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Geochemical and Isotope Study of Trichloroethene Degradation in a Zero-Valent Iron Permeable Reactive Barrier: A Twenty-Two-Year Performance Evaluation

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Abstract

This study provides a twenty-two-year record of in situ degradation of chlorinated organic compounds by a granular iron permeable reactive barrier (PRB). Groundwater concentrations of trichloroethene (TCE) entering the PRB were as high as 10,670 µg/L. Treatment efficiency ranged from 81 to >99% and TCE concentrations from <1 µg/L to 165 µg/L were detected within and hydraulically down-gradient of the PRB. After 18 years, effluent TCE concentrations were above the maximum contaminant level (MCL) along segments of the PRB exhibiting upward trending influent TCE. Degradation products included cis-dichloroethene (cis-DCE), vinyl chloride (VC), ethene, ethane, >C₄ compounds, and possibly CO_{2(aq)} and methane. Abiotic patterns of TCE degradation were indicated by compound-specific stable isotope data and the distribution of degradation products. δ¹³C values of methane within and down-gradient of the PRB varied widely from −94‰ to −16‰; these values cover most of the isotopic range encountered in natural methanogenic systems. Methanogenesis is a sink for inorganic carbon in zero-valent iron PRBs that competes with carbonate mineralization and this process is important for understanding pore-space clogging and longevity of iron-based PRBs. The carbon isotope signatures of methane and inorganic carbon were consistent with open-system behavior and 22% molar conversion of CO_{2(aq)} to methane.

Graphical Abstract

Supporting Information Available

Supporting Information includes additional site background, details on methods, quality control data, and tables of VOC, methane, and inorganic carbon isotope data.

Introduction

Contamination of groundwater with chlorinated solvents is a common problem at hazardous waste sites. In the United States, nearly 75 percent of the Superfund sites with groundwater remedies selected between 2012 and 2014 addressed contamination by halogenated (primarily chlorinated) hydrocarbons.¹ Over the past decade, the increased use of in situ groundwater treatment technologies (29% in 2004 to 53% in 2014) correlates with an overall decrease in the selection of aboveground pump-and-treat remedies (35% in 2004 to 17% in 2014).¹ These trends reflect acceptance and reliance on the innovative groundwater remediation technologies for site cleanup that were developed and first implemented during the 1980s and 1990s, including permeable reactive barriers (PRBs), in situ chemical oxidation, in situ chemical reduction, bioremediation, and thermal treatment. The continued application of these technologies will benefit from long-term performance data to improve system designs and guide the selection of remedial measures that best match site-specific hydrogeochemical conditions.

The seminal study by Gillham and O'Hannesin² on the degradation of chlorinated hydrocarbons by zero-valent iron (ZVI) kicked off a period of intense bench-scale analysis to understand parent-daughter relationships, rates, and mechanisms of reaction between ZVI and chlorinated methanes, ethanes, and ethenes.^{3–16} Parallel studies explored the degradation potential of reactive iron minerals that precipitate within ZVI PRBs.^{17–20} In ZVI systems, chlorinated ethene removal proceeds by a combination of reductive β -elimination reactions (producing chloroacetylene and breakdown products) and sequential hydrogenolysis reactions (producing cis-dichloroethene, vinyl chloride, and breakdown products).¹⁴ Recent studies developed and applied compound specific stable carbon isotope analysis to differentiate biotic and abiotic dechlorination processes and to evaluate the overall efficiency of contaminant degradation in field applications.^{21–33}

The first field demonstration of ZVI technology showed effective chlorinated solvent treatment over an initial five-year period of performance.³⁴ Warner et al.³⁵ reported on the hydraulic and chemical performance of the first commercial PRB constructed in the U.S. with granular iron metal after 10 years of operation. Phillips et al.³⁶ provided a 10-year performance evaluation of Europe's oldest commercially-installed granular iron PRB located in Northern Ireland. These studies showed effective treatment of trichloroethylene (TCE)

over a decade, although processes such as mineralization and gas generation within ZVI PRBs were identified as factors that could reduce the longevity of these engineered systems for groundwater cleanup.

The Elizabeth City ZVI PRB is one of the earliest full-scale PRBs in the United States. The PRB was constructed in 1996 to treat contaminated groundwater (TCE, hexavalent chromium) originating from a metal plating shop.^{37,38} Previous reports focused on mineralization, hydraulic performance, and treatment efficiency of the Elizabeth City PRB, mainly with respect to the removal of hexavalent chromium from groundwater.^{39–41} The current study examines a twenty-two-year history of TCE treatment, including analysis of daughter products and compound specific stable isotope data for chlorinated compounds, methane, and inorganic carbon. This study provides the longest available record of treatment performance of chlorinated compounds by ZVI and the first analysis of carbon and hydrogen stable isotope ratios in methane produced from a ZVI system.

Materials and Methods

Field Site –

The site is located on the southern bank of the Pasquotank River, about 5 km southeast of Elizabeth City, North Carolina. In June 1996, a 46 m long, 7.3 m deep, and 0.6 m wide PRB (continuous wall configuration) of ZVI (Peerless Metal Powders, Inc.) was installed approximately 30 m from the Pasquotank River^{37,38} (Figure 1; see Supporting Information). The PRB was designed to remediate hexavalent chromium-contaminated groundwater and portions of a larger overlapping plume of volatile chlorinated organic compounds, mainly TCE with lesser amounts of cis-dichloroethene (cis-DCE) and vinyl chloride (VC). Subsurface sampling points discussed here include monitoring wells screened in the aquifer at positions up-gradient (MW48) and down-gradient (MW46, MW47, MW49, MW50, and MW52) of the PRB, as well as transects consisting of multi-level well clusters (ML series; 15-cm screens) placed at depths ranging from 2 to 7 m below ground surface (BGS) at locations up-gradient, within, and down-gradient of the PRB (Figure 1; Table S1).

Groundwater Sampling –

Groundwater samples were collected from 1996 to 2018 using peristaltic (Alexis) or submersible centrifugal (Grundfos) pumps. Prior to sample collection, groundwater was pumped through a flow-cell containing calibrated electrodes to measure pH, oxidation-reduction potential, specific conductance, and dissolved oxygen. Samples for volatile organic compounds (VOCs) were collected with no headspace into 43-mL amber glass vials containing an acid preservative (pH<2). VOC analysis employed headspace gas chromatography-mass spectrometry (GC-MS; EPA Method 8260C). Dissolved gas (methane, ethane, and ethene) samples were collected into 60-mL serum bottles, preserved with sulfuric acid, and capped with crimp seals. Dissolved gas concentrations were determined using a GC equipped with a thermal conductivity detector.⁴² Samples for stable oxygen and hydrogen isotope compositions of water were collected into 20-mL glass vials; isotopic ratios of H₂O were analyzed by cavity ring-down spectrometry (CRDS; Picarro L2120i).

Duplicate field samples for analysis of reproducibility were randomly collected on about 15% of the samples. Groundwater samples were stored at 4°C in a mobile laboratory refrigerator and shipped to analytical laboratories packed in ice. Quality control samples included duplicates, blanks, matrix spikes, calibration check standards, and second-source quality control samples. Results of field and laboratory quality control samples are provided in the Supporting Information.

