

FINAL REPORT

Biologically Mediated Abiotic Degradation (BMAD) of Chlorinated Ethenes: A New Conceptual Framework

SERDP Project ER-2532

JUNE 2019

Michelle M. Scherer
Drew E. Latta
Anke Neumann
David M. Cwiertny
Rula Deeb
The University of Iowa

Distribution Statement A

This document has been cleared for public release



Page Intentionally Left Blank

This report was prepared under contract to the Department of Defense Strategic Environmental Research and Development Program (SERDP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

Page Intentionally Left Blank

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 02-12-2019		2. REPORT TYPE SERDP Final Report		3. DATES COVERED (From - To) Jun 2015 - Jun 2019	
4. TITLE AND SUBTITLE Final Report Biologically Mediated Abiotic Degradation (BMAD) of Chlorinated Ethenes: A New Conceptual Framework			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Scherer, Michelle M. Latta, Drew E. Neumann, Anke Cwiertny, David M. Deeb, Rula			5d. PROJECT NUMBER ER-2532		
			5e. TASK NUMBER N/A		
			5f. WORK UNIT NUMBER N/A		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The University of Iowa 2 Gilmore Hall Iowa City, IA 52242-1320			8. PERFORMING ORGANIZATION REPORT NUMBER ER-2532		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 17D03 Alexandria, VA 22350			10. SPONSOR/MONITOR'S ACRONYM(S) SERDP		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER-2532		
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The primary objective ER-2532 was to evaluate whether magnetite and Fe-containing clay minerals reduced perchloroethene (PCE) and trichloroethene (TCE) alone and then in the presence of ferrous iron (Fe(II)) or sulfide (S(-II)). Our goal was to evaluate pathways and factors controlling abiotic degradation of PCE and TCE by reactive minerals and evaluate which aquifer properties might be used as indicators for abiotic natural attenuation rates in anoxic PCE and TCE plumes. We found that magnetite and reduced Fe-containing clay minerals alone did not reduce PCE and TCE under anoxic conditions. We observed no reduction of PCE and TCE when sulfide was added to magnetite and clay mineral suspensions. We did, however, find that both magnetite and Fe-containing clay minerals reduced PCE and TCE to acetylene in the presence of high concentrations of Fe(II). In both cases our analyses indicated a transient mineral phase formed suggesting that dynamic conditions and high Fe(II) concentrations that favor active precipitation of minerals could abiotically attenuate anoxic PCE and TCE plumes.					
15. SUBJECT TERMS Abiotic dechlorination, magnetite, clay minerals, perchloroethylene (PCE), trichloroethylene (TCE), reactive mineral intermediates (RMI), Mössbauer spectroscopy, Fe(II), sulfide					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 111	19a. NAME OF RESPONSIBLE PERSON Michelle Scherer
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (include area code) 319-335-5654

Page Intentionally Left Blank



ER-2532 / Final Report

Project Start: 4 June 2015; Project End: 4 June 2019

Biologically Mediated Abiotic Degradation (BMAD) of
Chlorinated Ethenes: A New Conceptual Framework

Michelle Scherer (PI)

Drew Latta, Anke Neumann, David Cwiertny, and Rula Deeb

Executive Summary

Chlorinated solvents, such as tetrachloroethene (PCE) and trichloroethene (TCE), are one of the most prevalent pollutants at hundreds of Department of Defense (DoD) sites, and remain among the most difficult to remediate despite years of intense research and development. Biological degradation of PCE and TCE has been studied in some detail, however, there is still a significant knowledge gap in the understanding of how abiotic processes contribute to the degradation of PCE and TCE, in particular the formation of reactive iron (Fe) mineral phases through biologically mediated pathways.

The primary objective ER-2532 was to evaluate whether magnetite and Fe-containing clay minerals reduced perchloroethene (PCE) and trichloroethene (TCE) alone and then in the presence of ferrous iron (Fe(II)) OR sulfide (S(-II)). Our goal was to evaluate pathways and factors controlling abiotic degradation of PCE and TCE by reactive minerals and evaluate which aquifer properties might be used as indicators for abiotic natural attenuation rates and products in anoxic PCE and TCE plumes.

We found that magnetite and reduced Fe-containing clay minerals *alone* did not reduce PCE and TCE under *anoxic* conditions. Our findings suggest that it is unlikely that magnetite and reduced Fe-containing clay minerals *alone* reduce PCE and TCE fast enough to significantly contribute to the natural attenuation of PCE and TCE in contaminated, anoxic aquifer plumes. We also, somewhat surprisingly, found no reduced carbon products from PCE and TCE when sulfide was added to magnetite and Fe-containing clay mineral suspensions. We therefore suggest that PCE and TCE transformation by sulfide-reduced clay minerals is also likely not relevant in groundwater aquifers.

We did, however, find that both magnetite and Fe-containing clay minerals reduced PCE and TCE in the presence of high concentrations of Fe(II). In both cases, color changes in the mineral suspensions, as well as spectroscopy analyses indicated that another, transient mineral phase was forming suggesting that dynamic conditions and high Fe(II) concentrations that favor active precipitation of minerals could help abiotically attenuate anoxic PCE and TCE plumes. Specifically, we observed the formation of ferrous hydroxide (Fe(OH)₂(s)) in the presence of magnetite and clay minerals that was associated with accelerated rates of PCE and TCE reduction. Reduction rates were slow with carbon products up to only 30% accumulating over several months. Acetylene was the primary product suggesting that reductive β -elimination of PCE and TCE was likely the primary mechanism for reduction.



Reductive dechlorination products, including dichloroethenes and vinyl chloride, were measured, but not detected.

Our findings suggest that the presence of either magnetite or Fe-containing clay minerals in aquifer sediments is not sufficient to suggest that abiotic natural attenuation is likely. Rather, it appears that conditions that favor active precipitation of reactive minerals may be necessary. Our work suggests that zones of active Fe(II) precipitation in anoxic aquifers could result in PCE and TCE reduction that is sufficiently fast to help attenuate PCE and TCE plumes. Likely, there needs to be a source of Fe in the sediments and then conditions that are favorable to reducing and releasing that Fe into the dissolved phase. Those conditions could include a number of different Fe-reducing conditions driven by the microbiology or geochemical conditions. Some potential field protocols for abiotic degradation of PCE and TCE by Fe minerals include field screening methods for assessing extractable Fe and sulfide, as well as characterizing the electron accepting and donating capacity of the soils. Field screening methods for acid volatile sulfides targeting FeS and citrate-bicarbonate (CB) extractable Fe would provide a good indicator of readily available sources of Fe and sulfide.

Results from ER-2532 have significantly improved the understanding of pathways and factors controlling abiotic degradation of PCE and TCE as well as provided important insights on aquifer properties that are (and are not) important for predicting whether PCE and TCE plumes have the potential to be attenuated by abiotic mineral-based reactions. For this work, Dr. Scherer and her team received the 2018 SERDP Project-of-the-Year Award for this project (ER-2532).

Table of Contents

<i>Executive Summary</i>	<i>(i)</i>
1.0 Project Motivation and Team	1
2.0 Project Objectives and Plan	1
3.0 Project Results	4
3.1. PCE and TCE Degradation by Magnetite + Fe(II)	4
3.2 PCE and TCE Degradation by Fe-containing Clay Minerals + Fe(II)	35
3.3. PCE and TCE Degradation by Magn and Fe Clay Minerals + S(-II)	74
3.4. PCE and TCE Degradation by Aquifer Materials	92

1.0 Project Motivation

There is a need for improved understanding of long-term natural attenuation processes of contaminants in groundwater. Chlorinated solvents, such as tetrachloroethene (PCE) and trichloroethene (TCE), are by far the most prevalent priority pollutants at hundreds of Department of Defense (DoD) sites, and remain among the most difficult to remediate despite years of intense research and development. Past cleanup practices focused on restoring contaminated sites by achieving specific regulatory Maximum Contaminant Levels (MCLs) while minimizing costs. With ever growing concerns regarding carbon emissions and their impact on climate change, cleanup practices must now balance plume cleanup with costs, *as well as* the global environmental impact of energy consumption and subsequent carbon combustion. Including global environmental impacts in assessing cleanup practices has made it even more critical and urgent to understand when and where we can rely on or enhance natural biological, chemical, and physical processes (i.e., natural attenuation) to degrade PCE and TCE.

While biological degradation of PCE and TCE has been studied in some detail, there is still a significant knowledge gap in our understanding of how abiotic processes contribute to the degradation of PCE and TCE. In particular, the formation of reactive mineral phases through biologically mediated pathways has been identified as a **critically understudied process** in the SERDP-ESTCP August 2013 workshop report on *Long-Term Management of Contaminant Groundwater Sites*. Formation of reactive mineral phases is likely to be particularly important in aquifers of lower hydraulic conductivity where lower mobility zones contain accumulations of fine-grained sediments which promote the formation of reactive minerals.

ER-2532 Project Team

Michelle Scherer (PI) - University of Iowa
Drew Latta - University of Iowa
David Cwiertny - University of Iowa
Johnathan Culpepper - University of Iowa
Thomas Robinson - University of Iowa

Rula Deeb - Geosyntec Consultants
Eric Suchomel - Geosyntec Consultants

Anke Neumann - Newcastle University
James Entwistle - Newcastle University



Photo by Ben Zweig

2.0 Project Objectives and Plan

The overall objective of our work was to understand biologically mediated abiotic degradation (**BMAD**) of PCE and TCE by magnetite and Fe-bearing clays. While it has been long suspected that these minerals play an important role in BMAD of chlorinated solvents, BMAD performance has not been predictable or reproducible at the field scale, or even at the more controlled laboratory scale. Our goal

was to understand the factors controlling abiotic reduction of PCE and TCE by magnetite and Fe-bearing clay minerals in anoxic plumes. Our specific research objectives of ER-2532 were:

ER-2532 Project Research Objectives

- (1) to determine pathways and factors controlling abiotic degradation of PCE and TCE by reactive minerals formed from reaction of **aqueous ferrous iron (Fe^{II})** with Fe-containing aquifer sediments.
- (2) to understand pathways and factors controlling abiotic degradation of PCE and TCE by reactive minerals formed from reaction of **aqueous sulfides (S^{-II})** with Fe-containing aquifer sediments.
- (3) to evaluate aquifer properties that can be used as **indicators** of BMAD rates and products in PCE and TCE plumes and identify strategies to accelerate BMAD processes.

Our approach included measuring PCE and TCE reduction by magnetite and Fe-bearing clay minerals alone and in the presence of Fe(II) and sulfide. We conducted batch experiments over a wide range of conditions to determine PCE and TCE degradation rates and product distributions. We used isotope selective Mössbauer spectroscopy and X-ray Diffraction (XRD) to evaluate changes in mineral suspensions. In addition, we collected and measured rates of PCE and TCE reduction by aquifer materials alone and reacted with Fe(II) and S(-II). A detailed project plan and dates of completion is provided in **Table 1**.

Table 1. Completed Project Plan

1 Magnetite Synthesis (varying stoichiometry)  		
1.1	Magnetite Synthesis (varying stoichiometry)	Completed: 10/1/2016 
2 Measure PCE/TCE Transformation by magnetite  		
2.1	Measure rates of PCE and TCE removal after reaction with magnetite of varying stoichiometries.	Completed: 1/1/2016 
2.2	Measure rates of PCE and TCE removal by magnetite reacted with Fe(II)	Completed: 4/1/2016 
2.3	Quantify products from reduction of PCE and TCE by magnetite and magnetite reacted with Fe(II)	Completed: 8/1/2016 
3 Reduce clays with Fe(II) and dithionite and characteriz...  		
3.1	Reduce clays with Fe(II) and dithionite and characterize clays	Completed: 1/1/2016 

Table 1. Completed Project Plan (Continued)

4 Determine rates and extents of PCE/TCE reduction by...  		
4.1	Measure rates of PCE and TCE removal after reaction with dithionite-reduced clay minerals	Completed: 10/1/2017 
4.2	Measure rates of PCE and TCE removal after reaction with Fe(II)-reduced clay minerals	Completed: 10/1/2017 
4.3	Quantify products from reduction of PCE and TCE by reduced clays and evaluate mechanism of removal	Completed: 10/1/2017 
5 Reduce magnetites with sulfide and determine stoich...  		
5.1	Reduce magnetites with sulfide and determine stoichiometry and FeS products	Completed: 10/1/2016 
6 Measure PCE/TCE reduction with sulfide-reduced ma...  		
6.1	Measure rates of PCE and TCE removal after reaction with sulfide-reduced magnetite	Completed: 9/17/2018 
6.2	Quantify products from reduction of PCE and TCE by sulfide reduced magnetite and evaluate mechanism of removal	Completed: 9/17/2018 
7 Reduce clay minerals with sulfide and characterize  		
7.1	Reduce clay minerals with sulfide and characterize	Completed: 7/1/2017 
8 Measure PCE/TCE Transformation with sulfide-reduc...  		
8.1	Measure rates of PCE and TCE removal after reaction with sulfide-reduced clay minerals	Completed: 7/24/2018 
8.2	Quantify products from reduction of PCE and TCE by sulfide reduced magnetite and evaluate mechanism of removalQuantify products from reduction of PCE ...	Completed: 7/24/2018 
9 Identify sites and collect reduced aquifer materials  		
9.1	Identify sites and collect reduced aquifer materials	Completed: 9/1/2017 
10 Characterize aquifer sediments  		
10.1	Characterize aquifer sediments	Completed: 1/17/2018 

Table 1. Completed Project Plan (Continued)

11	React aquifer materials with Fe(II) and S(-II) and char...	 
11.1	React aquifer materials with Fe(II) and S(-II) and characterize	Completed: 7/24/2018 
12	Measure and correlate rates of PCE/TCE transformati...	 
12.1	Measure and correlate rates of PCE/TCE transformation by aquifer materialsion	Completed: 7/24/2018 
13	Reporting	 
13.1	Go/No Go White Paper - 1 (v1)	Completed: 3/1/2017  
13.2	Go/No Go White Paper - 2 (v1)	Completed: 8/7/2018  
13.3	Go/No Go White Paper - 3 (v1)	Completed: 4/24/2019  

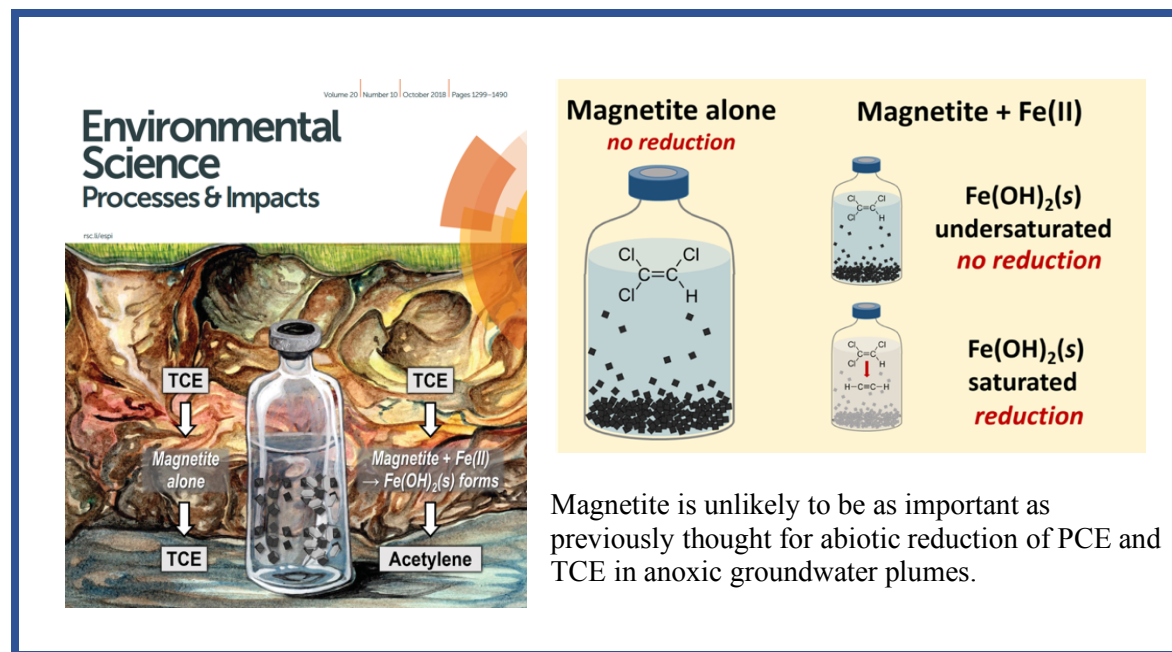
3.0 Project Results

3.1 PCE and TCE Degradation by Magnetite + Fe(II)

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 $\text{Fe}(\text{OH})_2(\text{s})$ 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.



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 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 (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 $\text{Fe}(\text{OH})_2(s)$, 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) (PIPES, 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 ($\sim 1.4 \text{ M FeCl}_2 \cdot 4\text{H}_2\text{O}$) 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 ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and 0.2 M ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 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 $63 \pm 7 \text{ m}^2 \text{ g}^{-1}$ using N_2 -BET analysis.³³

Mineral characterization. Magnetite stoichiometries ($x = \text{Fe}^{2+}/\text{Fe}^{3+}$) 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 ^{57}Co 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 $\text{Fe}(\text{OH})_2$.

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 $50 \mu\text{M}$ (8,291 and 6,570 $\mu\text{g/L}$ 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 ($[\text{Fe}(\text{II})]_f$) 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

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 products (in μ moles C) at time t , C_0 is the initial PCE or TCE amount (in μ 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} .

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

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

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 $5.2 \times 10^{-3} \text{ s}^{-1}$ (**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 ($\sim$ pH 8 and $\sim$ 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, $\text{Fe}(\text{OH})_2(\text{s})$, which was confirmed by X-ray diffraction of the filtered reactor solids (**Figure S2**).

To quantitatively evaluate if $\text{Fe}(\text{OH})_2(\text{s})$ precipitation was necessary for PCE and TCE reduction, we plotted k_{obs} values versus the saturation index (SI) for $\text{Fe}(\text{OH})_2(\text{s})$ (**Figure 4**). We calculated the SI as $\log(\text{IAP}/K_{\text{sp}})$ using the initial Fe(II) concentration and an $\text{Fe}(\text{OH})_2(\text{s})$ 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 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 Fe(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 Fe(II) concentration of these magnetite plus Fe(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 Fe(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 Fe(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. 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} $\text{L m}^{-2} \text{d}^{-1}$, 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 ($t_{1/2} \sim 3$ 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 **x** 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 $\text{Fe}(\text{II})$ ($> 13 \text{ mM}$, 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 $\text{Fe}(\text{II})$ 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 $\text{Fe}(\text{II})$ 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 $\text{Fe}(\text{II})$ ($> 13 \text{ mM}$, 726 mg/L) make these conditions unlikely to be relevant in groundwater aquifers where $\text{Fe}(\text{II})$ 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.

Conclusions and 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_{lab}) 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 $\text{Fe}(\text{II})$ added exceeds typical concentrations of $\text{Fe}(\text{II})$ 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 $\text{Fe}(\text{II})$ precipitates. Our work does, however, highlight that active precipitation of reactive $\text{Fe}(\text{II})$ 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 Weidemer et al.²⁵ between chlorinated ethene degradation and magnetic susceptibility is weak, with $r = 0.18$ and a Spearman's rank-order correlation coefficient of 0.41, making the correlation statistically non-significant at even a 90% confidence interval (critical $q = 0.49$).

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).^{34,51} 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.

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.

3.1 Figures

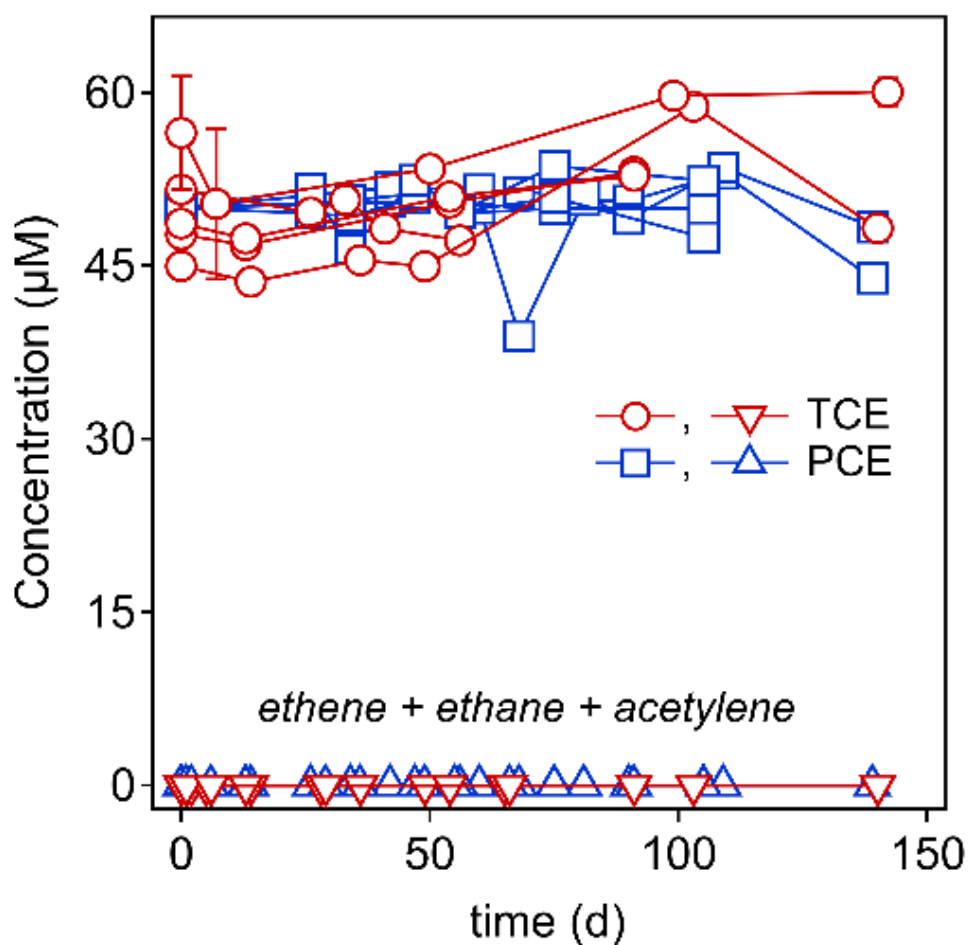


Fig. 1. PCE and TCE concentration versus time in the presence of stoichiometric magnetite ($x = \text{Fe}^{2+}/\text{Fe}^{3+} = 0.46 - 0.50$). Experimental conditions: 50 μM PCE/TCE, 10 mM MOPs/NaCl at pH 7.0, 7.5, and 8.0 for TCE reactors and pH 7.5 for PCE reactors, mass loading 5 - 20 g/L. Average 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)

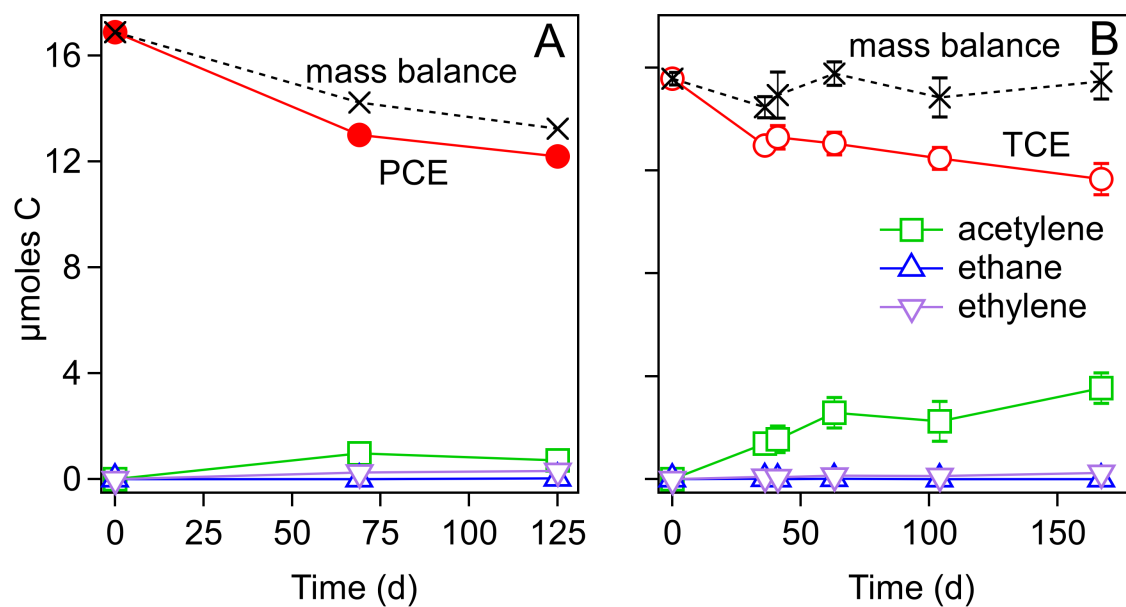


Fig. 2. Reduction of (A) PCE and (B) TCE over time with magnetite and aqueous Fe(II). Experimental conditions: (A) 54 μM PCE, 5 g/L Fe_3O_4 (s), 33 mM Fe(II), 10 mM MOPs/NaCl, pH 7.9, single reactor. (B) 50 μM TCE, 5 g/L Fe_3O_4 (s), 9.3 ± 0.6 mM Fe(II), 10 mM MOPs/NaCl, pH 8, for n from 3 to 12.

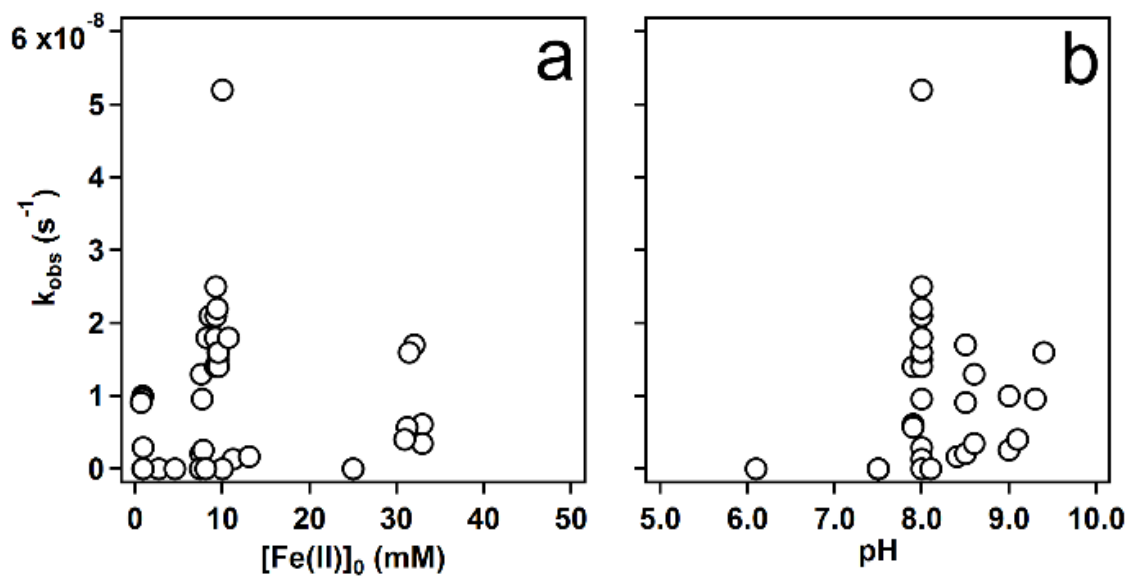


Fig. 3. Plots of k_{obs} for PCE and TCE reduction as a function of $[\text{Fe(II)}]_0$ (initial Fe(II) concentration) (a) and pH (b).

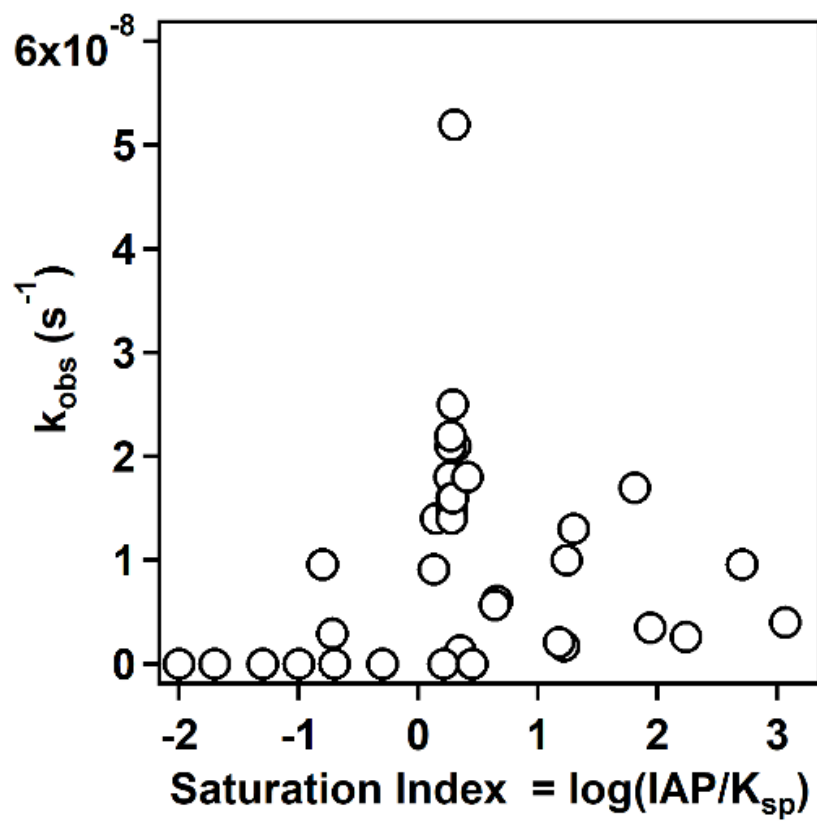


Fig. 4. Plot of k_{obs} for PCE and TCE reduction vs. the $\text{Fe}(\text{OH})_2(\text{s})$ initial saturation index (<0 undersaturated, 0 at saturation, >0 oversaturated).

