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Long-term evaluation of an EHC injection permeable reactive barrier in a sulfate-rich, high-flow aquifer

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Abstract

Permeable reactive barriers (PRBs) have traditionally been constructed via trenching backfilled with granular, long-lasting materials. Over the last decade, direct push injection PRBs with fine-grained injectable reagents have gained popularity as a more cost-efficient and less-invasive approach compared to trenching. A direct push injection PRB was installed in 2005 to intercept a 2,500 feet (760 meter) long carbon tetrachloride (CT) groundwater plume at a site in Kansas. The PRB was constructed by injecting EHC® in situ chemical reduction reagent slurry into a line of direct push injection points. EHC is composed of slow-release plant-derived organic carbon plus microscale zero-valent iron (ZVI) particles, specifically formulated for injection applications. This project was the first full-scale application of EHC into a flow-through reactive zone and provided valuable information about substrate longevity and PRB performance over time. Groundwater velocity at the site is high (1.8 feet per day) and sulfate-rich (~120 milligrams per liter), potentially affecting the rate of substrate consumption and the PRB reactive life. CT removal rates peaked 16 months after PRB installation with >99% removal observed. Two years post-installation removal rates decreased to approximately 95% and have since stabilized at that level for the 12 years of monitoring data available after injection. Geochemical data indicate that the organic carbon component of EHC was mostly consumed after 2 years; however, reducing conditions and a high degree of chloromethane treatment were maintained for several years after total organic carbon concentrations returned to background. Redox conditions are slowly reverting and have returned close to background conditions after 12 years, indicating that the PRB may be nearing the end of its reactive life. Direct measurements of iron have not been performed, but stoichiometric demand calculations suggest that the ZVI component of EHC may, in theory, last for up to 33 years. However, the ZVI component by itself would not be expected to support the level of treatment observed after the organic carbon substrate had been depleted. A longevity of up to 5 years was originally estimated for the EHC PRB based on the maximum expected longevity of the organic carbon substrate. While the organic carbon was consumed faster than expected, the PRB has continued to support a high degree of chloromethane treatment for a significantly longer time period of

over 12 years. Recycling of biomass and the contribution from a reduced iron sulfide mineral zone are discussed as possible explanations for the sustained reducing conditions and continued chloromethane treatment.

1 | INTRODUCTION

The long-term effectiveness of in situ remediation applications is often determined based on the amendment longevity. In permeable reactive barrier (PRB) applications, particularly in cases where the source has not been remediated, amendment longevity dictates the frequency of reapplication required and sharply impacts treatment economics. Granular zero-valent iron (ZVI) PRBs, traditionally installed via trenching, have been proven to last for over 10 years or more (Wilkin et al., 2018). Over the last decade, fine-grained injectable reagents have gained popularity as direct push injection is typically more cost-efficient and less invasive. EHC® (Peroxychem, Philadelphia, PA) is such a reagent, comprised of 40% microscale ZVI (~50–150 microns) and 60% slow-release organic carbon derived from plant fibers. It is formulated for direct injection and used to treat many halogenated compounds including chlorinated volatile organic carbons (CVOCs), pesticides, and organic explosives (Seech, Cairns, & Marvan, 1995).

The first full-scale EHC PRB was installed in April 2005 to intercept a 2,500-foot (ft) (760 meter[m]) long carbon tetrachloride (CT) groundwater plume. EHC was selected over granular ZVI following a bench-scale evaluation due to its ability to more effectively treat CT breakdown products by promoting both abiotic and biotic degradation pathways. Although CT is rapidly dechlorinated in the presence of ZVI alone through in situ chemical reduction (ISCR), typically a portion of the CT is converted to chloroform (CF) and a portion of the CF is converted to dichloromethane (DCM; Matheson & Tratnyek, 1994). DCM and chloromethane (CM) are not abiotically degraded in contact with ZVI but may instead be biologically degraded (Vidumsky, 2003). This biological degradation may occur naturally downgradient of a ZVI PRB from the release of hydrogen during ZVI corrosion acting as an electron donor for dechlorinating bacteria; however, it may be further enhanced by the addition of the organic carbon substrate in EHC.

This paper reviews the long-term performance and geochemical parameter changes following the installation of the EHC PRB over a 12-year data set. The estimated longevity and contribution from biotic, abiotic, and biogeochemical pathways are discussed.

2 | SITE BACKGROUND

Site groundwater was impacted with CT at concentrations of up to 2,700 micrograms per liter (μg/L). The CT plume extended approximately 2,500 ft (760 m) from grain elevators, across a residential neighborhood,

where it terminated at a small creek (Exhibit 1). The CT source area was unknown, but impacts were likely the result of its former use at the site in grain silo fumigation. The shale bedrock rises to approximately 10 ft (3 m) above the normal water table at the presumed source area, complicating site characterization. The CT is believed to have migrated along the bedrock surface to the downgradient aquifer.