Stable carbon isotope ratios for TCE, cis-DCE, and VC were determined by Microbial Insights (Knoxville, TN) using gas chromatography coupled to isotope-ratio mass spectrometry (GC-IRMS; samples collected 2016–2018). Carbon and hydrogen stable isotope ratios in methane and carbon isotope ratios in dissolved inorganic carbon (DIC) were determined by Isotech (Champaign, IL; samples collected 2016–2018; see Supporting Information). Carbon and hydrogen isotope values are reported in permil (‰) units relative to a reference standard using the δ notation:

$$\delta^{13}\text{C} = \left[\left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}} \right) - 1 \right] \times 1000 \quad (1)$$

and

$$\delta^2\text{H} = \left[\left(\frac{{}^2\text{H}/\text{H}_{\text{sample}}}{{}^2\text{H}/\text{H}_{\text{standard}}} \right) - 1 \right] \times 1000 \quad (2)$$

Carbon isotope values are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard and hydrogen isotope values are reported with respect to the Vienna Standard Mean Ocean Water (VSMOW) standard.

Results and Discussion

TCE and daughter products.

Near the center region of the PRB (Transect 2; see Figure 1), influent TCE concentrations from the ML21 well cluster ranged widely in time and space from <1 µg/L to 10,670 µg/L. The highest TCE concentrations in the up-gradient aquifer occurred at depth intervals near the PRB base at 6 to 7 m BGS; TCE concentrations in groundwater decreased upward in the aquifer. Lower levels of cis-DCE (<384 µg/L) and VC (<52 µg/L) were also present in influent groundwater, suggesting that limited biodegradation occurred in the aquifer up-gradient of the PRB. Over the 22-year history of monitoring, mean TCE concentrations from the seven-level ML21 well cluster located 2 m up-gradient of the PRB ranged from 150 µg/L ($10^{-5.94}$ mol/L) to 2,309 µg/L ($10^{-4.76}$ mol/L; Figure 2A). The mean influent trend in the ML21 well cluster was in good agreement with TCE concentrations tracked in MW48, a fully screened (4.3 to 7.3 m BGS) monitoring well located approximately 0.7 m to the east of the ML21 well cluster ($\text{MW48}_{\text{TCE}} = \text{MeanML21}_{\text{TCE}} \times 1.08$, $R^2 = 0.72$; Figure 2A and Figure S2). Within (ML24 well cluster) and down-gradient (ML25 well cluster) of the PRB, TCE concentrations ranged from 0.25 µg/L ($10^{-8.72}$ mol/L) to 165 µg/L ($10^{-5.90}$ mol/L) and concentrations tracked influent TCE (Figure 2A). TCE concentrations in the aquifer

hydraulically down-gradient of the PRB were in close agreement with concentrations within the PRB, except for several monitoring points early in the history of the PRB; these points might represent back-diffusion from the aquifer matrix or localized gradient fluctuations due to proximity of a tidally influenced river (Figure 2A). The efficiency of TCE removal by the PRB was estimated to range from 80.7 to 99.6% based on differences in median influent and effluent concentrations; the lowest removal percentage occurred in 2006 when influent TCE spiked (Figure 2A). The cause of the abrupt influent spike is not known; however, the 2006 sampling event represented a transition point from overall decreasing influent TCE prior to 2006 to increasing concentrations from 2007 to 2018. Over the last 5 years (2014–2018), although the apparent TCE removal efficiency was close to 98%, influent TCE concentrations continued an upward trend and mean TCE concentrations within and down-gradient of the PRB were above the Maximum Contaminant Level (MCL, 5 µg/L) in the vicinity of Transect 2 (Figure 2A).

Within and down-gradient of the PRB, residual TCE and daughter products cis-DCE, VC, ethene, and ethane were routinely detected. Their combined concentrations represented between 5 and 100% of influent TCE on a molar basis (Figure 2B). Interestingly, the highest mass recovery of residual TCE plus daughter products coincided with a period of low degradation efficiency in September 2006. Acetylene was not detected in groundwater. However, the results of head space gas analyses conducted between 2016 and 2018 indicated the presence of higher coupling products: propane, propene, i-butane, n-butane, i-pentene, n-pentene, and hexanes (Table S3). The detection of ethene, ethane, and >C4 compounds provides evidence for abiotic TCE degradation via β -elimination reactions.^{8,14} Production of cis-DCE and VC indicates that TCE dehalogenation was not exclusively by β -elimination and points to the competing hydrogenolysis degradation pathway. These results are consistent with laboratory batch testing with ZVI that showed multiple TCE dehalogenation pathways, including β -elimination and sequential hydrogenolysis. The absence of acetylene represents a departure from lab-based studies, where this intermediate product is frequently detected^{8,14,18,31,43}; whereas, field studies rarely report concentrations of acetylene.^{25,32,33} This finding suggests that acetylene rapidly reacts in the environment and has negligible residence time.

Down-gradient of the PRB (ML25 cluster), normalized molar fractions of measured daughter products showed decreasing trends with time for ethene and ethane and increasing trends for cis-DCE and residual TCE, providing evidence that treatment capacity of the PRB is waning at this location (Figure 2C).

The combined concentrations of cis-DCE and VC represent <10% of influent TCE on a molar basis, indicating low accumulation rates of undesired chlorinated products like VC and the predominance of the β -elimination degradation pathway.⁸ Over most of the 22-year monitoring history, a significant proportion of expected TCE degradation products were not accounted for (Figure 2B). Because TCE mainly enters the PRB near its base, there is a possibility that the TCE bypassed the treatment zone beneath the PRB. Results from down-gradient monitoring well MW50, screened from 8.1 to 9.7 m BGS, suggest that this under-flow scenario is unlikely. TCE concentrations in MW50 were <5 µg/L for most of the monitoring record of the PRB (Figure 3); however, it is acknowledged that a lack of deep

sampling points around the PRB limit the strength of this conclusion. Furthermore, hydrologic studies indicated no significant lateral diversion of groundwater in the central region of the PRB.⁴¹ Mass balance on chloride was not possible at this site because influent concentrations of chloride (1.3 mM) were much higher than influent concentrations of chlorinated compounds (~0.01 mM), so that increases in chloride expected during TCE degradation could not be discerned from the background chloride level. Other processes that could result in low mass balance estimates include volatilization and/or other contaminant transformation pathways. The unaccounted mass of TCE degradation products conceivably represents a very small percentage of other carbon reservoirs, such as CO₂ and CH₄. Although ethene and ethane are normally considered to be the final products of dechlorination reactions, CO₂ and CH₄ are also possible end points of anaerobic dehalogenation.^{44,45}

Wells in Transects 1 and 3 (Figure 1) were sampled less frequently compared to the Transect 2 well cluster (Figure S3). In May 2018, mean TCE concentrations in up-gradient ML11 and ML31 well clusters were 515 µg/L ($10^{-5.41}$ mol/L) and 65 µg/L ($10^{-6.31}$ mol/L), respectively, and in the corresponding down-gradient ML15 and ML35 well clusters, mean TCE concentrations were 1 µg/L and 0.7 µg/L ($\sim 10^{-8.1}$ mol/L), respectively, indicating effective treatment of TCE. The down-gradient concentrations measured in the ML15 and ML35 well clusters were consistent with results obtained from the nearby fully screened monitoring wells (MW49 and MW47) in which TCE concentrations were mainly <5 µg/L ($<10^{-7.4}$ mol/L; Figure 3). Thus, the center region of the PRB is the most challenged with respect to maintaining treatment levels below the MCL, primarily because influent TCE concentrations in this region of the PRB increased over 10-fold since 2008.