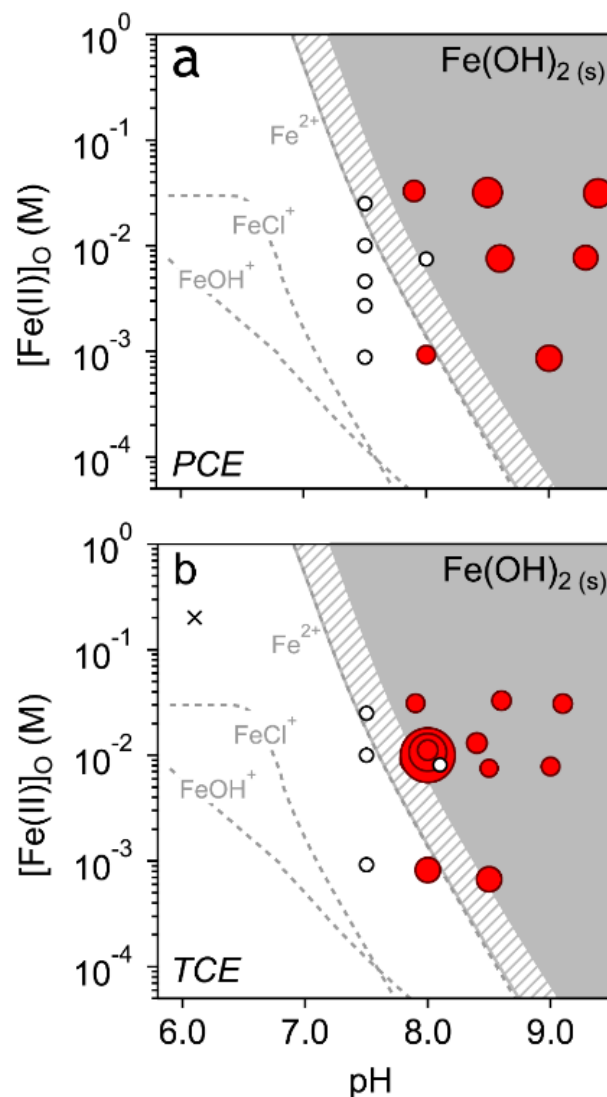


Fig. 5. $\text{Fe(OH)}_2(\text{s})$ solubility diagram with magnetite plus Fe(II) reactor conditions overlaid for (a) PCE and (b) TCE reactors. Fe(II) is plotted as the initial Fe(II) concentration – $[\text{Fe(II)}]_0$. Red markers represent PCE and TCE reactors where carbon products were observed and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

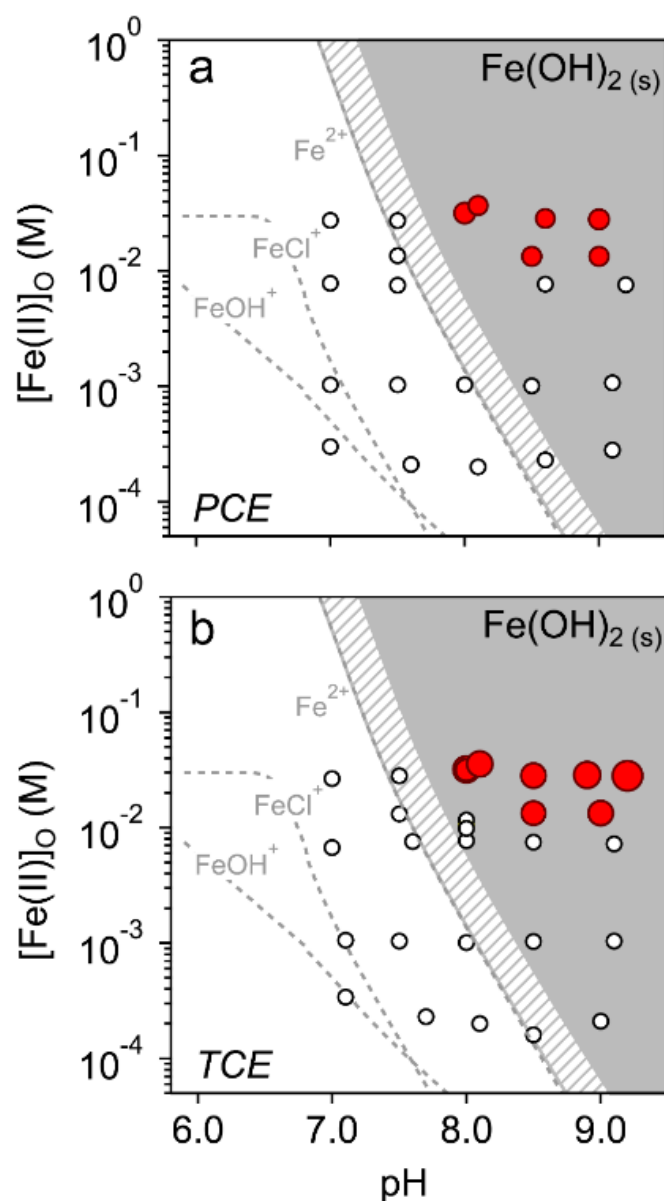


Fig. 6. $\text{Fe(OH)}_2(\text{s})$ solubility diagram with aqueous Fe(II) reactors without magnetite conditions overlaid for PCE and TCE reactors. Fe(II) is plotted as the initial Fe(II) concentration – $[\text{Fe(II)}]_0$. Red markers represent PCE and TCE reactors where products were observed and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

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.
5. Guyton, K. Z.; Hogan, K. A.; Scott, C. S.; Cooper, G. S.; Bale, A. S.; Kopylev, L.; Barone Jr, S.; Makris, S. L.; Glenn, B.; Subramaniam, R. P., Human health effects of tetrachloroethylene: key findings and scientific issues. *Environ. Health. Perspect.* **2014**, *122*, (4), 325.
6. Chiu, W. A.; Jinot, J.; Scott, C. S.; Makris, S. L.; Cooper, G. S.; Dzubow, R. C.; Bale, A. S.; Evans, M. V.; Guyton, K. Z.; Keshava, N., Human health effects of trichloroethylene: key findings and scientific issues. *Environ. Health. Perspect.* **2013**, *121*, (3), 303.
7. Lepom, P.; Brown, B.; Hanke, G.; Loos, R.; Quevauviller, P.; Wollgast, J., Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European Water Framework Directive. *J. Chromatogr. A* **2009**, *1216*, (3), 302-315.
8. Zogorski, J. S.; Carter, J. M.; Ivahnenko, T.; Lapham, W. W.; Moran, M. J.; Rowe, B. L.; Squillace, P. J.; Toccalino, P. L., Volatile organic compounds in the nation's ground water and drinking-water supply wells. *US Geological Survey Circular* **2006**, *1292*, 101.
9. Council, N. R., Alternatives for managing the nation's complex contaminated groundwater sites. National Academies Press: 2013.
10. Council, N. R., Contaminants in the subsurface: Source zone assessment and remediation. National Academies Press: 2005.
11. van der Zaan, B.; Hannes, F.; Hoekstra, N.; Rijnaarts, H.; de Vos, W. M.; Smidt, H.; Gerritse, J., Correlation of Dehalococcoides 16S rRNA and chloroethene-reductive dehalogenase genes with geochemical conditions in chloroethene-contaminated groundwater. *Appl. Environ. Microbiol.* **2010**, *76*, (3), 843-850.
12. Lee, P. K.; Macbeth, T. W.; Sorenson, K. S.; Deeb, R. A.; Alvarez-Cohen, L., Quantifying genes and transcripts to assess the in situ physiology of "Dehalococcoides" spp. in a trichloroethene-contaminated groundwater site. *Appl. Environ. Microbiol.* **2008**, *74*, (9), 2728-2739.
13. Lu, X.; Wilson, J. T.; Kampbell, D. H., Relationship between Dehalococcoides DNA in ground water and rates of reductive dechlorination at field scale. *Water Res.* **2006**, *40*, (16), 3131-3140.

14. Hendrickson, E. R.; Payne, J. A.; Young, R. M.; Starr, M. G.; Perry, M. P.; Fahnestock, S.; Ellis, D. E.; Ebersole, R. C., Molecular analysis of Dehalococcoides 16S ribosomal DNA from chloroethene-contaminated sites throughout North America and Europe. *Appl. Environ. Microbiol.* **2002**, *68*, (2), 485-495.
15. Damgaard, I.; Bjerg, P. L.; Bælum, J.; Scheutz, C.; Hunkeler, D.; Jacobsen, C. S.; Tuxen, N.; Broholm, M. M., Identification of chlorinated solvents degradation zones in clay till by high resolution chemical, microbial and compound specific isotope analysis. *J. Contam. Hydrol.* **2013**, *146*, 37-50.
16. Hunkeler, D.; Aravena, R.; Butler, B., Monitoring microbial dechlorination of tetrachloroethene (PCE) in groundwater using compound-specific stable carbon isotope ratios: microcosm and field studies. *Environ. Sci. Technol.* **1999**, *33*, (16), 2733-2738.
17. Mattes, T. E.; Alexander, A. K.; Coleman, N. V., Aerobic biodegradation of the chloroethenes: pathways, enzymes, ecology, and evolution. *FEMS Microbiol. Rev.* **2010**, *34*, (4), 445-475.
18. Findlay, M.; Smoler, D. F.; Fogel, S.; Mattes, T. E., Aerobic Vinyl Chloride Metabolism in Groundwater Microcosms by Methanotrophic and Etheneotrophic Bacteria. *Environ. Sci. Technol.* **2016**, *50*, (7), 3617-3625.
19. Bradley, P. M.; Landmeyer, J. E.; Dinicola, R. S., Anaerobic oxidation of [1, 2-¹⁴C] dichloroethene under Mn (IV)-reducing conditions. *Appl. Environ. Microbiol.* **1998**, *64*, (4), 1560-1562.
20. Haderlein, S. B.; Pecher, K., Mediation of organic pollutant reduction by iron oxides. *Abstr. Pap. Am. Chem. Soc.* **1997**, *213*, 129-GEOC.
21. Cwiertny, D. M.; Scherer, M. M., Abiotic Processes Affecting the Remediation of Chlorinated Solvents. In *In Situ Remediation of Chlorinated Solvent Plumes*, Stroo, H. F.; Ward, C. H., Eds. Springer New York: New York, NY, 2010; pp 69-108.
22. Vogel, T. M.; Criddle, C. S.; McCarty, P. L., Transformations of halogenated aliphatic compounds. *Environ. Sci. Technol.* **1987**, *21*, (8), 722-736.
23. Kriegman-King, M. R.; Reinhard, M., Reduction of hexachloroethane and carbon tetrachloride at surfaces of biotite, vermiculite, pyrite, and marcasite. In *Organic Substances and Sediments in Water*, Baker, R., Ed. Lewis: MI, 1991; Vol. 2, pp 349-364.
24. He, Y. T.; Wilson, J. T.; Su, C.; Wilkin, R. T., Review of Abiotic Degradation of Chlorinated Solvents by Reactive Iron Minerals in Aquifers. *Groundwater Monitoring & Remediation* **2015**, *35*, (3), 57-75.
25. 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.
26. Ferrey, M.; Wilkin, R.; Ford, R.; Wilson, J., Nonbiological removal of cis-dichloroethylene and 1,1-dichloroethylene in aquifer sediment containing magnetite. *Environ. Sci. Technol.* **2004**, *38*, (6), 1746-1752.

27. Lee, W.; Batchelor, B., Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and Magnetite. *Environ. Sci. Technol.* **2002**, *36*, (23), 5147-5154.
28. Sivavec, T. M.; Horney, D. P. In *Reduction of chlorinated solvents by Fe(II) minerals*, 213th National Meeting, San Francisco, CA, 1997; American Chemical Society: San Francisco, CA, 1997; pp 115-117.
29. Liang, X. M.; Philp, R. P.; Butler, E. C., Kinetic and isotope analyses of tetrachloroethylene and trichloroethylene degradation by model Fe(II)-bearing minerals. *Chemosphere* **2009**, *75*, (1), 63-69.
30. Pham, H. T.; Suto, K.; Inoue, C., Trichloroethylene Transformation in Aerobic Pyrite Suspension: Pathways and Kinetic Modeling. *Environ. Sci. Technol.* **2009**, *43*, (17), 6744-6749.
31. Pham, H. T.; Kitsuneduka, M.; Hara, J.; Suto, K.; Inoue, C., Trichloroethylene transformation by natural mineral pyrite: The deciding role of oxygen. *Environ. Sci. Technol.* **2008**, *42*, (19), 7470-7475.
32. Gorski, C. A.; Scherer, M. M., Determination of nanoparticulate magnetite stoichiometry by Mössbauer spectroscopy, acidic dissolution, and powder X-ray diffraction: A critical review. *Am. Mineral.* **2010**, *95*, (7), 1017-1026.
33. Gorski, C. A.; Nurmi, J. T.; Tratnyek, P. G.; Hofstetter, T. B.; Scherer, M. M., Redox behavior of magnetite: Implications for contaminant reduction. *Environ. Sci. Technol.* **2009**, *44*, (1), 55-60.
34. Tamura, H.; Goto, K.; Yotsuyan, T.; Nagayama, M., Spectrophotometric determination of iron(II) with 1,10-phenanthroline in presence of large amounts of iron(III). *Talanta* **1974**, *21*, (4), 314-318.
35. Lagarec, K.; Rancourt, D. G. *Recoil-Mössbauer spectral analysis software for Windows*, University of Ottawa, Ottawa, ON: 1998.
36. Latta, D. E.; Gorski, C. A.; Boyanov, M. I.; O'Loughlin, E. J.; Kemner, K. M.; Scherer, M. M., Influence of magnetite stoichiometry on U^v reduction. *Environ. Sci. Technol.* **2012**, *46*, (2), 778-786.
37. Gorski, C. A.; Nurmi, J. T.; Tratnyek, P. G.; Hofstetter, T. B.; Scherer, M. M., Redox behavior of magnetite: Implications for contaminant reduction. *Environ. Sci. Technol.* **2010**, *44*, (1), 55-60.
38. Pasakarnis, T. S.; Boyanov, M. I.; Kemner, K. M.; Mishra, B.; O'Loughlin, E. J.; Parkin, G.; Scherer, M. M., Influence of Chloride and Fe(II) Content on the Reduction of Hg(II) by Magnetite. *Environ. Sci. Technol.* **2013**, *47*, (13), 6987-6994.
39. Brown, R. A.; Wilson, J. T.; Ferrey, M., Monitored natural attenuation forum: The case for abiotic MNA. *Remediation Journal* **2007**, *17*, (2), 127-137.
40. Sivavec, T. M. Composition and method for ground water remediation. U.S. Patent 5,750,036, May 12, 1998.
41. Arnold, W. A.; Roberts, A. L., Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environ. Sci. Technol.* **2000**, *34*, (9), 1794-1805.
42. Gustafsson, J. P. *Visual MINTEQ*, 3.0; 2011.

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

3.1 Supporting Information

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 C_2 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 $>C_2$ were not analyzed in this study. We used Henry's law and the specific dimensionless coefficient H^* to calculate dissolved C_2 gases and headspace PCE and TCE.¹ The averaged values for the H^* 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: $k_{SA} = k_{obs}/SA = 1.9 \times 10^{-8}$ s⁻¹/(5 g/L·60 m²/g)·3.1536 $\times 10^7$ s/year = 2.0×10^{-3} L m² yr⁻¹

Assuming $\rho_{bulk} = 1700$ kg/m³, 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}):

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

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

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] ₀ (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]₀ 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	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>k</i> _{SA}	<i>k</i> _{field} ^h	<i>t</i> _{1/2 field}
μM						<i>x</i> _d ^d	<i>x</i> _{xrd} ^e					<i>s</i> ⁻¹	<i>L m</i> ⁻² <i>t</i> ⁻¹	<i>yr</i> ⁻¹	<i>years</i>
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^{-15.3}

^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 *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.

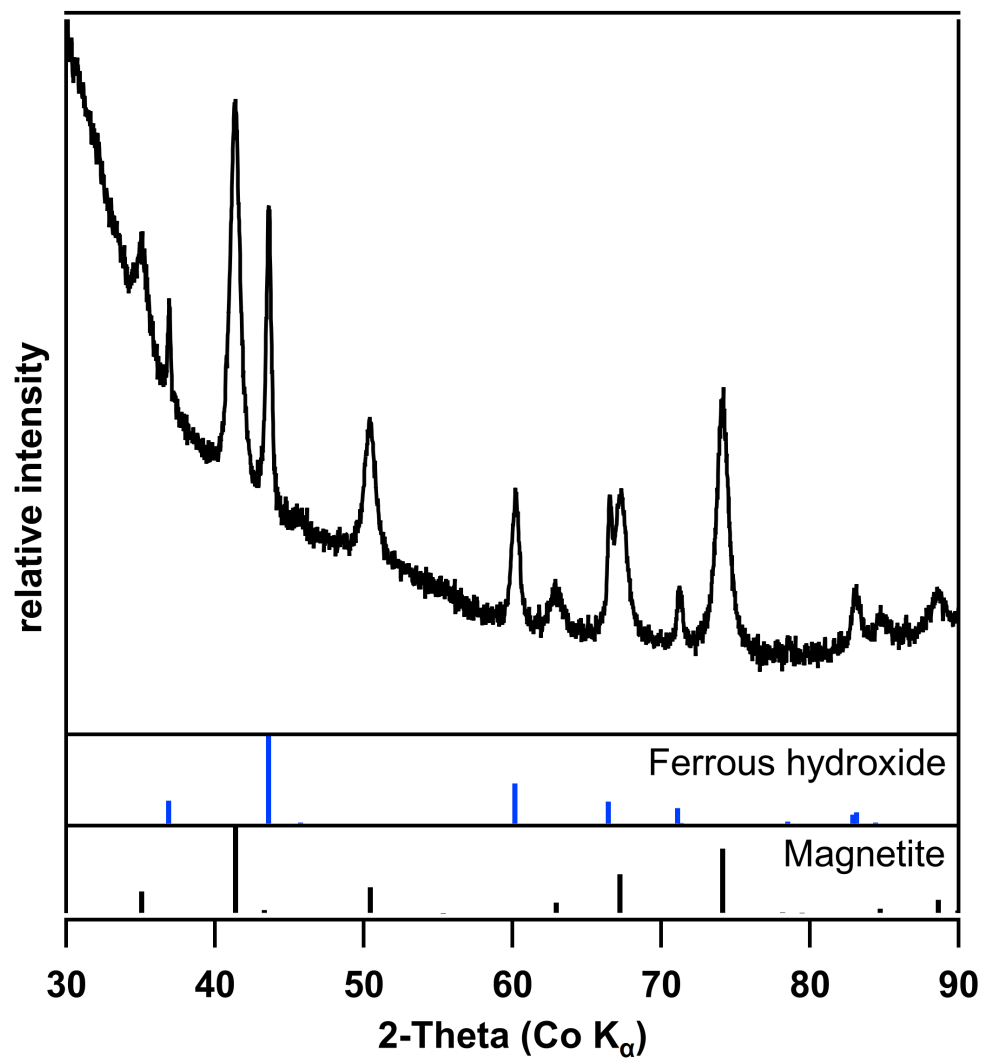


Figure S2. X-ray diffraction pattern of a TCE reactor with magnetite and Fe(II) where 30.0% products were observed after 167 days. Blue bars indicate ferrous hydroxide and black bars indicate magnetite. The background at $2\theta < 60^\circ$ is from the Kapton film used to seal the sample from air. Experimental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

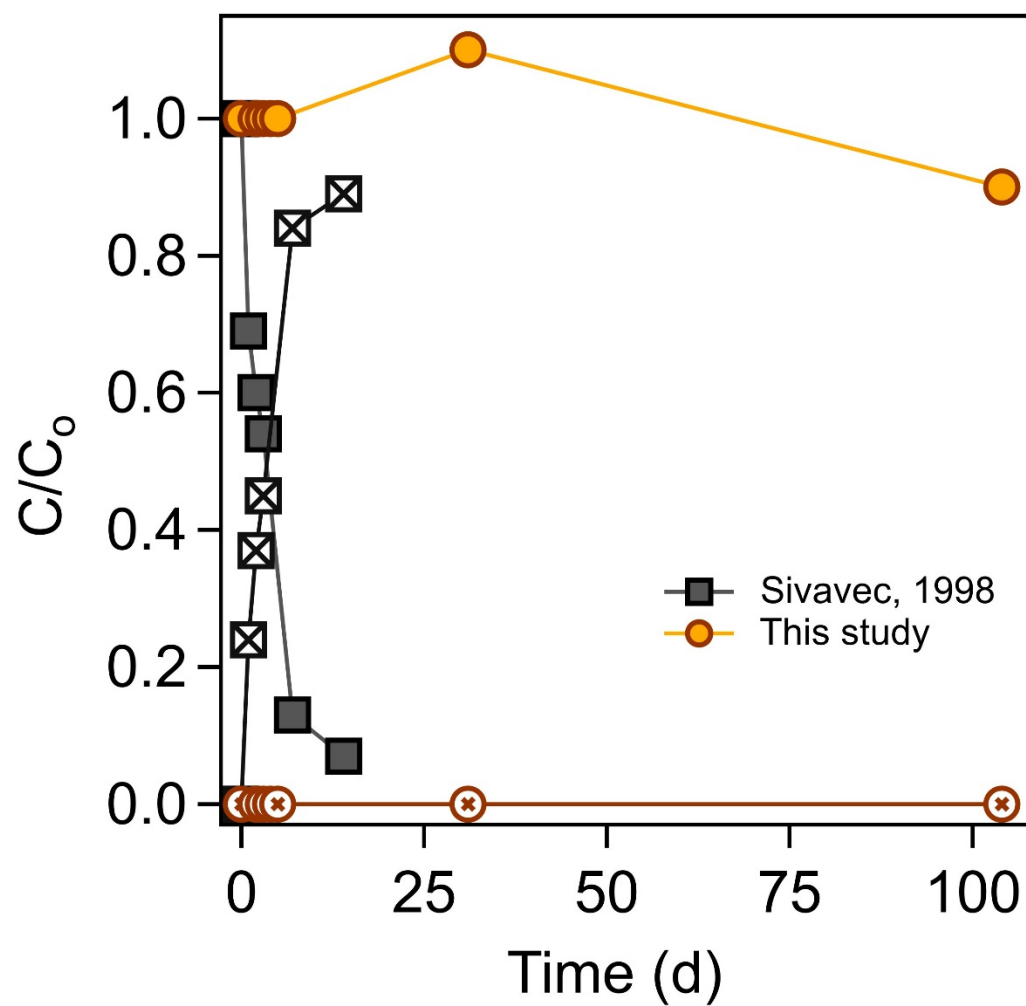


Figure S3. TCE reduction (or lack thereof) as reported in the Sivavec patent¹ and our attempt to reproduce the data under similar conditions. **Sivavec:** 7.0 μ M TCE, 217 g/L Fe_3O_4 (s), 200 mM Fe(II) , pH 6.0. **This study:** 22 μ M TCE, 147 g/L Fe_3O_4 (s), 201 ± 12 mM Fe(II) , 10 mM MOPs/NaCl, pH 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	$[\text{Fe(II)}]_0^b$ (mM)	Saturation Index ^c	$[\text{Fe(II)}]_f^b$ (mM)	% loss ^d	% products ^d	% C recovery ^d	Duration (day)	k_{obs} (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 $[\text{Fe(II)}]_0$ = initial Fe(II) concentration

^c Saturation index = $\log(\text{IAP}/K_{sp})$. 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.

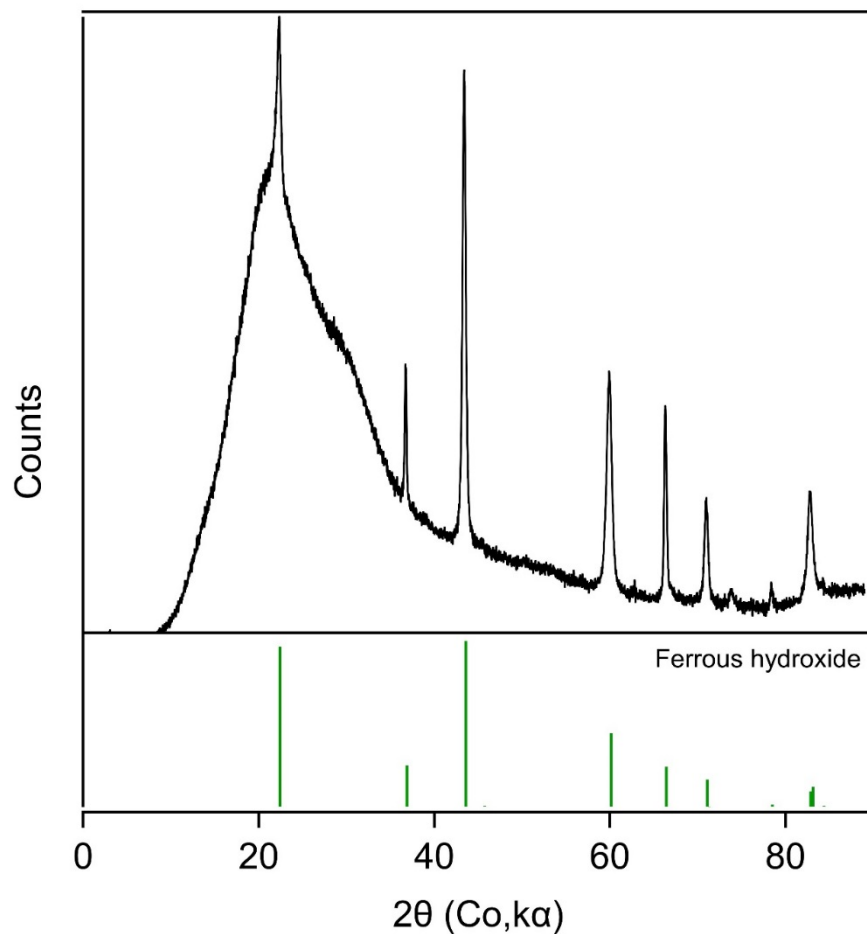
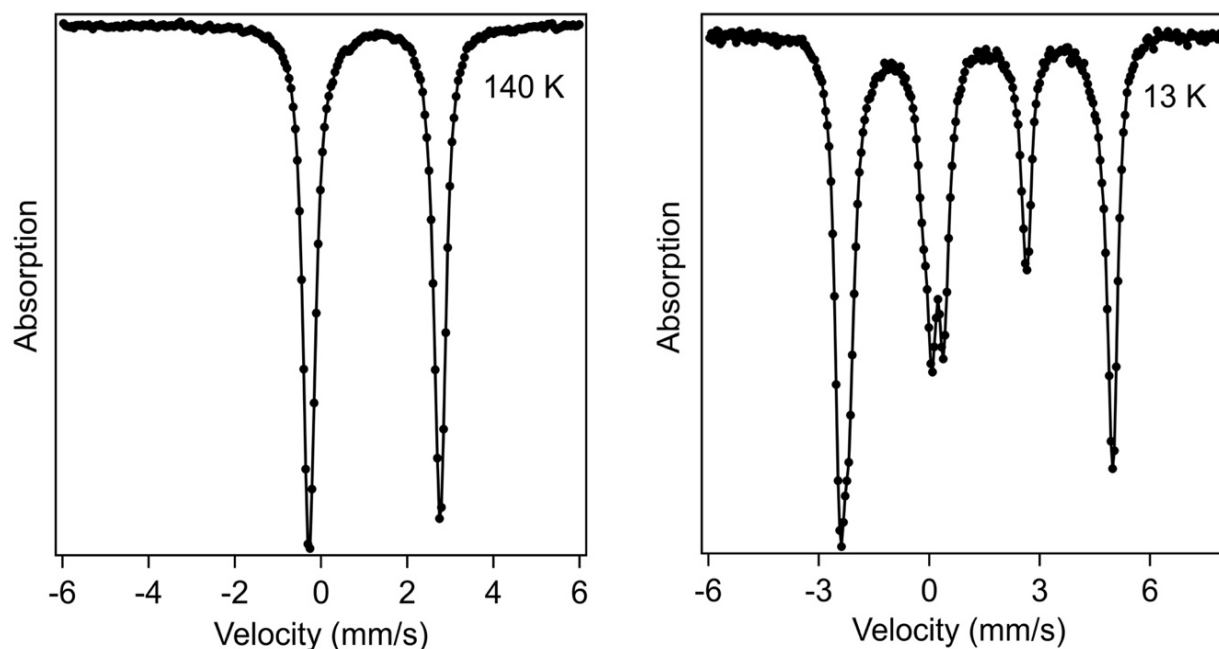


Figure S4. X-ray diffraction pattern of a TCE reactor with Fe(II) alone after 193 days where 9.0% products were observed. Light green bars indicate ferrous hydroxide. The background before 60° 2θ is due to Kapton film used to seal the sample from air. Experimental conditions: 60 μ M TCE, 10 mM MOPs/NaCl,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



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.

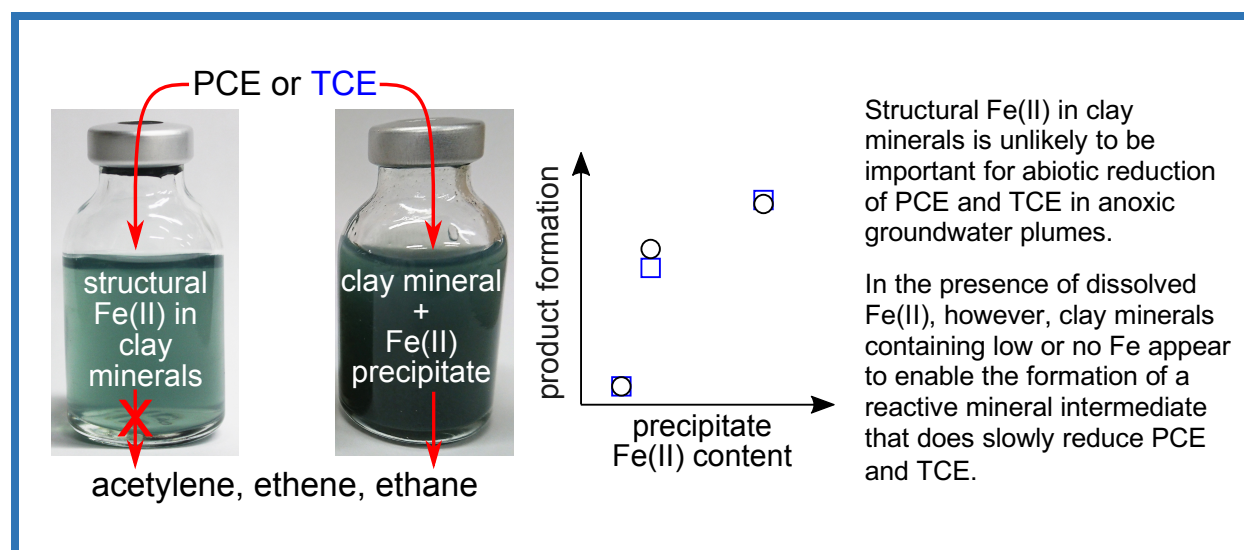
References

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.

3.2 PCE and TCE Degradation by Fe-containing Clay Minerals + Fe(II)

Abstract

For decades, there has been evidence that Fe-containing minerals might contribute to abiotic degradation of chlorinated ethene (CE) plumes. Here we evaluated whether Fe(II) in clay minerals reduces tetrachloroethene (PCE) and trichloroethene (TCE). We found that structural Fe(II) in both low (SWy-2) and high (Nau-1) Fe clay minerals did not reduce PCE or TCE under anoxic conditions. Adding 5 mM dissolved Fe(II) to the clay mineral suspensions also resulted in no reduction of PCE or TCE. In the presence of high Fe(II) concentrations (20 mM), however, PCE and TCE reduction products were observed in the presence of low Fe-content clay mineral SWy-2. Our Mössbauer spectroscopy results indicate that a mixed-valent Fe(II)-Fe(III) precipitate formed in the reactive SWy-2 suspensions. In contrast, in suspensions containing 20 mM Fe(II) alone or Fe-free clay mineral (Syn-1) we observed a purely Fe(II)-containing precipitate ($\text{Fe}(\text{OH})_2$) and also PCE and TCE reduction products. Interestingly, the amount of CE products decreased in the order Fe-free clay mineral Syn-1 > $\text{Fe}(\text{OH})_2$ > low Fe-content clay mineral SWy-2, suggesting that clay mineral Fe controlled the formation of the reactive mineral phase. Additional experiments with hexachloroethane (HCA) reveal that faster HCA reduction occurs as the clay mineral Fe content decreases. Kinetic modeling yielded invariable second-order rate constants and increasing concentrations of reactive Fe(II) as the Fe(II)/Fe(total) content of the precipitates increased. Our data suggests that clay mineral Fe(III) is a sink for electrons from added Fe(II) that might have reduced the CEs. Our findings are also consistent with the hypothesis that active precipitation of Fe(II)-containing reactive mineral intermediates (RMI) may be important to CE reduction and suggest that RMI formation depends on clay mineral presence and Fe content.



Introduction

Large, dilute plumes of chlorinated ethenes (CEs) remain a challenge to conventional remediation approaches and are commonly found at contaminated sites such as the USEPA National Priority List (Superfund) sites, of which more than 60% are polluted with trichloroethene (TCE).¹ Despite substantial investment and efforts over the past 30 years, over 125,000 sites in the USA alone remain contaminated at levels above cleanup goals. Many of these sites are difficult to remediate due to their complex hydrogeology and contamination.² As legacy contaminants, the pathways of CE degradation have been extensively investigated. It is widely accepted that biodegradation is the predominant degradation pathway in large, dilute plumes, which is supported by extensive laboratory results,^{3–5} as well as field data.^{6–9} Although dominant, biodegradation is not the most beneficial or desired pathway for CE transformation, because dechlorination becomes slower and less complete for CEs with fewer chlorine atoms,¹⁰ fails at medium to low flow velocities,¹¹ and often stalls at vinyl chloride (VC), which is much more toxic and carcinogenic compared to the parent compounds such as TCE or tetrachloroethene (PCE).¹⁰

In contrast, abiotic CE reduction often results in the formation of innocuous gaseous products acetylene, ethene, or ethane.¹² Thus, there has been interest in abiotic degradation for decades now and a recent review summarized the evidence that Fe-containing minerals might be an important reductant for CE degradation.¹ Among the large variety of naturally occurring Fe minerals, Fe sulfides are the most promising as consistent reduction has been observed in laboratory studies^{13–16} and compelling evidence has been collected at field scale.^{17–19}

For the other Fe minerals, however, evidence for abiotic degradation, is limited and, in some cases, not consistent. For example, in our recent work with magnetite, we found that despite previous work demonstrating limited, yet detectable dechlorination of CEs,^{15,20} magnetite alone was not capable of reducing PCE or TCE.²¹ Significant formation of gaseous products, suggesting CE degradation via a reductive β -elimination pathway, was observed only once the reaction conditions led to the precipitation of an even more reactive Fe(II) mineral, Fe(OH)₂, which was responsible for the observed CE transformation. Similarly, previous work on green rusts reported gaseous product formation during reaction with CEs,^{20,22} yet recent work suggests little to no direct reduction by Fe(II) in green rust.²³ However, transformation of CEs by green rusts as bulk reductant was significantly enhanced when transition metals such as Cu²⁴ or organic materials capable of mediating electron transfer such as char²⁵ were added.

