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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, $Fe(OH)_2(s)$. 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 $Fe(OH)_2(s)$ alone and found that, compared to in the presence of magnetite, $Fe(OH)_2(s)$ 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 $Fe(OH)_2(s)$ 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.

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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 (Fe_3O_4), a common mixed-valent Fe mineral, has been suggested to be responsible for chlorinated ethene attenuation at some field sites[24-26] 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 (FeS_2) 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, ≥ 99%) and trichloroethylene (TCE, ≥ 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 ≥ 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 $m^2\ g^{-1}$ 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-phenathroline 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 ^{57}Co source. Unless otherwise noted, Mössbauer spectra were collected at 140 K. Spectra were fit using the Recoil software[35] 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 N_2/H_2 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 $FeCl_2$ 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 ($x = Fe^{2+}/Fe^{3+} \approx 0.5$) 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 ± 8% for $n = 7$; PCE: 98 ± 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.

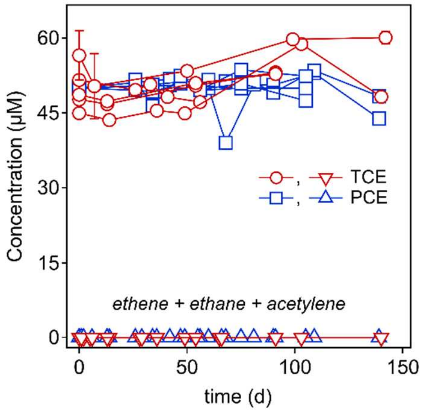

Fig. 1. PCE and TCE concentration versus time in the presence of stoichiometric magnetite ($x = Fe^{2+}/Fe^{3+}$ = 0.46 – 0.50). Experimental conditions: 50 µM PCE/TCE, 10 mM MOPs/NaCl at pH 7.0, 7.5, and 8.0 for TCE reactors and pH 7.5 for PCE reactors, mass loading 5 - 20 g/L. Average carbon recoveries,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

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 4.5×10^{-4} L m^{-2} d^{-1} (half-life of 19 days),[28] more recent studies[26-29] reported about 100-fold slower rates ($k_{SA} \approx 10^{-6}$ L m^{-2} d^{-1}) than those in Sivavec and Horney.[28] . In addition, carbon reduction products were only reported in one study[29], 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 products[28] 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 ~ 1 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]

Nevertheless, this work[26] 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 ± 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.

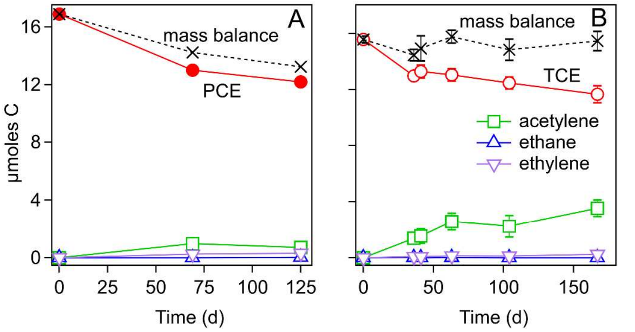

Fig. 2. Reduction of (A) PCE and (B) TCE over time with magnetite and aqueous Fe(II). Experimental conditions: (A) 54 µM PCE, 5 g/L Fe_3O_4 (s), 33 mM Fe(II), 10 mM MOPs/NaCl, pH 7.9, single reactor. (B) 50 µM TCE, 5 g/L Fe_3O_4 (s), 9.3 ± 0.6 mM Fe(II), 10 mM MOPs/NaCl, pH 8, for *n* from 3 to 12.

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 products (in µmoles C) at time t,

C_0 is the initial PCE or TCE amount (in µmoles 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}.

$$P(t) = C_0\left(1 - e^{-k_{obs} \cdot t}\right) \qquad (1)$$

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

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 5.2×10^{-8} 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 (~ pH 8 and ~ 10 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 ($k_{obs} > 0$), 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, $Fe(OH)_2(s)$, which was confirmed by X-ray diffraction of the filtered reactor solids (**Figure S2**).

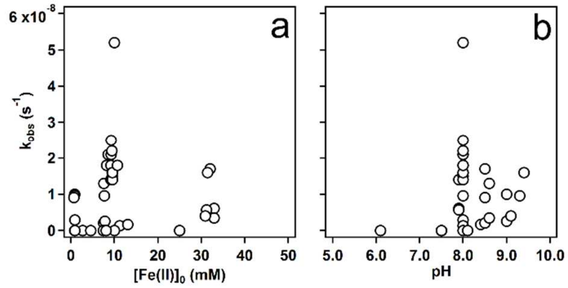

Fig. 3. Plots of k_{obs} for PCE and TCE reduction as a function of $[Fe(II)]_0$ (initial Fe(II) concentration) (a) and pH (b

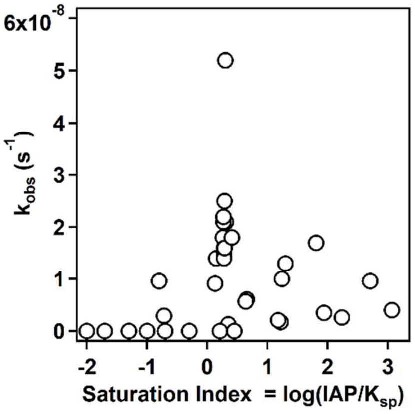

Fig. 4. Plot of k_{obs} for PCE and TCE reduction vs. the $Fe(OH)_2(s)$ initial saturation index (<0 undersaturated, 0 at saturation, >0 oversaturated).