Effective treatment of TCE over 22 years was indicated by most of the near-field PRB wells. However, further down-gradient in monitoring wells MW46 and MW52 (Figure 1), TCE concentrations were erratic and elevated, ranging from ~8 µg/L to 630 µg/L (Figure S4). In these monitoring wells, upward trends in TCE concentrations were apparent over the last 5 years of monitoring (2013–2018), consistent with concentration trends in the region up-gradient of the PRB. Geochemical signatures in these wells suggest previous interaction with ZVI, e.g., detected methane, depleted sulfate, and non-detectable hexavalent chromium concentrations. The persistence of TCE points to complicating effects of potential down-gradient contaminant sources and possible back-diffusion from the aquifer matrix.⁴⁶

Carbon isotopes of TCE, cis-DCE, and VC.

Fractionation of stable carbon isotopes during abiotic degradation of chlorinated ethenes has been investigated in laboratory systems containing ZVI.^{21,23,25,26,31,47} Carbon isotope fractionation occurs because of differences in reaction rates between ¹³C- and ¹²C-bearing molecules, typically leading to ¹³C-enrichment in residual reactant molecules and depletion of ¹³C in the products of degradation reactions. The development of isotopic tools has mainly relied on controlled laboratory experiments, although several studies have applied this method at the field-scale to help understand reaction mechanisms and the extent of contaminant degradation.^{24,29,32,33,48}

Stable carbon isotope analyses were performed on samples collected from 2016 to 2018, or after 20 years of PRB operation (Table S4). Up-gradient of the treatment zone, TCE was characterized by uniform $\delta^{13}\text{C}$ values of $-24.7 \pm 0.2\text{‰}$ ($n = 10$; Figure 4A). At deeper levels in the aquifer where TCE was most concentrated ($>2,000 \mu\text{g/L}$), concentrations of cis-DCE and VC were typically $<1 \mu\text{g/L}$ indicating negligible up-gradient degradation in the most concentrated portion of the chlorinated plume (see Supporting Information; Table S4). At shallower sampling intervals (3.0 to 4.5 m BGS), TCE, cis-DCE, VC, and ethene were present; co-occurring cis-DCE and VC had $\delta^{13}\text{C}$ values of $-20.8 \pm 0.1\text{‰}$ ($n = 3$) and $-18.0 \pm 2.1\text{‰}$ ($n = 3$), respectively, indicating degradation and isotopic fractionation in the aquifer up-gradient of the PRB at depths near 4 m BGS (Figure 4A). The isotope patterns for cis-DCE and VC are characteristic of late stages of microbial cultures when dechlorination products become enriched in ^{13}C compared to the initial substrate molecules.⁴⁹

Within and down-gradient of the PRB, the carbon isotopic composition of TCE showed consistent enrichment in ^{13}C compared to influent TCE (range $\delta^{13}\text{C}_{\text{TCE}}$: -20.5‰ to -2.9‰ ; Figure 4B), or in terms of the isotopic ratio (R/R_0) of the product (R) and initial reactant (R_0), $R/R_0 = [\delta + 1000/\delta_0 + 1000] = 1.005$ to 1.022 ($n = 19$), evidence that TCE underwent degradation with accompanying isotopic fractionation. The observed pattern of carbon isotope fractionation indicates that sorption of VOCs to nonreactive sites was not a primary mechanism of VOC removal from groundwater because sorption does not significantly fractionate carbon isotopes ($<0.5\text{‰}$ or $R/R_0 = 1.001$)^{50, 51}, although sorption could have played a more important role in removing VOCs during the early history of the PRB when isotopic data were not collected.⁵² The extent of carbon isotope fractionation documented here is similar to results obtained at a ZVI PRB installed at the F.E. Warren Air Force Base ($R/R_0 = 1.001$ to 1.018)²⁹ and significantly greater than a pilot-scale ZVI PRB (max $R/R_0 = 1.002$).³²

Compared to TCE, the carbon isotope composition of cis-DCE within and down-gradient of the PRB was more restricted (range -24.6‰ to -12.3‰ ; mean = $-22.4 \pm 2.8\text{‰}$, $n = 19$) and always depleted in ^{13}C by 1.6‰ to 18.4‰ (Figure 4c). The concentration of cis-DCE within and down-gradient of the PRB was up to $36\times$ greater than concentrations entering the PRB so the isotope signal largely reflects processes occurring within the treatment zone. The most negative values of $\delta^{13}\text{C}_{\text{cis-DCE}}$ occurred when TCE was the most depleted in ^{13}C and |

$\delta^{13}\text{C}_{\text{cis-DCE-TCE}}$ increased with increasing $\delta^{13}\text{C}_{\text{TCE}}$ (Figure 4d), i.e., $\alpha_{\text{cis-DCE-TCE}}$ was not constant ($\alpha_{\text{cis-DCE-TCE}} = [(\delta^{13}\text{C}_{\text{cis-DCE}} + 1000)/(\delta^{13}\text{C}_{\text{TCE}} + 1000)] = 0.990 \pm 0.005$; $n = 18$). This further supports that degradation processes operated on TCE and that cis-DCE was a breakdown product. Laboratory experiments with ZVI show that cis-DCE produced during TCE degradation is depleted in ^{13}C relative to TCE by about 11‰ to 16‰ and the isotopic separation increases at the highest levels of TCE consumption.^{23,25,31} The more restricted isotopic composition of cis-DCE may be the result of initial production of ^{13}C -depleted cis-DCE from TCE followed by subsequent degradation and transformation of cis-DCE resulting in ^{13}C -enrichment, i.e., opposing isotopic fractionation during production and subsequent transformation.⁵³ Interestingly, in laboratory studies with ZVI, Bill et al.²³ observed a constant 16‰ fractionation between cis-DCE and TCE. Non-constant fractionation is apparent in the experimental results of Schüth et al.²⁵ and Elsner et al.³¹, as was observed here. Thus, it is possible that $\delta^{13}\text{C}_{\text{cis-DCE}}$ values and trends with $\delta^{13}\text{C}_{\text{TCE}}$

provide information about the relative rates of production and transformation of cis-DCE. Three data points for VC within and down-gradient of the PRB showed a stable carbon isotope composition ranging from -19.4‰ to -13.4‰ ; co-existing $\delta^{13}\text{C}$ values for TCE and cis-DCE indicated that VC was more depleted in ^{13}C compared to TCE but enriched in ^{13}C compared to co-existing cis-DCE (Table S4). These trends further reveal the complexity of isotope patterns formed during sequential transformation⁵³ and indicate a strong fractionating process for VC during reductive dechlorination.^{49,54,55}

