10 ⁻⁶	0.52	1.3
45.8	9.4	5	31.4	3.64	3.86	0.52 ± 0.03	0.50	41	15	74	125	1.6 × 10 ⁻⁸	4.6 × 10 ⁻⁶	0.86	0.81
TCE															
55.3	8.0	5	0.82	-0.80	n.d.	0.54 ± 0.03	0.51	28	11	83	139	9.6 × 10 ⁻⁹	2.8 × 10 ⁻⁶	0.97	0.72
50.8	8.0	5	8.23	0.30	4.85	0.53 ± 0.01	0.48	24	24	99	167	1.8 × 10 ⁻⁸	5.2× 10 ⁻⁶	1.3	0.52
51.6	8.0	5	8.54	0.31	4.23	0.53 ± 0.01	0.48	27	28	101	167	2.1 × 10 ⁻⁸	6.1× 10 ⁻⁶	1.1	0.62
51.1	7.9	5	9.19	0.15	4.13	0.53 ± 0.01	0.48	26	18	93	167	1.4 × 10 ⁻⁸	4.0× 10 ⁻⁶	1.2	0.59
49.7	8.0	5	9.19	0.26	5.09	0.53 ± 0.01	0.48	14	24	110	167	1.8 × 10 ⁻⁸	5.2 × 10 ⁻⁶	0.80	0.86
51.1	8.0	5	9.24	0.29	4.34	0.53 ± 0.01	0.48	31	30	99	167	2.5 × 10 ⁻⁸	7.2 × 10 ⁻⁶	0.86	0.81
49.7	8.0	5	9.24	0.27	5.2	0.53 ± 0.01	0.48	29	26	97	167	2.1 × 10 ⁻⁸	6.0 × 10 ⁻⁶	0.75	0.92
50.1	8.0	5	9.42	0.27	5.23	0.53 ± 0.01	0.48	28	30	102	167	2.2 × 10 ⁻⁸	6.3 × 10 ⁻⁶	0.86	0.81
49.8	8.0	5	9.49	0.28	5.48	0.53 ± 0.01	0.48	25	24	99	167	1.5 × 10 ⁻⁸	4.3 × 10 ⁻⁶	2.8	0.25
49.3	8.0	5	9.50	0.28	5.36	0.53 ± 0.01	0.48	22	24	102	167	1.6 × 10 ⁻⁸	4.6 × 10 ⁻⁶	0.97	0.72
50.5	8.0	5	9.52	0.28	4.98	0.53 ± 0.01	0.48	25	19	94	167	1.4 × 10 ⁻⁸	4.0 × 10 ⁻⁶	0.070	9.9
51.1	8.0	5	9.52	0.29	4.18	0.53 ± 0.01	0.48	24	20	97	167	1.6 × 10 ⁻⁸	4.6 × 10 ⁻⁶	0.31	2.3
54	8.0	5	10.0	0.30	n.d.	0.48 ± 0.03	0.56	75	46	71	168	5.2 × 10 ⁻⁸	1.5 × 10 ⁻⁵	0.091	7.6
51.2	8.0	5	10.69	0.41	4.57	0.53 ± 0.01	0.48	27	26	99	167	1.8 × 10 ⁻⁸	5.2 × 10 ⁻⁶	0.49	1.4
61.2	8.0	5	11.2	0.35	n.d.	0.48 ± 0.03	0.56	10	5	94	287	1.3 × 10 ⁻⁹	3.7 × 10 ⁻⁷	0.11	6.2
49.5	7.9	5	31.2	0.64	19.56	0.48 ± 0.03	0.45	-0.8	3	103	69	5.7 × 10 ⁻⁹	1.6 × 10 ⁻⁶	0.19	3.7
69.3	8.4	5	13.1	1.22	n.d.	0.48 ± 0.03	0.56	22	5	83	287	1.7 × 10 ⁻⁹	4.9 × 10 ⁻⁷	0.14	5.0
53.9	8.5	5	0.67	0.13	n.d.	0.54± 0.03	0.51	25	11	85	139	9.1 × 10 ⁻⁹	2.6 × 10 ⁻⁶	0.21	3.2
51.1	8.5	5	7.55	1.18	4.18	0.48 ± 0.03	0.45	5	2	97	125	2.1 × 10 ⁻⁹	6.0 × 10 ⁻⁷	0.97	0.72
51.5	8.6	5	32.9	1.94	3.50	0.48 ± 0.03	0.45	4.5	4	99	125	3.5 × 10 ⁻⁹	1.0 × 10 ⁻⁶	1.3	0.52
54.2	9.0	5	7.83	2.24	0.58	0.48 ± 0.03	0.45	13	3	90	125	2.6 × 10 ⁻⁹	7.5 × 10 ⁻⁷	1.1	0.62
52.2	9.1	5	30.9	3.07	1.87	0.48 ± 0.03	0.45	11	4	93	125	4.0 × 10 ⁻⁹	1.2 × 10 ⁻⁶	1.2	0.59