Clay minerals are another Fe-containing class of minerals for which there is limited data for CE reduction. This is surprising given that their fine-grained nature and swelling characteristics make clay minerals a predominant feature of low-permeability CE source zones and of some fractured aquifers or aquitards.^{5,26} Clay minerals are also the material of choice for engineered barriers to mitigate the movement of dense non-aqueous phase liquid-containing plumes, which CEs tend to form.²⁷ Because clay and clay-mineral-containing zones often take up significant masses of dissolved-phase CEs during plume expansion, they can serve as long

term sources of CEs to groundwater even after the source zone is remediated.²⁶ Although the general trend is for clay-containing sediments to act as a source, evidence also suggests that degradation at or near low permeability zones can significantly impact contaminant mass fluxes to the aquifer.²⁸

Despite their importance in determining CE fate in the subsurface, the reaction of CEs with Fe(II) in clay minerals is crucially understudied. Only few results have been published and range from findings of no observable reduction products over 24 h reaction time,²⁹ to reduction of PCE, TCE, dichloroethenes, and VC by dithionite reduced clay minerals with and without added Fe(II) and quantified via chloride formation,³⁰ as well as partial reduction of PCE to TCE by clay minerals in the presence of dithionite.³¹ More recently, Fe-bearing clay minerals in natural sediments have been identified as key to oxidative CE degradation at the anoxic-oxic interface.³²

Here, we evaluated whether Fe(II) in Fe-containing clay minerals was a viable reductant for CE degradation over a range of conditions. We varied the initial reductant for clay mineral Fe (dithionite vs dissolved Fe(II)), the initial aqueous Fe(II) concentration between 2 and 20 mM, and investigated clay minerals with no (Syn-1), low (SWy-2) and high Fe content (NAu-1). We complemented our degradation study with Mössbauer analyses of the reduced clay minerals as well as kinetic modeling to connect Fe(II) speciation to observed reactivity. Our findings indicate that clay mineral Fe(II) *alone* cannot degrade CEs. We only observed CE reduction product formation when reaction conditions, i.e. added Fe(II) concentration and pH value, were conducive to Fe(OH)₂ formation *and* in the absence of clay mineral or in the presence of clay minerals with no (Syn-1) or low (SWy-2) Fe content. This work highlights that clay mineral Fe is a sink for electrons and controls the active precipitation of reactive mineral intermediates necessary for CE degradation.

Materials and Methods

Clay mineral preparation

The clay minerals used in this study were nontronite NAu-1 (19.8 wt% Fe), montmorillonite SWy-2 (2.5 wt% Fe), and Fe-free montmorillonite Syn-1 (0 wt% Fe) purchased from the Source Clays Repository of The Clay Minerals Society (www.clays.org). The clay minerals were dried, crushed in a ball mill, and then size-fractionated and Na⁺-homoionized as previously described.³³ Once the purity of the prepared clay minerals was verified using Fourier-transform infrared spectroscopy (FTIR) and Mössbauer spectroscopy, the clay minerals were freeze-dried and stored until use.

All clay mineral reduction procedures and the subsequent handling of Fe(II)-containing solutions and suspensions were carried out in an anaerobic glovebox (N₂: 100%, O₂<1 ppm, GS Glovebox Systemtechnik GmbH). To maintain anoxic conditions at all times, solutions were bubbled with N₂ for at least 2 h before transfer into the glovebox and plastic and glassware was brought into the glovebox at least 24 hours prior to use to remove sorbed O₂. Chemical reduction of Fe in the clay minerals followed an adapted version³⁴ of the citrate-bicarbonate-dithionite method³⁵ and used dithionite either in excess to achieve as complete clay

mineral Fe reduction as possible, or in stoichiometric amount for partly reduced N_{Au}-1. The chemically reduced clay minerals were Na⁺-homoionized, washed clear of excess ions with deionized water (DI water: $\rho = 18.2 \text{ M}\Omega\text{cm}$), and stored as 20 g L⁻¹ suspension in 0.05 M NaCl until further use.

For clay mineral Fe reduction with aqueous Fe(II), Fe(II) stock solutions (100 mM Fe(II), ~0.1M HCl) were prepared by reacting metallic Fe with HCl and subsequent filtration and dilution with DI water. For preparing clay minerals for degradation experiments with perchloroethylene (PCE), tetrachloroethylene (TCE), and hexachloroethane (HCA), Fe(II) stock solution was prepared from metal Fe of natural composition (or natural abundance, n.a., ⁵⁶Fe/ Σ^i Fe: ~92%; ⁵⁷Fe/ Σ^i Fe: ~2.1%).³⁶ For clay mineral preparation for Mössbauer analysis, Fe(II) stock solution was produced from metal Fe enriched in the ⁵⁶Fe isotope (⁵⁶Fe/ Σ^i Fe: 99.92%, Isoflex, San Francisco, CA, USA) or enriched in the ⁵⁷Fe isotope (⁵⁶Fe/ Σ^i Fe: 95.06%, Isoflex, San Francisco, CA, USA). Clay mineral Fe reduction was initiated by adding clay mineral powder (final concentration: 5 g L⁻¹) to solution that contained aqueous Fe(II) of the desired isotopic composition and at the desired concentration (2-20 mM), pH buffer (0.01 M 3-(N-morpholino)propanesulfonic acid (MOPS) adjusted to pH 8.0), and ionic strength buffer (0.05 M NaCl). After 24 hours, reduction was stopped either by centrifugation for 30 minutes at 4000 rpm at 4 °C in a swing bucket rotor (samples for Mössbauer analysis) or by adding the target contaminant (degradation experiments).

PCE, TCE, and HCA degradation experiments

Reactors for PCE and TCE degradation experiments were assembled in 160 mL serum bottles with 155 mL aqueous phase and 5 mL headspace, following the reactor design described previously.²¹ Experiments with HCA were run in 25 mL serum bottles with 20 mL aqueous phase and 5 mL headspace. The aqueous phase contained MOPS buffer adjusted to pH 8.0 (0.01 M) and 0.05 M NaCl and additionally either dithionite-reduced or Fe(II)-reacted clay mineral (final concentration: 5 g L⁻¹). Control conditions included reactors that contained only buffer solution (to test for volatilization), non-reduced clay mineral (to quantify contaminant sorption to the mineral), and 20 mM aqueous Fe(II) (to test for precipitate formation in the absence of clay minerals). All reactor conditions are summarized in Table S2 for the degradation experiments with PCE and TCE, in Table 2 for the HCA degradation reactors, and in Table 1 for the experiments for Mössbauer spectroscopy. Volatilization and sorption to the minerals was negligible for both PCE and TCE (Figure S1). Similarly, volatilization of HCA was limited (8.6±0.1%) and there was some sorption to all native clay minerals (17±0.5, Figure S2).

Degradation experiments were initiated by adding 50 μ L of a methanolic spike solution containing PCE, TCE, or HCA to the crimp-capped and aluminum foil-wrapped reactors and yielded an initial contaminant concentration of ~60 μ M (PCE), ~70 μ M (TCE) or ~45 μ M (HCA). For HCA, additional exhaustion experiments for mineral-free and Syn-1 containing suspensions were set up with higher initial HCA concentrations (1-1.3 mM) and run for 750 hours. Using a gas-tight glass syringe, an initial aqueous sample (420 μ L) was withdrawn after mixing the suspension vigorously using a Vortex shaker and extracted into 600 μ L n-pentane

containing the internal standard 1-chloro-3-fluorobenzene (CFB, 20 μ M). The reactors were placed horizontally on a reciprocal shaker and sampled at given intervals up to a maximum of 343 days ($\sim$ 1 year). Aqueous samples were withdrawn and extracted as described and stored at -18 °C until analysis. Headspace samples of 250 μ L were withdrawn immediately following aqueous phase sampling using a gas-tight glass syringe equipped with a sample lock, and were analyzed instantly.

Chlorinated compounds and gaseous products. Gas chromatography with mass detection (GC-MS; Agilent) was used to quantify the concentrations of all chlorinated compounds, i.e. the reactants HCA, PCE, and TCE, as well as the dichloroethane (DCE) dechlorination products cis-DCE, trans-DCE, and 1,1-DCE. The compounds were separated on a Rtx-VMS fused silica capillary column (Restek).

Analysis of ethane, ethene, acetylene, and vinylchloride (VC) was performed on a Thermo Trace GC coupled to a flame ionization detector (FID). Samples were directly injected onto an Agilent CP-Silica Plot column and identified and quantified by using gas standards (acetylene, 1 % in N₂, and ethene, ethane, and VC, all 1% in N₂, Calgaz). Details of the GC methodology and correction calculations are included in the Supporting Information (SI).

Fe analysis. Aqueous Fe(II) and Fe(total) concentrations were measured using the 1,10-phenanthroline method.³⁷ Solid phase Fe concentrations were measured following HF digestion using a modified 1,10-phenanthroline method,^{38,39} as described previously.³⁴

Mössbauer spectroscopy. Reactors prepared for Mössbauer analysis were sacrificed before addition of contaminants. The solid phase was transferred onto and sealed in Kapton tape to prevent oxidation during the transfer to the Mössbauer spectrometer. Mössbauer spectra were calibrated against α -Fe metal. Further details on the Mössbauer analyses are provided in the SI.

Data evaluation. The kinetic data, i.e. concentrations of HCA and its reduction product PCE measured at predetermined time points, were analyzed for the reaction rate constant using the differential equations given in the Results and Discussion section. The equations were solved numerically using Mat- lab's ODE15s routine, as described previously.⁴⁰

Results and Discussion

PCE and TCE transformation by Fe(II)-containing clay minerals.

To determine whether tetrachloroethene (PCE) and trichloroethene (TCE) could be transformed by structurally bound Fe(II) in clay minerals, we reacted PCE and TCE with chemically reduced clay minerals NAu-1 and SWy-2. As expected from previous work,^{40,41} dithionite reduced a significant amount of the structural Fe(III) resulting in Fe(II)/Fe(total) ratios of 90% in NAu-1 and 81% in SWy-2. Based on mediated electrochemical measurements, these extents of reduction correspond to reduction potentials of -0.51 V for NAu-1 and -0.21 V for SWy-2.⁴² Both of these reduction potentials are similar to or more negative than the one- and two-electron reduction potentials of PCE and TCE (PCE: $E_1 = -0.358$ V, $E_2 = 0.582$ V; TCE: $E_1 =$

-0.578 V, $E_2 = 0.543$ V),¹² indicating that PCE and TCE transformation by chemically-reduced clay minerals is thermodynamically feasible. Despite favorable thermodynamics for PCE/TCE reduction by reduced NAu-1 and SWy-2, we did, however, not observe reduction over a timeframe of almost 1 year (343 days) (Figure 1, top row). More specifically, we detected neither a decrease in PCE or TCE concentrations nor the formation of degradation products in our experiments with dithionite-reduced NAu-1 and SWy-2 (Figure 1). Our results suggest that structural Fe(II) in clay minerals alone does not degrade PCE and TCE under anoxic conditions, consistent with the previously observed stability of PCE and TCE in the presence of dithionite-reduced, Fe-rich smectite SWa-1 (16 wt% Fe).²⁹

While structural Fe(II) in clay minerals does not reduce PCE and TCE under anoxic conditions, there is some evidence that reduction will occur after Fe(II) amendment, with 10% reduction of both PCE and TCE observed after addition of aqueous to dithionite-reduced montmorillonite.³⁰ We tested whether adding Fe(II) to native Fe-containing clay mineral suspensions would result in PCE and TCE reduction and varied initial aqueous Fe(II) concentrations from 1.9 mM to 20.1 mM (Table S2). In contrast to previous observations, we did not observe any chlorinated ethene transformation products for NAu-1 regardless of how much Fe(II) we added (Figure 1, second and third row). Furthermore, we observed no reduction of PCE and TCE with SWy-2 amended with low to moderate Fe(II) concentrations (≤ 4.9 mM, Figure 1) similar to those reported previously to result in PCE and TCE reduction.³⁰

Only at our highest aqueous Fe(II) concentration of 20.1 mM *and* in the presence of the Fe- poor clay mineral SWy-2 did we detect reduction products (Figure 1, third column). The primary products formed were acetylene, ethene, and ethane with no measurable chlorinated transformation products (TCE, dichloroethenes, vinylchloride; Table S3). Both observations are consistent with reductive β -elimination rather than a stepwise hydrogenolysis process, which has been suggested to be indicative of abiotic transformation.¹² Over the initial 100 days of reaction, degradation products increased to 17% and 15% of initially present PCE and TCE, somewhat higher than the 10% found for Fe(II)-reacted, dithionite-reduced montmorillonite over the same reaction time.³⁰ We note that although we observed the formation of significant amounts of reaction products, the amount of PCE and TCE remained largely unchanged in our reactors. The 15-17% transformation quantified from product formation falls, however, within the standard deviation of our measurements of PCE and TCE (Figure 1) and is thus not detectable from the reactant data alone. After the initial 100 days of reaction until the end of the reaction time (343 days), the degradation products remained at the same level, suggesting that Fe(II)-reacted SWy-2 could degrade only a finite fraction of the PCE and TCE present in our experiments and that the reactive species responsible for reducing PCE and TCE had become consumed.

Our observations of PCE and TCE reduction only at high Fe(II) concentrations is similar to what we previously observed for magnetite. We found that magnetite alone could not transform PCE and TCE unless enough Fe(II) was added to exceed the saturation of Fe(OH)₂ and we suggested that conditions favoring the formation of reactive mineral intermediates (RMI) such as Fe(OH)₂ was necessary for reduction to occur.²¹ To evaluate whether an RMI might have formed and be responsible for PCE and TCE reduction in our experiments, we calculated

whether our conditions were conducive to $\text{Fe}(\text{OH})_2$ formation. We found that our reactors yielding transformation products were also oversaturated with respect to $\text{Fe}(\text{OH})_2$, whereas reactors with lower $\text{Fe}(\text{II})$ concentrations were at or below the $\text{Fe}(\text{OH})_2$ solubility product ($\log K_{\text{sp}}$: -14.30,^{43–45} Figure S3). We ran controls at similar conditions (20.1 mM $\text{Fe}(\text{II})$ at pH 8) and in the absence of clay mineral to confirm that both $\text{Fe}(\text{OH})_2$ formed and that PCE and TCE were reduced (Figure 1, fourth row). A white precipitate formed and we observed similar extents of product formation (PCE: 21%, TCE: 20%, Figure 1, fourth column) and similar product distribution (Table S3) in the clay mineral-free reactors and in reactors also containing SWy-2 (PCE: 17%, TCE: 15%). Note, we observed more reduction with $\text{Fe}(\text{OH})_2$ alone than we did in our previous work (15-17% here compared to 0.3-13% previously²¹). We suspect that these differences might have been the result of some slight differences in experimental conditions such as $\text{Fe}(\text{II})$ concentration, equilibration time before PCE and TCE addition or amount of base added during pH adjustment.²¹

Reactive mineral intermediate formation in the presence of clay minerals

It appears that conditions that favor formation of a reactive mineral intermediate such as $\text{Fe}(\text{OH})_2$ may be necessary for PCE and TCE reduction to occur in the presence of clay minerals. Yet, the precipitation of $\text{Fe}(\text{OH})_2$ as an RMI under conditions conducive to its formation does not explain why we observed PCE and TCE degradation with low Fe-content clay mineral SWy-2 but not with high Fe-content clay mineral NAu-1 for the same initial $\text{Fe}(\text{II})$ concentration and pH (Figure 1, Table S2). However, the striking color of our clay mineral suspensions after reaction with $\text{Fe}(\text{II})$ and the differences in color for different reaction conditions suggest the formation of RMIs different from $\text{Fe}(\text{OH})_2$. While NAu-1 exhibited the same color change from light green to dark blue after both addition of aqueous $\text{Fe}(\text{II})$ and reduction with dithionite (Figure S4), low Fe-content clay mineral SWy-2 showed a marked color change from its native beige only after addition of aqueous $\text{Fe}(\text{II})$ and a gradual color evolution from orange to dark blue with increasing $\text{Fe}(\text{II})$ concentrations (Figure S5). The intense blue color of our SWy-2 suspensions reacted with 20 mM $\text{Fe}(\text{II})$ could be indicative of the presence of $\text{Fe}(\text{II})$ - $\text{Fe}(\text{III})$ precipitates,⁴⁶ for example a green rust-like phase as suggested in previous work.^{47,48} However, the ability of green rusts to reductively degrade PCE and TCE has recently been called into question,²³ although previous work has demonstrated gaseous product formation during reaction of chlorinated ethenes with green rusts.^{20,22}

To better understand what makes the precipitates reactive for PCE and TCE degradation, we used Mössbauer spectroscopy to determine their Fe speciation. We reacted aqueous $\text{Fe}(\text{II})$ enriched in the Mössbauer-visible ^{57}Fe -isotope ($^{57}\text{Fe}/\sum^i\text{Fe} \geq 95\%$) with clay minerals such that the presence of ^{57}Fe in the clay mineral structure contributed less than 3% to the overall Mössbauer signal. This enabled us to study the precipitates' Fe speciation without significant interference from clay mineral Fe comprising ^{57}Fe in its natural abundance (2.2 % $^{57}\text{Fe}/\sum^i\text{Fe}$). Analysis of the Mössbauer spectra yielded relative $\text{Fe}(\text{II})$ contents, i.e. $\text{Fe}(\text{II})/\text{Fe}(\text{total})$ ratios, of the precipitates formed after reaction of $^{57}\text{Fe}(\text{II})$ with SWy-2 and NAu-1 from

25% at 2 mM Fe(II) to 80% at 20 mM Fe(II) (Figure S6, Table S4). The Mössbauer parameters center shift (CS) and quadrupole split (QS) for both Fe(II) and Fe(III) are in the typical range for these species. For precipitates formed at Fe(II) concentrations ≥ 4.9 mM, the parameters are also similar to published values of Fe(II) and Fe(III) in green rust.^{49–51} However, both color (Figure S5) and Fe(III) content (Table S4) of most of our precipitates are atypical for green rust (typical range: 0.25–0.33 Fe(III)/Fe(total)^{49–51}), confirming that mineral identity cannot be unambiguously assigned based on Mössbauer data alone. Regardless of the specific identity of the precipitates formed, the range of Fe(III) content of the precipitates is remarkable (20–75%, Table S4) and must have resulted from the oxidation of the aqueous Fe(II) that had been added. Indeed, the precipitates formed from mineral-free solution contained only Fe(II), ruling out that accidental Fe(II) oxidation had occurred. Even more compelling, Fe(III) was also absent after Fe-free clay mineral Syn-1 had been reacted with Fe(II) (Figure S7, Table S4), suggesting that clay mineral Fe controlled the Fe(III) content of the precipitate formed.

To confirm that clay mineral Fe controlled the precipitates' Fe speciation by functioning as a sink for electrons from the added Fe(II), we quantified the speciation of Fe in the clay mineral structure in complementary experiments with Mössbauer-invisible aqueous ⁵⁶Fe(II). Similar to previous reports, reaction of low Fe-content clay mineral SWy-2 with aqueous Fe(II) led to the reduction of a substantial portion of clay mineral structural Fe(III),^{52,53} as indicated by the decrease in the Fe(III) doublet present in the native clay mineral and a simultaneous formation and increase of an Fe(II) doublet (Figure S8). We observed final structural Fe(II)/Fe(total) ratios of 78–93% for ⁵⁶Fe(II)-reacted SWy-2 (Table S4), which are comparable to the Fe reduction extent obtained via chemical reduction with dithionite (81%). As we have observed before,³³ the Fe reduction extent in NAu-1 was much smaller when aqueous Fe(II) was the reductant than when dithionite was used (7–15% vs 90%, respectively). However, the amount of clay mineral Fe reduced was very similar across the range of aqueous Fe(II) concentrations used (24–54 μ mol, Table 1). This observation is consistent with previous reports on a similar Fe-rich smectite (NAu-2), which also exhibited an upper limit of Fe reduction that could be achieved with aqueous Fe(II) as a reductant.⁵⁴ Interestingly, the total amount of clay mineral Fe reduced in clay mineral SWy-2 (35–42 μ mol, Table 1) is slightly lower than in Fe-rich clay mineral NAu-1, despite similar or even higher Fe(II) uptake from solution, and is most likely limited by the total amount of Fe present in the clay mineral structure (45 μ mol).

When comparing the Mössbauer results from ⁵⁷Fe(II)- and ⁵⁶Fe(II)-addition, we found that the amount of added Fe(II) oxidized was very similar to the amount of clay mineral Fe(III) reduced (Table 1). The complete electron balance confirms that clay mineral Fe controls the Fe speciation of the precipitates formed, as it oxidizes sorbed Fe(II) via interfacial electron transfer. Our findings further identified that the relative Fe(II) and Fe(III) content of the precipitates formed is determined by (a) the amount (or concentration) of aqueous Fe(II) in the system and (b) the Fe content of the clay mineral (Table 1). These results also reveal that the low Fe content in SWy-2 was key to the higher Fe(II)/Fe(total) content of the precipitates formed compared to those observed in the presence of Fe-rich clay mineral NAu-1 (Table 1). Interestingly, we observed PCE and TCE transformation only in those three reactors which contained precipitates

with the lowest Fe(III)/Fe(total) content (≤ 0.2), indicating that limited electron transfer to clay mineral Fe is more likely to result in the formation of reactive precipitates. Due to the limited overall PCE and TCE transformation extent as well as the small number of experiments, further interpretation of the relationship between precipitate Fe(II) content and its reactivity in dechlorination reactions would be highly speculative.

Evaluating the reactivity of mineral intermediates using HCA as kinetic probe

To better resolve the differences in mineral intermediate reactivity, we used the more readily reducible hexachloroethane (HCA) as kinetic probe. We chose the same reactions conditions as for the experiments with PCE and TCE, including Fe-bearing clay minerals NAu-1 and SWy-2, Fe-free mineral Syn-1, and mineral-free conditions at initial aqueous Fe(II) concentrations between 5.1 mM and 21.2 mM (Table 2). For all reaction conditions, we observed a decrease in HCA concentration and a simultaneous increase in PCE concentration over 30-80 hours of reaction (Figure 2). The exclusive and quantitative transformation of HCA into PCE is consistent with the reduction following a β -elimination pathway⁵⁵ like we observed for PCE and TCE. At reaction times longer than 50 hours, both HCA and PCE concentrations remained stable, indicating that the reaction had ceased (in the presence of NAu-1 and SWy-2) or was complete (Syn-1 and mineral-free reactors, Figure 2). Previous work has demonstrated that structural Fe(II) in Fe-rich clay mineral (ferruginous smectite SWa-1, 12.6 wt% Fe) is capable of transforming HCA to PCE over extended time periods (≥ 1000 hours).⁵⁵ However, our reference experiments with fully dithionite-reduced low Fe-content SWy-2 and partly reduced high Fe-content NAu-1 exhibiting the same reduction extents achieved after reaction with aqueous Fe(II) (Table S4), demonstrate the absence of HCA transformation by clay mineral Fe(II) over our reaction time of 80 h (Figure S2).

To quantify HCA reduction, we initially applied the simplest kinetic rate law that has been used to evaluate chlorinated solvent degradation.⁵⁶ In a first-order kinetic rate law, the change in HCA concentration over time (rate) depends only on the HCA concentration and the rate constant k (equation 1):

$$\frac{d[\text{HCA}]}{dt} = -k[\text{HCA}]$$

Although the total Fe(II) concentration of ≥ 5 mM in our reactors is 50-200-fold the amount required to completely transform 50 μ M HCA to PCE via a 2-electron reduction, the measured data was not described well by a first-order kinetic model (Figure S9). We therefore applied a second-order rate law that takes into account changes in both HCA (equation 2) and *reactive* Fe(II) concentration (equation 3) as well as the transfer of 2 electron from Fe(II) to HCA (stoichiometric factor $\nu = 2$).

$$\frac{d[\text{HCA}]}{dt} = -k[\text{HCA}][\text{Fe(II)}_r]$$

$$\frac{d[\text{Fe(II)}_r]}{dt} = -k[\text{HCA}][\text{Fe(II)}_r] \cdot \nu$$

Our second-order kinetic model very well describes the measured changes in HCA concentration for all reaction conditions (Figure 2) and yields values of both the rate constant k and the initial *reactive* Fe(II) concentration, $[\text{Fe(II)}_r]_0$. We found that the rate constant k was very similar for all reaction conditions (Table 2), suggesting that the same or very similar Fe(II) species and/or of similar intrinsic reactivity⁵⁶ were responsible for the observed HCA degradation.

In contrast, the initial *reactive* Fe(II) concentrations span more than one order of magnitude from the least (NAu-1 reacted with 5.5 mM Fe(II)) to the most reactive condition (Syn-1 reacted with 21 mM Fe(II)) and ranged between 14 μM and 263 μM (Table 2). For the reactors containing Fe-bearing clay minerals, these Fe(II) concentrations are less than the reduction equivalents required to completely transform all HCA to PCE, consistent with the apparent exhaustion of reactive species observed. For the reactors where no interfacial electron transfer occurred (Syn-1 and mineral-free conditions), reactive Fe(II) was in excess (up to 3.3-fold) with respect to complete HCA transformation, again in agreement with the observed data. Overall, only a small fraction of the Fe(II) present was reactive in HCA degradation (0.25-1.3%, Table 2), suggesting that the identity of these Fe(II) species cannot be resolved using bulk characterization methods, including Mössbauer spectroscopy. Even for those conditions where all HCA was reduced to PCE (Syn-1 and mineral-free reactors, Figure 2), exhaustion experiments suggest that only up to 444-560 μM Fe(II), or 2.1-2.7% of the total Fe(II), were reactive (Table S5).

Our observation of HCA degradation for all reaction conditions enable us to explore the trends of observed reactivity, i.e. of both rate constant and reactive Fe(II) concentration. As we found for PCE and TCE degradation, the initial total Fe(II) concentration alone does not control contaminant dechlorination and we thus used the precipitates' relative Fe(II) content to further analyze our data. When plotting rate constant k against the precipitate Fe(II)/Fe(total) ratio, we observed no correlation (Figure 3). In contrast, when we plotted $\log [\text{Fe(II)}_r]_0$ against precipitate Fe(II)/Fe(total), we observed a trend: reactive Fe(II) concentrations increased with increasing relative Fe(II) content of the precipitates (Figure 3). These two findings suggest that the effective reactive species and/or its intrinsic reactivity was independent of the mineral identity of the bulk precipitates in our experiments⁵⁶ but that its abundance was controlled by the precipitate Fe(II)/Fe(total) ratio and, in turn, controlled the overall rate of contaminant dechlorination.

Although the precipitates' relative Fe(II) content could explain the reactivity trends observed with HCA, it remains unclear how these findings can be extrapolated to PCE and TCE. However, our results do not enable us to rationalize why PCE and TCE were not degraded when the precipitate Fe(II)/Fe(total) value was lower than 0.2, whereas HCA was transformed for all precipitate Fe(II)/Fe(total) values. We still suggest that HCA might be useful as an additional and more convenient probe molecule to test for the potential of PCE and TCE degradation as HCA transforms more quickly and is less volatile. When HCA is used as a probe molecule and no degradation is observed, PCE and TCE transformation can be ruled out. In case of HCA degradation, reduction kinetics can be analyzed for the reactive Fe(II) concentration in the

system and to estimate the maximum extent of PCE and TCE degradation that could be expected. When we quantify the Fe(II) consumed by PCE and TCE degradation in the experiments with SWy-2 reacted with 20 mM Fe(II), we obtain a value of 38-68 μM (Table S3), which agrees well with the amount of reactive Fe(II) determined using HCA (65 μM , Table 2). In the mineral-free and Syn-1 containing reactors, a lower reactive Fe(II) concentration resulted from the PCE and TCE reduction products quantified (52-90 μM and 59-98 μM , respectively; Table S3) compared to the reactive Fe(II) determined from the analysis of HCA kinetics (116 μM and 263 μM ; Table 2). When we take into account that not all reactive Fe(II) was utilized in the transformation of HCA to PCE, the reactive Fe(II) consumed by HCA and PCE/TCE reduction was similar (HCA: 81-94 μM). Because our data set is small and reactive Fe(II) utilization might have been limited by the available concentration of HCA (as explored in the exhaustion experiments), the agreement between HCA and PCE/TCE degradation experiments should be confirmed with a larger data set and tested for its applicability to other reductive mineral systems, which is outside the scope of this work.

Environmental significance

Our results clearly demonstrate that structural Fe(II) in clay minerals *alone* is not capable of reductively transforming PCE or TCE over almost a year of reaction. Under our conditions, we therefore conclude that direct reduction by clay mineral Fe(II) will not contribute to natural attenuation at sites contaminated with CEs. Only once we added aqueous Fe(II) under conditions that exceeded the solubility of ferrous hydroxide ($\text{Fe}(\text{OH})_2$) did we observe dechlorination products. Our findings are consistent with what we previously observed with magnetite, which alone could not degrade CEs but only did so once conditions were conducive to the formation of the reactive mineral intermediate (RMI) $\text{Fe}(\text{OH})_2$.²¹

In contrast to the passive role of stoichiometric ($\text{Fe}(\text{II})\text{Fe}(\text{III})_2\text{O}_4$) magnetite in RMI formation and PCE and TCE degradation, clay mineral Fe is active in redox reactions, which affect RMI formation and, consequently, its reactivity for CE transformation. We demonstrated that in the absence of clay mineral Fe(III), i.e. in clay mineral-free experiments and in the presence of Fe-free clay mineral, $\text{Fe}(\text{OH})_2$ precipitated and controlled CE degradation, just as found for Fe(II)-reacted magnetite.²¹ Once Fe-bearing clay minerals were present, the Fe(II) content of the precipitates decreased, which was directly linked to a decreased reactivity of the precipitates and was caused by interfacial electron transfer from aqueous to clay mineral Fe. Fe-bearing clay minerals thus acted as a sink for electrons that might have reduced the CEs. We found that both higher aqueous Fe(II) concentration and lower clay mineral Fe content led to increased dechlorination rates, suggesting that these parameters should be included when assessing the feasibility of CE degradation in real sediments.

Previous work on contaminant degradation (U(VI), nitroaromatic compounds) by Fe(II)-reacted clay minerals suggested that the Fe(II)-Fe(III) precipitate green rust dominated the suspensions' redox reactivity.^{48,57} In our work here we cannot rule out or confirm this tentative identification, yet our reactive precipitates contain either lower (0.20-0.23) or higher (0.37) Fe(III)/Fe(total) content than expected for green rusts (0.25-0.33).⁴⁹⁻⁵¹ More importantly, our

kinetic analyses indicate that the intrinsic reactivity of the *reactive* Fe(II) species was identical for all reaction conditions, irrespective of whether Fe(OH)₂ or an Fe(II)-Fe(III) phase precipitated, suggesting that the identity of the bulk precipitate phase was not the primary control on the reactivity observed. We found that the differences in HCA degradation rates were explained by the formation of different amounts of reactive Fe(II), which correlated with the precipitate's Fe(II)/Fe(total) content. Despite significant quantities of precipitate formed (3.72-14.1 mM Fe removed from solution, Table 1), our quantification of *reactive* Fe(II) from kinetic fits shows that the *reactive* Fe(II) in our systems comprise a very small portion of the total Fe(II) (0.2-1.3%, Table 2), suggesting that reactive Fe(II) species might become exhausted unless they are regenerated continuously, for example via active precipitation. Although the precipitate Fe(II) content might be a useful parameter for assessing abiotic natural attenuation, it will be difficult to measure in natural sediments, where isotopic labeling of *in-situ* produced aqueous Fe(II) for Mössbauer spectroscopy will be the major challenge.