Restricted access to residential properties further complicated source area cleanup. A passive PRB, installed at the first available roadway was thus selected as an interim measure.

PRB compliance requirements were set forth in the site Voluntary Cleanup Plan (VCP) which required a minimum 95% CT concentration reduction (relative to baseline) at compliance points located 70 and 140 ft (21 and 42 m) downgradient. The baseline monitoring event occurred in March 2005, a month before the PRB installation.

2.1 | PRB area lithology

The site geology consists of braided stream channel deposits (sand and clay) overlying shale bedrock. Soil borings were installed along the length of the planned PRB location to develop a vertical cross section to identify the optimum depths in which to install the EHC PRB (Exhibit 2). Two primary saturated sand units were identified as water bearing and targeted during the injection. The upper sand unit was approximately 3–4 ft (0.9–1.2 m) thick at the proposed PRB location. The thickness of the lower sand unit varied considerably across the plume, ranging from 0 to -13 ft (0–4 m) thick across the PRB area. Groundwater was encountered at approximately 23 ft (7 m) below ground surface (bgs) and CT impacts extended down to approximately 45 ft (14 m) bgs.

2.2 | Hydrogeology

Horizontal hydraulic gradients across the plume area range from 0.002 ft/ft in the central portion of the plume to 0.004 ft/ft in the north and south portions of the plume area. Groundwater seepage velocity range from 1.0 to 2.2 ft/day across the plume (Biteman, Foote, MacFabe, Mueller, & Molin, 2006) and was estimated at 1.8 ft/day at the PRB location within the water-bearing sand units. The effective porosity was estimated at 15% for the water-bearing sand units.

3 | BENCH-SCALE REAGENT EVALUATION

Bench-scale testing was conducted using soil and groundwater collected from the plume area to identify the preferred reagent for
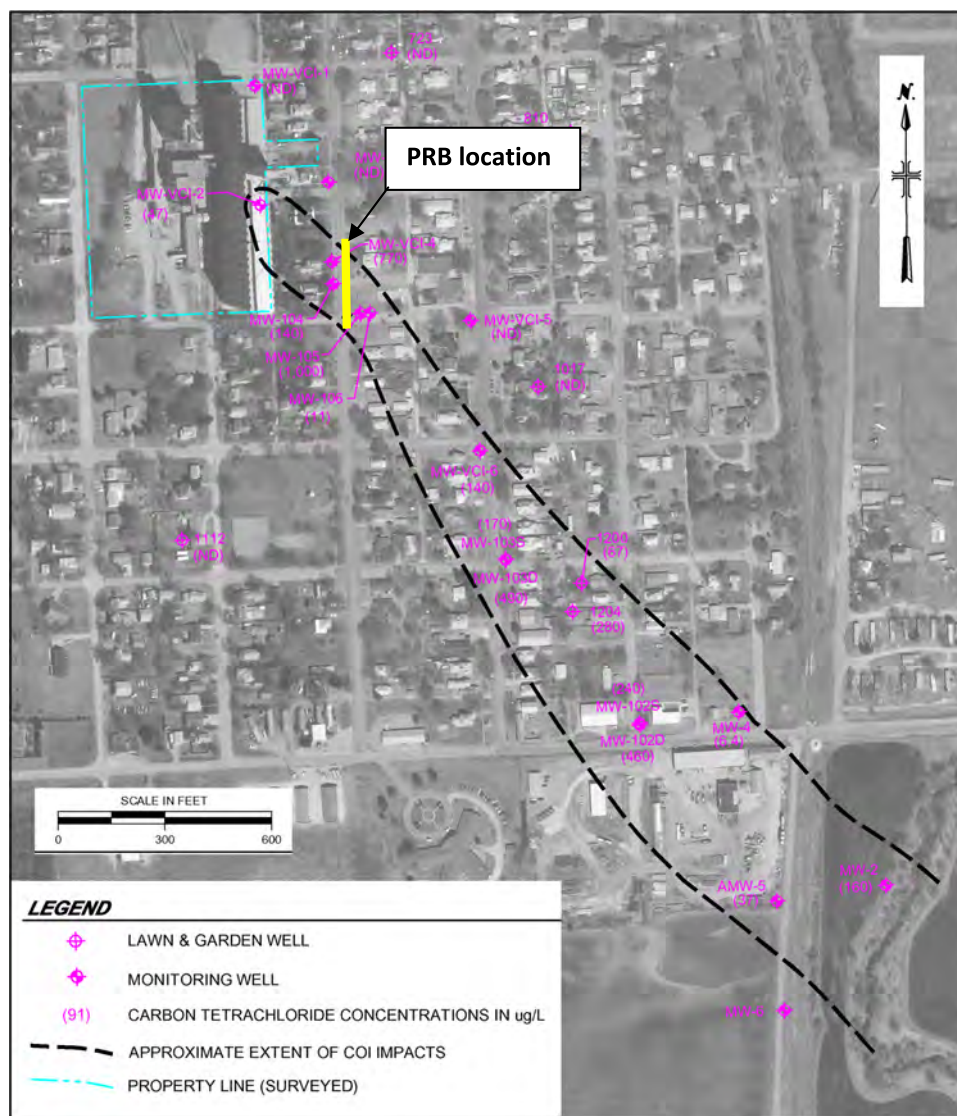
EXHIBIT 1 Carbon tetrachloride (CT) groundwater plume map showing the EHC PRB location and the March 2005 baseline CT concentrations