Measured carbon isotope ratios of TCE can also be used to examine the extent and mechanism of transformation in well-constrained systems.^{28,30,56} Laboratory derived isotope trends are typically examined using the Rayleigh equation: $\delta^{13}\text{C} - \delta^{13}\text{C}_0 \approx \epsilon \ln(C/C_0)$, where $\delta^{13}\text{C} - \delta^{13}\text{C}_0$ is the carbon isotope separation, for example, between TCE at time t and time zero, ϵ is the process-dependent bulk enrichment factor: $(\alpha - 1)10^3$, and C/C_0 is the fraction of reactant remaining at time t . Thus, in batch studies bulk enrichment factors are determined by linear regression of $\delta^{13}\text{C} - \delta^{13}\text{C}_0$ versus $\ln(C/C_0)$ and this approach has shown promise for discriminating biotic and abiotic degradation pathways and for estimating the extent of TCE degradation.^{27,28,30,31,56}

Applying this method at PRB sites is challenging because multiple degradation processes are possible (so a unique value of ϵ cannot be assumed) and C_0 may vary widely in heterogeneous systems, e.g., in cases where influent TCE concentrations are not constant in time or space. We estimated C/C_0 by computing the molar ratio $[\text{TCE}/(\text{TCE} + \text{cis-DCE} + \text{VC} + \text{ethene} + \text{ethane})]$ in samples collected within and down-gradient of the PRB, assuming that measured daughter product concentrations correlate with the amount of degraded TCE and that concentrations of daughter products entering the PRB were negligible. This method is similar to the f_{abiotic} ratio used by Whiting et al.⁵⁷ to quantify the degree of biological versus abiological transformation of TCE; however, it is noted that production of cis-DCE, VC, ethene, and ethane is not unique to either the biotic or abiotic pathways of transformation, so no *a priori* conclusion can be drawn from this ratio alone. Furthermore, this approach does not uniquely account for TCE degraded through the β -elimination pathway. Using this approach to estimate C/C_0 , apparent bulk enrichment factors ranged from -2‰ to -26‰ with a median value of -14‰ ($n = 20$; Figure 4e); the median value is in close agreement with a laboratory derived enrichment factor determined for Peerless ZVI ($\epsilon = -13.9\text{‰}$).²⁶ Bulk enrichment factors determined for biotic degradation of TCE fall in the range from about -2.5‰ to -15‰ ^{30,49} and values less than about -14‰ are typical for abiotic degradation.³¹ The most negative ϵ values reported are from systems where TCE degraded in the presence of iron sulfide (-27.9‰).³⁰ Taken at face value, the results shown in Figure 4e indicate that multiple transformation pathways occurred in the PRB. About 70% of the estimated ϵ values were characteristic of abiotic TCE degradation (Fig. 4e), consistent with low cis-DCE and VC production and predominance of the β -elimination degradation pathway. Note that the compound-specific isotope evaluation presented here is biased to samples in which TCE degradation is incomplete ($\text{TCE} > 1 \mu\text{g/L}$). Approximately 43% of the possible sampling locations in the ML24 and ML25 well clusters (in wall and down-gradient positions) showed non-detectable TCE concentrations and could not be examined using the stable isotope method because of detection level constraints. In addition, the

estimate of C/C_0 represents a maximum value given that, on average, the molar quantities of all transformation products have not been accounted for as previously indicated.

Sulfate Reduction and Methanogenesis.

Iron corrosion reactions within the PRB create a H_2 -rich environment in which sulfate-reducing bacteria and methane-producing archaea flourish without normal competition constraints.^{58,59} Over the 22-year study period, the mean influent sulfate concentration (ML21 well cluster) was 1.01 mM ($n = 154$). Within the PRB (ML24 well cluster), sulfate concentrations ranged from <0.01 to 0.49 mM (mean = 0.06 mM; $n = 154$; Figure S5), indicating sustained sulfate removal efficiency of about 94% (Supporting Information; Figure S6). Reduction of sulfate to sulfide and precipitation of mackinawite (FeS) is the primary fate of sulfate within the Elizabeth City PRB based on electron diffraction and acid-volatile sulfide measurements.^{40,60} X-ray absorption spectroscopy and electron microscopy studies revealed the importance of neo-formed mackinawite for removing hexavalent chromium in the PRB and it is possible that iron sulfides have had a long-term beneficial impact on TCE degradation via sustained natural sulfidation within the reactive medium.^{61,62} In addition to the previous solid-phase studies, this possibility is also supported by isotopic data, i.e., low apparent bulk enrichments factors ($\epsilon \approx -25\%$).

Measured carbon-containing molecules in groundwater up-gradient, within, and down-gradient of the PRB include: dissolved carbonic acid/bicarbonate/carbonate, halogenated organic compounds, daughter products produced during TCE degradation, and methane (Figure 5a). The difference between inorganic carbon concentrations in up-gradient and in-wall locations is often used as a monitoring parameter to estimate the quantity of carbonate mineralization within ZVI treatment zones, e.g., aragonite/calcite, chukanovite/siderite, and carbonate green rust.^{40,63} Carbonate minerals precipitate in ZVI treatment zones through progressive exposure to groundwater at elevated pH and carbonate mineralization is commonly viewed as one of the primary processes responsible for reducing ZVI reactivity and permeability.^{40,63–66}

Methane concentrations have not been commonly reported from field ZVI systems. Zolla et al.⁵⁹ noted that groundwater samples collected from a ZVI PRB in Avigliana, Italy contained elevated methane levels (>0.31 mM) within and down-gradient of the PRB and influent groundwater contained non-detectable methane levels. At the Elizabeth City PRB, methane concentrations were determined during initial performance monitoring events (1996–1997).³⁸ Within the PRB, methane concentrations ranged between 0.02 and 0.70 mM (median = 0.18 mM; $n = 55$). Between 1998 and 2012, methane concentrations were not tracked. Starting in 2013, methane concentrations were again measured as part of this study and methane isotopic signatures (C and H) were measured from 2016 to 2018. Methane concentrations from 0.27 to 0.89 mM (median = 0.44 mM; $n = 42$) were measured in the ML24 well cluster from 2013 to 2018. These results suggest that, like sulfate-reduction, methanogenesis has occurred over the entire history of the PRB.

Dissolved inorganic carbon represents the most likely source of carbon for methanogenesis, although potential sources of solid-phase carbon in the PRB and down-gradient aquifer cannot be excluded. Hardy and Gillham⁶⁷ detected low levels of methane to C5

hydrocarbons produced via the reduction of aqueous CO₂ by ZVI in laboratory experiments. In their experiments, methane concentrations were detected at trace levels (<0.008 mM) and were presumably formed as a consequence of abiotic reactions. However, recent studies emphasize that ZVI enhances biocathodic carbon dioxide reduction to methane and methanogenic consortia possibly increase the rate of anaerobic iron corrosion by lowering the H₂ partial pressure.⁶⁸ In addition, the use of ZVI for methane bioenergy production is being examined with increased interest.⁶⁹ Based on data collected in Transect 2 from 2016 to 2018, approximately 20% of the dissolved inorganic carbon entering the PRB was transformed to methane (Figure 5a). Thus, estimates of carbonate mineralization in the treatment zone, based on the change in DIC concentrations, provide an over-estimate of carbonate precipitation when methanogenesis is not considered.