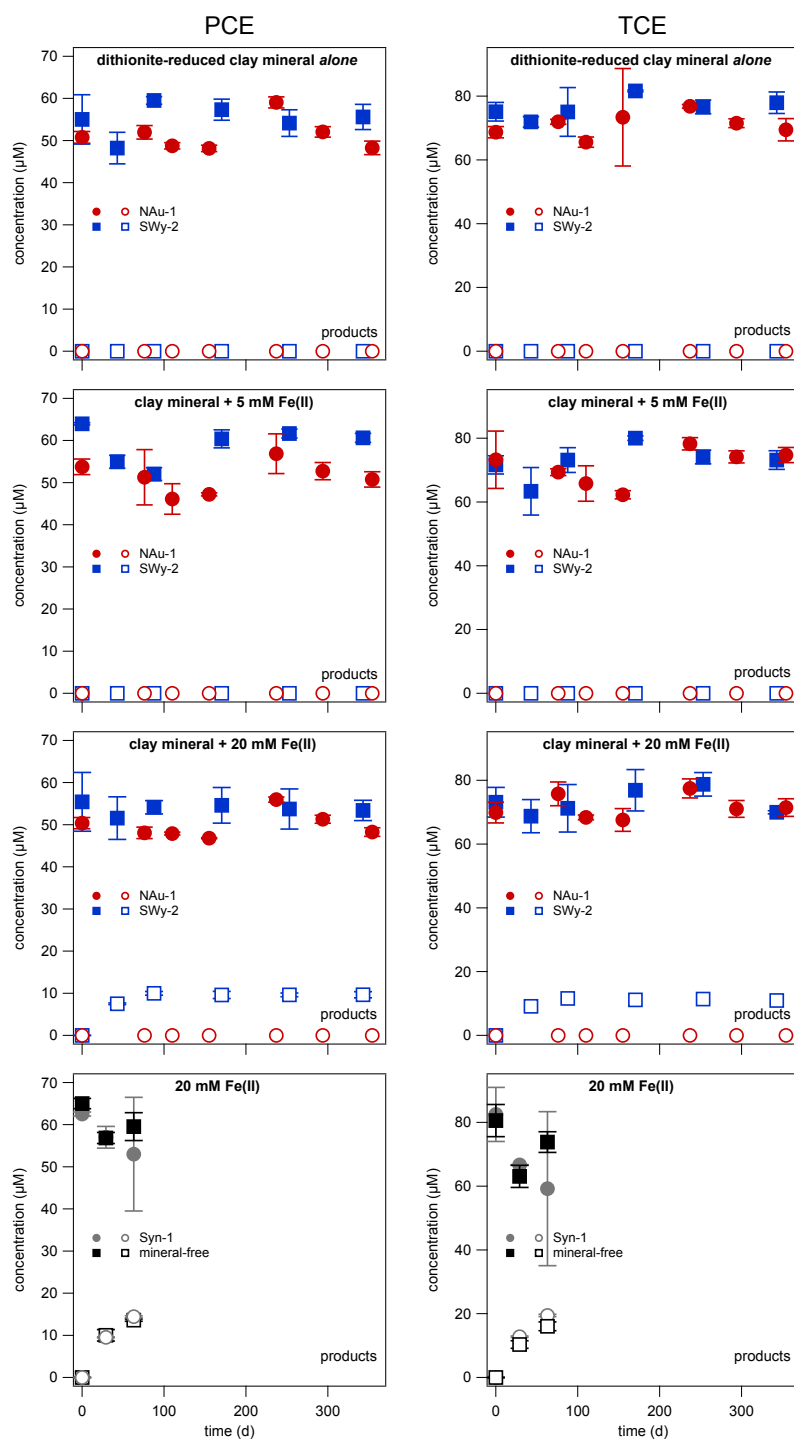
Our results also enable us to re-interpret previous results of PCE/TCE and HCA reduction by Fe(II)-reacted, dithionite-reduced clay minerals.^{30,56} Because treatment with dithionite will reduce all available Fe in the clay mineral structure to Fe(II),³⁵ as also demonstrated in this study, subsequently added aqueous Fe(II) will not undergo interfacial electron transfer with this clay mineral Fe(II). Hence, addition of aqueous Fe(II) to dithionite-reduced clay minerals is more likely to result in the formation of (reactive) precipitates, especially when reaction conditions would predict Fe(OH)₂ supersaturation, i.e. at high Fe(II) concentrations and pH values. Although it was suggested that reactive surface-bound Fe(II) formed and degraded PCE and TCE in suspensions of Fe(II)-reacted, dithionite-reduced biotite, montmorillonite, and vermiculite,³⁰ our calculations suggest that at 4.3 mM Fe(II) concentration and pH values ≥ 8.0 , Fe(OH)₂ was near saturation or was expected to precipitate (saturation index = $\log(\text{IAP}/K_{\text{sp}})$: -0.17 to 0.83 for pH 8.0 to 8.5, with $K_{\text{sp}}(\text{Fe(OH)}_2) = 5 \times 10^{-15} \text{ M}^3$ ⁴³⁻⁴⁵). Hence, reduction of PCE and TCE might have been caused by a reactive mineral precipitate, similar to what we observed in the absence of electron transfer to clay mineral Fe, i.e. for Fe(II)-reacted Fe-free clay mineral Syn-1. In contrast, circumneutral pH value (7.2) and low Fe(II) concentration (1 mM) is unlikely to have resulted in the formation of a reactive precipitate that could explain the HCA reduction observed previously.⁵⁶ We note though that the second-order rate constant reported for HCA reduction of $\log k = 0.7$ (converted from a surface normalized, pseudo-first order rate constant) is much lower than the consistent rate constant we obtained in our experiments ($\log k = 3.3$), suggesting that a different reactive Fe(II) species was controlling the overall reactivity. This lower reactivity could be due to HCA reduction by structural Fe(II) in the clay mineral, which was much slower for dithionite-reduced clay minerals compared to our Fe(II)-reacted clay minerals (1000 hours⁵⁵ vs 80 hours to completion) and was not evaluated in this previous study.⁵⁶

Recently, a study on natural sediments has called into question whether abiotic reduction of PCE and TCE was at all relevant at contaminated sites. It was found that oxidative degradation of TCE during the oxygenation of reduced sediments was orders of magnitude faster and more complete than reductive degradation.³² Because we only have few data points

for PCE and TCE degradation, we cannot derive reliable rate constants (or half-life values) for reaction with our RMIs, for comparison to the sediment data. Comparing the amount of degradation product acetylene formed in our reactors with that reported to arise from reduction in reducing sediments, we found, however, a more than tenfold larger degradation extent (7-8 μM vs 0.3 μM) despite the much lower initial concentration of TCE (and PCE) in our experiments (55-70 μM PCE/TCE vs 3 mM TCE). The apparent discrepancy between these two transformation efficiencies might be due to the difference of several parameters, including pH value, solid Fe(II) content, as well as clay mineral content, identity, and Fe content. Interestingly, our data also showed that reduction ceases after about 100 hours, and thus is limited under static conditions, whereas experiments in the study using natural sediments was limited to 100 days and thus did not capture this effect. Hence our results suggest that abiotic reductive degradation could contribute to at least a small extent to the natural attenuation of PCE and TCE, when reactive Fe(II) precipitates are being actively formed and regenerated, for example under dynamic conditions typical for natural subsurface environments.

Active precipitation of RMIs might have also played a major role in a recent remediation study, where a mixture of dissolved Fe(II) and fermentable substrates was applied to simultaneously stimulate abiotic and biotic CE transformation.⁵⁸ For all 24 field sites, a significant increase in CE degradation rates and extents was observed when both dissolved Fe(II) and fermentable substrates were used compared to fermentable substrates only. Because no data on mineralogy or geochemistry at the field sites were collected, we can only speculate that this type of treatment may have resulted in RMI formation similar to what we observed here and previously.²¹ Importantly, the simultaneous stimulation of microbial respiration, which could have led to clay mineral Fe reduction, and addition of dissolved Fe(II) could have led to RMIs with very low Fe(III) content, similar to what we found for Fe-free clay mineral Syn-1. Future work should aim to test this hypothesis and involve both laboratory experiments and field measurements.

3.2 Figures and Tables



20

Figure 1: PCE (first column) and TCE concentrations (second column) in suspensions of dithionite-reduced and Fe(II)-reacted (5 mM, 20 mM) clay minerals NAu-1 (red circles) and SWy-2 (blue squares) over 343 days of reaction. Dechlorination products (open markers) were detected only for low Fe-content clay mineral SWy-2 reacted with 20 mM Fe(II). Similar rates and extents of dechlorination product formation were observed at 20 mM Fe(II) in mineral-free solution (black squares) and in the presence of Fe-free clay mineral Syn-1 (grey circles, fourth row). Error bars represent the standard deviation of duplicate reactors.

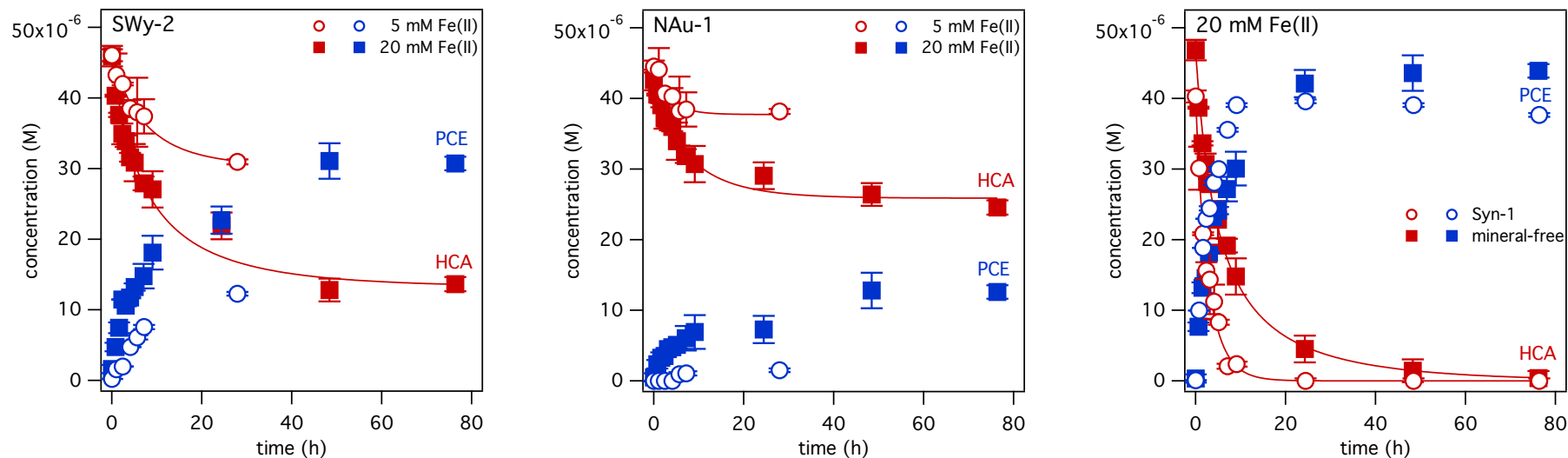


Figure 2: Transformation of hexachloroethane (HCA, red) to PCE (blue) in suspensions of SWy-2 and NAu-1 reacted with 5 mM Fe(II) (open circles) and 20 mM Fe(II) (filled squares). For comparison, HCA degradation in 20 mM Fe(II) solution without the addition of clay mineral (filled squares) and in the presence of Fe-free Syn-1 (open circles) is shown. The general trend of reactivity at the same Fe(II) concentration is Syn-1>mineral-free>>SWy-2>NAu-1 and the same clay mineral exhibits higher reactivity at higher Fe(II) concentration. Solid lines are fits to the second-order kinetic model (equations 2-3). Error bars represent the standard deviation of duplicate reactors.

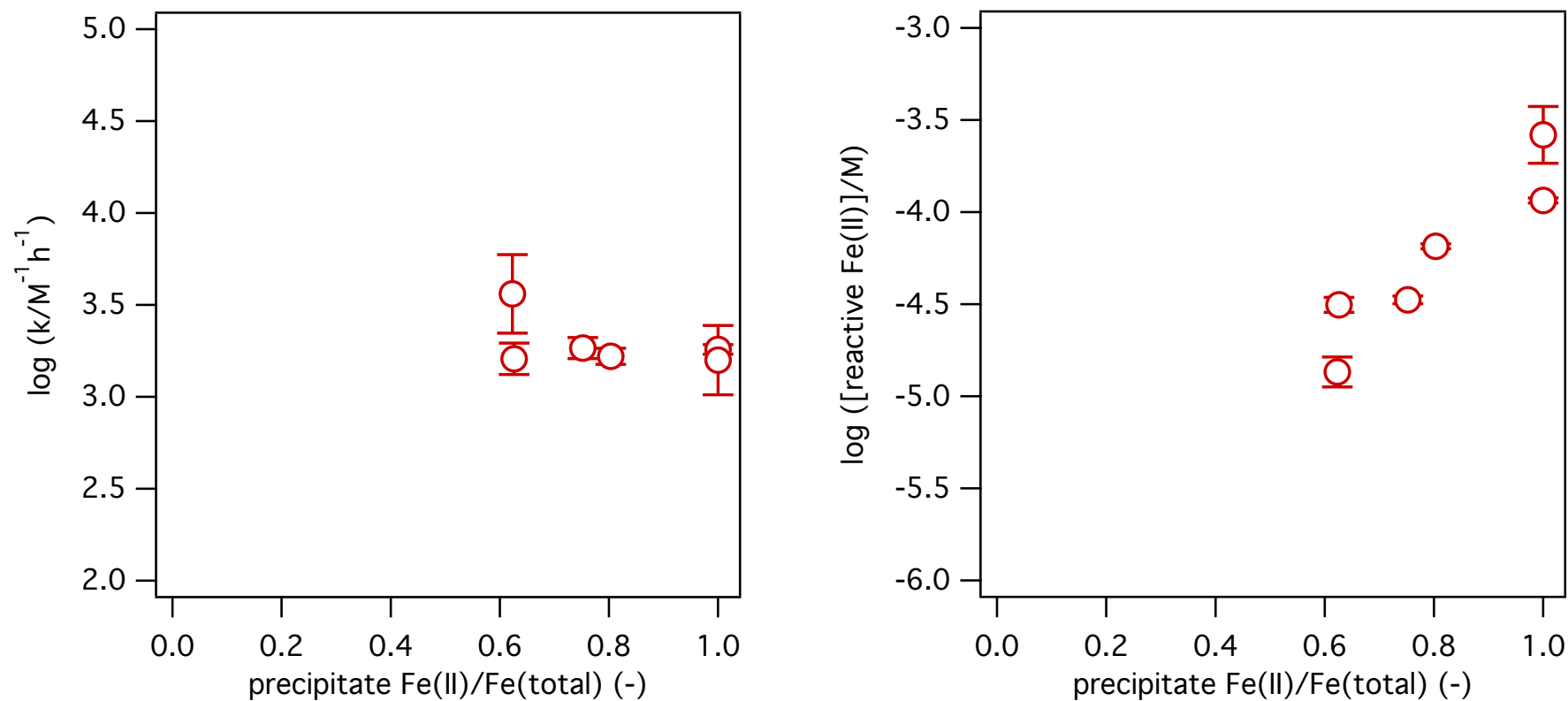


Figure 3: Kinetic parameters for HCA degradation obtained from fits of all measured data to the second order kinetic model (equations 2-3): second order rate constant k ($M^{-1}h^{-1}$) and initial concentration of reactive Fe(II) (M). The parameter values are plotted as logarithms and as a function of the relative Fe(II) content (Fe(II)/Fe(total) ratio) of the precipitate formed (data from Table S4). Error bars represent the standard deviations from the least squares fit.

Table 1: Electron balances for experiments with Fe-bearing clay minerals SWy-2 and NAu-1 at different initial aqueous Fe(II) concentrations. The amount of aqueous Fe taken up and oxidized and the amount of clay mineral Fe reduced are in good agreement. Values in parentheses are standard deviations.

clay mineral	aqueous Fe(II)			Fe taken up				clay mineral Fe		
	nominal <i>mM</i>	initial ^a <i>mM</i>	final ^a <i>mM</i>	total Fe(II) ^b <i>μmol</i>	Fe(II) oxidized % ^c	Fe(II) oxidized <i>μmol</i> ^d	Fe(II) remaining ^e <i>μmol</i>	total ^f <i>μmol</i>	Fe(III) reduced % ^g	Fe(III) reduced <i>μmol</i> ^h
SWy-2	2	2.28(0.27)	0.10(0.01)	43.6(0.3)	74.6(0.3)	32.6(0.2)	11.1(0.4)	45.4(1.8)	77.8(2.0)	35.3(1.7)
SWy-2	5	5.67(0.75)	0.22(0.20)	109(1)	37.4(0.3)	40.8(0.4)	68.3(0.9)	45.4(1.8)	79.4(3.8)	36.0(2.2)
SWy-2	20	21.5(2.2)	7.37(2.19)	282(3)	19.7(0.6)	55.6(1.7)	226(4)	45.4(1.8)	92.5(1.9)	42.0(1.9)
NAu-1	5	3.79(0.85)	0.08(0.04)	74.2(0.9)	37.7(0.4)	28.0(0.4)	46.2(1.0)	354(11)	6.9(0.6)	24.4(2.1)
NAu-1	20	17.9(3.7)	6.46(2.46)	228(4)	23.1(0.1)	52.7(1.1)	175(5)	354(11)	15.4(0.7)	54.4(2.5)

^a Average values from experiments with ⁵⁶Fe(II) and ⁵⁷Fe(II). Aqueous Fe(II) concentrations were measured using the 1,10-phenanthroline method.³⁷

^b Calculated from the difference of initial and final aqueous Fe(II) concentration and the reactor volume of 0.02 L.

^c Relative area of Fe(III) doublets in the Mössbauer spectra of ⁵⁷Fe(II)-reacted clay minerals. Data from Table S4.

^d Calculated using the total Fe(II) removed from solution and the relative area of Fe(III) doublets in the Mössbauer spectra of ⁵⁷Fe(II)-reacted clay minerals.

^e Calculated as difference between total Fe(II) taken up and Fe(II) oxidized. ^f Calculated from the clay mineral concentration and the clay mineral Fe content determined via HF digestion and quantification using the 1,10-phenanthroline method.^{35,39} SWy-2: 5 g L⁻¹, 0.454±0.018 mmol g⁻¹ Fe; NAu-1: 5 g L⁻¹, 3.54±0.11 mmol g⁻¹ Fe.

^g Relative area of Fe(II) doublets in the Mössbauer spectra of ⁵⁶Fe(II)-reacted clay minerals. Data from Table S4. ^h Calculated using the amount of clay mineral Fe and the relative area of Fe(II) doublets in the Mössbauer spectra of ⁵⁶Fe(II)-reacted clay minerals.

Table 2: Degradation experiments with HCA: reactor composition, rate constants, and initial concentrations of reactive Fe(II). Kinetic parameters were determined from fits of the measured data (Figure 2) to the kinetic model (equations 2-3). Values in parentheses are standard deviations of replicate reactors or from the least squares fit.

clay mineral ^a	initial HCA	initial Fe(II)	log k	[Fe(II) _{reactive}]	log([Fe(II) _{reactive}])	reactive Fe(II)/total Fe(II)	reactive Fe(II) excess ^b
	M	mM	(k/M ⁻¹ h ⁻¹)	M	([Fe(II) _{reactive}]/M)	%	
SWy-2	4.61(0.22) × 10 ⁻⁵	5.08(0.02)	3.21(0.09)	3.14(0.03) × 10 ⁻⁵	-4.50(0.04)	0.62	0.34
SWy-2	4.59(0.09) × 10 ⁻⁵	21.1(0.1)	3.22(0.04)	6.53(0.02) × 10 ⁻⁵	-4.19(0.01)	0.31	0.71
NAu-1	4.45(0.09) × 10 ⁻⁵	5.50(0.51)	3.56(0.21)	1.36(0.02) × 10 ⁻⁵	-4.87(0.08)	0.25	0.15
NAu-1	4.26(0.15) × 10 ⁻⁵	21.2(0.5)	3.27(0.06)	3.34(0.02) × 10 ⁻⁵	4.48(0.02)	0.16	0.39
Syn-1	4.03(0.31) × 10 ⁻⁵	20.9(0.3)	3.20(0.19)	2.63(0.11) × 10 ⁻⁴	-3.58(0.15)	1.26	3.26
- ^c	4.69(0.17) × 10 ⁻⁵	21.1(0.2)	3.26(0.03)	1.16(0.01) × 10 ⁻⁴	-3.94(0.01)	0.55	1.24

^a Clay mineral concentrations were 5 g L⁻¹. ^b Calculated as the ratio of the concentration of reactive Fe(II) determined and the reduction equivalents required to quantitatively reduce HCA to PCE, which requires the transfer of 2 electrons per HCA molecule: $\frac{[\text{Fe(II)}_{\text{reactive}}]}{[\text{HCA}] \cdot 2}$.

^c Initially mineral-free reactors that formed a white precipitate, presumably Fe(OH)₂.

References

- (1) He, Y. T.; Wilson, J. T.; Su, C.; Wilkin, R. T. Review of Abiotic Degradation of Chlorinated Solvents by Reactive Iron Minerals in Aquifers. *Groundwater Monitoring and Remediation* **2015**, *35*, 57–75.
- (2) Council, N. R. *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites*; The National Academies Press: Washington, DC, 2013; p 422.
- (3) Bradley, P. M.; Chapelle, F. H. Kinetics of DCE and VC Mineralization under Methanogenic and Fe(III)-Reducing Conditions. *Environ Sci Technol* **1997**, *31*, 2692–2696.
- (4) Darlington, R.; Lehmicke, L.; Andrachek, R. G.; Freedman, D. L. Biotic and abiotic anaerobic transformations of trichloroethene and cis-1,2-dichloroethene in fractured sandstone. *Environ Sci Technol* **2008**, *42*, 4323–4330.
- (5) Damgaard, I.; Bjerg, P. L.; Bælum, J.; Scheutz, C.; Hunkeler, D.; Jacobsen, C. S.; Tuxen, N.; Broholm, M. M. Identification of chlorinated solvents degradation zones in clay till by high resolution chemical, microbial and compound specific isotope analysis. *J Contam Hydrol* **2013**, *146*, 37–50.
- (6) Lee, M. D.; Odom, J. M., Jr.; R. J. B. New perspectives on microbial dehalogation of chlorinated solvents: Insights from the Field. *Annu Rev Microbiol* **1998**, *52*, 423–452.
- (7) Hunkeler, D.; Aravena, R.; Butler, B. J. Monitoring Microbial Dechlorination of Tetrachloroethene (PCE) in Groundwater Using Compound-Specific Stable Carbon Isotope Ratios: Microcosm and Field Studies. *Environ Sci Technol* **1999**, *33*, 2733–2738.
- (8) Lu, X.; Wilson, J. T.; Kampbell, D. H. Relationship between *Dehalococcoides* DNA in ground water and rates of reductive dechlorination at field scale. *Water Res* **2006**, *40*, 3131–3140.
- (9) Lee, P. K. H.; Macbeth, T. W.; Sorenson, K. S.; Deeb, R. A.; Alvarez-Cohen, L. Quantifying Genes and Transcripts To Assess the In Situ Physiology of *Dehalococcoides* spp. in a Trichloroethene-Contaminated Groundwater Site. *Appl Environ Microbiol* **2008**, *74*, 2728–2739.
- (10) Vogel, T. M.; Criddle, C. S.; McCarty, P. L. Transformations of halogenated aliphatic compounds. *Environ Sci Technol* **1987**, *21*, 722–736, doi:10.1021/es00162a001.

- (11) Mendoza-Sanchez, I.; Autenrieth, R. L.; McDonald, T. J.; Cunningham, J. A. Biological Limitations of Dechlorination of cis-Dichloroethene during Transport in Porous Media. *Environ Sci Technol* **2018**, *52*, 684–691.
- (12) Arnold, W. A.; Lynn Roberts, A. Pathways of chlorinated ethylene and chlorinated acetylene reaction with Zn(O). *Environ Sci Technol* **1998**, *32*, 3017–3025.
- (13) Butler, E. C.; Hayes, K. F. Kinetics of the Transformation of Trichloroethylene and Tetrachloroethylene by Iron Sulfide. *Environ Sci Technol* **1999**, *33*, 2021–2027
- (14) Butler, E. C.; Hayes, K. F. Factors influencing rates and products in the transformation of trichloroethylene by iron sulfide and iron metal. *Environ Sci Technol* **2001**, *35*, 3884–3891.
- (15) Lee, W.; Batchelor, B. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and magnetite. *Environ Sci Technol* **2002**, *36*, 5147–5154.
- (16) Shen, H.; Wilson, J. T. Trichloroethylene Removal from Groundwater in Flow-Through Columns Simulating a Permeable Reactive Barrier Constructed with Plant Mulch. *Environ Sci Technol* **2007**, *41*, 4077–4083.
- (17) Kennedy, L. G.; Everett, J. W.; Becvar, E.; DeFeo, D. Field-scale demonstration of induced biogeochemical reductive dechlorination at Dover Air Force Base, Dover, Delaware. *J Contam Hydrol* **2006**, *88*, 119–136.
- (18) Kennedy, L. G.; Everett, J. W.; Gonzales, J. Assessment of biogeochemical natural attenuation and treatment of chlorinated solvents, Altus Air Force Base, Altus, Oklahoma. *J Contam Hydrol* **2006**, *83*, 221–236.
- (19) Butler, E. C.; Chen, L.; Darlington, R. Transformation of Trichloroethylene to Predominantly Non-Regulated Products under Stimulated Sulfate Reducing Conditions. *Ground Water Monit Remediat* **2013**, *33*, 52–60.
- (20) Liang, X.; Paul Philp, R.; Butler, E. C. Kinetic and isotope analyses of tetrachloroethylene and trichloroethylene degradation by model Fe(II)-bearing minerals. *Chemosphere* **2009**, *75*, 63–69.
- (21) Culpepper, J. D.; Scherer, M.; Robinson, T. C.; Neumann, A.; Cwiertny, D.; Latta, D. E. Reduction of PCE and TCE by magnetite revisited. *Environ Sci Process Impacts* **2018**, *20*, 1340–1349.
- (22) Lee, W.; Batchelor, B. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 2. Green rust. *Environ Sci Technol* **2002**, *36*, 5348–5354.

- (23) Mangayayam, M. C.; Dideriksen, K.; Tobler, D. J. Can or cannot green rust reduce chlorinated ethenes? *Energy Procedia* **2018**, *146*, 173–178.
- (24) Maithreepala, R. A.; Doong, R.-a. Enhanced Dechlorination of Chlorinated Methanes and Ethenes by Chloride Green Rust in the Presence of Copper(II). *Environ Sci Technol* **2005**, *39*, 4082–4090.
- (25) Ai, J.; Yin, W.; Hansen, H. C. Fast Dechlorination of Chlorinated Ethylenes by Green Rust in the Presence of Bone Char. *Environ Sci Technol Letters* **2019**, *6*, 191–196.
- (26) Parker, B. L.; Chapman, S. W.; Guilbeault, M. A. Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. *Journal of Contaminant Hydrology* **2008**, *102*, 86 – 104, Partial Source Zone Removal.
- (27) Ayral-Cinar, D.; Otero-Diaz, M.; Demond, A. H. A mechanism of basal spacing reduction in sodium smectitic clay materials in contact with DNAPL wastes. *Chemosphere* **2016**, *159*, 577 – 583.
- (28) Rasa, E.; Chapman, S. W.; Bekins, B. A.; Fogg, G. E.; Scow, K. M.; Mackay, D. M. Role of back diffusion and biodegradation reactions in sustaining an MTBE/TBA plume in alluvial media. *Journal of Contaminant Hydrology* **2011**, *126*, 235 – 247.
- (29) Cervini-Silva, J.; Larson, R. A.; Wu, J.; Stucki, J. W. Transformation of chlorinated aliphatic compounds by ferruginous smectite. *Environ Sci Technol* **2001**, *35*, 805–809.
- (30) Lee, W.; Batchelor, B. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates. *Chemosphere* **2004**, *56*, 999–1009.
- (31) Nzengung, V. A.; Castillo, R. M.; Gates, W. P.; Mills, G. L. Abiotic transformation of perchloroethylene in homogeneous dithionite solution and in suspensions of dithionite-treated clay minerals. *Environ Sci Technol* **2001**, *35*, 2244–2251.
- (32) Schaefer, C. E.; Ho, P.; Berns, E.; Werth, C. Mechanisms for Abiotic Dechlorination of Trichloroethene by Ferrous Minerals under Oxidic and Anoxic Conditions in Natural Sediments. *Environ Sci Technol* **2018**, *52*, 13747–13755.
- (33) Neumann, A.; Olson, T. L.; Scherer, M. M. Spectroscopic Evidence for Fe(II)–Fe(III) Electron Transfer at Clay Mineral Edge and Basal Sites. *Environ Sci Technol* **2013**, *47*, 6969–6977.
- (34) Neumann, A.; Petit, S.; Hofstetter, T. B. Evaluation of redox-active iron sites in smectites using middle and near infrared spectroscopy. *Geochim Cosmochim Acta* **2011**, *75*, 2336–2355.
- (35) Stucki, J. W.; Golden, D. C.; Roth, C. B. Preparation and Handling of Dithionite-Reduced

Smectite Suspensions. *Clays Clay Miner* **1984**, 32, 191–197.

- (36) Taylor, P. D. P.; Maeck, R.; De Bièvre, P. Determination of the absolute isotopic composition and Atomic Weight of a reference sample of natural iron. *Int. J. Mass Spectrom* **1992**, 121, 111–125.
- (37) Schilt, A. A. *Analytical applications of 1, 10-phenanthroline and related compounds: international series of monographs in analytical chemistry*; Pergamon Press, 1969.
- (38) Stucki, J. W. The quantitative assay of minerals for Fe²⁺ and Fe³⁺ using 1,10-phenanthroline: 2. A photochemical method. *Soil Sci Soc Am J* **1981**, 45, 638–641.
- (39) Amonette, J. E.; Templeton, J. C. Improvements to the quantitative assay of nonrefractory minerals for Fe(II) and total Fe using 1, 10-phenanthroline. *Clays Clay Miner* **1998**, 46, 51–62.
- (40) Neumann, A.; Hofstetter, T. B.; Lüssi, M.; Cirpka, O. A.; Petit, S.; Schwarzenbach, R. P. Assessing the redox reactivity of structural iron in smectites using nitroaromatic compounds as kinetic probes. *Environ Sci Technol* **2008**, 42, 8381–8387.
- (41) Gorski, C. A.; Aeschbacher, M.; Soltermann, D.; Voegelin, A.; Baeyens, B.; Marques Fernandes, M.; Hofstetter, T. B.; Sander, M. Redox properties of structural Fe in clay minerals. 1. Electrochemical quantification of electron-donating and -accepting capacities of smectites. *Environ Sci Technol* **2012**, 46, 9360–9368.
- (42) Gorski, C. A.; Klüpfel, L.; Voegelin, A.; Sander, M.; Hofstetter, T. B. Redox properties of structural Fe in clay minerals. 2. Electrochemical and spectroscopic characterization of electron transfer irreversibility in ferruginous smectite, SWa-1. *Environ Sci Technol* **2012**, 46, 9369–9377.
- (43) Gustafsson, J. P. Visual MINTEQ, 3.0. 2011.
- (44) Bohnsack, G. Löslichkeit und thermodynamische Daten von Eisen(II)-Hydroxid durch analytische Bestimmung des Eisens und Leitfähigkeitsmessung im System Eisen-Wasser. *Berichte der Bunsengesellschaft für physikalische Chemie* **1988**, 92, 797–802.
- (45) Sawyer, C. N.; McCarty, P. L.; Parkin, G. F. *Chemistry for environmental engineering and science*; 2016.
- (46) Hansen, H. C. B. Composition, stabilization, and light absorption of Fe(II)Fe(III) hydroxycarbonate ('green rust'). *Clay Minerals* **1989**, 24, 663–669.

- (47) Zhu, Y.; Elzinga, E. J. Formation of layered Fe(II)-hydroxides during Fe(II) sorption onto clay and metal-oxide substrates. *Environ Sci Technol* **2014**, *48*, 4937–4945.
- (48) Jones, A. M.; Murphy, C. A.; Waite, T. D.; Collins, R. N. Fe(II) interactions with smectites: temporal changes in redox reactivity and the formation of green rust. *Environ Sci Technol* **2017**, *acs.est.7b01793*.
- (49) Refait, P.; Génin, J. M. The oxidation of ferrous hydroxide in chloride-containing aqueous media and pourbaix diagrams of green rust one. *Corrosion Science* **1993**, *34*, 797–819.
- (50) Refait, P. H.; Abdelmoula, M.; Génin, J. M. R. Mechanisms of formation and structure of green rust one in aqueous corrosion of iron in the presence of chloride ions. *Corrosion Science* **1998**, *40*, 1547–1560, doi:10.1016/S0010-938X(98)00066-3.
- (51) Génin, J. M.; Abdelmoula, M.; Aïssa, R.; Ruby, C. Ordering in FeII-III hydroxysalt green rusts from XRD and Mössbauer analysis (chloride, carbonate, sulphate, oxalate...); about the structure of hydrotalcite-like compounds. *Hyperfine Interactions* **2005**, *166*, 391–396.
- (52) Latta, D. E.; Neumann, A.; Premaratne, W. A. P. J.; Scherer, M. M. Fe(II)–Fe(III) Electron Transfer in a Clay Mineral with Low Fe Content. *ACS Earth Space Chem* **2017**, *1*, 197–208.
- (53) Soltermann, D.; Marques Fernandes, M.; Baeyens, B.; Dähn, R.; Joshi, P. A.; Scheinost, A. C.; Gorski, C. A. Fe(II) uptake on natural montmorillonites. I. Macroscopic and spectroscopic characterization. *Environ Sci Technol* **2014**, *48*, 8688–8697.
- (54) Schaefer, M. V.; Gorski, C. A.; Scherer, M. M. Spectroscopic evidence for interfacial Fe(II)-Fe(III) electron transfer in a clay mineral. *Environ Sci Technol* **2011**, *45*, 540–545.
- (55) Neumann, A.; Skarpeli-liati, M.; Schwarzenbach, R. P. Ethanes and Carbon Tetrachloride. *Environ Sci Technol* **2009**, *43*, 4082–4089.
- (56) Elsner, M.; Schwarzenbach, R. P.; Haderlein, S. B. Reactivity of Fe(II)-Bearing Minerals toward Reductive Transformation of Organic Contaminants. *Environ Sci Technol* **2004**, *38*, 799–807.
- (57) Tsarev, S.; Waite, T. D.; Collins, R. N. Uranium Reduction by Fe(II) in the Presence of Montmorillonite and Nontronite. *Environ Sci Technol* **2016**, *50*, 8223–8230.
- (58) Davis, D.; Miller, O. J. Addition of divalent iron to electron donor mixtures for remediation of chlorinated ethenes: A study of 100 wells. *Remed J* **2018**, *29*, 37–44.