the PRB construction. The groundwater contained approximately 1,300–1,600 µg/L CT with trace concentrations of degradation products. The studies evaluated two in situ treatment technologies for degrading CT and related compounds: (a) chemical reduction using ZVI; and (b) EHC for combined enhanced anaerobic biodegradation coupled with chemical reduction. Both EHC and ZVI were tested in flow-through columns to model PRB-type applications. Two types of PRBs were simulated. For the EHC materials, one set of columns simulated low-weight percentage of EHC dispersed in site soil to mimic application via injection. Dose rates of 0.66% and 3.3% (weight to weight [wt/wt]) EHC by soil mass were evaluated. A second set of columns was established with higher loadings of EHC (26% wt/wt) or granular ZVI (100% wt/wt) to simulate a trench or panel-injection type PRB. After passing through each column, the groundwater effluent was pumped through a flow-through jar with sand only to mimic the

potential for continued treatment in the downgradient zone. Groundwater was sampled both immediately following the treatment column and following the downgradient sand jar. CT, CF, DCM, and CM were analyzed using solid phase microextraction followed by gas chromatography desorption and analysis at Adventus' in-house laboratory.

3.1 | Results from simulated injected PRB columns

Following 58 days of operation, the low dosage, dispersed EHC columns supported complete removal of CT to below the detection limit of 0.4 µg/L in response to both the low and the high reagent dosages (Exhibit 3). The low dose showed better overall treatment with only 0.9 µg/L of CF remaining. No DCM or CM were present in the effluent from either system. The residence time within the dispersed columns was approximately 1.3 days.
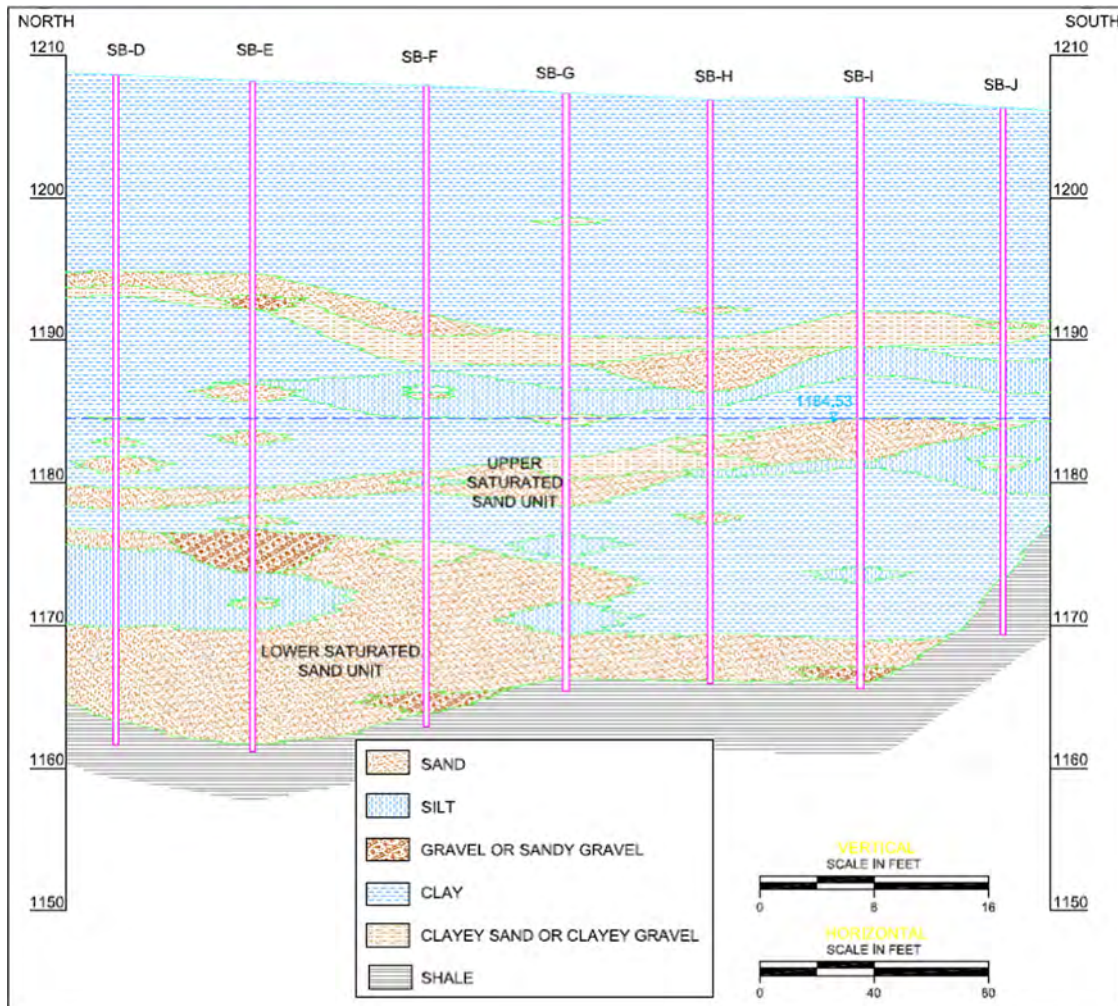
EXHIBIT 2 Vertical cross section from the PRB area showing the upper and lower saturated sand units depicted from the soil coring locations (SB-D to SB-J) installed across the length of the planned PRB