Methane concentrations persist in well cluster ML25, MW47, and MW49 (~2–3 m down-gradient of the PRB) at similar levels present within the treatment zone (Figure S7). However, further down-gradient (~17 m) methane concentrations drop by a factor of ~3 in MW46 and by a factor of ~200 in MW52 compared to methane levels within the PRB (Figure S7).

The $\delta^{13}\text{C}$ values of methane within and down-gradient of the PRB vary widely from –94‰ to –16‰ (mean = $-47.9 \pm 20\text{‰}$, n = 34; Supporting Information; Table S6); co-existing $\delta^{13}\text{C}$ values of dissolved inorganic carbon vary from –18.7‰ to 1.1‰ (mean = $-9.2 \pm 4.4\text{‰}$, n = 23). Up-gradient of the PRB, $\delta^{13}\text{C}$ values of dissolved inorganic carbon are comparatively uniform and more depleted in ^{13}C (mean = $-18.1 \pm 1.9\text{‰}$; n = 17). The apparent carbon fractionation factors between carbon dioxide and methane [$\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4} = (\delta^{13}\text{C}_{\text{CO}_2} + 1000)/(\delta^{13}\text{C}_{\text{CH}_4} + 1000)$] ranged from 1.086 to 0.988 (median = 1.041; n = 23; Figure 5b). Remarkably, the span of $\delta^{13}\text{C}$ values for methane reported here covers most of the range displayed in all methanogenic groundwater environments combined (i.e., from about –100‰ to about –40‰).⁷⁰ The initial hypothesis tested with methane/carbon dioxide isotope studies was that methane production would dominantly follow the hydrogenotrophic methanogenesis pathway (CO₂ reduction) with expected $\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ values >1.058.⁷¹ However, the data covered a wider range including the region expected for acetoclastic methanogenesis ($\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4} = 1.039$ to 1.058)⁷¹, and lower apparent fractionation factors atypical of methanogenic environments (<1.020; Figure 5b). Acetoclastic methanogenesis is not entirely unexpected because it involves the formation of acetate from CO₂ and H₂, and is thermodynamically favorable in high-H₂ environments characteristic of ZVI systems.⁷⁰ In addition to biotically mediated reactions between CO₂ and H₂, acetate is a possible breakdown product of acetylene⁷², which was not detected as previously noted, but is an expected product of abiotic dechlorination reactions; thus, multiple methanogenesis pathways could be envisioned in ZVI systems and current studies are underway to better understand the controlling factors (D. Hakob, pers. communic.). One sample with a low apparent $\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ value of 0.99 was from the shallowest well in the ML25 down-gradient cluster and was probably influenced by methane oxidation/consumption; other data points in Figure 5b are considered to be reflective of methane production.

Vinson et al.⁷⁰ recently challenged conventional interpretation of $\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ values by noting that non-methanogenic processes such as sulfate reduction, iron reduction, and

carbonate mineralization can cause the apparent carbon isotopic fractionation between methane and carbon dioxide to differ from the true methanogenic fractionation. An alternative pathway-independent analysis considers mass balance between methane and carbon dioxide in an open-system^{70,73–75}:

$$\delta^{13}\text{C}_{\text{input}} \approx f(\delta^{13}\text{C}_{\text{CH}_4}) + (1 - f)(\delta^{13}\text{C}_{\text{CO}_2}) \quad (3)$$

where $\delta^{13}\text{C}_{\text{input}}$ is any available carbon source that is consumed without accumulating in groundwater. When all available carbon is routed through methanogenesis, the value of f goes to 1. When $f = 0$, no methanogenesis occurs. High f values are characteristic of systems with sources of highly biodegradable organic carbon, such as peat and oils.⁷⁰ Lower f values, such as observed here, can occur in cases where non-methanogenic processes (e.g., sulfate reduction) compete with methanogenesis for substrates. In the system described here, CO_2 represents the dominant apparent carbon source for methanogenesis (so $\delta^{13}\text{C}_{\text{input}} = \delta^{13}\text{C}_{\text{CO}_2 \text{ input}}$). Note that apparent $\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ values fall along a trend represented by $f = 0.22 \pm 0.04$ (Figure 5b), equivalent to the apparent fraction of dissolved inorganic carbon in up-gradient groundwater that is converted to methane in the PRB (Figure 5a).

Apparent carbon fractionation factors between methane and carbon dioxide reinforce the concept that dissolved inorganic carbon represents the primary source of carbon in methane. The wide range of apparent carbon isotope fractionation and $\delta^{13}\text{C}_{\text{CH}_4}$ values are considered to be a function of: 1) lower f values indicating competition for substrate and associated isotope effects; 2) rate dependent fractionation where more alkaline environments result in greater isotopic fractionation; and, 3) potential impact of carbonate mineralization within the PRB.⁷⁶ Unfortunately, because the carbon reservoir of TCE and daughter products is very small compared to inorganic carbon and methane, stable isotope signatures are not an effective tool to evaluate whether CO_2 and CH_4 represent end-products of TCE degradation. However, values of $\delta^{13}\text{C}$ for TCE co-existing with methane show that samples with TCE enriched in ^{13}C correspond to more depleted methane (Figure 5c).

Hydrogen isotope compositions of methane and co-existing water also provide constraints on methanogenesis. The δD value of groundwater can be compared with that of the co-produced methane in a given well. Groundwater values of δD were uniform ($-25.1 \pm 1.6\text{‰}$; $n = 52$) and the difference in δD between water and methane was $307 \pm 16\text{‰}$ ($n = 32$; Table S6), significantly greater than the 180‰ value typically associated with the hydrogenotrophic methanogenesis pathway in marine sediments.⁷⁷ Sugimoto and Wada⁷⁸ conducted incubation experiments in freshwater systems and determined much larger differences in δD in freshwater compared to marine settings. Based on the mean water composition from the Elizabeth City site, $\delta\text{D}_{\text{CH}_4}$ values of $334 \pm 20\text{‰}$ for CO_2 reduction and $303 \pm 15\text{‰}$ for acetoclastic methanogenesis were predicted based on the models of Sugimoto and Wada⁷⁸, and both results are consistent with the data presented here. No significant difference in δD of CH_4 between hydrogenotrophic methanogenesis and acetoclastic methanogenesis is expected when δD of water is close to SMOW.⁷⁸

Implications for Field Applications of ZVI for Groundwater Remediation.

This study shows for the first time that subsurface installations of ZVI can remain biogeochemically active for 20-plus years, supporting methanogenesis, microbial sulfate reduction, and degradation of chlorinated ethenes. Methanogenesis is a sink for inorganic carbon that competes with carbonate mineralization. The common assumption is false that DIC removal in ZVI PRBs translates solely to carbonate precipitation and pore space reduction. Estimation of the carbonate mineral mass or volume that precipitates, based on the differences between up-gradient and down-gradient DIC concentrations, requires additional evaluation of methane production. Furthermore, methane can be used as a near-field probe in down-gradient regions to evaluate whether reductive geochemical processes remain active within the treatment zone. Long-term sulfate reduction and creation of secondary reactivity through the formation of iron sulfide improves the treatment performance of ZVI by enhancing abiotic degradation. This is consistent with daughter-product and compound-specific isotope analysis indicating that abiotic processes were dominantly responsible for TCE degradation.