^a [CE]₀ = Initial chloroethylene concentration

^b [Fe(II)]_{0,f} = initial or final Fe(II) concentration, respectively

^c Saturation index = log(IAP/K_{sp}). The ion activity product (IAP) was determined with initial Fe(II) concentration and pH for each experiment. K_{sp} = [Fe²⁺] [OH⁻]² = 5 × 10⁻¹⁵.

^d *x*_d = Magnetite Fe(II)/Fe(III) ratio from dissolution

^e *x*_{xrd} = Magnetite Fe(II)/Fe(III) ratio from x-ray diffraction.

^f % PCE or TCE loss, % Products and % Carbon recovery are taken from the final reported time point.

^g (n.d.) indicates not determined.

^h *k*_{aquifer} calculated with the assumptions: sediment magnetite content = 1 g/kg, ρ_{bulk} = 1700 kg/m³, effective porosity: η_e = 0.2, that the aquifer magnetite specific surface area is 60 m²/g.

TABLE S3. PCE/TCE with Magnetite + aqueous Fe(II) reactors without products.

[C] ₀ ^a (μM)	pH	Mass loading (g/L)	[Fe(II)] ₀ ^b (mM)	Saturation Index ^c	Stoichiometry		% loss ^f	% products ^f	% C recovery ^f	Duration (day)
					<i>x</i> _d ^d	<i>x</i> _{xrd} ^e				
PCE										
51.7	7.5	5	0.88	-1.7	0.54 ± 0.03	0.51	26	0	74	140
~50	7.5	5	2.7	-1.3	0.55 ± 0.02	0.53	10	0	90	78
~50	7.5	5	4.6	-1.0	0.39 ± 0.03	0.54	2.8	0	97	78
65	7.5	17	10.0	-0.70	0.50 ± 0.06	n.d. ^g	-24.5	0	125	91
~70	7.5	17	25.0	-0.30	0.50 ± 0.06	n.d.	-14.5	0	115	91
48.9	8.0	5	7.47	0.21	0.52 ± 0.03	0.5	6.4	0	96	125
TCE										
22 ^h	6.1	147	201 ^h	-2.0	0.43	n.d.	3.8	0	96	104
51	7.5	20	10.0	-0.70	0.50 ± 0.06	n.d.	4.0	0	96	128
50.5	7.5	20	25.0	-0.30	0.50 ± 0.06	n.d.	-2.0	0	102	128
55.2	8.1	5	8.11	0.45	0.48± 0.03	0.45	6	0	94	195
55.9	7.5	5	0.92	-1.7	0.54 ± 0.03	0.51	26	0	74	139

* The magnetite Fe₃O₄ mineral used in the reactor was freshly precipitated and not freeze dried.

^a [C]₀ = Initial chloroethylene concentration

^b [Fe(II)]₀ = initial Fe(II) concentration, respectively

^c Saturation index = log(IAP/K_{sp}). The ion activity product (**IAP**) was determined with initial Fe(II) concentration and pH for each experiment. $K_{sp} = [Fe^{2+}] [OH^-]^2 = 5 \times 10^{-15}$.³

^d x_d = Magnetite Fe(II)/Fe(III) ratio from dissolution

^e x_{xrd} = Magnetite Fe(II)/Fe(III) ratio from x-ray diffraction.

^f % **PCE or TCE loss**, % **Products** and % **Carbon recovery** are taken from the final reported time point.

^g (**n.d.**) indicates not determined.

^h 22 g of a mixture of freeze dried magnetite with the stoichiometry determined by a weighted average.

Figure S1. Photographs of reactors containing 5 g/L magnetite reacted with low Fe(II) (~1 mM, left) and high Fe(II) (~10 mM, right). The solids on the right contain white $\text{Fe}(\text{OH})_2(\text{s})$. Conditions: 10 mM MOPS buffer at pH 8.0, and 50 μM TCE.