3.2 | Results from simulated trenched PRB columns

After 46 days of continuous operation, the 100% ZVI column effluent yielded the overall lowest concentrations of CVOCs of the trench systems (Exhibit 4). However, DCM remained at significant concentrations and little additional treatment was observed

EXHIBIT 3 Influence of simulated injected PRB treatments on column effluent CVOC concentrations after 58 days of operation

Column	CT (µg/L)	CF (µg/L)	DCM (µg/L)	CM (µg/L)
Influent	1,570	79.7	ND (<40)	ND (<40)
Injected PRB column effluents				
Sand control	1,530	78.1	ND (<40)	ND (<40)
EHC high dose (3.3%)	ND (<0.4)	26	ND (<2)	ND (<2)
EHC low dose (0.66%)	ND (<0.4)	0.9	ND (<2)	ND (<2)

Abbreviations: CF, chloroform; CM, chloromethane; CT, carbon tetrachloride; CVOC, chlorinated volatile organic carbons; DCM, dichloromethane; ND, not detected; PRB, permeable reactive barrier.

following the downstream attenuation jar. Interestingly, the sand-only control system contained elevated levels of CF and DCM following the downstream column, suggesting that some CT was naturally degraded, but at rates slower than in the amended systems.

In the presence of 100% ZVI, the half-lives for CT and CF adjusted for groundwater temperatures were calculated to 0.4 and 9.6 hr, respectively. It was estimated that 29% (molar basis) of the CT was transformed to CF and about 22% (molar basis) of CF was converted to DCM (Mueller et al., 2004).

Although the studies suggested that ZVI alone was equally effective as EHC at treating CT, EHC was selected for full-scale application due to its ability to provide more complete degradation of the CT metabolites DCM and CM. The low-dose dispersed EHC column showed the overall highest removal of CVOCs, indicating that a lower EHC dose dispersed over a longer residence time (injected PRB scenario) was more effective than applying a higher dose rate over a shorter residence time (trench PRB scenario). On the basis of these results, an injection EHC PRB approach was selected for full-scale implementation.

EXHIBIT 4 Influence of simulated trench PRB treatments on column effluent CVOC concentrations after 46 days of operation

Column	CT (µg/L)	CF (µg/L)	DCM (µg/L)	CM (µg/L)
Influent	1,350	77.7	ND (<40)	ND (<40)
Trenched PRB column effluents				
Sand control	1,260	73.5	194	ND (<40)
ZVI (100%)	2.7	0.3 (<0.4)	57.7	3.3
EHC (26%)	ND (<4)	134	135	ND (<20)
Downgradient sand column effluents				
Sand control	ND (<4)	469	149	ND (<20)
ZVI (0%)	ND (<0.4)	ND (<0.4)	117	3
EHC (0%)	ND (<40)	84.4	ND (<200)	ND (<200)

Abbreviations: CF, chloroform; CM, chloromethane; CT, carbon tetrachloride; CVOC, chlorinated volatile organic carbons; DCM, dichloromethane; ND, not detected; PRB, permeable reactive barrier; ZVI, zero-valent iron.

4 | EHC PRB DESIGN AND INSTALLATION

Extrapolating from the bench study results, a dispersed injection PRB with a low dose of EHC was selected as the preferred remedy for the site. In addition to facilitating more complete treatment of CT breakdown products, implementation via direct push injection was viewed as a less intrusive and a more cost-effective approach for the site relative to a trench or panel-type PRB. Due to its multiple degradation pathways, EHC is less reliant on uniform reagent placement and, therefore, may effectively be installed via standard high-pressure direct injection. Although the EHC reagent itself will not move with groundwater following placement, organic carbon fermentation will serve to release volatile fatty acids (e.g., acetic, propionic, and butyric) that will diffuse from the EHC reagent seams into the surrounding groundwater and distribute via advection, dispersion, and diffusion. As the ZVI undergoes corrosion, it will release ferrous iron that also will transport with groundwater flow and may precipitate as reactive ferrous iron minerals in the downgradient zone. These mechanisms will serve to extend the effective treatment zone beyond the reagent placement zone and help bridge between uneven reagent distribution. Elevated concentrations of dissolved organic carbon supportive of biological reductive dechlorination may be found at significant distances downgradient from EHC injection zones (Molin, Mueller, Moreno, Valkenburg, & Duchene, 2010). In contrast, direct abiotic degradation in contact with ZVI will require direct contact with the reagent itself and will be limited to the reagent seams.