The stable isotope results obtained in this study showed ^{13}C enrichment in treated TCE ranging from about 5‰ to 22‰ relative to influent TCE. About 70% of the estimated ϵ values were characteristic of abiotic TCE degradation. This coupled with low cis-DCE and VC production indicates that the β -elimination degradation pathway was dominantly responsible for TCE treatment over the 22-year monitoring history. A more restricted range of carbon isotope compositions for cis-DCE possibly reflects opposing isotopic fractionation during production from TCE (^{13}C depletion) and subsequent degradation (^{13}C enrichment). Decreasing concentration trends with time for ethene and ethane and increasing trends for cis-DCE and residual TCE within in-wall and near-field down-gradient monitoring points are the most apparent indicators of impending or lost treatment capacity of ZVI. Fluctuations and/or upward-trending influent contaminant concentrations can lead to reduced performance efficiency. Thus, coupling up-gradient source treatment with PRB technology utilizing granular ZVI, in appropriate hydrologic and geochemical settings, can result in sustained groundwater treatment over decadal timescales.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- (1). US EPA (2017). Superfund Remedy Report, 15th edition. EPA/542/R-17-001.
- (2). Gillham RW; O'Hannesin SF Enhanced degradation of halogenated aliphatics by zero-valent iron. *Groundwater* 1994, 32 (6), 958–967.
- (3). Matheson LJ; Tratnyek PG Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* 1994, 28 (12), 2045–2053. [PubMed: 22191743]

- (4). Burris DR; Campbell TJ; Manoranjan VS Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron-water system. *Environ. Sci. Technol.* 1995, 29 (11), 2850–2855. [PubMed: 22206534]
- (5). Reardon EJ Anaerobic corrosion of granular iron: measurement and interpretation of hydrogen evolution rates. *Environ. Sci. Technol.* 1995, 29 (12), 2936–2945. [PubMed: 22148199]
- (6). Orth WS; Gillham RW Dechlorination of trichloroethene in aqueous solution using Fe^0 . *Environ. Sci. Technol.* 1996, 30 (1), 66–71.
- (7). Johnson TL; Scherer MM; Tratnyek PG Kinetics of halogenated organic compound degradation by iron metal. *Environ. Sci. Technol.* 1996, 30 (8), 2634–2640.
- (8). Roberts AL; Totten LA; Arnold WA; Burris DR; Campbell TJ Reductive elimination of chlorinated ethylenes by zero-valent metals. *Environ. Sci. Technol.* 1996, 30 (8), 2654–2659.
- (9). Campbell TJ; Burris DR; Roberts AL; Wells JR Trichloroethylene and tetrachloroethylene reduction in a metallic iron-water-vapor batch system. *Environ. Toxicol. Chem.* 1997, 16 (4), 625–630.
- (10). Fennelly JP; Roberts AL Reaction of 1,1,1-trichloroethane with zero-valent metals and bimetallic reductants. *Environ. Sci. Technol.* 1998, 32 (11), 1980–1988.
- (11). Wüst WF; Köber R; Schlicker O; Dahmke A Combined zero- and first-order kinetic model of the degradation of TCE and cis-DCE with commercial iron. *Environ. Sci. Technol.* 1999, 33 (23), 4304–4309.
- (12). Su C; Puls RW Kinetics of trichloroethene reduction by zerovalent iron and tin: pretreatment effect, apparent activation energy, and intermediate products. *Environ. Sci. Technol.* 1999, 33 (1), 163–168.
- (13). Deng B; Burris DR; Campbell TJ Reduction of vinyl chloride in metallic iron-water systems. *Environ. Sci. Technol.* 1999, 33 (15), 2651–2656.
- (14). Arnold WA; Roberts AL Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with $\text{Fe}(0)$ particles. *Environ. Sci. Technol.* 2000, 34 (9), 1794–1805.
- (15). Scherer MM; Richter S; Valentine RL; Alvarez PJ Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean-up. *Crit. Rev. Microbiol.* 2000, 26 (3), 221–264. [PubMed: 11192023]
- (16). Köber R; Schlicker O; Ebert M; Dahmke A Degradation of chlorinated ethylenes by Fe^0 : inhibition processes and mineral precipitation. *Environ. Geol.* 2002, 41 (6), 644–652.
- (17). Butler EC; Hayes KF Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide. *Environ. Sci. Technol.* 1999, 33 (12), 3884–3891.
- (18). Butler EC; Hayes KF Factors influencing rates and products in the transformation of trichloroethylene by iron sulfide and iron metal. *Environ. Sci. Technol.* 2001, 35 (19), 3884–3891. [PubMed: 11642448]
- (19). Lee W; Batchelor B Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 2. Green rust. *Environ. Sci. Technol.* 2002, 36 (23), 5348–5354. [PubMed: 12521160]
- (20). He YT; Wilson JT; Wilkin RT Impact of iron sulfide mineral transformation on its reactivity toward TCE degradation. *Geochim. Cosmochim. Acta* 2010, 74 (7), 2025–2039.
- (21). Dayan H; Abrajano T; Sturchio NC; Winsor L Carbon isotopic fractionation during reductive dehalogenation of chlorinated ethenes by metallic iron. *Org. Geochem.* 1999, 30 (8), 755–763.
- (22). Sherwood Lollar B; Slater GF; Ahad J; Sleep B; Spivack J; Brennan M; MacKenzie P Contrasting carbon isotope fractionation during biodegradation of trichloroethylene and toluene: implications for intrinsic bioremediation. *Org. Geochem.* 1999, 30 (8), 813–820.
- (23). Bill M; Schüth C; Barth JAC; Kalin RM Carbon isotope fractionation during abiotic reductive dehalogenation of trichloroethene (TCE). *Chemosphere* 2001, 44 (5), 1281–1286. [PubMed: 11513419]
- (24). Slater GF; Sherwood Lollar B; Sleep BE; Edwards EA Variability in carbon isotopic fractionation during biodegradation of chlorinated ethenes: implications for field applications. *Environ. Sci. Technol.* 2001, 35 (5), 901–907. [PubMed: 11351533]