3.2 Supporting Information

Analytical procedures

Chlorinated compounds

GC-MS analysis of PCE, TCE, and DCE isomers was performed on an Agilent 7890A GC using split/split-less injection at 260 °C with Helium as the carrier gas (flow rate of 1 mL min⁻¹, initial pressure of 50 kPa, and split at 50 mL min⁻¹) and an Agilent 5975C MSD for mass detection. Compound separation was performed on a Restek fused silica capillary column (60 m × 0.25 mm i.d.) coated with 1.41 μm Rtx-VMS phase, applying a GC temperature program (initial temperature: 30 °C, hold for 8 minutes; ramp to 260 °C at 15 °C min⁻¹; hold at 260 °C for 6 minutes). The mass separation was performed using an Agilent 5975C MSD (electron voltage 70 eV, source temperature 230 °C), quad temperature 150 °C, multiplier voltage 1200 V, interface temperature 260 °C). The acquired data was processed using Chemstation, using an internal (CFB) and external standards. The measured concentrations were corrected for the extraction efficiency into n-pentane and for partitioning into the headspace, as detailed below.

Gaseous products

Analysis of gaseous compounds (VC, acetylene, ethene, ethane) was performed on a Thermo Trace GC coupled to a flame ionization detector (FID). An Agilent CP-Silica Plot column (30 m × 0.32 mm i.d.) coated with a film 41 μm phase in conjunction with the GC temperature program (initial temperature: 75 °C, hold for 50 minutes; ramp to 225 °C at 15 °C min⁻¹; hold at 225 °C for 30 minutes) was used for compound separation. Target compounds were identified and quantified by comparing to a series of calibration curves which were created by injecting known volumes of gas standards (acetylene, 1% in N₂ balance, Calgaz; ethene, ethane, and VC, all 1% in N₂ balance, Calgaz). The total amounts of C₂ gases were calculated taking into account compound partitioning between aqueous and gas phase as well as the changing ratio of aqueous to gas phase due to aqueous phase sampling, as detailed below.

Mössbauer spectroscopy

Samples for Mössbauer were analyzed using a MS4 Mössbauer spectrometer (SEE Co., Edina, MN, U.S.A.) in transmission mode and calibrated against 71 μm α-Fe(0) foil. Temperature during spectra acquisition was controlled with a closed cycle cryostat (SHI-850, Janis Research Co., Wilmington, MA, U.S.A.) at either 13 K (reactors containing aqueous ⁵⁶Fe(II)) or 77 K (reactors containing removed from solution, respectively). Mössbauer spectra were analyzed using the software Recoil and its Voigt-based fitting routine, which also provides the uncertainties of the fit parameters.

Data evaluation

Responses from GC-MS analysis for PCE, TCE, and HCA were first normalized to the internal standard CFB and then converted into concentrations via linear regression of external standards. Concentrations were corrected for sample dilution (0.4 mL sample extracted into 0.6 mL n-pentane) and extraction efficiencies (Table S1), which were determined by comparing responses from standards prepared in n-pentane with those prepared in aqueous solution and subsequently extracted into n-pentane. Finally, total concentrations ($c_{i,tot}$) were calculated from the measured concentrations $c_{i,m}$, taking into account partitioning into the headspace of the reactors and changes in the volumes of headspace (V_g) and aqueous phase (V_{aq}) over the reaction time, which was due to repeated (x) removal of an aqueous sample of volume $V_{s,aq}$ (420 μ L):

$$c_{i,tot} = \frac{K_{iH}(V_g + xV_{s,aq})c_{i,m} + (V_{aq} - xV_{s,aq})c_{i,m}}{V_{tot}}$$

The compounds' dimensionless Henry's constants K_{iH} were taken from a recent compilation and are listed in Table S1, together with values for the parameters in equation 4.

Similarly, the amounts of gaseous products (acetylene, ethene, ethane) obtained from GC-FID ($n_{i,m}$) were converted into total amounts ($n_{i,tot}$), using the dimensionless Henry's constants K_{iH} (Table S1), the volumes of headspace (V_g) and aqueous phase (V_{aq}), as well as sampling (x) of aqueous phase ($V_{s,aq}$ = 420 μ L) and headspace ($V_{s,g}$ = 250 μ L):

$$n_{i,tot} = \frac{n_{i,m}}{V_{s,g}}(V_g + xV_{s,aq}) + \frac{1}{K_{iH}} \frac{n_{i,m}}{V_{s,g}}(V_{aq} - xV_{s,aq})$$

Table S1: Parameters used to evaluate the total concentrations of PCE, TCE, and HCA as well as the total amounts of acetylene, ethene, and ethane in the reactors.

parameter	PCE	TCE	HCA	actetylene	ethene	ethane
extraction efficiency	93.8%	80.7 %	94.5 %	n.a. ^b	n.a. ^b	n.a. ^b
K_{iH} ^a	1.186	0.367	0.098	0.984	8.583	21.23
V_g	5 mL	5 mL	5 mL	5 mL	5 mL	5 mL
V_{aq}	155 mL	155 mL	20 mL	155 mL	155 mL	155 mL
V_{tot}	160 mL	160 mL	25 mL	160 mL	160 mL	160 mL

^a Dimensionless Henry's constant, $K_{iH} = \frac{c_{i,g}}{c_{i,aq}}$, values taken from a recent compilation.

^b n.a.: not applicable.

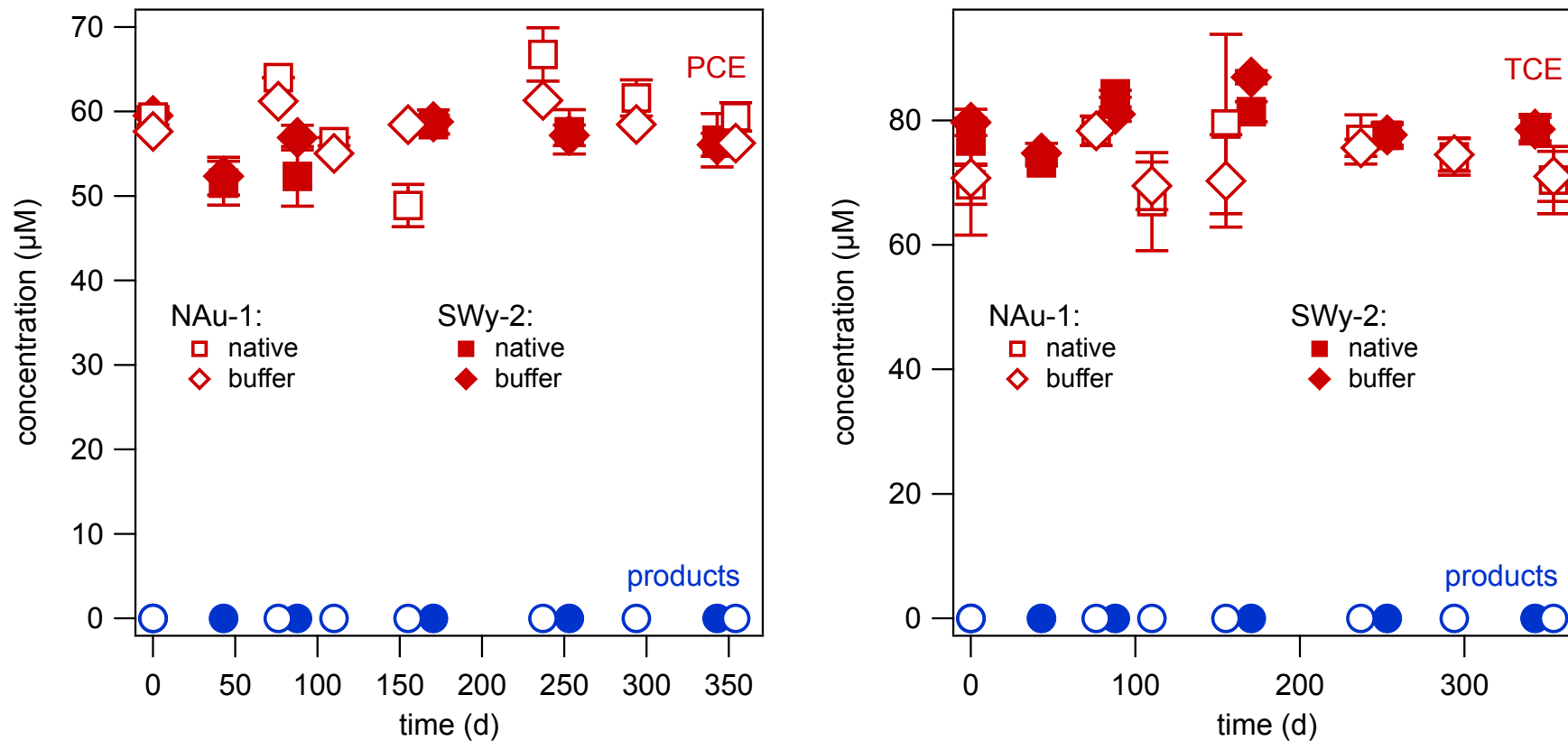


Figure S1: PCE and TCE concentrations in reference reactors containing buffer only to control for reactant loss due to volatilization or clay minerals NAu-1 or SWy-2 in their native form (buffered to pH 8) to quantify sorption to the mineral surfaces. No dechlorination products were detected in any of these reactors. Error bars represent the standard deviation of duplicate reactors.

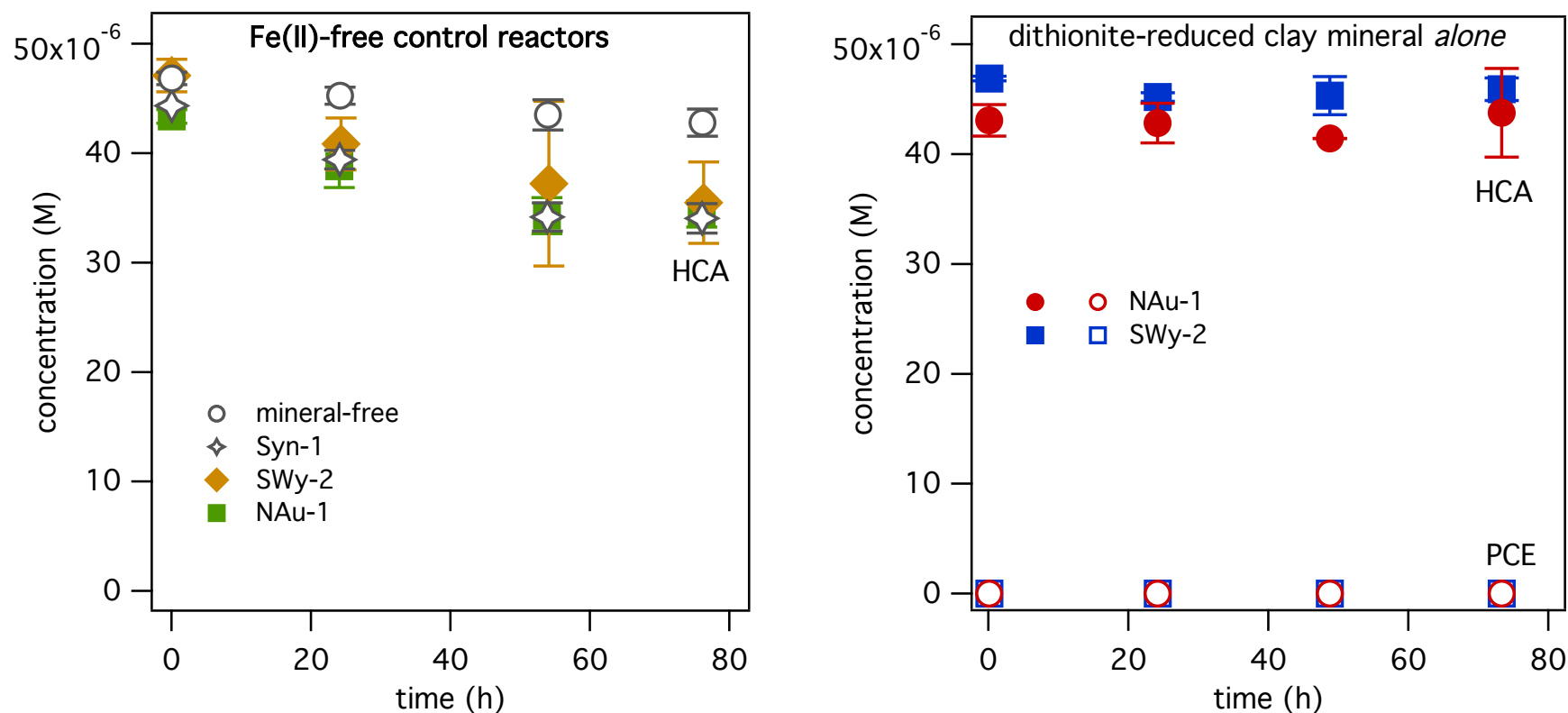


Figure S2: HCA concentrations measured in reference reactors containing no added aqueous Fe(II) (left) and in the presence of dithionite-reduced clay minerals (right). Left: Mineral-free reactors (grey open circles) monitored any losses of HCA due to volatilization (limited: $8.6 \pm 0.1\%$) and native mineral reactors monitored losses of HCA due to sorption (small: $17 \pm 0.5\%$). There is no statistically significant difference between Fe-free clay mineral Syn-1 (grey open stars) and Fe-bearing clay minerals SWy-2 and NAu-1 (filled orange diamonds and green squares, respectively). Right: Similar to PCE and TCE, HCA was not degraded by structural Fe(II) in clay minerals alone over the time frame of the experiments (80 hours). We note that loss due to volatilization and sorption was smaller in experiments with dithionite-reduced NAu-1 (red circles) and SWy-2 (blue squares) compared to the native clay minerals. Error bars represent standard deviations from replicate experiments.

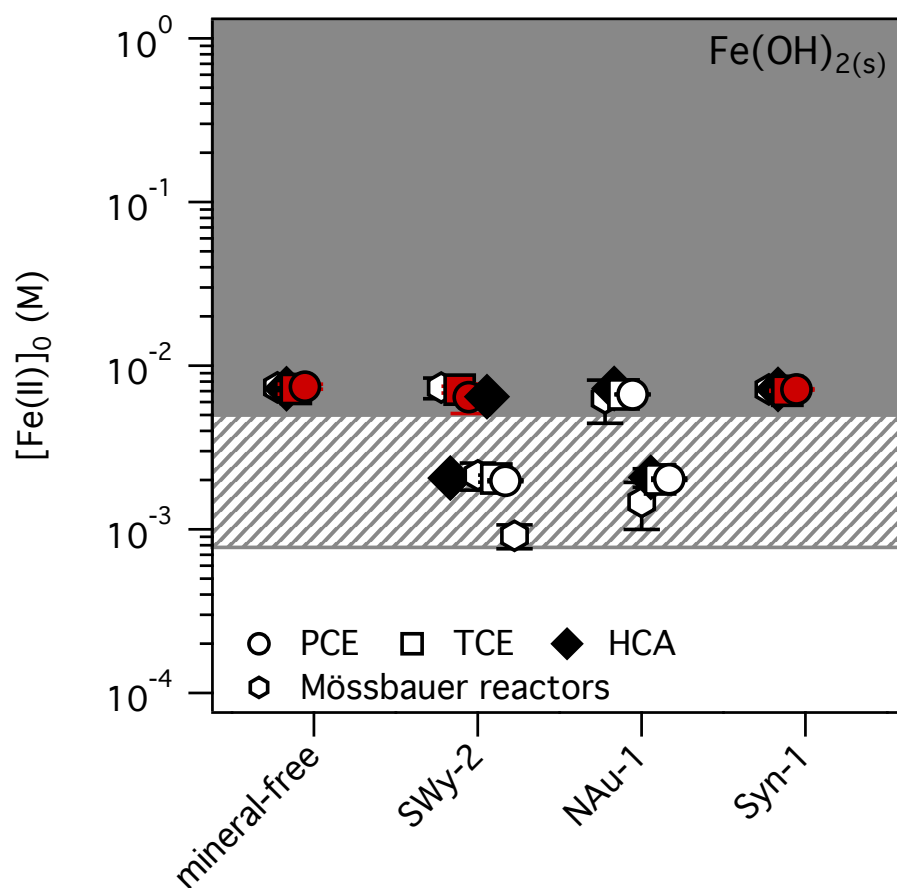


Figure S3: Initial Fe(II) activities in PCE, TCE, HCA, and Mössbauer reactors containing clay minerals and mineral-free suspension, overlaid with the solubility of $\text{Fe}(\text{OH})_2$. Filled markers represent reactors in which dechlorination products were detected and open black markers are reactors without product formation. The grey hatched and shaded areas represent the Fe(II) concentrations expected to lead to $\text{Fe}(\text{OH})_2$ precipitation and were calculated based on the range of published solubility product values ($-15.11 < \log K_{\text{sp}}(\text{Fe}(\text{OH})_2) < -14.30$). Measured Fe(II) concentrations were converted into activities based on the ionic strength in the reactors (details in Table S6).

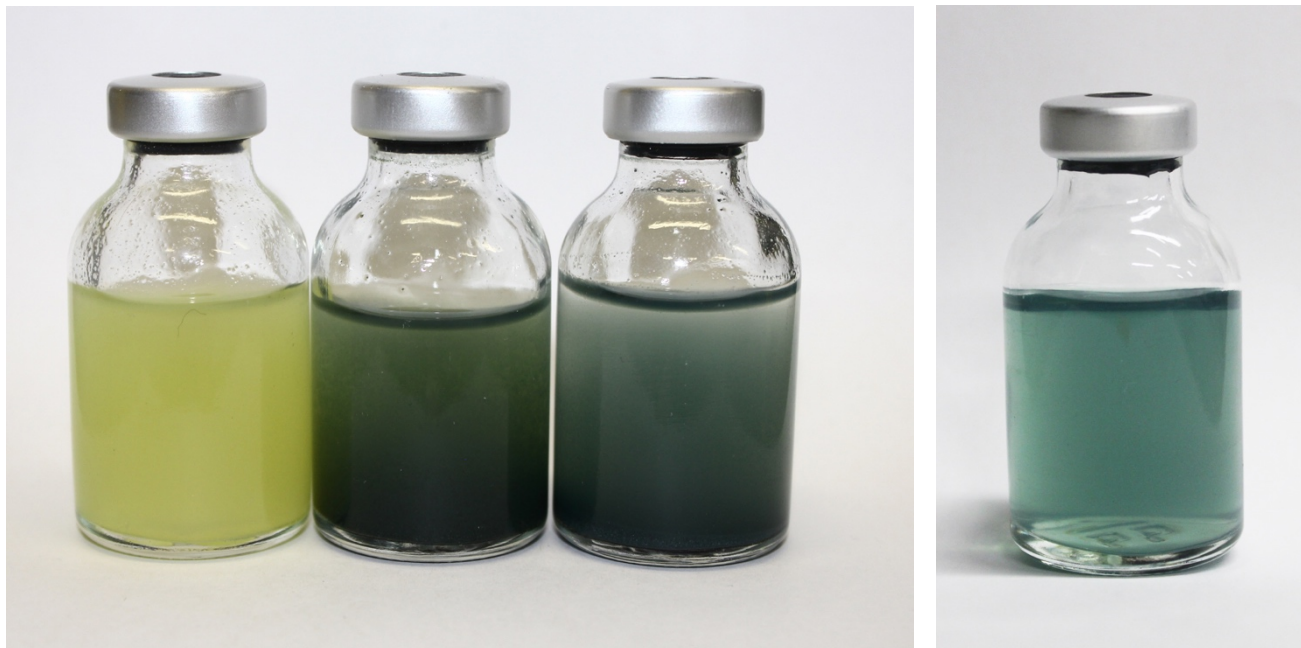


Figure S4: Reactors of differently prepared high Fe content clay mineral NAu-1: native, amended with aqueous Fe(II) at concentrations of 4.4 mM or 20.5 mM, and dithionite-reduced (from left to right).



Figure S5: Reactors of differently prepared low Fe content clay mineral SWy-2: native, amended with aqueous Fe(II) at concentrations of 1.9 mM, 4.9 mM, or 20.1 mM, and dithionite-reduced (from left to right).

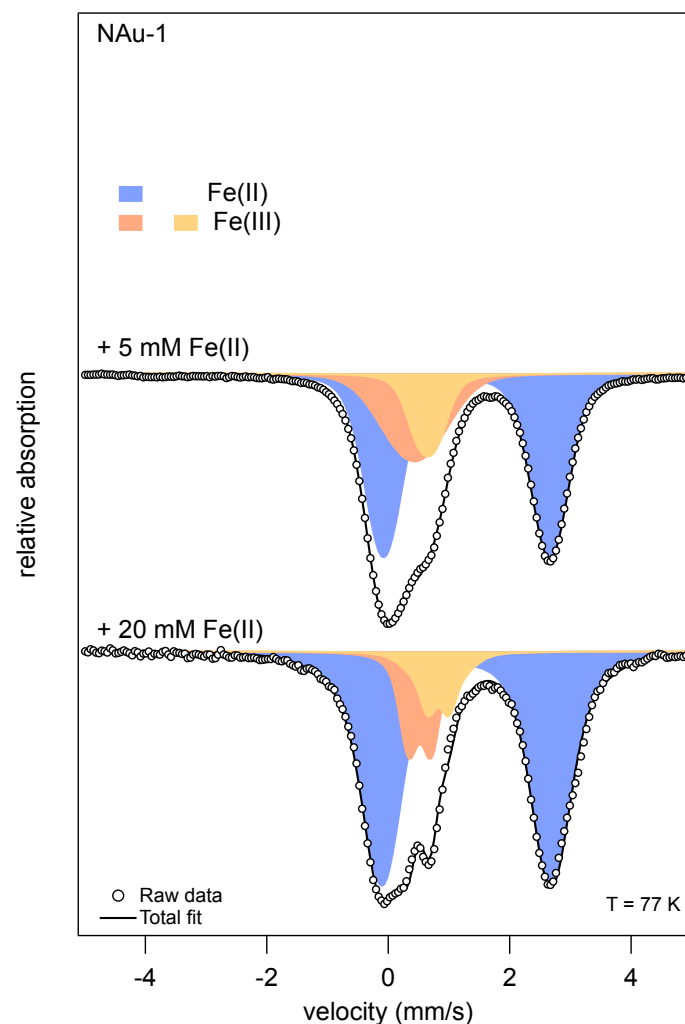
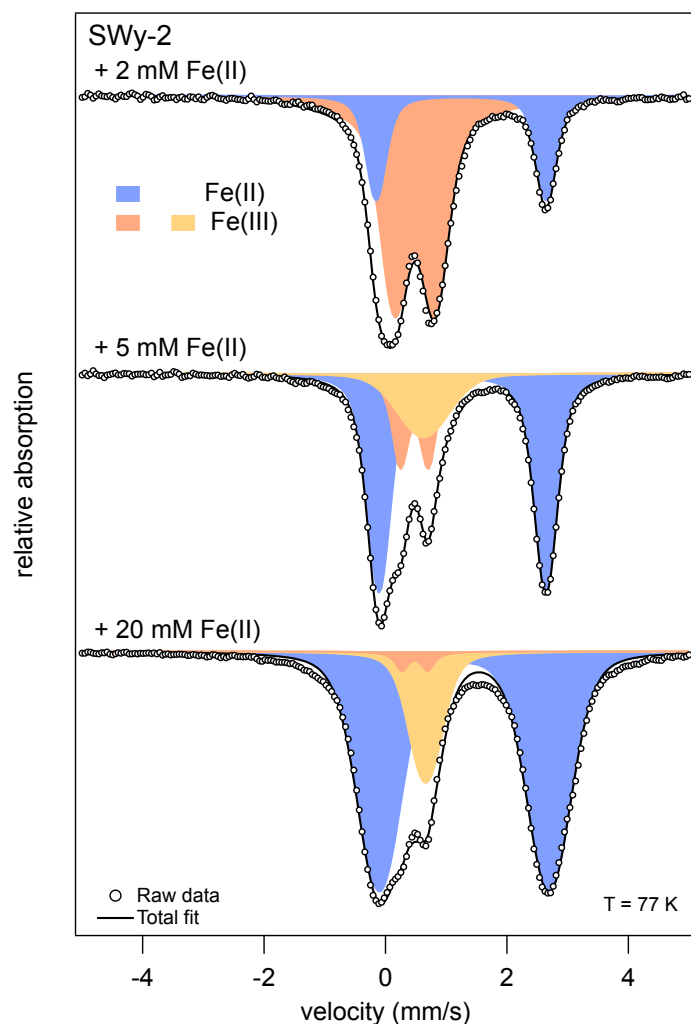


Figure S6: Mössbauer spectra of low Fe content clay mineral SWy-2 (left) and high Fe content clay mineral NAu-1 (right) after reaction with different concentrations of Mössbauer-visible $^{57}\text{Fe(II)}$. The signal associated with ^{57}Fe in both clay minerals comprises $\leq 3.2\%$ of the total spectral area and the spectra thus reflect exclusively the Fe speciation of Fe(II) added and taken up from solution. The presence of both blue and yellow doublets indicates that all precipitates contain Fe(II) and Fe(III), respectively, and the ratio of Fe(II)/Fe(total) increased with increasing aqueous Fe(II) concentration from 25% to 80% for SWy-2 and from 62% to 75% for NAu-1 (Table S4). Spectra were collected at 77 K.

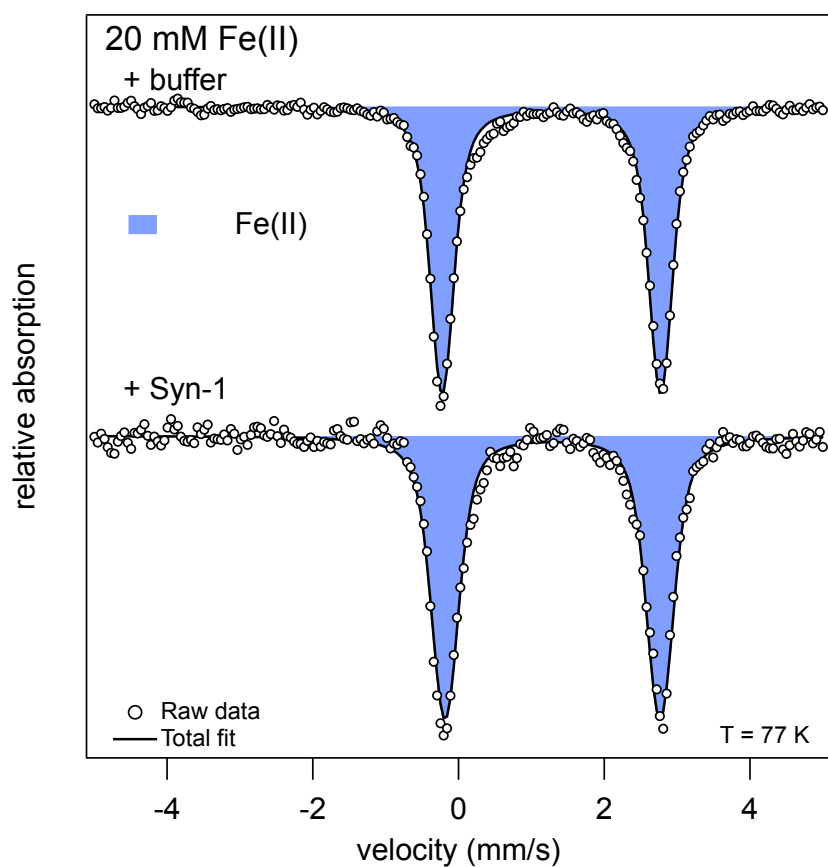


Figure S7: Mössbauer spectra of the precipitates formed in 20 mM $^{57}\text{Fe}(\text{II})$ solution in the absence of clay mineral (top) and in the presence of Fe-free clay mineral Syn-1 (bottom) show the presence of exclusively Fe(II) (blue doublet), indicating the absence of electron transfer and accidental oxidation. Spectra were collected at 77 K.

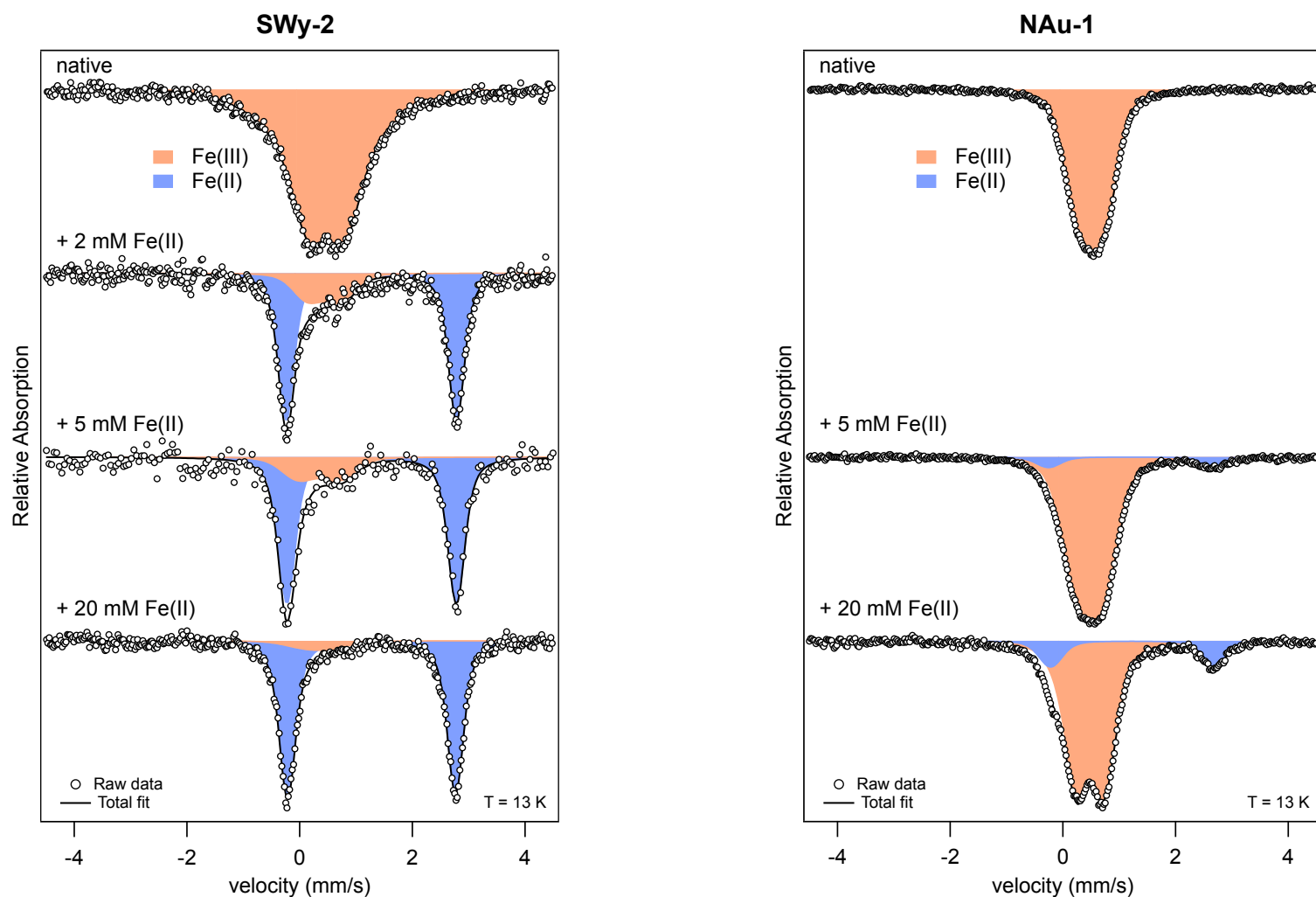


Figure S8: Mössbauer spectra of low Fe content clay mineral SWy-2 (left) and high Fe content clay mineral NAu-1 (right) before and after reaction with different concentrations of Mössbauer-invisible $^{56}\text{Fe(II)}$. While both native clay minerals only contain Fe(III), as indicated by the presence of the yellow doublet, reaction with $^{56}\text{Fe(II)}$ led to the formation of Fe(II) in the clay mineral structure (blue doublets). Clay mineral Fe reduction extents achieved were 78-93% for SWy-2 and 7-15% for NAu-1 (Table S4). Spectra were collected at 13 K.