Figure S2. X-ray diffraction pattern of a TCE reactor with magnetite and Fe(II) where 30.0% products were observed after 167 days. Blue bars indicate ferrous hydroxide and black bars indicate magnetite. The background at $2\theta < 60^\circ$ is from the Kapton film used to seal the sample from air. Experimental conditions: 51 μ M TCE, 10 mM MOPs/NaCl, 9.2 mM Fe(II), pH 8.0.

Figure S3. TCE reduction (or lack thereof) as reported in the Sivavec patent⁴ and our attempt to reproduce the data under similar conditions. **Sivavec:**⁴ 7.0 μM TCE, 217 g/L Fe_3O_4 (s), 200 mM Fe(II), pH 6.0. **This study:** 22 μM TCE, 147 g/L Fe_3O_4 (s), 201 ± 12 mM Fe(II), 10 mM MOPs/NaCl, pH 6.1

Table S4. PCE/TCE with aqueous Fe(II) alone and no products

[C] ₀ ^a (μM)	pH	[Fe(II)] ₀ ^b (mM)	Saturation Index ^c	[Fe(II)] _f ^b (mM)	% loss ^d	% products ^d	% C recovery _d	Duration (day)
PCE								
58.2	7.0	0.3	-3.0	0.16	20	0	80	138
55.2	7.0	1.03	-2.7	1.08	29.6	0	82	134
53.3	7.0	7.79	-1.8	7.52	19.1	0	81	117
50.2	7.0	27.41	-1.3	n.d. ^e	16	0	84	140
56.1	7.5	1.03	-1.6	1.06	20.4	0	70.4	134
51.2	7.5	7.52	-0.78	7.17	17.7	0	82	117
49.2	7.5	13.52	-0.52	n.d.	13	0	87	140
50.3	7.5	27.32	-0.28	n.d.	14	0	78	140
56.3	7.6	0.21	-2.3	0.21	26.1	0	74	138
57.2	8.0	1.03	-0.62	1.04	16.4	0	80	134
57	8.1	0.2	-1.2	0.18	21.9	0	78	138
53.6	8.5	1.01	0.35	1.02	16.4	0	84	134
59.1	8.6	0.23	-0.22	0.2	8.5	0	92	138
51.4	8.6	7.67	1.3	1.56	15.9	0	84	117
57	9.1	0.28	0.93	0.14	19	0	81	138
52.7	9.1	1.07	1.4	0.37	15.6	0	85	134
55.7	9.2	7.58	2.5	1.15	25.2	0	75	117
TCE								
49.4	7.0	6.71	-1.9	8.08	1	0	99	117
54.1	7.0	26.54	-1.3	n.d.	21	0	79	140
51.9	7.1	0.34	-3.0	0.33	1	0	99	138
53.3	7.1	1.06	-2.5	1.02	4.1	0	96	134
53.5	7.5	1.04	-1.6	1.08	4.1	0	96	134
52.6	7.5	13.13	-0.59	n.d.	14	0	86	140
56.9	7.5	28.16	-0.25	n.d.	16	0	84	140
53	7.6	0.23	-2.2	0.2	2.4	0	98	138
51.1	7.6	7.59	-0.70	7.64	1	0	99	117
51.7	8.0	1.01	-0.71	1.06	2.2	0	98	134
66.3	8.0	9.84	0.29	n.d.	23.5	0	77	75
152.9	8.0	9.9	0.30	n.d.	-36.6	0	33.2	75
~50 ^f	8.0	10.27	0.31	n.d.	2.3	0	98	75
~50 ^f	8.0	11.54	0.36	n.d.	3.1	0	97	75
79.9	8.0	11.64	0.37	n.d.	35	0	65	75
~50 ^f	8.0	11.79	0.37	n.d.	6.3	0	94	75
52.5	8.1	0.2	-1.2	0.24	11.1	0	89	138
53.5	8.1	7.71	0.21	6.27	5.5	0	95	117
53.8	8.5	0.16	-0.43	0.25	4.5	0	96	138
52.7	8.5	1.03	0.35	1	2.7	0	97	134
52.8	8.5	7.48	1.2	1.99	6.5	0	94	117
52.1	9.0	0.21	0.55	0.16	1.1	0	99	138
53.9	9.1	1.04	1.4	0.46	6.3	0	94	134
52	9.1	7.23	2.3	0.88	2.7	0	97	117

^a [C]₀ = Initial chloroethylene concentration

^b [Fe(II)]_{0,f} = initial or final Fe(II) concentration, respectively

^c Saturation index = log(IAP/K_{sp}). The ion activity product (**IAP**) was determined with initial Fe(II) concentration and pH for each experiment. $K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 5 \times 10^{-15}$.³

^d % **PCE or TCE loss**, % **Products** and % **Carbon recovery** are taken from the final reported time point.