- (25). Schüth C; Bill M; Barth JAC; Slater GF; Kalin RM Carbon isotope fractionation during reductive dechlorination of TCE in batch experiments with iron samples from reactive barriers. *J. Contam. Hydrol.* 2003, 66 (1–2), 25–37. [PubMed: 14516939]
- (26). VanStone NA; Focht RM; Mabury SA; Sherwood Lollar B Effect of iron type on kinetics and carbon isotopic enrichment of chlorinated ethylenes during abiotic reduction on Fe(0). *Groundwater* 2004, 42 (2), 268–276.
- (27). Schmidt TC; Zwank L; Elsner M; Berg M; Meckenstock RU; Haderlein SB Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Anal. Bioanalytical Chem.* 2004, 378 (2), 283–300.
- (28). Elsner M; Zwank L; Hunkeler D; Schwarzenbach RP A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environ. Sci. Technol.* 2005, 39 (18), 6896–6916. [PubMed: 16201610]
- (29). VanStone N; Przepiora A; Vogan J; Lacrampe-Couloume G; Powers B; Perez E; Mabury S; Sherwood Lollar B Monitoring trichloroethene remediation at an iron permeable reactive barrier using stable carbon isotopic analysis. *J. Contam. Hydrol.* 2005, 78 (4), 313–325. [PubMed: 16026893]
- (30). Liang X; Dong Y; Kuder T; Krumholz LR; Philp RP; Butler EC Distinguishing abiotic and biotic transformation of tetrachloroethylene and trichloroethylene by stable carbon isotope fractionation. *Environ. Sci. Technol.* 2007, 41 (20), 7094–7100. [PubMed: 17993153]
- (31). Elsner M; Chartrand M; Vanstone N; Lacrampe C; Sherwood Lollar B Identifying abiotic chlorinated ethene degradation: characteristic isotope patterns in reaction products with nanoscale zero-valent iron. *Environ. Sci. Technol.* 2008, 42 (16), 5963–5970. [PubMed: 18767652]
- (32). Lojkasek-Lima P; Aravena R; Shouakar-Stash O; Frapce SK; Marchesi M; Fiorenza S; Vogan J Evaluating TCE abiotic and biotic degradation pathways in a permeable reactive barrier using compound specific isotope analysis. *Ground Water Monit. Remediation* 2012, 32 (4), 53–62.
- (33). Audí-Miró C; Cretnik S; Torrentó, Rosell M; Shouakar-Stash O; Otero N; Palau J; Elsner M; Soler A C, Cl and H compound-specific isotope analysis to assess natural versus Fe(0) barrier-induced degradation of chlorinated ethenes at a contaminated site. *J. Haz. Mater.* 2015, 229, 747–754.
- (34). O'Hannesin SF; Gillham RW (1998). Long-term performance of an in situ “iron wall” for remediation of VOCs. *Groundwater* 1998, 36 (1), 164–170.
- (35). Warner SD; Longino BL; Zhang M; Bennett P; Szerdy FS; Hamilton LA The first commercial permeable reactive barrier composed of granular iron: hydraulic and chemical performance at 10 years of operation. In *Permeable Reactive Barriers, Proceedings of the International Symposium*, Belfast Ireland, pp. 32–42, 2005.
- (36). Phillips DH; Van Nooten T; Bastiaens L; Russell MI; Dickson K; Plant S; Ahad JME; Newton T; Elliot T; Kalin RM Ten year evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater. *Environ. Sci. Technol.* 2010, 44 (10), 3861–3869. [PubMed: 20420442]
- (37). Blowes DW; Gillham RW; Ptacek CJ; Puls RW; Bennett TA; O'Hannesin SF; Hanton-Fong CJ; Bain JG An in situ permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in ground water: Volume 1, Design and installation. U.S. Environmental Protection Agency, EPA Report, EPA/600/R-99/095a, 1999.
- (38). Blowes DW; Puls RW; Gillham RW; Ptacek CJ; Bennett TA; Bain JG; Hanton-Fong CJ; Paul CJ An in situ permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in ground water: Volume 2, Performance monitoring. U.S. Environmental Protection Agency, EPA Report, EPA/600/R-99/095b, 1999.
- (39). Puls RW; Blowes DW; Gillham RW Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard Support Center, Elizabeth City, North Carolina. *J. Hazard. Mater.* 1999, 68 (1–2), 109–124. [PubMed: 10518667]
- (40). Wilkin RT; Puls RW; Sewell GW Long-term performance of permeable reactive barriers using zero-valent iron: geochemical and microbiological effects. *Groundwater* 2003, 41 (4), 493–503.

- (41). Wilkin RT; Acree SD; Ross RR; Puls RW; Lee TR Woods LL Fifteen-year assessment of a permeable reactive barrier for treatment of chromate and trichloroethylene in groundwater. *Sci. Total Environ.* 2014, 468–469, 186–194. [PubMed: 24742557]
- (42). Kampbell DH; Vandegrift SA Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *J. Chromatographic Sci.* 1998, 36 (5), 253–256.
- (43). Hwang H-T; Jeon S-W; Sudicky EA; Illman WA Determination of rate constants and branching ratios for TCE degradation by zero-valent iron using a chain decay multispecies model. *J. Contam. Hydrol.* 2015, 177–178, 43–53.
- (44). Vogel TM; McCarty PL Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Appl. Environ. Microbiol.* 1985, 49 (5), 1080–1083. [PubMed: 3923927]
- (45). Bradley PM; Chapelle FH Accumulation of dechlorination daughter products: A valid metric of chloroethene biodegradation. *Remediation* 2007, 17 (4), 7–22.
- (46). Parker BL; Chapman SW; Guilbeault MA Plume persistence caused by back-diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. *J. Contam. Hydrol.* 2008, 102 (1–2), 86–104. [PubMed: 18775583]
- (47). Slater GF; Sherwood Lollar B; King RA; O'Hannesin S Isotopic fractionation during reductive dechlorination of trichloroethene by zero-valent iron: influence of surface treatment. *Chemosphere* 2002, 49 (6), 587–596. [PubMed: 12430646]
- (48). Hunkeler D; Aravena R; Butler BJ 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.
- (49). Bloom Y; Aravena R; Hunkeler D; Edwards E; Frape SK Carbon isotope fractionation during microbial dechlorination of trichloroethene, cis-1,2-dichloroethene, and vinyl chloride: Implications for assessment of natural attenuation. *Environ. Sci. Technol.* 2000, 34 (13), 2768–2772.
- (50). Slater GF; Ahad JME; Sherwood Lollar B; Allen-King R; Sleep B Carbon isotope effects resulting from equilibrium sorption of dissolved VOCs. *Anal. Chem.* 2000, 72 (22), 5669–5672. [PubMed: 11101247]
- (51). Schüth C; Taubald H; Bolaño N; Maciejczyk K Carbon and hydrogen isotope effects during sorption of organic contaminants on carbonaceous materials. *J. Contam. Hydrol.* 2003, 64 (3–4), 269–281. [PubMed: 12814884]
- (52). Burris DR; Allen-King RM; Manoranjan VS; Campbell TJ; Loraine GA; Deng B Chlorinated ethene reduction by cast iron: sorption and mass transfer. *J. Environ. Engineer.* 1998, 124 (10), 1012–1019.
- (53). Braeckvelt M; Fisher A; Kästner M Field applicability of compound-specific isotope analysis (CSIA) for characterization and quantification of in situ contaminant degradation in aquifers. *Appl. Microbiol. Biotechnol.* 2012, 94, 1401–121. [PubMed: 22573267]
- (54). Hunkeler D; Aravena R; Cox E Carbon isotopes as a tool to evaluate the origin and fate of vinyl chloride: laboratory experiments and modeling of isotope evolution. *Environ. Sci. Technol.* 2002, 36 (15), 3378–3384. [PubMed: 12188368]
- (55). Courbet C; Rivière A; Jeannotat S; Rinaldi S; Hunkeler D; Bendjoudi H; de Marsily G Complementing approaches to demonstrate chlorinated solvent biodegradation in a complex pollution plume: mass balance, PCR and compound-specific stable isotope analysis. *J. Contam. Hydrol.* 2011, 126, 315–329. [PubMed: 22115095]
- (56). Meckenstock RU; Morasch B; Griebler C; Richnow HH Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated aquifers. *J. Contam. Hydrol.* 2004, 75 (3–4), 215–255. [PubMed: 15610901]
- (57). Whiting K; Evans PJ; Lebrón C; Henry B; Wilson JT; Becvar E Factors controlling in situ biogeochemical transformation of trichloroethene: field survey. *Groundwater Monit. Remediation* 2014, 34 (3), 79–94.