Although the bench study demonstrated effective treatment at a dose rate of 0.66% EHC by soil mass, a higher dose rate of 1% EHC was selected for the full-scale PRB design to add a level of safety and to maximize the expected longevity. A PRB longevity of up to 5 years was estimated based on the expected maximum longevity of the organic carbon portion of EHC.

In April 2005, 48,000 pounds (lbs) (21,818 kilograms [kg]) of EHC was injected into an area measuring approximately 270 ft (82.3 m) long by 15 ft (4.6 m) wide by 9.7 ft (3.0 m) deep on average to form a PRB. The PRB was installed along the side of a road and extended across the plume. The EHC powder, comprised of 40% microscale ZVI and 60% organic carbon, was mixed with water on site to form a 30% slurry and injected using direct push technology. The injections specifically targeted the two saturated sand and gravel units identified during the preinjection field investigation. Injections were not attempted into the surrounding clay layers as these were not deemed to be water bearing. The EHC was emplaced at an average application rate of approximately 1.0% (wt/wt) EHC by soil mass within the sand units.

During field implementation, after one injection point had been completed using a bottom-up injection approach using a disposable probe tip, five verification borings were performed around the injection point to confirm EHC placement. EHC slurry was found to have distributed in discrete bands or fractures and was visually detected in soil cores collected up to 5 ft (1.6 m) away from the injection location, this suggested a radius of influence of at least 5 ft (1.6 m). The EHC reagent was observed as darker bands within the soil matrix (Exhibit 5). Horizontal as well as vertically rising fractures

Chem Grout mixing and pump unit and direct push probe

Horizontal EHC fracture

Vertically dipping fracture

EXHIBIT 5 Injection set-up and soil verification borings showing EHC material emplaced in discrete bands (darker material)
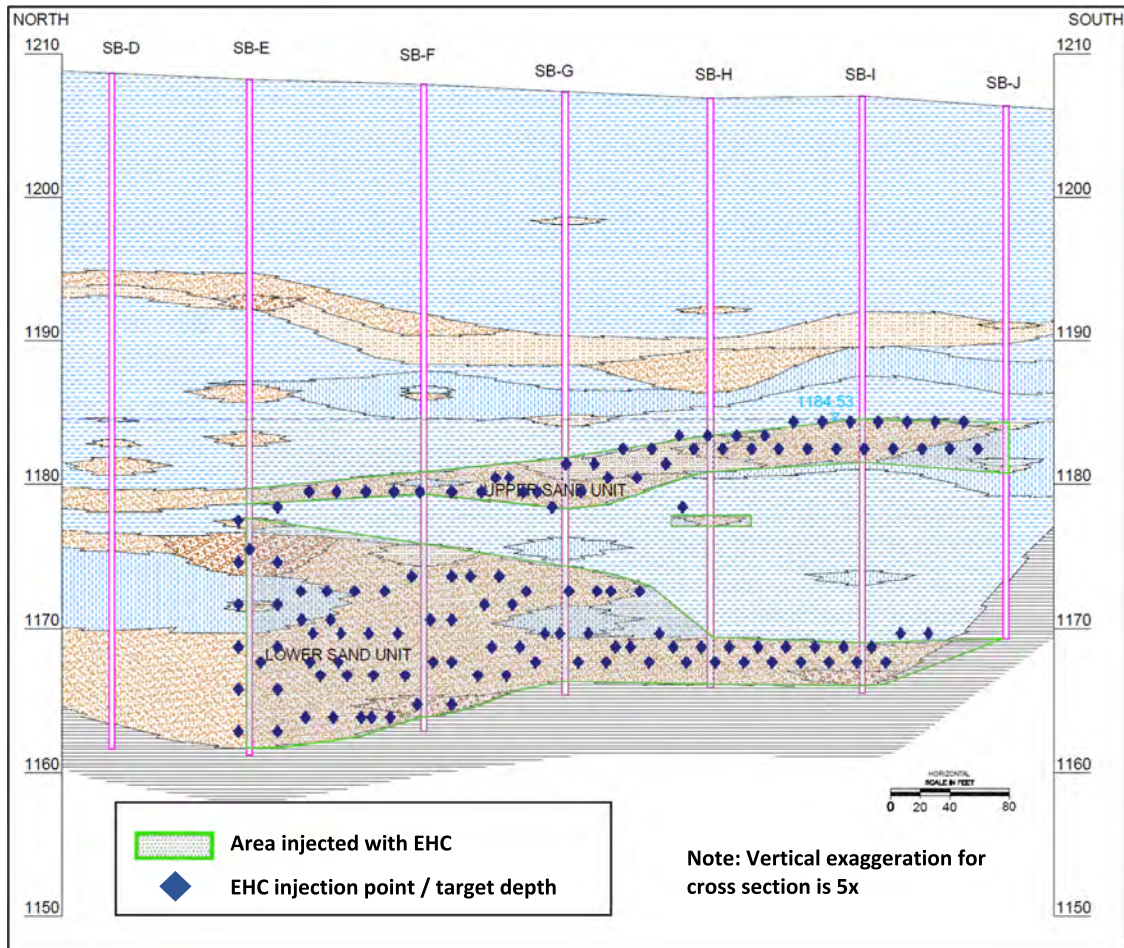
EXHIBIT 6 Cross-section from PRB area showing the individual depths targeted for injection
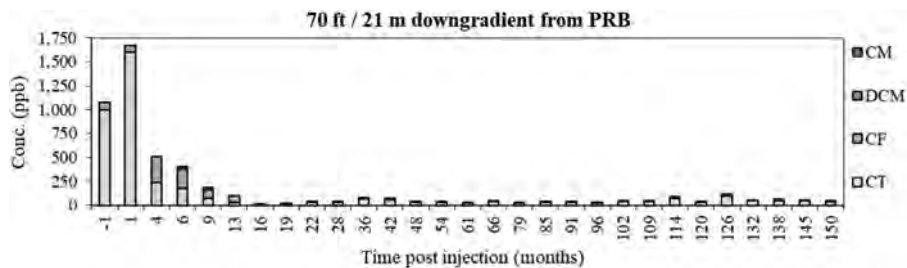