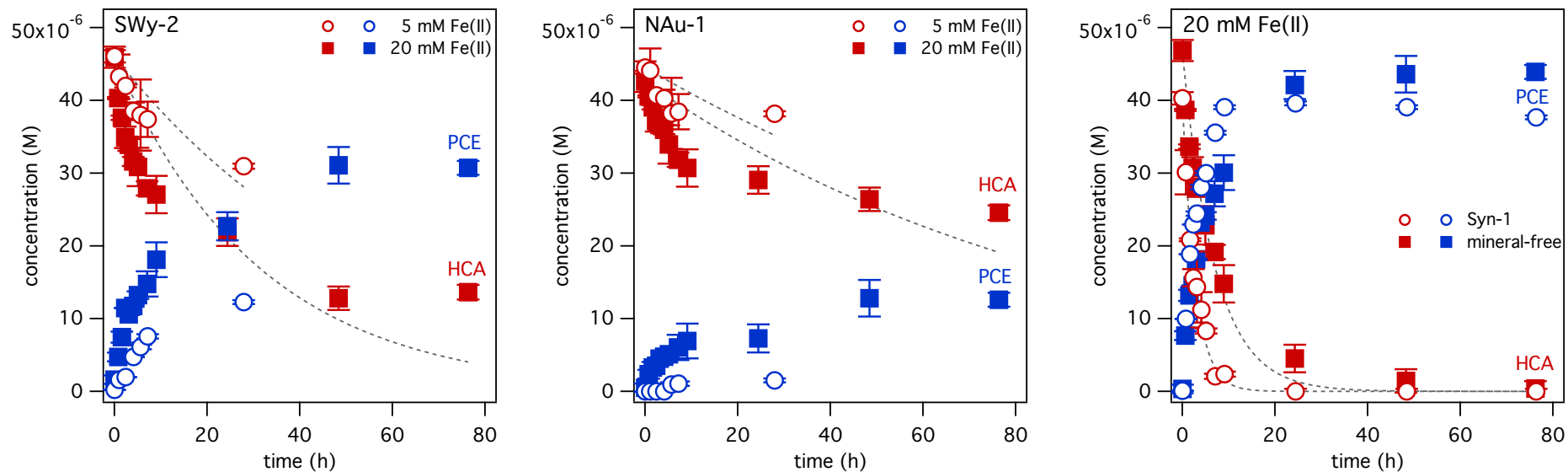


Figure S9: Kinetic data of the transformation of hexachloroethane (HCA, red) to PCE (blue) in suspensions of SWy-2 and NAu-1 reacted with 5 mM Fe(II) (open circles) and 20 mM Fe(II) (filled squares) as well as in 20 mM Fe(II) solution without the addition of clay mineral (filled squares) and in the presence of Fe-free Syn-1 (open circles). Dashed lines are fits to the first-order kinetic model (equation 1), which does not describe the data well. Error bars represent the standard deviation of duplicate reactors.

Table S2: Summary of reactor conditions for PCE and TCE degradation experiments, including reactant loss and product formation observed. Errors are standard deviations from replicate reactors.

Clay mineral	reactor condition	clay mineral Fe(II)/Fe(total) ^a %	clay mineral concentration $g\ L^{-1}$	initial reactant concentration μM		reactant loss ^b %		product formation ^c %	
				PCE	TCE	PCE	TCE	PCE	TCE
NAu-1	5 mM Fe(II)	6.9(0.6)	5	53.8(1.9)	73.3(9.0)	5.6(0.3)	-2.0(0.4)	0	0
	20 mM Fe(II)	15.4(0.7)	5	50.4(1.3)	69.9(3.3)	4.2(0.2)	-2.3(0.2)	0	0
	Dithionite-reduced	90.1(0.3)	3.5	50.8(1.4)	68.7(1.8)	4.9(0.3)	-1.1(0.1)	0	0
	Native	n.d. ^e	5	59.3(0.1)	69.7(3.1)	-0.1(0.0)	-1.1(0.1)	0	0
	Buffer	–	–	57.6	70.7(9.2)	2.4	-0.4(0.1)	0	0
SWy-2	5 mM Fe(II)	79.4(3.8)	5	64.0(0.3)	71.7(2.9)	5.2(0.1)	-2.1(0.1)	0	0
	20 mM Fe(II)	92.5(1.9)	5	55.4(7.0)	73.0(4.6)	3.7(0.5)	4.3(0.3)	17.4(1.3)	15.0 ^d
	Dithionite-reduced	80.9 ^f	4.15	55.0(5.9)	75.1(2.9)	-1.0(0.2)	-3.8(0.3)	0	0
	Native	n.d. ^e	5	58.8(1.5)	76.7(3.7)	3.7(0.2)	-2.5(0.2)	0	0
	Buffer	–	–	59.5(1.1)	79.7(2.1)	5.8(0.2)	1.4(0.1)	0	0
Syn-1	20 mM Fe(II)	–		62.5(0.5)	82.5(8.5)	15(4)	28(12)	23.1(0.3)	23.6(0.4)
–	20 mM Fe(II)	–	–	65.0(1.2)	80.6(5.1)	8.4(0.5)	8.4(0.6)	20.9(0.4)	19.9(1.7)

^a Reduction extent of the clay mineral Fe as measured by HF digestion or Mössbauer spectroscopy (latter data from Table S4).

^b Relative to the initial reactant concentration. ^c Refers to the sum of products formed in reactors containing either PCE or TCE as a starting reactant; relative to the initial reactant concentration. ^d Only one replicate reactor yielded products. ^e Not detected using Mössbauer spectroscopy.

^f Only one replicate sample was subjected to the HF digestion and subsequent 1,10-phenanthroline analysis.

Table S3: Distribution of products formed in reactors containing 20 mM aqueous Fe(II) and different (clay) minerals. Errors are standard deviations from replicate reactors.

Reactor condition	PCE transformation					TCE transformation				
	products % of initial	ethane % of overall products	ethene	acetylene	[Fe(II) _r] ^a M	products % of initial	ethane % of overall products	ethene	acetylene	[Fe(II) _r] ^a M
SWy-2	17.4(1.3)	13.6(1.0)	27.3(3.6)	59.1(7.3)	6.84×10^{-5}	15.0 ^b	6.8 ^b	22.9 ^b	70.2 ^b	3.77×10^{-5}
Syn-1	23.1(0.3)	10.1(0.2)	20.3(1.2)	69.7(1.4)	9.84×10^{-5}	23.6(0.4)	7.8(0.2)	20.3(1.2)	71.9(2.0)	5.90×10^{-5}
mineral-free	20.9(0.4)	10.9(0.2)	22.8(1.2)	66.4(2.0)	9.02×10^{-5}	19.9(1.7)	9.9(0.9)	27.4(2.7)	62.7(10.1)	5.23×10^{-5}

^a Calculated from the initial concentration of PCE or TCE, the amounts of products formed, and the stoichiometric factor ν accounting for the transfer of 10(8), 8(6), or 6(4) electrons from reactive Fe(II) for the formation of ethane, ethene, or acetylene from PCE(TCE), respectively.

^b Only one replicate reactor yielded products.

Table S4: Mössbauer hyperfine parameters from clay minerals reacted with aqueous $^{56}\text{Fe(II)}$ to determine structural Fe reduction extent and reacted with $^{57}\text{Fe(II)}$ to determine the Fe speciation of the precipitates formed. Spectra were acquired at 13 K and 77 K, respectively. Voigt-based fitting was used to evaluate the Mössbauer parameters.

	χ^2	Site	CS ^a mm/s	QS (σ) ^b mm/s	area (σ) ^c %
⁵⁶ Fe(II)-reacted clay minerals					
SWy-2					
native	0.64	Fe(III)	0.48	10.9(0.92)	100
+2 mM Fe(II)	0.54	Fe(II)	1.27	3.02(0.17)	77.8(2.0)
		Fe(III)	0.43	0.61(0.39)	22.2(2.0)
+5 mM Fe(II)	0.55	Fe(II)	1.28	3.01(0.19)	79.4(3.8)
		Fe(III)	0.34	0.76(0.45)	20.6(3.8)
+20 mM Fe(II)	0.57	Fe(II)	1.27	2.98(0.18)	92.5(1.9)
		Fe(III)	0.32	0.64(0.47)	7.5(1.9)
NAu-1					
native	0.58	Fe(III)	0.50	0.50(0.34)	100
+5 mM Fe(II)	0.62	Fe(II)	1.20	2.91(0.33)	6.9(0.6)
		Fe(III)	0.49	0.53(0.35)	93.1(0.6)
+20 mM Fe(II)	0.69	Fe(II)	1.23	2.89(0.30)	15.4(0.7)
		Fe(III)	0.49	0.55(0.34)	84.6(0.7)
⁵⁷ Fe(II)-reacted clay minerals					
SWy-2					
+2 mM Fe(II)	1.50	Fe(II)	1.25	2.80(0.22)	25.4(0.3)
		Fe(III)	0.48	0.96(0.93)	74.6(0.3)
+5 mM Fe(II)	1.26	Fe(II)	1.27	2.75(0.26)	62.6(0.2)
		Fe(III) 1	0.47	0.46(0.13)	19.4(0.2)
		Fe(III) 2	0.62	0.60(0.45)	18.0(0.2)
+20 mM Fe(II)	12.46	Fe(II)	1.30	2.79(0.62)	80.3(0.5)
		Fe(III) 1	0.48	0.43(0)	2.4(0.4)
		Fe(III) 2	0.66	0.34(0.25)	17.3(0.4)
NAu-1					
+5 mM Fe(II)	6.31	Fe(II)	1.29	2.74(0.51)	62.3(0.3)
		Fe(III) 1	0.43	0.76(0.56)	24.4(0.3)
		Fe(III) 2	0.65	0.35(0.24)	13.3(0.2)
+20 mM Fe(II)	2.19	Fe(II)	1.29	2.85(0.79)	75.2(0.1)
		Fe(III) 1	0.50	0.39(0.01)	11.9(0.1)
		Fe(III) 2	0.70	0.29(0.01)	11.2(0.1)
Syn-1					
+20 mM Fe(II)	0.72	Fe(II)	1.29	2.95(0.26)	100
mineral-free					
+20 mM Fe(II)	0.97	Fe(II)	1.27	3.00(0.20)	100

^a Center shift relative to $\alpha\text{-Fe(0)}$.

^b Standard deviation of QS from the Gaussian distribution of the QS parameter used in the model. ^c Standard deviation due to uncertainty.

Table S5: Data from exhaustion experiments using HCA, at initial Fe(II) concentrations of ~ 20 mM. From both decrease in HCA concentration and increase in PCE concentration, maximum reactive Fe(II) concentration and its proportion of the total Fe(II) in the reactors were calculated. Experiments were run for 750 hours.

Reactor	HCA				PCE		
	initial <i>mM</i>	final <i>mM</i>	reactive Fe(II) ^a <i>mM</i>	reactive Fe(II)/Fe(total) ^b %	final <i>mM</i>	reactive Fe(II) ^c <i>mM</i>	reactive Fe(II)/Fe(total) ^b %
Syn-1	1.33(0.01)	1.16(0.01)	0.34(0.01)	1.62	0.22(0.00)	0.44(0.01)	2.12
mineral-free	1.02(0.02)	0.85(0.01)	0.33(0.02)	1.54	0.28(0.00)	0.56(0.01)	2.65

^a Reactive Fe(II) was calculated as the difference of initial and final HCA concentration and taking into account the stoichiometry of the reduction of HCA to PCE requiring the oxidation of two Fe(II): $[\text{Fe(II)}]_{\text{reactive}} = 2 \times ([\text{HCA}]_{\text{initial}} - [\text{HCA}]_{\text{final}})$ ^b Total Fe(II) was taken from Table 2. For reactors containing Syn-1: 20.9 mM, for mineral-free reactors: 21.1 mM. ^c Reactive Fe(II) was calculated taking into account the stoichiometry of the reduction of HCA to PCE requiring the oxidation of two Fe(II): $[\text{Fe(II)}]_{\text{reactive}} = 2 \times [\text{PCE}]_{\text{final}}$.

Table S6: Overview of Fe(II) concentrations in the experimental reactors and conversion calculation into activities for comparison to the solubility product of Fe(OH)₂ (Figure S3).

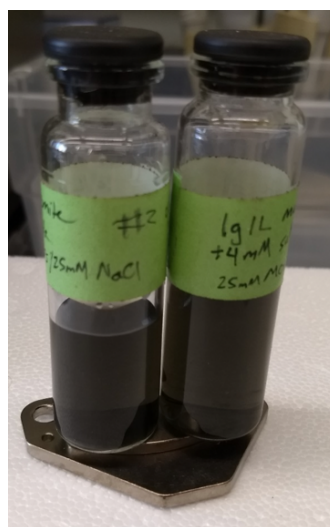
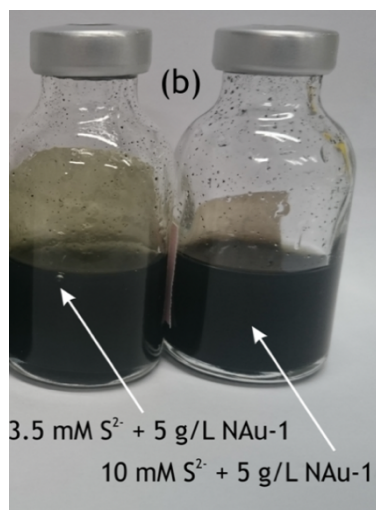
Reactor	2 mM				5 mM				20 mM			
	initial concentration ^a <i>mM</i>	ionic strength ^b <i>M</i>	activity coefficient ^c	activ- ity <i>mM</i>	initial concentration ^a <i>mM</i>	ionic strength ^b <i>M</i>	activity coefficient ^c	activ- ity <i>mM</i>	initial concentration ^a <i>mM</i>	ionic strength ^b <i>M</i>	activity coefficient ^d	activ- ity <i>mM</i>
PCE												
mineral-free									21.9(0.6)	0.121	0.34	7.45(0.27)
SWy-2					5.21(0.05)	0.071	0.38	1.98(0.03)	18.3(2.7)	0.110	0.35	6.44(1.32)
NAu-1					5.34(0.05)	0.071	0.38	2.03(0.03)	19.1(0.1)	0.112	0.35	6.68(0.05)
Syn-1									20.9(0.1)	0.118	0.34	7.18(0.06)
TCE												
mineral-free									21.0(1.0)	0.118	0.34	7.22(0.50)
SWy-2					5.41(0.19)	0.071	0.38	2.05(0.10)	20.8(0.7)	0.117	0.34	7.15(0.34)
NAu-1					5.31(0.04)	0.071	0.38	2.02(0.02)	19.1(0.4)	0.112	0.35	6.68(0.18)
Syn-1									20.4(0.08)	0.116	0.35	7.04(0.04)
HCA												
mineral-free									21.1(0.2)	0.118	0.34	7.24(0.11)
SWy-2					5.08(0.02)	0.070	0.38	1.94(0.01)	21.1(0.1)	0.118	0.34	7.23(0.04)
NAu-1					5.50(0.51)	0.071	0.38	2.08(0.27)	21.2(0.47)	0.119	0.34	7.26(0.23)
Syn-1									20.9(0.3)	0.118	0.34	7.17(0.14)
Mössbauer^e												
mineral-free ^f									21.6	0.120	0.34	7.38
SWy-2	2.28(0.27)	0.062	0.40	0.91(0.15)	5.67(0.75)	0.072	0.38	2.14(0.40)	21.5(2.2)	0.119	0.34	7.35(1.07)
NAu-1					3.79(0.85)	0.066	0.39	1.47(0.47)	17.9(3.7)	0.109	0.35	6.30(1.86)
Syn-1 ^f									20.9	0.118	0.34	7.18

^a Average values from duplicate experiments. Aqueous Fe(II) concentrations were measured using the 1,10-phenanthroline method. ^b The ionic strength I was calculated from the measured concentrations c_i and the charge of the ions, z_i : $I = \frac{1}{2} \sum c_i z_i^2$. Ions present in solution were: Fe(II), Cl⁻ (2x the concentration of Fe(II)), Na⁺ and Cl⁻ (0.05 M), and MOPS anion (0.01 M). ^c The activity coefficient f was calculated using the Güntelberg approximation: $\log f = -0.5z^2 \frac{\sqrt{I}}{1+\sqrt{I}}$. ^d The activity coefficient f was calculated using the Davies approximation: $\log f = -0.5z^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right)$. ^e Average values from experiments with ⁵⁶Fe(II) and ⁵⁷Fe(II). ^f Only one reactor was prepared for Mössbauer analysis.

3.3. PCE and TCE Degradation by Magnetite and Fe Clay Minerals + Sulfide

Abstract

Our goal here was to determine pathways and factors controlling abiotic degradation of PCE and TCE by reactive minerals formed from reaction of aqueous sulfide (S^{2-}) with magnetite and Fe-bearing clay minerals. As expected, sulfide alone does not reduce TCE but when Fe(II) + S(-II) are mixed together, mackinawite forms which reduces TCE to acetylene. When S(-II) is added to a suspension of magnetite or Fe-bearing clay minerals, however, only a small amount of TCE reduction to acetylene was observed over a one month time frame for magnetite and no reduction was observed over a three month time frame for the clay minerals. When both Fe(II) and S(-II) were added to magnetite, about 20% reduction of TCE to acetylene was observed. Together these data offer a suggestion that reaction of sulfide with Fe(II,III) minerals may potentially reduce the reactivity of Fe(II,III) minerals toward contaminants, although this may depend significantly on the contaminant of concern as well as the aquifer conditions.



Addition of sulfide to both clay minerals (left) and magnetite (right) results in formation of black, non-magnetic particles as expected. Little reduction of PCE and TCE, however, were observed.

Results and Discussion

Addition of sulfide to Fe-containing clay minerals. Our findings show that the extent of structural Fe reduction for SWy-2 increased as the concentration of S^{2-} increased (Figure 1, Table 1). At low sulfide concentrations, the extent of clay mineral Fe reduction could be explained by a two-electron transfer from sulfide, which would result in elemental sulfur formation. At higher sulfide concentrations,

this relationship did not hold (Table 3). In contrast, the observed reduction extent for NAu-1 is much lower than for SWy-2 (Figure 1, Table 1), which is similar to results from our work with aqueous Fe⁰. Also, no relationship between sulfide concentration and clay mineral reduction extent could be established (Table 2).

Despite a distinct color change for reactors containing NAu-1 (Figure 2), we did not detect any additional Fe-S phases, with neither Mössbauer spectroscopy, XRD, nor Raman spectroscopy. Our results contrast previous reports of mackinawite and/or greigite formed during dissolution of nontronite, which led to structural Fe release and subsequent precipitation of iron sulfides. Consequently, in the absence of additional reactive Fe(II) phases, we have not detected any transformation products from PCE and TCE after 3 months of reaction (Figures 3 + 4). We therefore suggest that PCE and TCE transformation by sulfide-reduced clay minerals is likely to be slow and potentially not relevant in anoxic, groundwater aquifers and that the presence of clay minerals may potentially inhibit the formation of iron sulfides which would be more reactive towards PCE and TCE.

Addition of sulfide to magnetite. Sulfide alone does not reduce TCE (**Figure 5**). As expected, Fe(II) + S(-II) resulted in formation of a black precipitate (mackinawite by XRD, **Figure 10**) and the resulting solid reduced TCE to primarily acetylene after about one month (**Figure 6**). Magnetite (5 g/L) reacted with 5 mM sulfide resulted in a small amount of TCE reduction to acetylene (~2.2% of the total mass of TCE added) (**Figure 7**). Magnetite reacted with Fe(II) (1 mM) less than the Fe(OH)₂ solubility limit (**Figure 8**) also resulted in a similar amount of acetylene production (3.3% of total TCE). Mixing a suspension of 5 g/L magnetite with 10 mM Fe(II) resulted in precipitation of ferrous hydroxide at pH 8.0, and precipitation of putative FeS when reacted with 5 mM sulfide. Similar to the positive Fe(II) and sulfide control, these solids resulted in significant TCE reduction to acetylene (21%) (**Figure 9**).

Finally, we explored whether sulfide-reduced magnetite and Fe(III) minerals reacted with hexachloroethane (HCA). As expected, 4 mM Fe(II) mixed with 4 mM S(-II) precipitated putative FeS, which quickly reduced all the HCA to perchloroethene (PCE) (**Figure 11**). The mass balance was poor, likely due to rapid PCE reduction to acetylene or other C₂ products (not quantified). When we reacted both stoichiometric ($x_{MB} = 0.50$) and non-stoichiometric ($x_{MB} = 0.42$) magnetites with HCA (**Figure 11a and 12a**), we observed significant reduction of HCA to PCE over the 6 days of our experiment. Mass balances were better, as magnetite alone does not reduce PCE. However, when we reacted both stoichiometric and non-stoichiometric magnetite with 4 mM sulfide and HCA, we observed significantly less HCA reduction to PCE (**Figure 11b and 12b**). In general, PCE production in sulfide-reacted magnetites was similar to both a 4 mM sulfide control and other Fe(III) oxides reacted with sulfide (**Figure 13**). Together these data offer a suggestion that reaction of sulfide with Fe(II,III) minerals may potentially reduce the reactivity of Fe(II,III) minerals toward contaminants, although this may depend significantly on the contaminant of concern, as we noted a small amount of TCE reduction over a much longer time frame in the first part (Figure 3 in the first part).

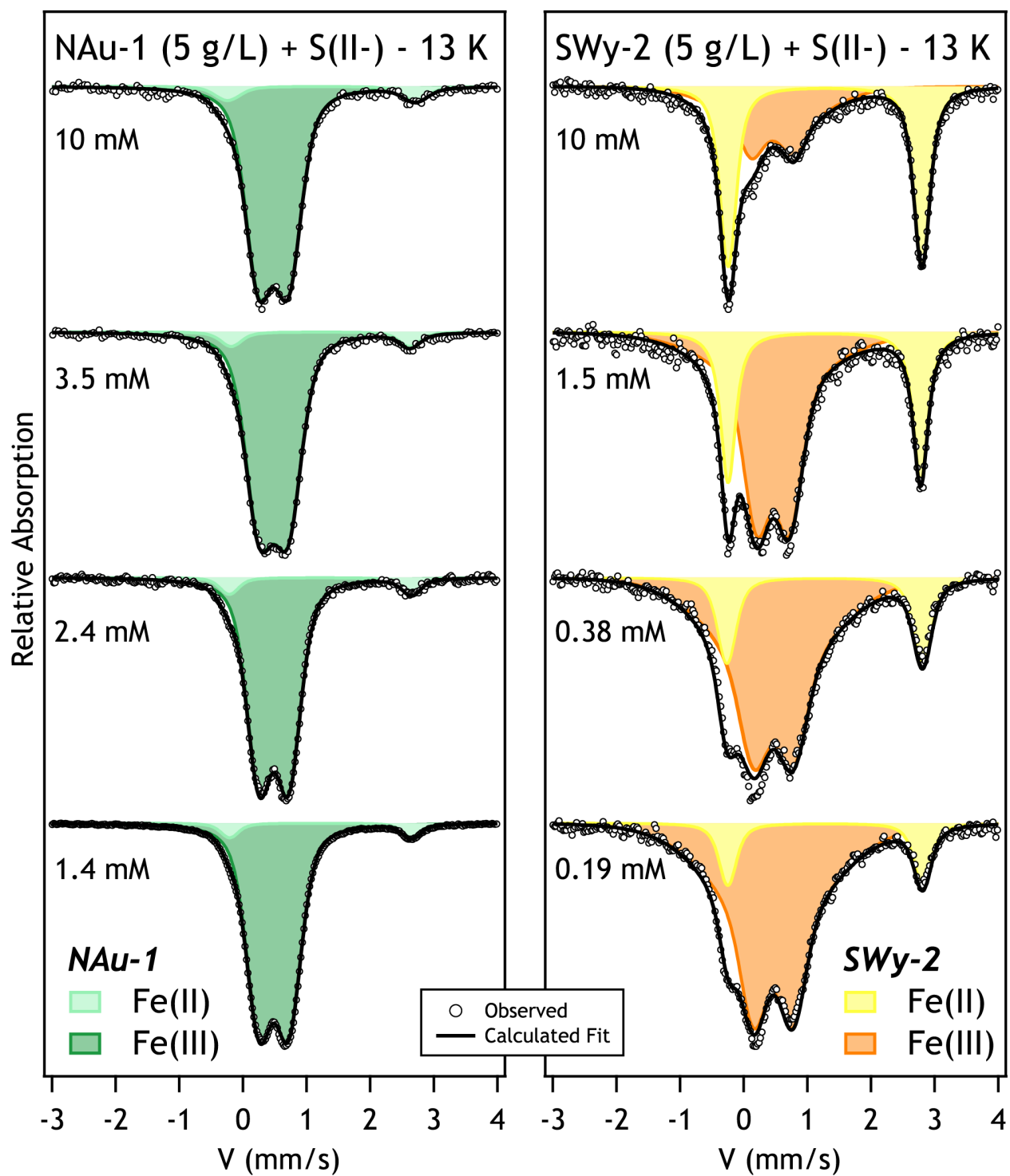


Figure 1. Mössbauer spectra of sulfide reduced NAu-1 and SWy-2. Experimental conditions: 5 g/L mineral loading, 50 mM HEPES, 25 mM NaCl, pH 8.0. All spectra were acquired at 13 K and fitted based on a Voigt-based approach.

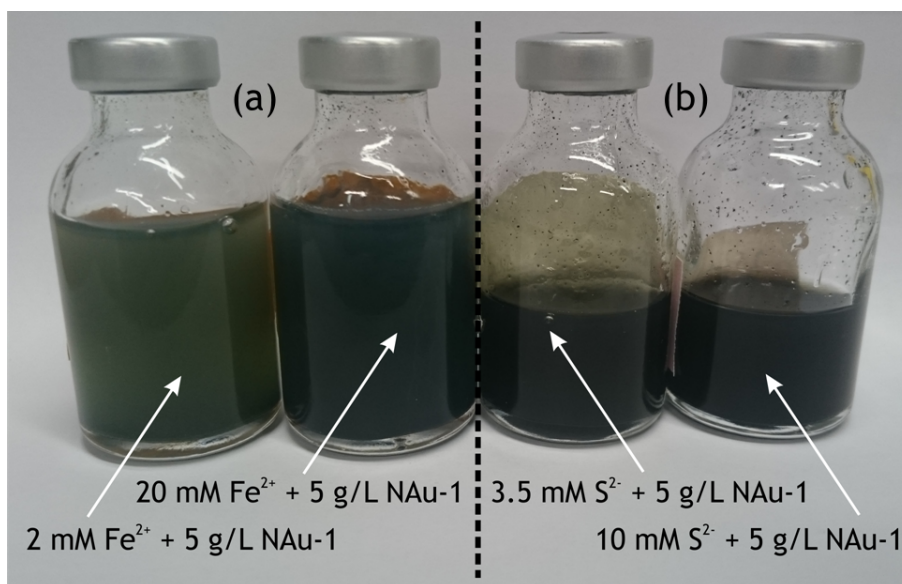


Figure 2. Color differences of precipitate that formed when NAu-1 was in the presence of (a) aqueous Fe^{II} or (b) aqueous S^{II}. Most notable difference is the formation of a greenish-blue precipitate in the presence of Fe^{II}, but a black precipitate in the presence of S^{II}.

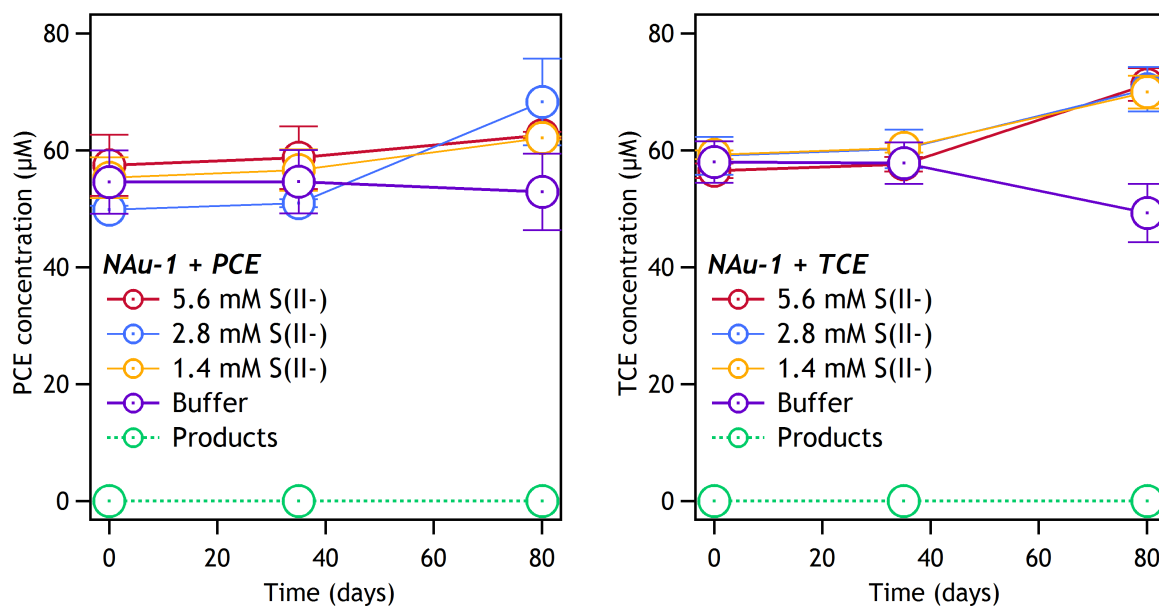


Figure 3. PCE and TCE concentration versus time in the presence of sulfide-reduced NAu-1 at various sulfide concentrations. No products were detected in either the aqueous or gas phase. Experimental conditions: 5 g/L NAu-1, 50 mM HEPES, 25 mM NaCl, pH 8.0. Experiments at higher sulfide concentrations were not carried out due to lack of mineral changes detected with Mössbauer spectroscopy.

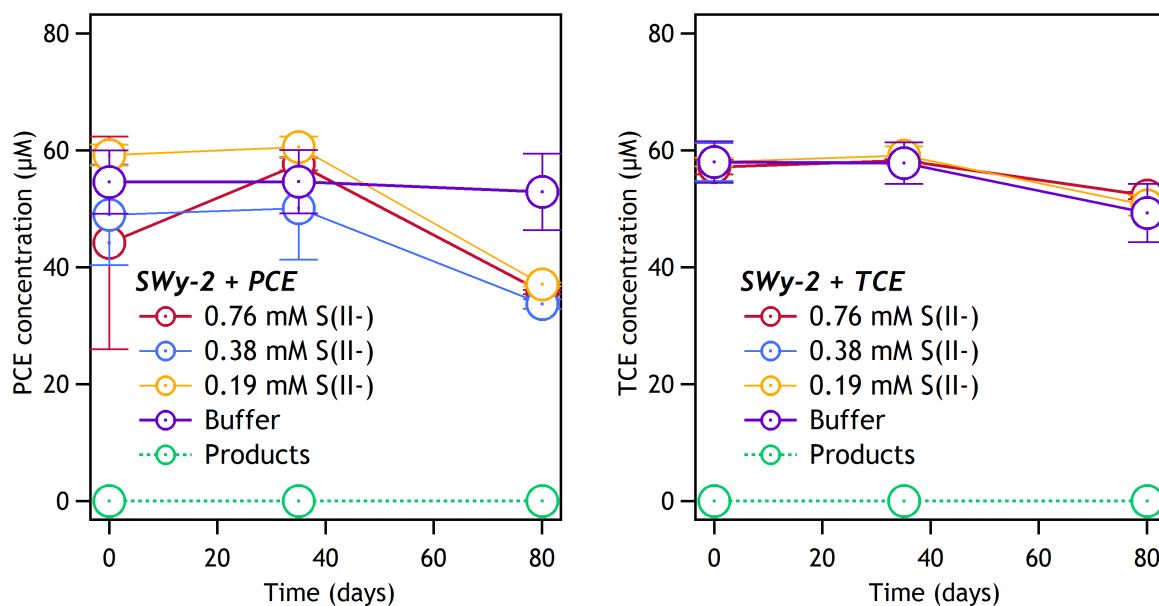


Figure 4. PCE and TCE concentration versus time in the presence of sulfide-reduced SWy-2 at various sulfide concentrations. No products were detected in either the aqueous or gas phase. Experimental conditions: 5 g/L N_{Au}-1, 50 mM HEPES, 25 mM NaCl, pH 8.0. Experiments at higher sulfide concentrations were not carried out due to lack of mineral changes detected with Mössbauer spectroscopy.