- (58). Chapelle FH; McMahon PB; Dubrovsky NM; Fujii RF; Oaksford ET; Vroblesky DA Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resources Research* 1995, 31 (2), 359–371.
- (59). Zolla V; Freyria FS; Sethi R; Di Molfetta A Hydrogeochemical and biological processes affecting the long-term performance of an iron-based permeable reactive barrier. *J. Environ. Quality* 2009, 38 (3), 897–908.
- (60). Furukawa Y; Kim J; Watkins J; Wilkin RT Formation of ferrihydrite and associated corrosion products in permeable reactive barriers of zero-valent iron. *Environ. Sci. Technol.* 2002, 36 (24), 5469–5475. [PubMed: 12521177]
- (61). Wilkin RT; Su C; Ford RG; Paul CJ Chromium removal processes during groundwater remediation by a zerovalent iron permeable reactive barrier. *Environ. Sci. Technol.* 2005, 39 (12), 4599–4605. [PubMed: 16047798]
- (62). Fan D; Lan Y; Tratnyek PG; Johnson RL; Filip J; O'Carroll DM; Garcia AN; Agrawal A Sulfidation of iron-based materials: A review of processes and implications for water treatment and remediation. *Environ. Sci. Technol.* 2017, 51, 13070–13085. [PubMed: 29035566]
- (63). McMahon PB; Dennehy KF; Sandstrom MW Hydraulic and geochemical performance of a permeable reactive barrier containing zero-valent iron, Denver Federal Center. *Groundwater* 1999, 37 (3), 396–404.
- (64). Vogan JL; Focht RM; Clark DK; Graham SL Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater. *J. Hazard. Mater.* 1999, 68 (1), 97–108. [PubMed: 10518666]
- (65). Jeen SW; Jambor JL; Blowes DW; Gillham RW Precipitates on granular iron in solutions containing calcium carbonate with trichloroethene and hexavalent chromium. *Environ. Sci. Technol.* 2007, 41 (6), 1989–1994. [PubMed: 17410795]
- (66). Henderson AD; Demond AH Long-term performance of zero-valent iron permeable reactive barriers: A critical review. *Environ. Eng. Sci.* 2007, 24 (4), 401–423.
- (67). Hardy LI; Gillham RW Formation of hydrocarbons from the reduction of aqueous CO₂ by zero-valent iron. *Environ. Sci. Technol.* 1996, 30 (1), 57–65.
- (68). Dykstra CM; Pavlosthathis SG Zero-valent iron enhances biocathodic carbon dioxide reduction to methane. *Environ. Sci. Technol.* 2017, 51 (21), 12956–12964. [PubMed: 28994592]
- (69). Ma L; Zhou L; Mbading SM; Gu J; Mu B Accelerated CO₂ reduction to methane for energy by zero-valent iron in oil reservoir production waters. *Energy* 2018, 147, 663–671.
- (70). Vinson DS; Blair NE; Martini AM; Larter S; Orem WH; McIntosh JC Microbial methane from in situ biodegradation of coal and shale: A review and reevaluation of hydrogen and carbon isotope signatures. *Chem. Geol.* 2017, 453, 128–145.
- (71). Whiticar MJ Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* 1999, 161 (1–3), 291–314.
- (72). Miller LG; Baesman SM; Kirshtein J; Voytek MA; Oremland RS A biogeochemical and genetic survey of acetylene fermentation by environmental samples and bacterial isolates. *Geomicrobiol. J.* 2013, 30 (6), 501–516.
- (73). Blair N The $\delta^{13}\text{C}$ of biogenic methane in marine sediments: the influence of Corg deposition rate. *Chem. Geol.* 1998, 152 (1–2), 139–150.
- (74). Brown A Identification of source carbon for microbial methane in unconventional gas reservoirs. *AAPG Bull.* 2011, 95 (8), 1321–1338.
- (75). Hayes JM Fractionation of carbon and hydrogen isotopes in biosynthetic processes In: *Stable Isotope Geochemistry: Reviews in Mineralogy and Geochemistry v. 43* Edited by Valley JW and Cole DR. Mineralogical Society of America, pp. 225–277, 2001.
- (76). Miller HM; Chaudhry N; Conrad ME; Bill M; Kopf SH; Templeton AS Large carbon isotope variability during methanogenesis under alkaline conditions. *Geochim. Cosmochim. Acta* 2018, 237 (15), 18–31.
- (77). Whiticar MJ; Faber E; Schoell M Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation-isotope evidence. *Geochim. Cosmochim. Acta* 1986, 50 (5), 693–709.

- (78). Sugimoto A; Wada E Hydrogen isotopic composition of bacterial methane: CO₂/H₂ reduction and acetate fermentation. *Geochim. Cosmochim. Acta* 1995, 59 (7), 1329–1337.

Figure 1.
Site map.

Figure 2.

A) Twenty-two-year record of TCE concentrations in Transect 2 multilevel wells and MW48. B) In-PRB distribution of TCE and daughter products compared to influent TCE. C) Normalized molar fractions of TCE and daughter products in ML25 (down-gradient of PRB; see Figure 1). The maximum contaminant level (MCL) for TCE is 5 $\mu\text{g/L}$.

Figure 3.

TCE concentrations measured in monitoring wells positioned down-gradient from the PRB (MW50, MW47, MW49) compared to concentrations in up-gradient monitoring well MW48 and the mean TCE concentration from the ML21 well cluster (up-gradient). See Figure 1 for the locations of the monitoring points and Table S1 for screened intervals.

Figure 4.

A) $\delta^{13}\text{C}$ values of TCE, cis-DCE, and VC in groundwater up-gradient of the PRB. B) $\delta^{13}\text{C}$ values of TCE in groundwater within and down-gradient of the PRB (2016–2018). C) $\delta^{13}\text{C}$ values of cis-DCE and VC in groundwater within and down-gradient of the PRB. The cis-DCE data point marked by an asterisk did not have an accompanying value for $\delta^{13}\text{C}$ of TCE due to detection level constraints. D) Relationship between $\delta^{13}\text{C}$ values of cis-DCE and TCE. E) Estimates of bulk enrichment factors. The trend lines show representative bulk enrichment factors for TCE degradation by iron sulfide, ZVI, and microbial processes.

Figure 5.

A) Concentrations of dissolved inorganic carbon (DIC), volatile organic compounds (VOCs) up-gradient of the PRB compared to concentrations of DIC and methane within and down-gradient of the PRB (2016–2018). Mineralized carbonate (MinC) is equal to $\text{DIC}_{\text{up-gradient}} - [\text{DIC}_{\text{In-wall}} + \text{Methane}_{\text{In-wall}}]$. B) $\delta^{13}\text{C}$ values and methane versus $\text{CO}_{2(\text{aq})}$ and contoured $\alpha^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ values. C) Comparison of $\delta^{13}\text{C}$ values of methane and co-existing TCE and contoured $\alpha^{13}\text{C}_{\text{TCE-CH}_4}$ values.