To quantitatively evaluate if $Fe(OH)_2(s)$ precipitation was necessary for PCE and TCE reduction, we plotted k_{obs} values versus the saturation index (SI) for $Fe(OH)_2(s)$ (**Figure 4**). We calculated the SI as $\log(IAP/K_{sp})$ using the initial Fe(II) concentration and an $Fe(OH)_2(s)$ 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 occurs under experimental conditions that are saturated (or super-saturated) with respect to $Fe(OH)_2(s)$ based on the amount of Fe(II) added and the pH value the reactor was set at. We note that after precipitation of $Fe(OH)_2$, 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.

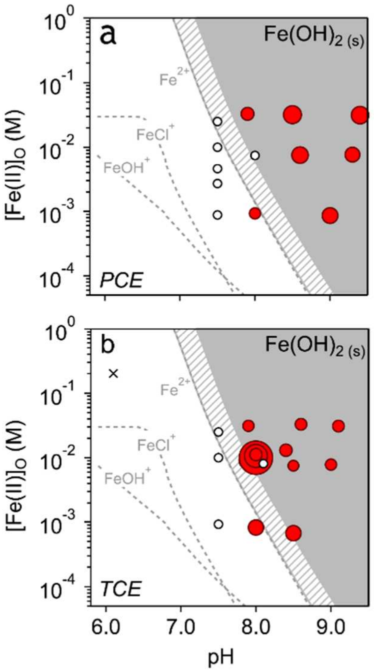

Fig. 5. $Fe(OH)_2(s)$ solubility diagram with magnetite plus Fe(II) reactor conditions overlaid for (a) PCE and (b) TCE reactors. Fe(II) is plotted as the initial Fe(II) concentration – $[Fe(II)]_0$. Red markers represent PCE and TCE reactors where carbon products were observed and the markers are scaled 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 Ksp ($[Fe(OH)_2(s)] = [Fe^{2+}] [OH^-]^2$) of $10^{-14.51}$ to $10^{-15.11}$[42-44]. The grey hatched and shaded areas represent the region where $Fe(OH)_2$ 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.

To better visualize the influence of $Fe(OH)_2(s)$ precipitation on PCE and TCE reduction, we also plotted the initial pH and Fe(II) concentration of these magnetite plus Fe(II) experiments on an $Fe(OH)_2(s)$ 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 Fe(II) concentration and pH values were such that $Fe(OH)_2(s)$ 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 $Fe(OH)_2(s)$ 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 Fe(II) to the magnetite suspensions resulted in reduction of PCE and TCE when $Fe(OH)_2(s)$ 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. Surface-area normalized first-order rate coefficients (k_{SA}) estimated from carbon product accumulation ranged from 3.7×10^{-7} to 1.5×10^{-5} L m^{-2} 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 ($t_{1/2}$ ~ 3 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.

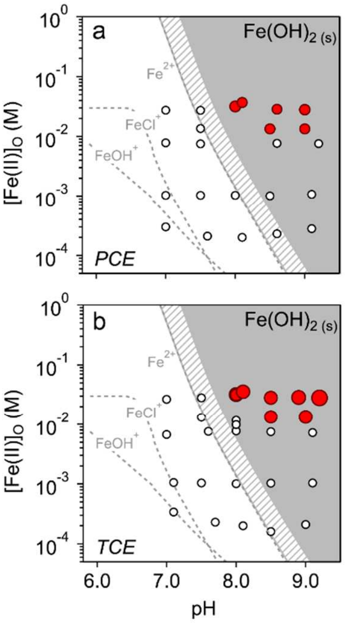

Fig. 6. $Fe(OH)_2(s)$ solubility diagram with aqueous Fe(II) reactors without magnetite conditions overlaid for PCE and TCE reactors. Fe(II) is plotted as the initial Fe(II) concentration – $[Fe(II)]_0$. Red markers represent PCE and TCE reactors where products were observed and the markers are scaled 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 Ksp ($[Fe(OH)_2(s)] = [Fe^{2+}] [OH^-]^2$) of $10^{-14.51}$ to $10^{-15.11}$.[42-44] The grey hatched and shaded areas therefore represent the region where $Fe(OH)_2$ 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.

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

Our observation that $Fe(OH)_2(s)$ precipitation is necessary for PCE and TCE reduction to occur in the presence of magnetite led us to wonder whether $Fe(OH)_2(s)$ or even aqueous Fe(II) alone can reduce TCE. To evaluate whether $Fe(OH)_2(s)$ 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 $Fe(OH)_2(s)$ 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 $Fe(OH)_2(s)$ 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 1.8×10^{-10} s^{-1} to 1.8×10^{-8} 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 $Fe(OH)_2(s)$. However, XRD and Mössbauer spectroscopy of the solids after 150 days indicated no additional phases present other than $Fe(OH)_2(s)$ (**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 $Fe(OH)_2$ 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 $Fe(OH)_2$ precipitates the saturation index will likely be near 0.

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 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 $\rho = 0.49$).

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 FeS[57] 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.

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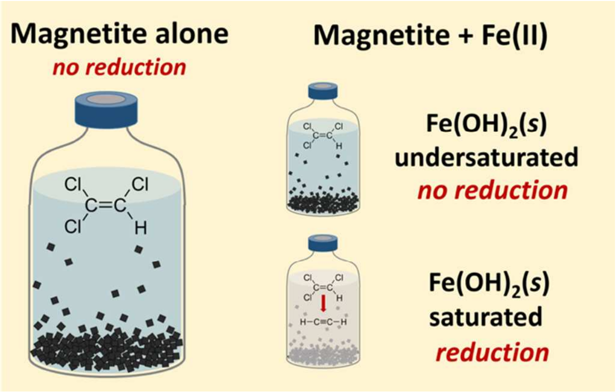
Table of Contents Artwork



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