EXHIBIT 7 CT and degradation products measured in compliance well located 70 ft (21 m) downgradient from PRB at the center of the plume. CF, chloroform; CM, chloromethane; CT, carbon tetrachloride; DCM, dichloromethane; PRB, permeable reactive barrier
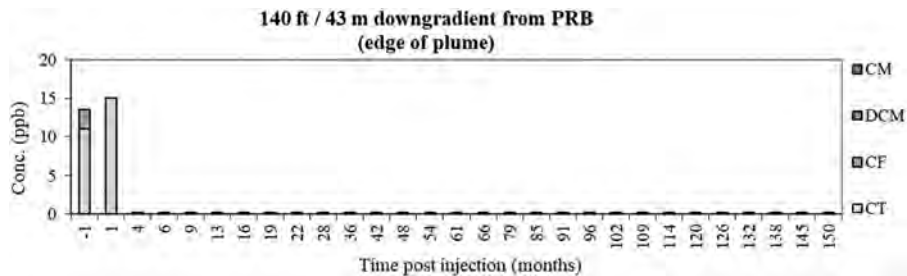
EXHIBIT 8 CT and degradation products measured in compliance well located 140 ft (42 m) downgradient from PRB at the edge of the plume. CF, chloroform; CM, chloromethane; CT, carbon tetrachloride; DCM, dichloromethane; PRB, permeable reactive barrier

EXHIBIT 9 CT and degradation products measured 600 ft (183 m) downgradient from PRB. CF, chloroform; CM, chloromethane; CT, carbon tetrachloride; DCM, dichloromethane; PRB, permeable reactive barrier
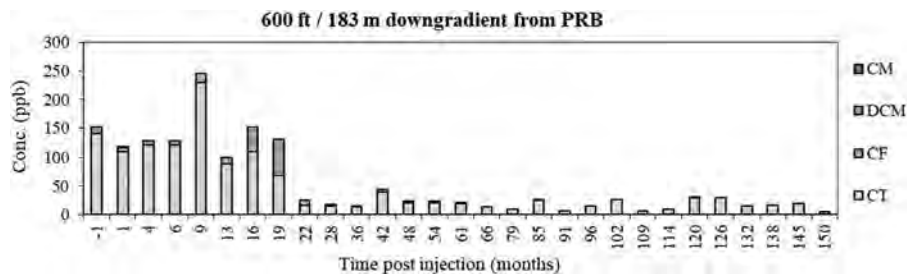
were observed with an increasing dip observed with distance from the injection location. The most substantial reagent seam was found at the bottom injection interval just above the shale, indicating preferential placement of the reagent to this interval.

An injection spacing of 10 ft (3 m) was used based on observations from the soil coring. Concurrently, it was decided to install individual borings for each depth interval at each location to ensure proper vertical distribution and to avoid preferential placement just above the shale. This injection approach was necessary at the time as more modern targeted injections tools were not available. The individual depths targeted for injection are depicted as blue dots on the vertical cross section from the injection area (Exhibit 6). Installation was completed in 12 days (between March 30, and April 10, 2005).