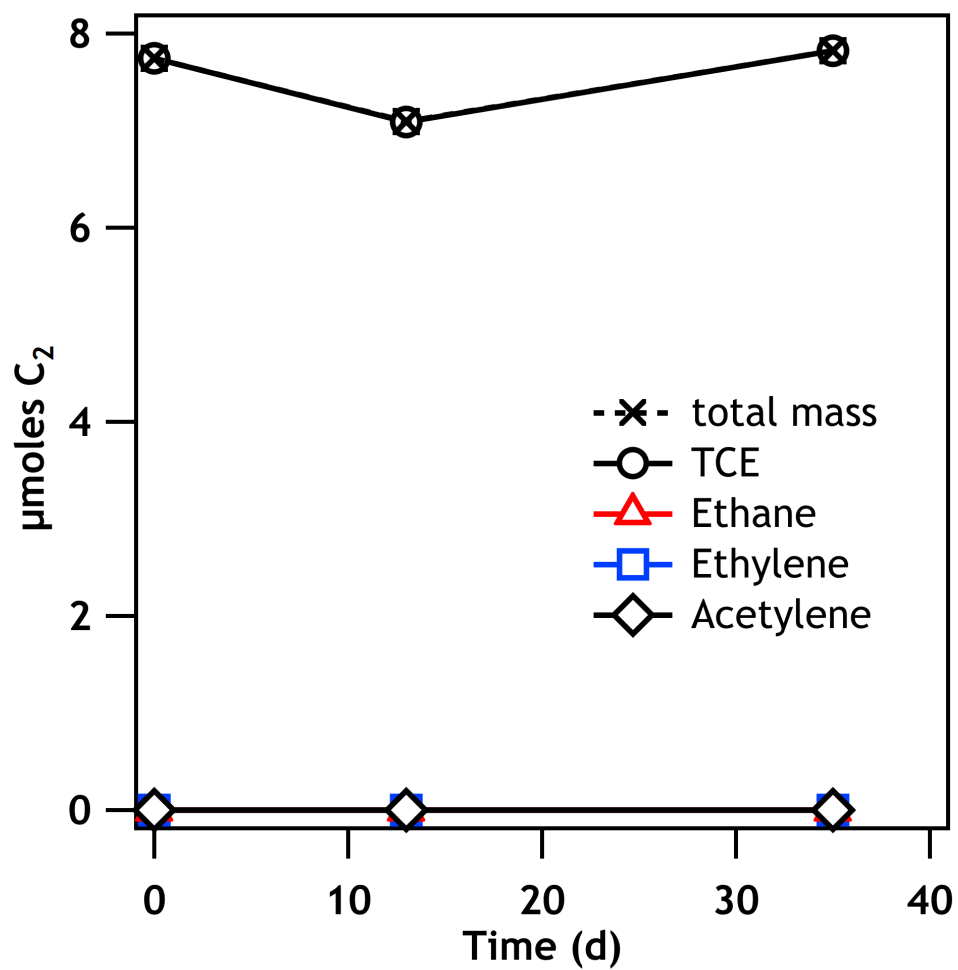


Figure 5. Reaction of TCE with 10 mM sulfide (control). Conditions: 10 mM NaHS in pH 8.0, 50 mM HEPES, 25 mM NaCl buffer, 50 μ M nominal TCE spike.

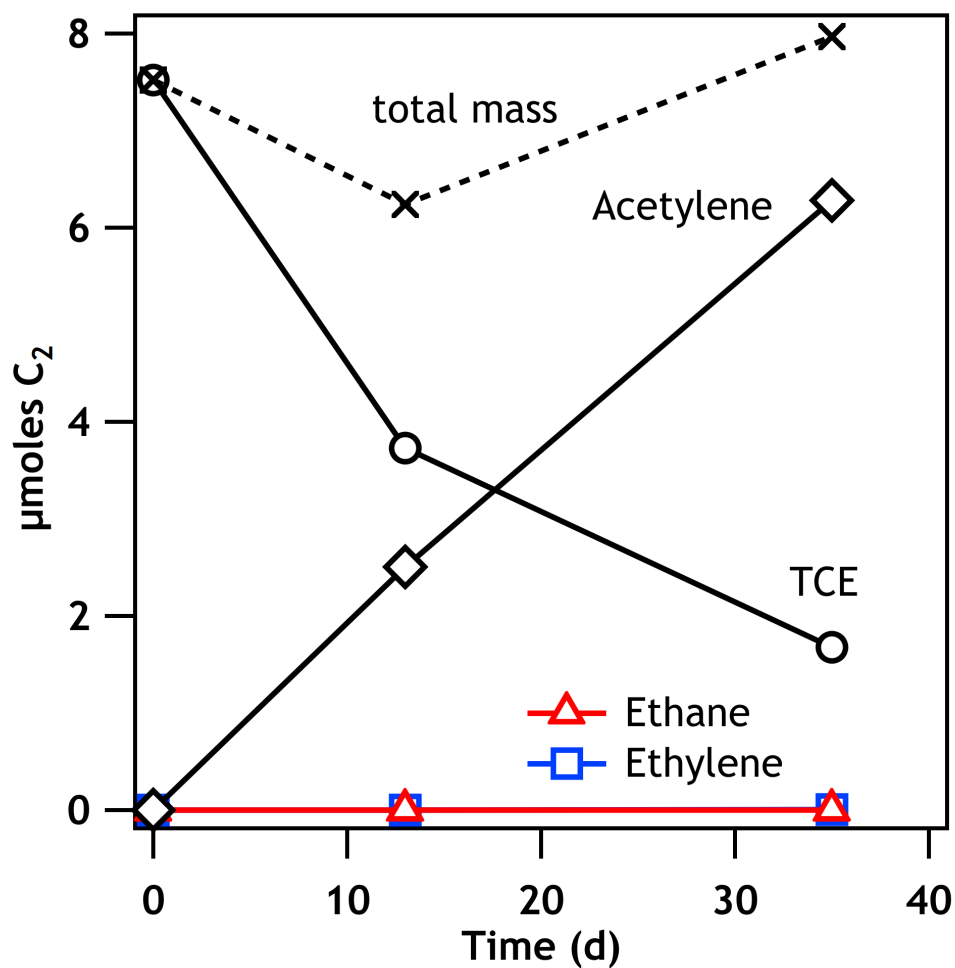


Figure 6. Reaction of TCE with 10 mM sulfide and 10 mM Fe(II). Conditions: 10 mM FeCl₂, 10 mM NaHS in pH 8.0, 50 mM HEPES, 25 mM NaCl buffer, 50 μM nominal TCE spike. Final Products = 79% of initial TCE.

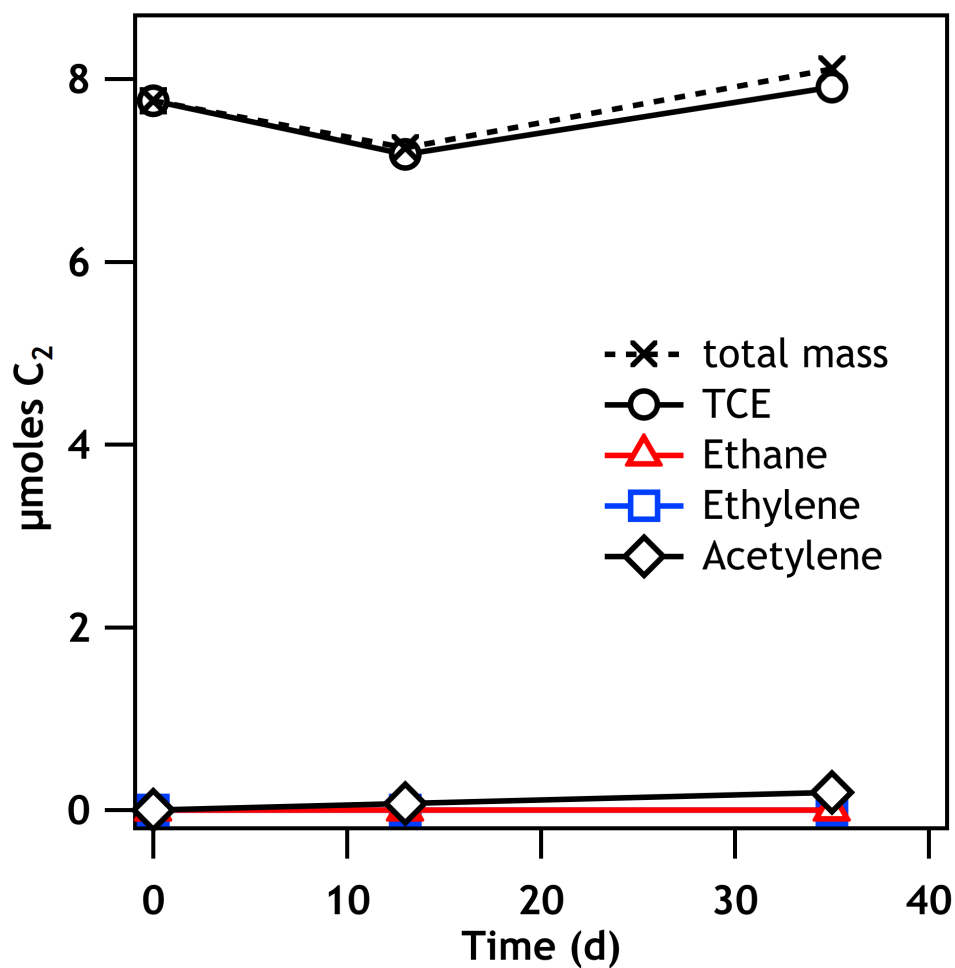


Figure 7. Reaction of TCE with 5 g/L magnetite and 5 mM sulfide. Conditions: 5 g/L magnetite (batch 23), 5 mM NaHS in pH 8.0, 50 mM HEPES, 25 mM NaCl buffer, 50 μ M nominal TCE spike. Final Products = 2.2% of initial TCE.

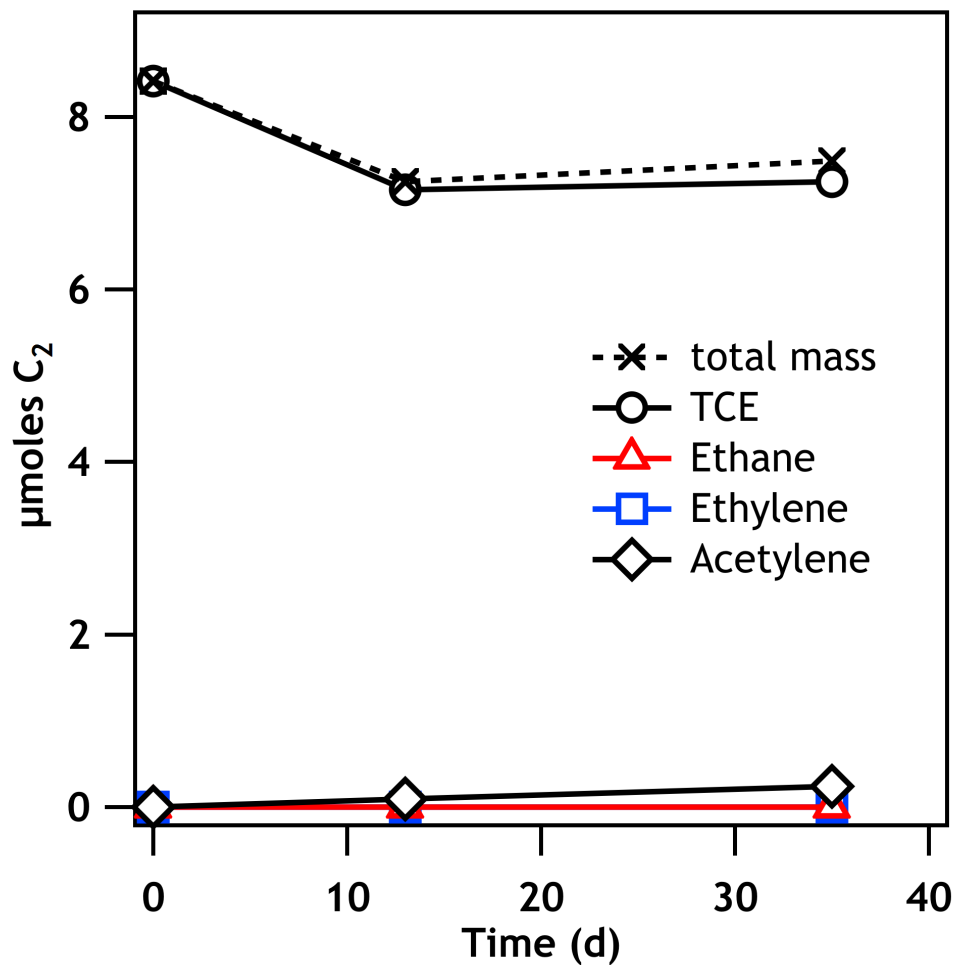


Figure 8. Reaction of TCE with 5 g/L magnetite, 1 mM Fe(II), 5 mM sulfide. Saturation index of $\text{Fe}(\text{OH})_2 < 1$. Conditions: 5 g/L magnetite (batch 23), 1 mM FeCl_2 , 5 mM NaHS in pH 8.0, 50 mM HEPES, 25 mM NaCl buffer, 50 μM nominal TCE spike. Final Products = 3.3% of initial TCE.

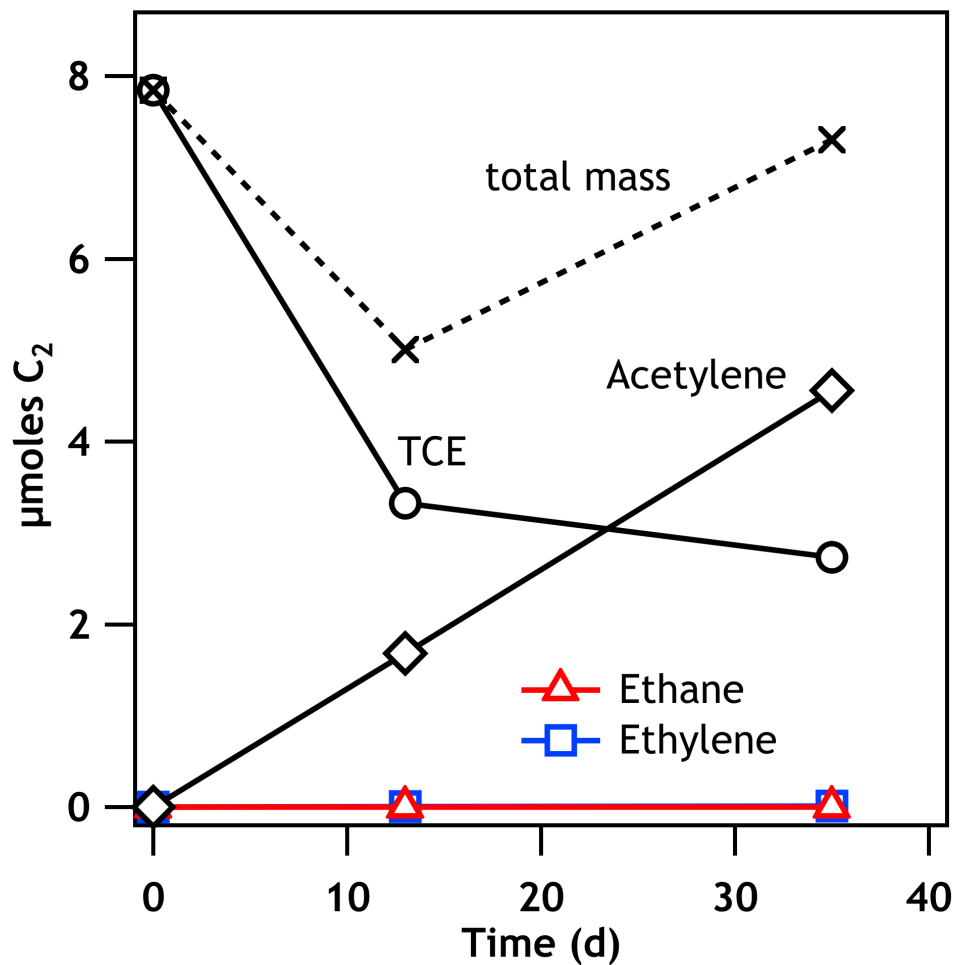


Figure 9. Reaction of TCE with 5 g/L magnetite, 10 mM Fe(II), 5 mM sulfide. Saturation index of $\text{Fe}(\text{OH})_2 > 1$. Conditions: 5 g/L magnetite (batch 23), 10 mM FeCl_2 , 5 mM NaHS in pH 8.0, 50 mM HEPES, 25 mM NaCl buffer, 50 μM nominal TCE spike. Final Products = 63% of initial TCE.

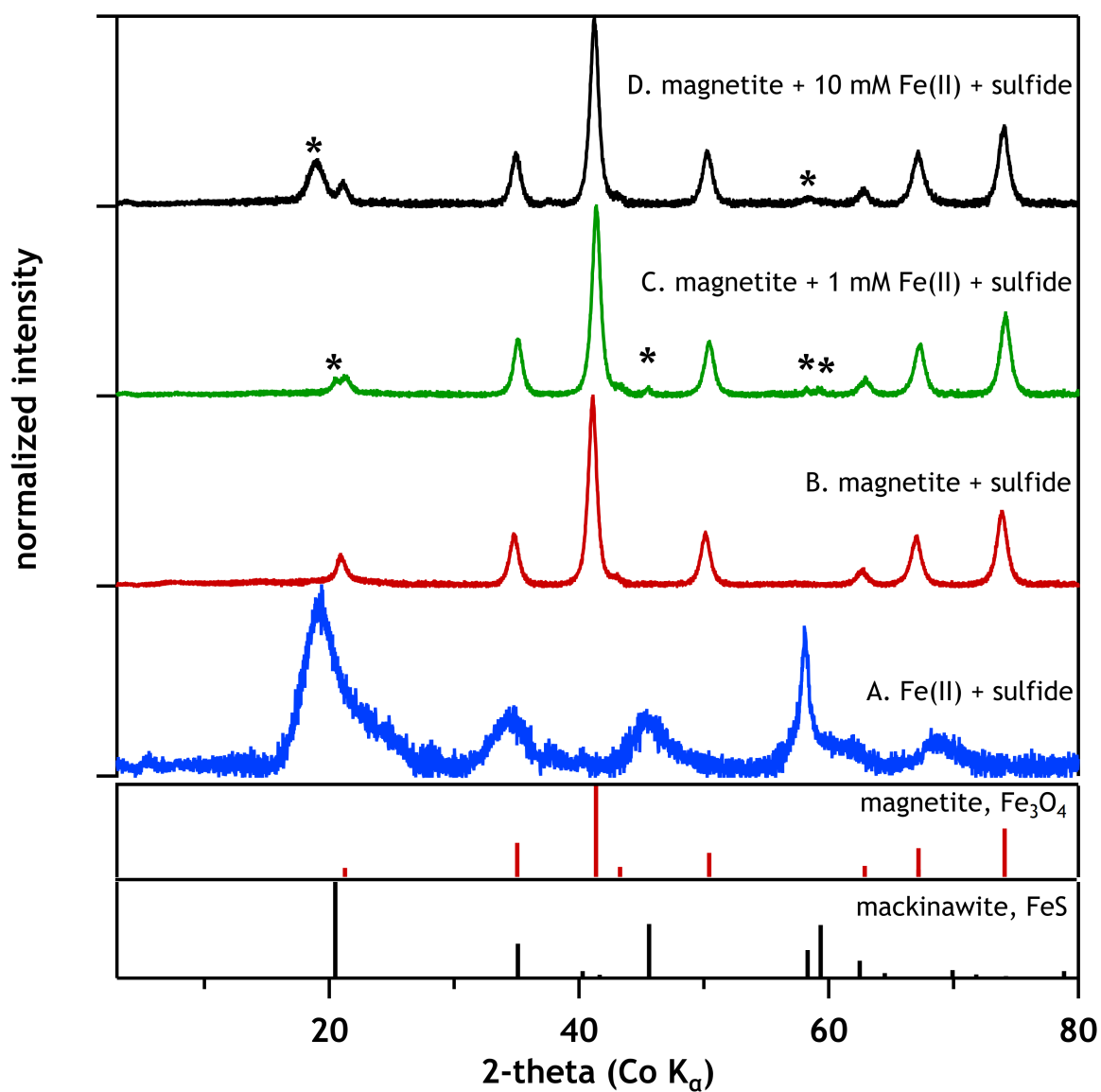


Figure 10 X-ray powder diffraction patterns of (A) 10 mM Fe(II) reacted with 10 mM sulfide, (B) 5 g/L magnetite + 5 mM sulfide, (C) 5 g/L magnetite spiked with 1 mM Fe(II) and 5 mM sulfide (below Fe(OH)₂ saturation), and (D) 5 g/L magnetite spiked with 10 mM Fe(II) and 5 mM sulfide (above Fe(OH)₂ saturation). *Denotes the presence of a peak consistent with that of mackinawite.

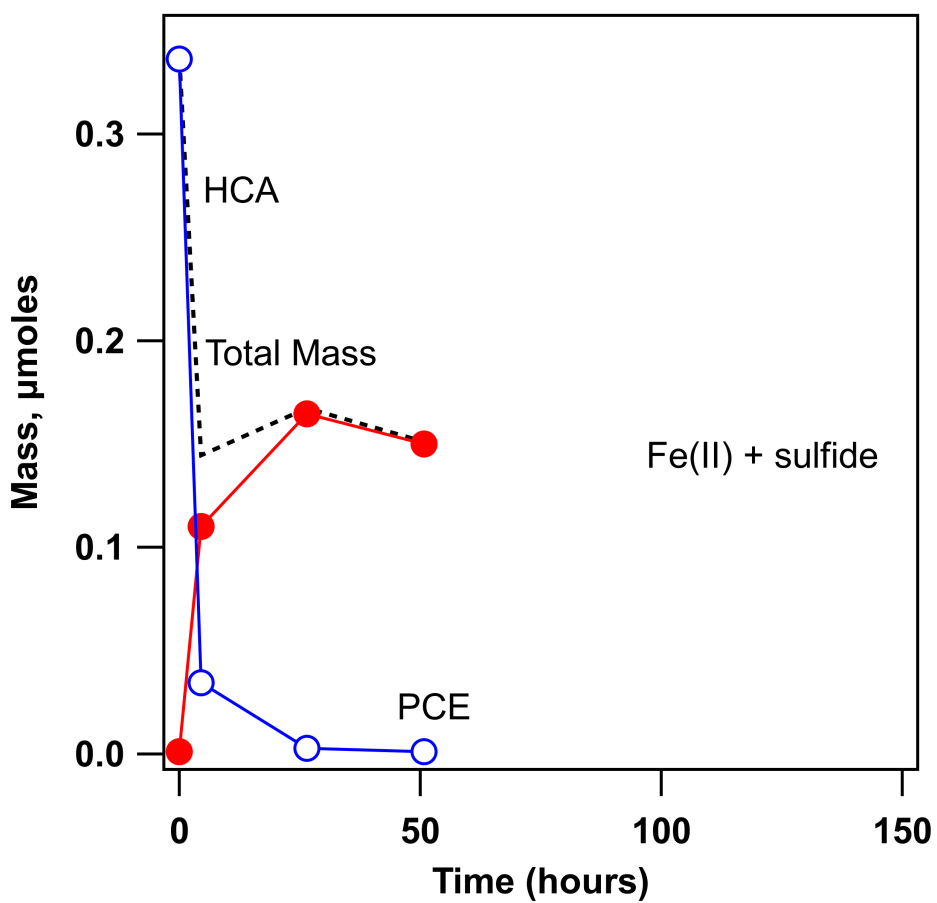


Figure 11. Hexachloroethane (HCA) reduction by FeS. Conditions: 4 mM Fe(II), 4 mM sulfide, pH 7.2, 25 mM MOPS/NaCl buffer.

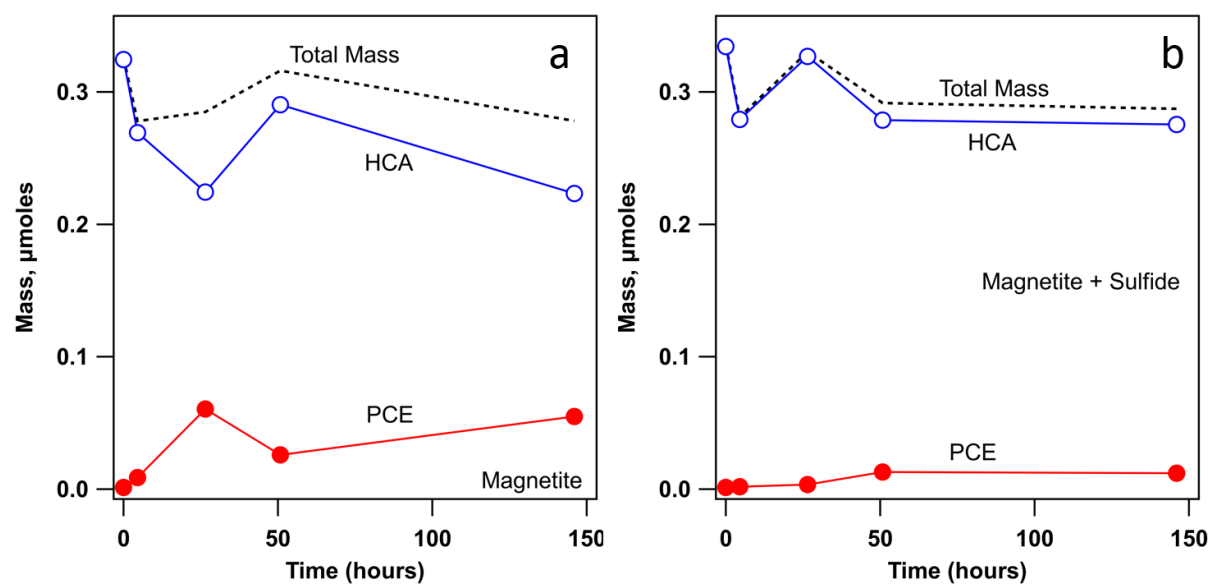


Figure 12. Reduction of HCA by (a) stoichiometric magnetite and (b) stoichiometric magnetite + 4 mM sulfide. Conditions: 1 g/L magnetite, pH 7.2, 25 mM MOPS/NaCl buffer, 6 $\mu\text{moles/L}$ HCA.

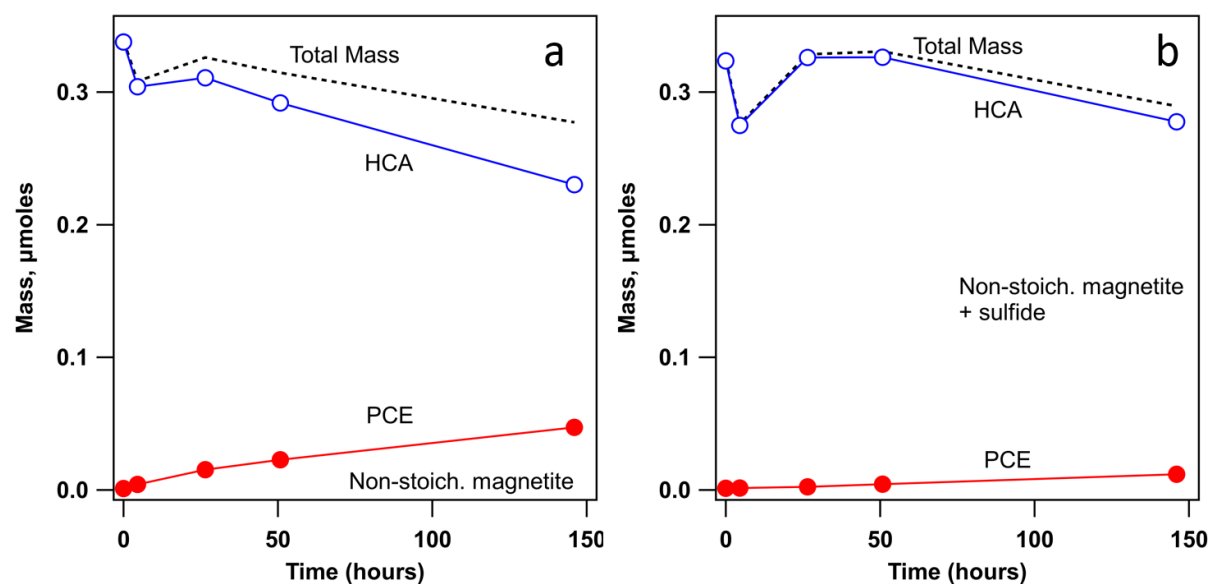


Figure 13. Reduction of HCA by (a) non-stoichiometric magnetite and (b) non-stoichiometric magnetite + 4 mM sulfide. Conditions: 1 g/L magnetite, pH 7.2, 25 mM MOPS/NaCl buffer, 6 $\mu\text{moles/L}$ HCA

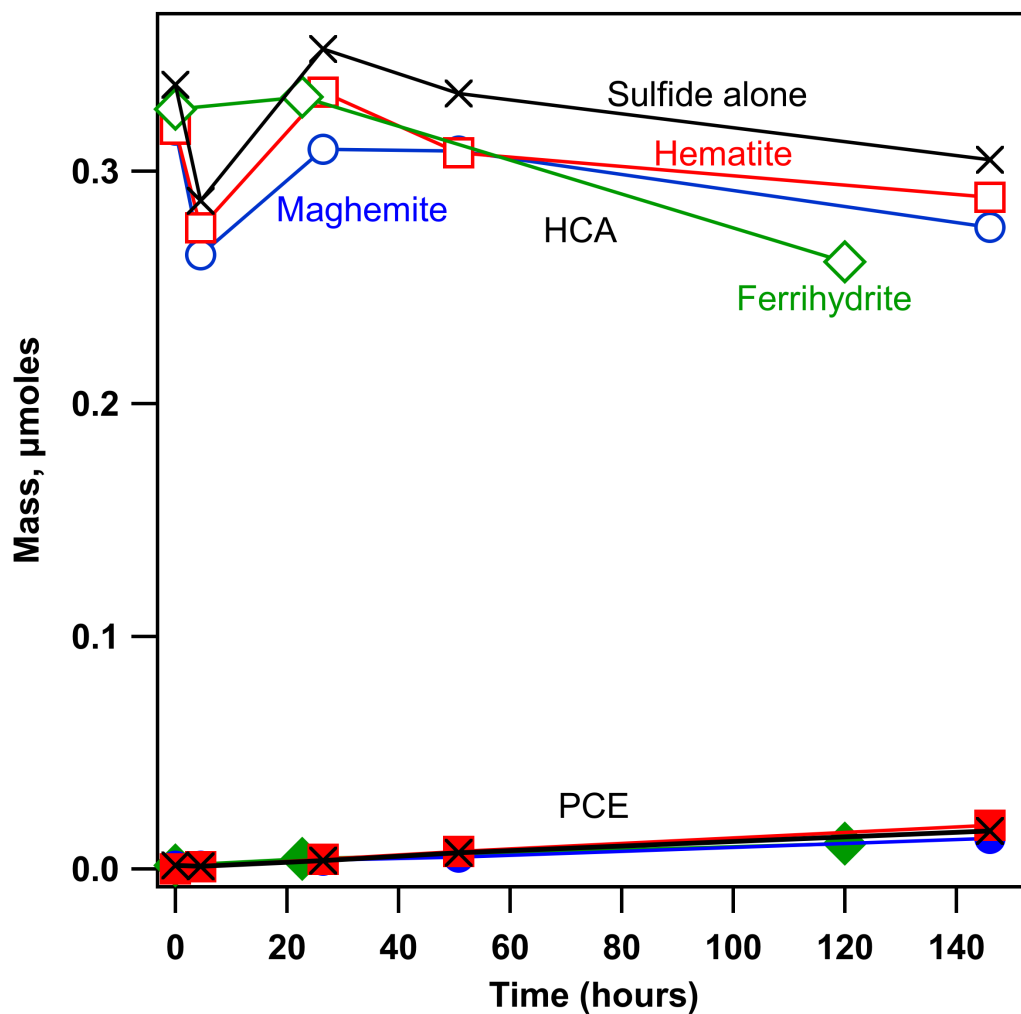


Figure 14. Reduction of HCA by Fe(III) oxides + 4 mM sulfide and in a buffer control with 4 mM sulfide. Conditions: 1 g/L oxide, pH 7.2, 25 mM MOPS/NaCl buffer, 6 μmoles/L HCA

Table 1. Mössbauer hyperfine parameters for sulfide-reduced NAu-1 and SWy-2 spectra with standard deviation for QS and site proportion.