^e (**n.d.**) indicates not determined.

^f First time point determined was not at time zero, and thus the [C]₀ is reported as a nominal concentration.

Table S5. PCE/TCE with aqueous Fe(II) alone, with products

[C] ₀ ^a (μM)	pH	[Fe(II)] ₀ ^b (mM)	Saturation Index ^c	[Fe(II)] _f ^b (mM)	% loss ^d	% products ^d	% C recovery ^d	Duration (day)	<i>k_{obs}</i> (s ⁻¹)
PCE									
50.2	8.0	31.7	0.80	1.99	27.6	2.7	75	193	1.7×10^{-9}
54.0	8.1	36.80	1.1	33.99	23.3	1.1	77	156	8.5×10^{-10}
52.7	8.5	~13.34	1.4	n.d. ^e	14	1.0	86	140	1.3×10^{-8}
54.0	8.6	28.52	1.9	1.39	39.0	0.3	61	188	1.8×10^{-10}
51.2	9.0	~13.34	2.4	n.d.	19	1.0	74	140	1.8×10^{-8}
44.4	9.0	28.00	2.7	0.63	11.9	2.0	90	188	4.8×10^{-10}
TCE									
196.9	8.0	31.62	0.80	9.39	-21.5	3.8	125	193	2.3×10^{-9}
58.9	8.0	31.98	0.81	15.19	26.6	9	82	193	5.6×10^{-9}
52.6	8.1	35.66	0.95	33.9	7	8	100.6	156	2.5×10^{-9}
50.2	8.5	28.26	1.8	1.73	5	7.2	102	193	4.3×10^{-9}
50.9	8.5	29.21	1.8	1.57	-7.9	1.2	109	193	6.6×10^{-10}
56.2	8.5	~13.34	1.4	n.d.	29	6	75	140	3.0×10^{-9}
51	8.9	28.55	2.6	0.46	7.4	9	102	193	5.7×10^{-9}
55.6	9.0	~13.34	2.4	n.d.	24	7	83	140	5.7×10^{-9}
51.5	9.2	28.08	3.1	0.33	23.3	13	90	193	7.7×10^{-9}

^a [C]₀ = Initial chloroethylene concentration

^b [Fe(II)]₀ = initial Fe(II) concentration

^c Saturation index = log(IAP/K_{sp}). The ion activity product (**IAP**) was determined with initial Fe(II) concentration and pH for each experiment. $K_{sp} = [\text{Fe}^{2+}] [\text{OH}^-]^2 = 5 \times 10^{-15}$.³

^d % **PCE or TCE loss**, % **Products** and % **Carbon recovery** are taken from the final reported time point. Negative loss numbers indicate higher measured TCE concentrations at the final time point than the initial time point.

^e n.d. = not determined.

Figure S4. X-ray diffraction pattern of a TCE reactor with Fe(II) alone after 193 days where 9.0% products were observed. Light green bars indicate ferrous hydroxide. The background before 60° 2θ is due to Kapton film used to seal the sample from air. Experimental conditions: 60 μ M TCE, 10 mM MOPs/NaCl, 32 mM Fe(II), pH 8.0.

Figure S5. Mössbauer spectrum of the white precipitate in Fe(II) alone reactors after reacting with 60 μ M TCE, 10 mM MOPs/NaCl, pH 8.0 for 193 days where 9.0% products were observed. Note: 32 mM Fe(II) was the initial concentration of dissolved iron added.

References

1. Sander, R., Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics* **2015**, *15*, (8), 4399-4981.
2. Wiedemeier, T. H.; Wilson, B. H.; Ferrey, M. L.; Wilson, J. T., Efficacy of an In-Well Sonde to Determine Magnetic Susceptibility of Aquifer Sediment. *Groundwater Monitoring & Remediation* **2017**, *37*, (2), 25-34.
3. Sawyer, C. N.; McCarty, P. L.; Parkin, G. F., Chemistry for environmental engineering and science. In 5th ed.; McGraw-Hill: New York, 2003.
4. Sivavec, T. M. Composition and method for ground water remediation. U.S. Patent 5,750,036, May 12, 1998.