5 | RESULTS

Following PRB installation, quarterly performance monitoring was conducted for 3 years before switching to semiannual monitoring in April 2008. Monitoring included analyses of target compounds (chloromethanes) and geochemical parameters.

5.1 | Groundwater quality response

Since the PRB installation groundwater sampling results have shown a significant reduction in total chloromethane concentrations (EPA Method 8260B) measured in the designated downgradient compliance wells (Exhibit 7 and Exhibit 8). CT removal rates peaked 16 months after PRB installation with >99% removal observed 70 ft (21 m) downgradient (from a baseline of 1,000 to < 5 µg/L measured in March 2005). Two years after installation these rates decreased to approximately 95–98% removal and stabilized at that level for 7 additional years. In October 2014, 9.5 years after the PRB installation, breakthrough

was first observed relative to the 95% VCP guideline. However, in the most recent sampling data available (October 2017), removal rates were back within guidelines. Concentrations at the second compliance well, located 140 ft (43 m) downgradient from the PRB and at the edge of the plume, have remained nondetect for all analytes since August 2005 (since 4 months after PRB installation).

CF concentrations initially increased following the PRB installation; however, by February 2007, CF had decreased below the baseline and upgradient concentrations at the VCP compliance wells. DCM and CM have remained below detection limits in both upgradient and downgradient wells since May 2006.

In February 2007, 22 months after PRB installation, PRB effects were observed 600 ft (183 m) downgradient of the PRB (Exhibit 9). In the most recent sampling data from this well, CT was detected at 5.6 µg/L and all degradation products were below detection limits (96% reduction relative to baseline).

Over more than 12 years since installation of the PRB, inflowing concentrations have fluctuated with a high of 2,700 µg/L CT and 120 µg/L CF measured in February 2007 (Exhibit 10). Most recently, inflowing concentrations were measured at 689 µg/L CT and 34 µg/L CF (October 2017).

Exhibit 11 illustrates the CT plume progression before and after EHC PRB installation, showing a large decrease in the downgradient plume size.

5.2 | Geochemical response

Significant total organic carbon (TOC, Method SM 5310C11) increases were measured 70 ft (21 m) downgradient of the PRB during the first 2 years. During this early phase, redox conditions reached their most strongly negative point concurrently with significant reductions in inflowing nitrate and sulfate. TOC levels have since returned close to background levels suggesting that the more readily degradable organic carbon component (cellulose) has

EXHIBIT 10 Inflowing concentrations measured in well located 85 ft (26 m) upgradient from PRB. ORP, oxidation–reduction potential; PRB, permeable reactive barrier
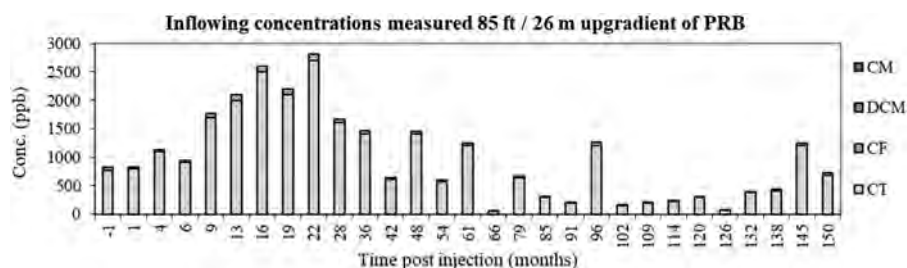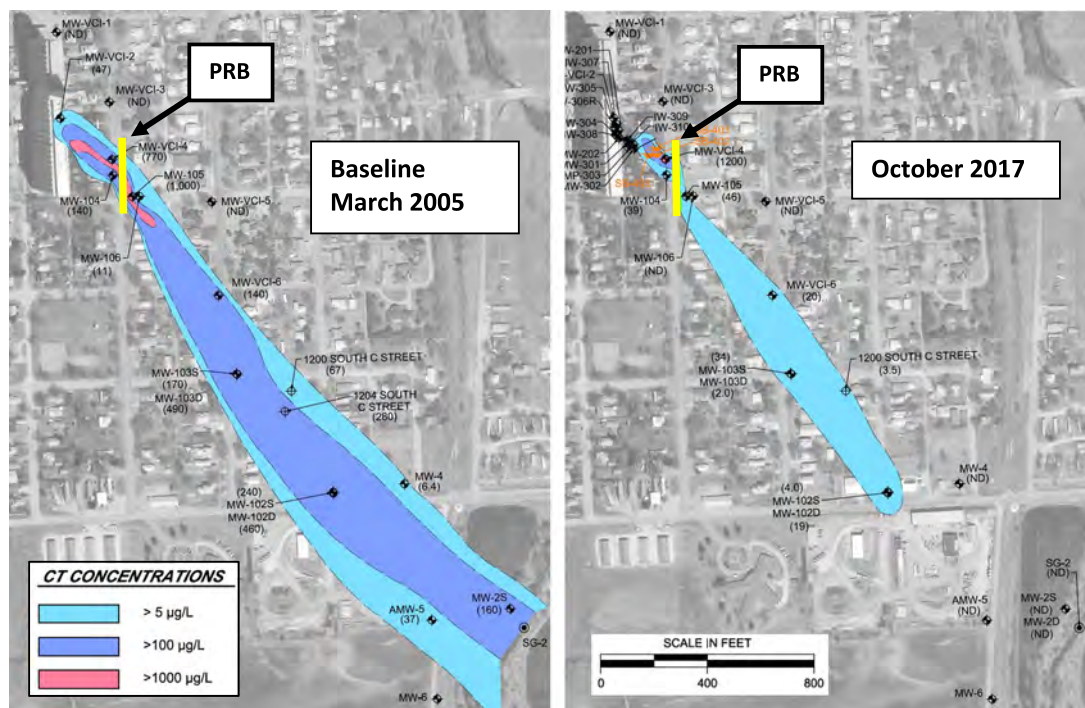
EXHIBIT 11 Impact of EHC PRB on the extent of CT plume. CT, carbon tetrachloride; PRB, permeable reactive barrier
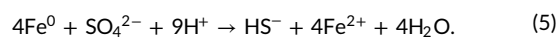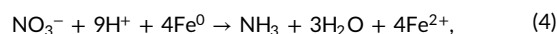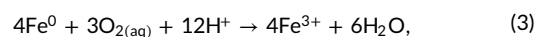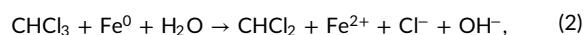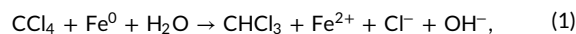
been consumed. After TOC levels returned closer to background, sulfate levels (Method SM 4500-SO4 E-11) also moved closer to inflowing concentrations while oxidation–reduction potential (ORP) and nitrate (method SM 4500-NO3 F-11) have remained significantly below background. No significant change in inflowing concentrations of TOC, nitrate, or sulfate was observed over time (Exhibit 12).