	Reduced χ^2	Site	IS $mm\ s^{-1}$	QS (σ) $mm\ s^{-1}$	Proportion (σ) %
NAu-1 + 10 mM S^{2-}	0.65	Fe(II)	1.24	2.85 (0.24)	7.35 (0.90)
		Fe(III)	0.48	0.48 (0.27)	92.65 (0.90)
NAu-1 + 3.5 mM S^{2-}	0.53	Fe(II)	1.22	2.81 (0.21)	6.18 (0.94)
		Fe(III)	0.48	0.47 (0.28)	93.82 (0.94)
NAu-1 + 2.8 mM S^{2-}	0.83	Fe(II)	1.22	2.86 (0.19)	6.73 (0.52)
		Fe(III)	0.49	0.48 (0.26)	93.27 (0.52)
NAu-1 + 1.4 mM S^{2-}	3.03	Fe(II)	1.22	2.86 (0.17)	5.59 (0.12)
		Fe(III)	0.49	0.48 (0.27)	94.41 (0.12)
SWy-2 + 10 mM S^{2-}	0.66	Fe(II)	1.28	3.04 (0.13)	57.42 (0.58)
		Fe(III)	0.46	0.98 (0.73)	42.58 (0.58)
SWy-2 + 1.5 mM S^{2-}	0.67	Fe(II)	1.27	3.03 (0.08)	30.68 (0.87)
		Fe(III)	0.46	0.83 (0.80)	69.32 (0.87)
SWy-2 + 0.38 mM S^{2-}	1.59	Fe(II)	1.27	3.07 (0.18)	19.54 (0.23)
		Fe(III)	0.47	1.08 (0.91)	80.46 (0.23)
SWy-2 + 0.19 mM S^{2-}	1.20	Fe(II)	1.28	3.06 (0.16)	13.78 (0.46)
		Fe(III)	0.46	1.09 (0.92)	86.22 (0.46)

Table 2. Conditions for reduction of NAu-1 with sulfide with calculated maximum reduction extents assuming either a transfer of 8 electrons from sulfide to the clay mineral and formation of sulfate, or a transfer of 2 electrons and the formation of elemental sulfur.

Sulfide Concentration	Maximum Reduction Equivalents to SO_4^{2-}	Maximum Reduction Extent to SO_4^{2-}	Maximum Reduction Equivalents to S(0)	Maximum Reduction Extent to S(0)	Observed Structural Fe Reduction Extent
<i>(mM)</i>	<i>(mM)</i>	<i>(%)</i>	<i>(mM)</i>	<i>(%)</i>	<i>(%)</i>
10	80	357	20	89	7.4
3.5	28	125	7	31	6.2
2.8	22	100	5.6	25	6.7
1.4	11	50	2.8	12.5	5.6

Table 3. Conditions for reduction of SWy-2 with sulfide with calculated maximum reduction extents assuming either a transfer of 8 electrons from sulfide to the clay mineral and formation of sulfate, or a transfer of 2 electrons and the formation of elemental sulfur.

Sulfide Concentration	Maximum Reduction Equivalents to SO_4^{2-}	Maximum Reduction Extent to SO_4^{2-}	Maximum Reduction Equivalents to S(0)	Maximum Reduction Extent to S(0)	Observed Structural Fe Reduction Extent
<i>(mM)</i>	<i>(mM)</i>	<i>(%)</i>	<i>(mM)</i>	<i>(%)</i>	<i>(%)</i>
10	80	2631	20	658	57
1.5	12	394	3	98	31
0.38	3.04	100	0.76	25	20
0.19	1.52	50	0.38	12.5	14

3.4 PCE and TCE Degradation by Aquifer Materials

Abstract

Here we provide a summary of our work focusing on our last task which was to measure rates of PCE and TCE degradation by aquifer materials. Our hope was to correlate rates of PCE or TCE degradation with sediment properties such as mineral content or extractable iron. We received sediment and groundwater samples from the Middlefield – Ellis – Whisman Field site in California provided by Geosyntec Consultants. These sediments were reacted with TCE, Fe(II) and S(-II) to investigate the potential reactivity of the sediment. The take home message is that we observed little to no TCE degradation over two months (and longer time periods for some reactors) with aquifer materials taken from four different monitoring wells spanning a range of conditions. It is difficult to draw any significant conclusion from our findings other than that the eight different sediments samples tested were not able to degrade TCE over several months even when we attempted to simulate Fe(II) and sulfide generation by microbes by adding it directly to the reactors.

Results and Discussion

We found little TCE degradation by aquifer materials or aquifer materials amended with Fe(II) or sulfide. The sediment and groundwater samples were from the Middlefield – Ellis – Whisman Field site in California provided by Geosyntec Consultants. The sediments were reacted with TCE, Fe (II) and S (-II) to investigate the potential reactivity of the sediment. The take home message is that we have observed little to no TCE degradation over two months (and longer time periods) with aquifer materials taken from four different monitoring wells spanning a range of conditions. It is difficult to draw any significant conclusion from our findings other than that the eight different sediments samples tested were not able to degrade TCE over several months even when we attempted to simulate Fe(II) and sulfide generation by microbes by adding it directly to the reactors

Materials and Methods. Aquifer sediment reactors were 161 ml vials with approximately 150 ml of 25 mM MOPS buffer with 25 mM NaCl at pH 7.5. The sediment loading was 100 g/L or ~15 g of sediment per bottle. The volume is approximate as to get 150 ml an empty reactor was filled with 150 ml of liquid and then marked with a sharpie. This marked bottle was then used as a reference to fill other reactors while accounting for the volume of the sediment itself. Each reactor was spiked with 50 mM TCE and then stored on a shake table rotating at 100 rpm. Reactors were also spiked with ferrous iron (prepared from FeCl₂) and sulfide (mostly at a concentration of 5 mM).

Results and Discussion

Aquifer sediment characterization. Initial X-ray Diffraction (XRD) analysis of the sediments suggested that the makeup was mostly quartz and finer particulate clays (kaolinite, montmorillonite, etc.) for W89-9 (19.5' -20' depth) (**Figure 1**). The Mössbauer spectrum of the W89-9 19.5' to 20' sample at 77K (**Figure 2**) indicates that Fe(II) makes up 63% of the total Fe, and Fe(III) the remainder (37%). At 13 K, an Fe(III) sextet is present as ~13% of the total spectral area, but the relatively low area makes it difficult to assign the sextet to a particular oxide. The sextet could arise from very small particulate Fe(III) oxides due to the low temperature at which the sextet appears (<77K), but could also be attributed to some Fe(III) in clay minerals magnetically ordering or undergoing slow paramagnetic relaxation at

13K. At 13K the Fe(II) and Fe(III) in clay minerals or other Fe silicates. The presence of Fe(II) in the sediments and initial site data (**Table 1**) led us to begin sediment reactivity analysis with sediment from MW W89-9 at a depth of 19.5'-20'. MW W89-9 was selected because of the relatively high TCE and iron concentrations measured at the site.

Groundwater site characterization. Table 1 provides a summary of the groundwater characteristics measured on site. As a quality control check, we calculated the charge balance for groundwater samples provided from each well and found that based on major cations and anions the overall charge balance was within 15% (**Figures 3 - 6**).

TCE degradation experiments. The first experiment conducted was of W89-9 sediment under three different conditions: TCE alone (**E1**), TCE + 5 mM Fe (II) (**E2**), and 5 mM S (-II) (**E3**). This experiment was conducted for the longest period of time (105 days). For the first three sampling points, no significant loss of TCE was observed. However, as seen in **Figure 7**, large unquantified peaks of methane arose and TCE concentrations in the bottles disappeared in both **E1** and **E2**. We suspect that a methanogen colony formed and consumed the chlorinated solvents present in these reactors. The next set of experiments were conducted starting in the spring where **E4** is 75A sediment at a depth of 21.6'-22' spiked with 50 mM TCE. **Figure 8** shows the lack of acetylene, ethene, and ethane production over a period of 89 days. The final set of prior experiments, **E5**, was W89-9 sediment at a depth of 19.5' to 20' spiked with 10 mM Lactate and 50 mM TCE. **Figure 9** shows the lack of acetylene, ethene, and ethane production over a period of 93 days.

After this initial set of reactors revealed no TCE degradation, we set up thirty additional reactors using sediment samples from each of the four monitoring wells (Table 2). We ran a sediment alone, sediment + Fe(II), and sediment + S(-II) for each monitoring well. The reactors were run between 50 and 70 days and no degradation products were observed. Based on these findings, the only conclusions we can draw is that these sediment samples were not able to degrade TCE over several months even when we attempted to simulate Fe(II) and sulfide generation by microbes by adding Fe(II) and sulfide directly to the reactors. Perhaps this is not surprising given that we detected mostly quartz and clays. The clay minerals, however, did contain some Fe which we had thought might be reactive. While we cannot draw any significant conclusions our findings of no degradation are consistent with other findings from this project that suggest reactive mineral intermediate phases (RMIs) might be the relevant phases contributing to abiotic TCE degradation in contaminated aquifers.

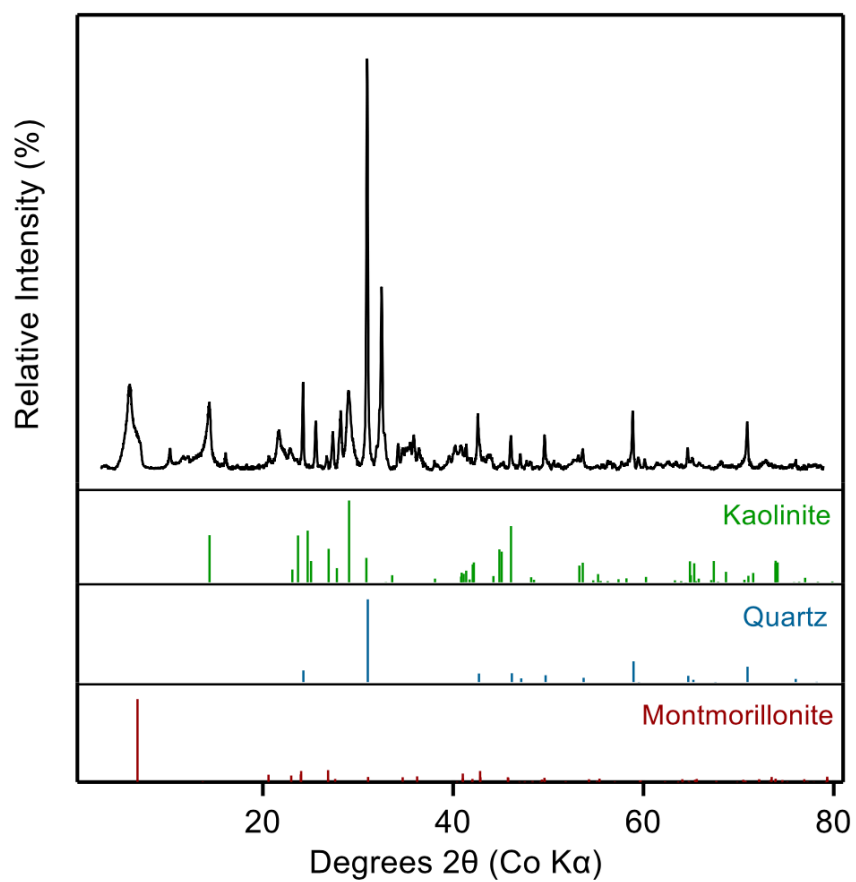


Figure 1. XRD patterns of W89-9 sediment from a depth of 19.5' to 20'.

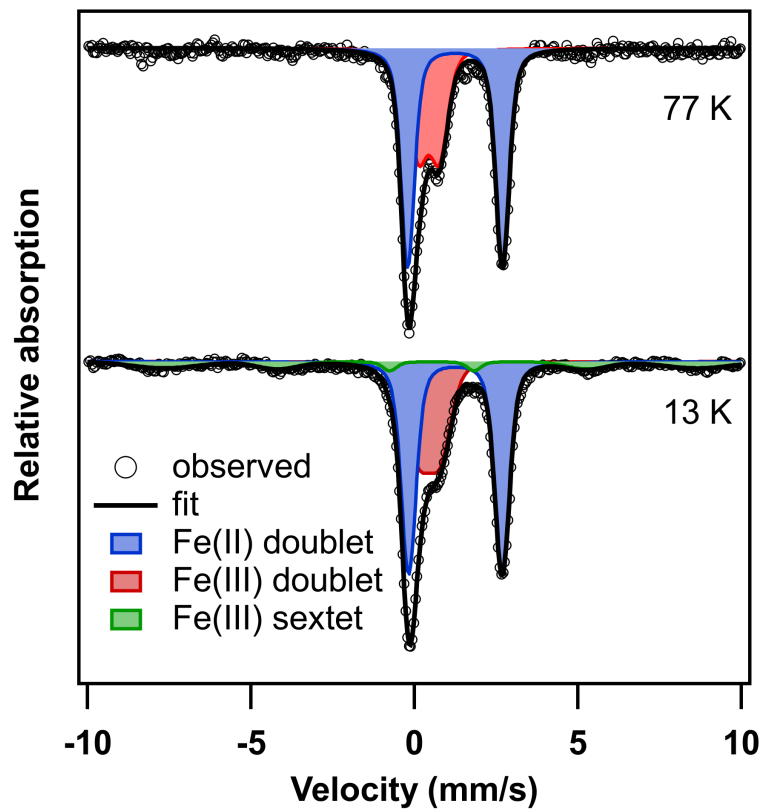


Figure 2. Mossbauer spectra of W89-9 from a depth of 19.5' to 20'.

Mössbauer spectral parameters derived from fitting MEW sample W89-9 from 19.5' to 20' BGS.

Sample	Temp. (K)	Component	Relative area (%)	Center shift, CS (mm/s)	Quadrupol e splitting, QS ^b (mm/s)	Hyperfin e Field, H (T)	$\sigma(H)^c$ (mm/s)	χ^2
W89-9 19.5'-20'	77	Fe(II)	62.7 (0.65)	1.25	2.90 (0.30)	-	-	0.97
		Fe(III)	37.3 (0.65)	0.45	0.66 (0.39)	-	-	
	13	Fe(II)	54.4 (0.64)	1.26	2.86 (0.35)	-	-	1.02
		Fe(III)	32.2 (0.47)	0.45	0.74 (0.48)	-	-	
		Fe(III) sextet	13.4 (0.85)	0.53	-0.01	50.7	6.05	

^a value in parenthesis reflects the error (1σ) in determination of the relative area for each component

^b $\sigma(H)$ = standard deviation of the hyperfine field distribution

* Fixed during fitting

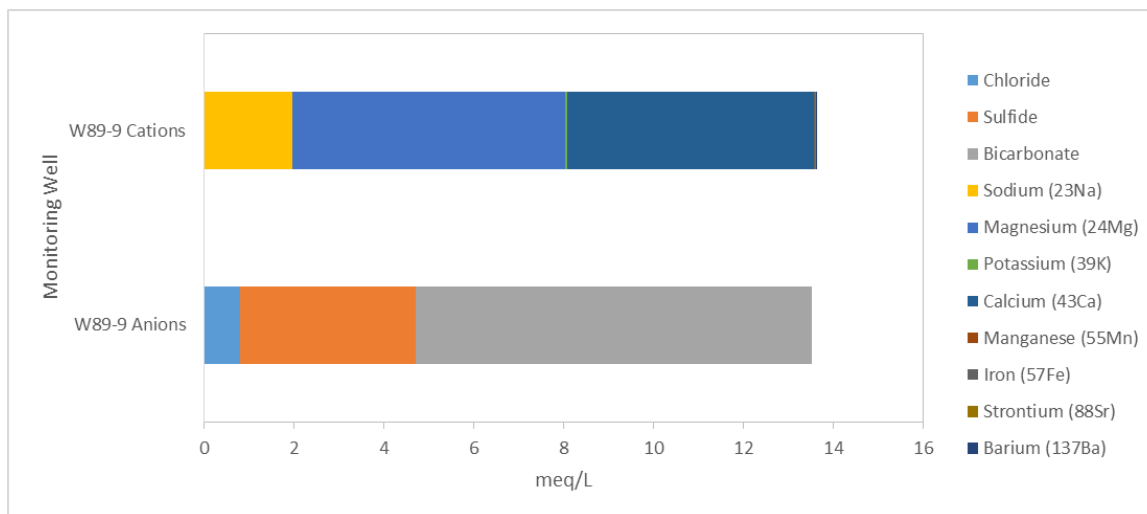


Figure 3. Charge balance of groundwater from monitoring well W89-9.

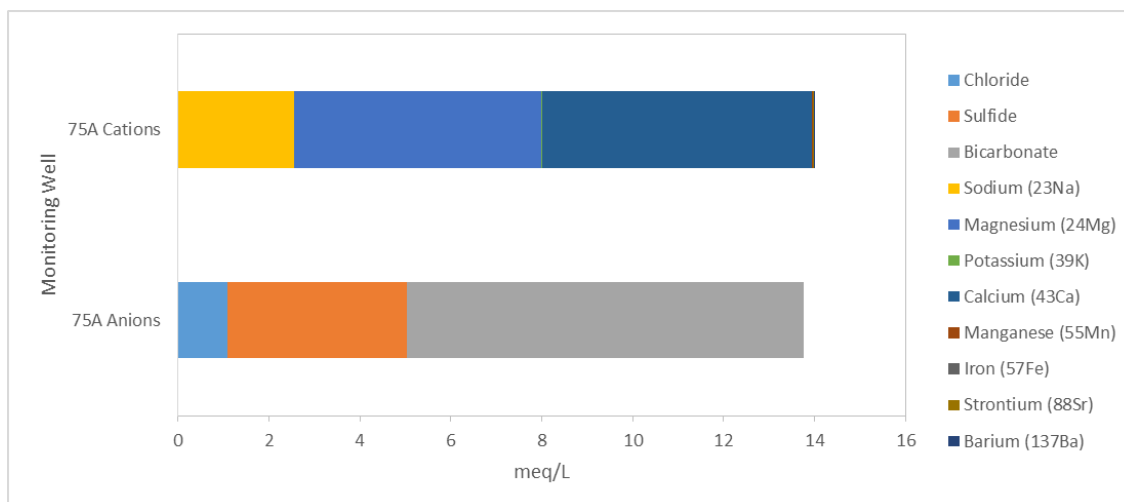


Figure 4. Charge balance of groundwater from monitoring well 75A.

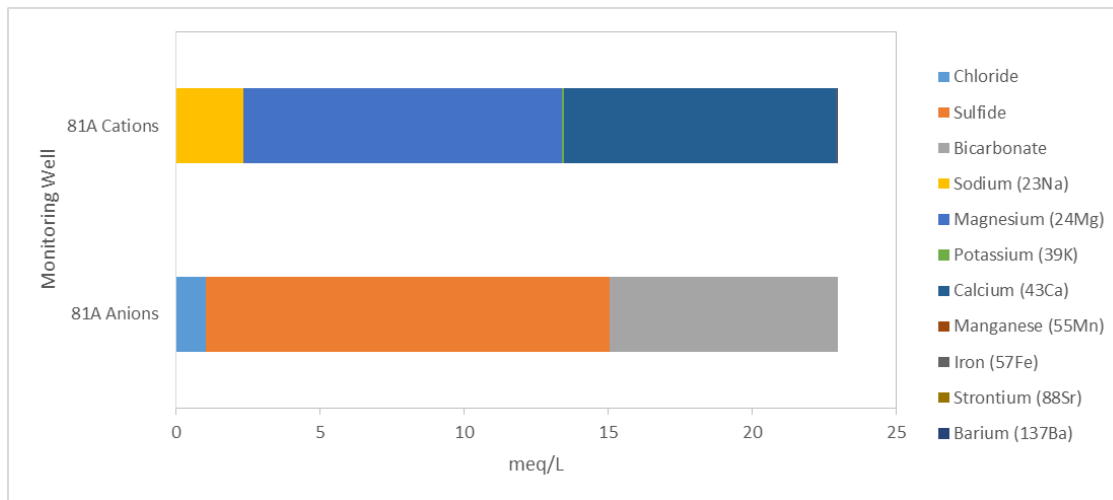


Figure 5. Charge balance of groundwater from monitoring well 81A.

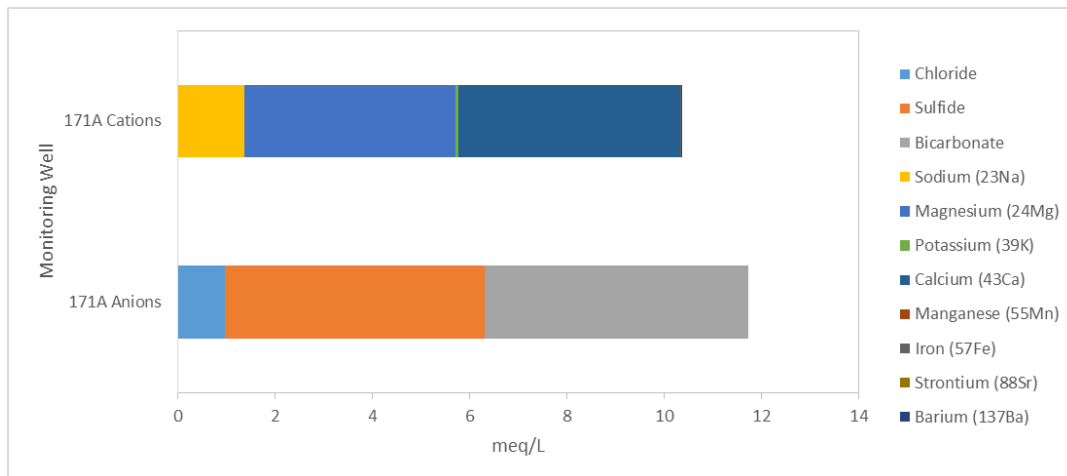


Figure 6. Charge balance of groundwater from monitoring well 171A.

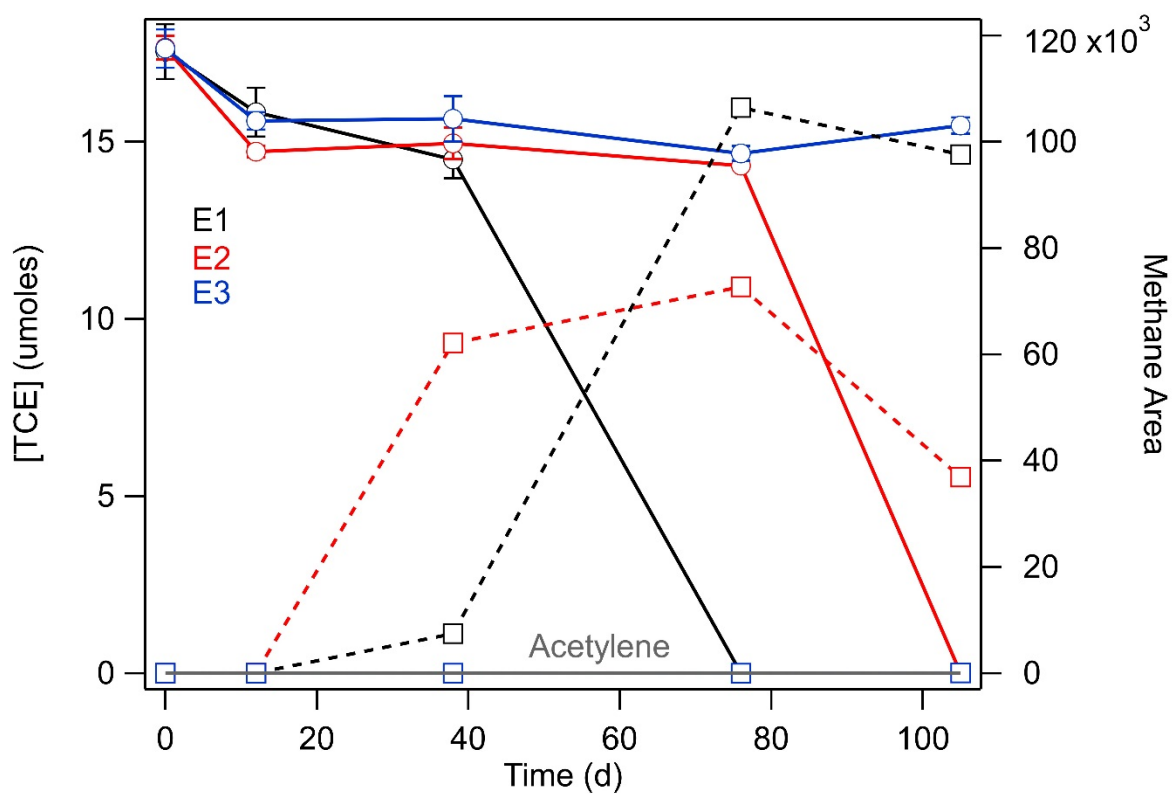


Figure 7. Experiments 1-3 of TCE loss with Sediment collected from monitoring well W89-9 at the Middlefield-Ellis-Whisman Superfund Site, CA. Note: acetylene, ethene, and ethane were all measured and all were non-detect. Experimental Conditions: 15 g of sediment (100 g/L) was added to 150 ml of 25 mM MOPS buffer with 25 mM NaCl and adjusted to pH 7.5. Amendments were made in Experiments 2 and 3 with either 5 mM Fe(II) or S(-II).

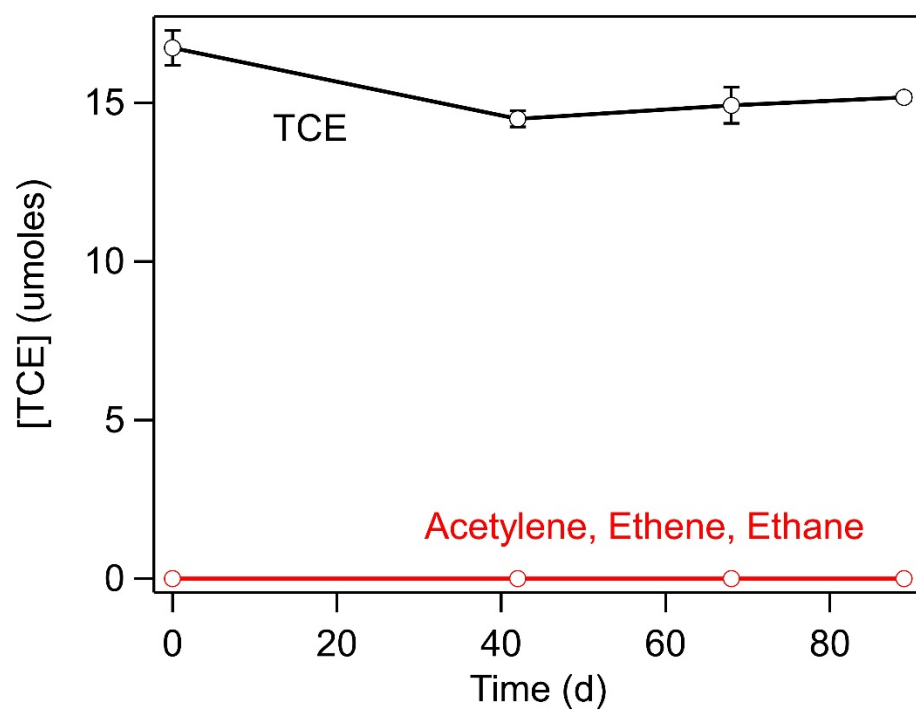


Figure 8. Experiment 4 of TCE loss with Sediment from monitoring well 75A from the Middlefield-Ellis-Whisman Superfund site, CA. Note: acetylene, ethene, and ethane were all measured and all were non-detect.

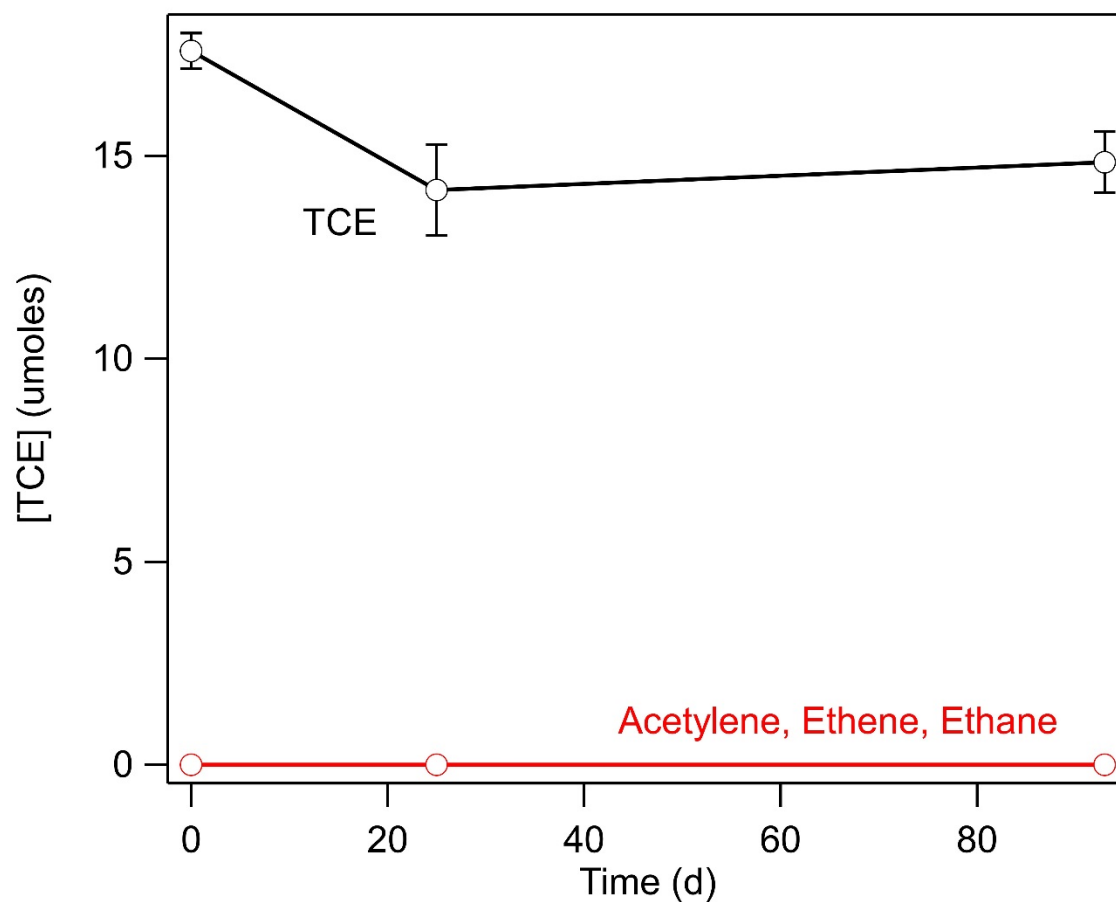


Figure 9. Experiment 5 of TCE loss with Sediment from monitoring well W89-9 from the Middlefield-Ellis-Whisman Superfund site, CA. Note: acetylene, ethene, and ethane were all measured and all were non-detect.

Table 1. Initial Site Data for MEW Monitoring Wells

Well Name	Dissolved Iron (mg/L)	pH	Volatile Organic Carbon Concentrations				Biological Results	
			TCE (ug/L)	DCE (ug/L)	VC (ug/L)	PCE (ug/L)	Dhc (cells/L)	vcrA (gene copies/L)
75A	0.12	7.28	5.1	270	9.7	<1.3	300	ND<2,000
81A	0.54	7.24	14	1500	3.4	<.50	Inconclusive	ND<2,000
171A								
W89-9	0.59	5.9	99	140	7.6	<1.0	10,000	10,000

Table 2. Summary of experimental conditions for second set of aquifer sediment TCE reactors.

Reactor Number	Sediment	Aq. Fe (II)	S (-II)
1	W89-9 21' - 20'6"	-	-
2		5	-
3		-	5
4		-	-
5	W89-9 20'6" - 20'	-	-
6		5	-
7		-	5
8		5	-
9	75A 22' - 21'5.5"	-	-
10		5	-
11		-	5
12		-	5
13	75A 20'11" - 20' 4.5"	-	-
14		5	-
15		-	5
16	81A 21' - 22'	-	-
17		10	-
18		-	5
19		-	-
20	81A 18' - 19'	-	-
21		10	-
22		-	5
23		10	-
24	171A 19'2" - 20'	-	-
25		10	-
26		-	5
27		-	5
28	171A 17' - 17'9"	-	-
29		10	-
30		-	5

Reactors containing Fe (II)

Reactors containing S (-II)