6 | THEORETICAL CALCULATIONS OF REAGENT CONSUMPTION

In evaluating EHC reagent longevity, several consumption mechanisms need to be considered, including: ZVI oxidation and carbon fermentation due to consumption (reduction) of terminal electron acceptors (TEAs); anaerobic ZVI corrosion by water; organic contaminant reduction; and trace metal reduction and precipitation. These processes are not functionally independent. However, for the purpose of this evaluation, consumption rates and longevity are discussed separately for the ZVI and organic carbon components. It should be noted that this discussion is theoretical and that actual in-situ consumption rates are subject to variability due to many factors that introduce complexity to the in-situ reaction zone, such as heterogeneous amendment distribution, groundwater flow, geochemistry, and microbial activity. It also does not consider treatment kinetics or the length of treatment, but rather estimates the potential lifespan of the substrate itself.

6.1 | ZVI consumption

ZVI oxidation rates are impacted by the TEA concentrations of inflowing groundwater entering the PRB. Reductive dechlorination of CT and CF and the corresponding ZVI oxidation can be expressed by Equations (1) and (2). Naturally occurring TEAs, including oxygen, nitrate, and sulfate, will also consume the ZVI (Equations (3)–(5)).

$$CCl_4 + Fe^0 + H_2O \rightarrow CHCl_3 + Fe^{2+} + Cl^- + OH^-, \quad (1)$$

$$CHCl_3 + Fe^0 + H_2O \rightarrow CHCl_2 + Fe^{2+} + Cl^- + OH^-, \quad (2)$$

$$4Fe^0 + 3O_{2(aq)} + 12H^+ \rightarrow 4Fe^{3+} + 6H_2O, \quad (3)$$

$$NO_3^- + 9H^+ + 4Fe^0 \rightarrow NH_3 + 3H_2O + 4Fe^{2+}, \quad (4)$$

$$4Fe^0 + SO_4^{2-} + 9H^+ \rightarrow HS^- + 4Fe^{2+} + 4H_2O. \quad (5)$$

Anaerobic ZVI corrosion occurs independently of oxidized species in groundwater with its rate largely dictated by surface area. Tests conducted with various ZVI materials show water corrosion rates on the order of 0.1–1 mmol/kg·Fe/day, with a value of 0.8 mmol/kg·Fe/day estimated for the particulate ZVI used in the EHC reagent (Reardon, 2005). This equates to an estimated 1.6% of the ZVI being consumed via corrosion per year.

To evaluate ZVI consumption rates and the resultant expected longevity, theoretical calculations were performed using the site data. Based on the assumptions presented in Exhibit 13 (shaded cells), an estimated 27% of the ZVI would be consumed per year if
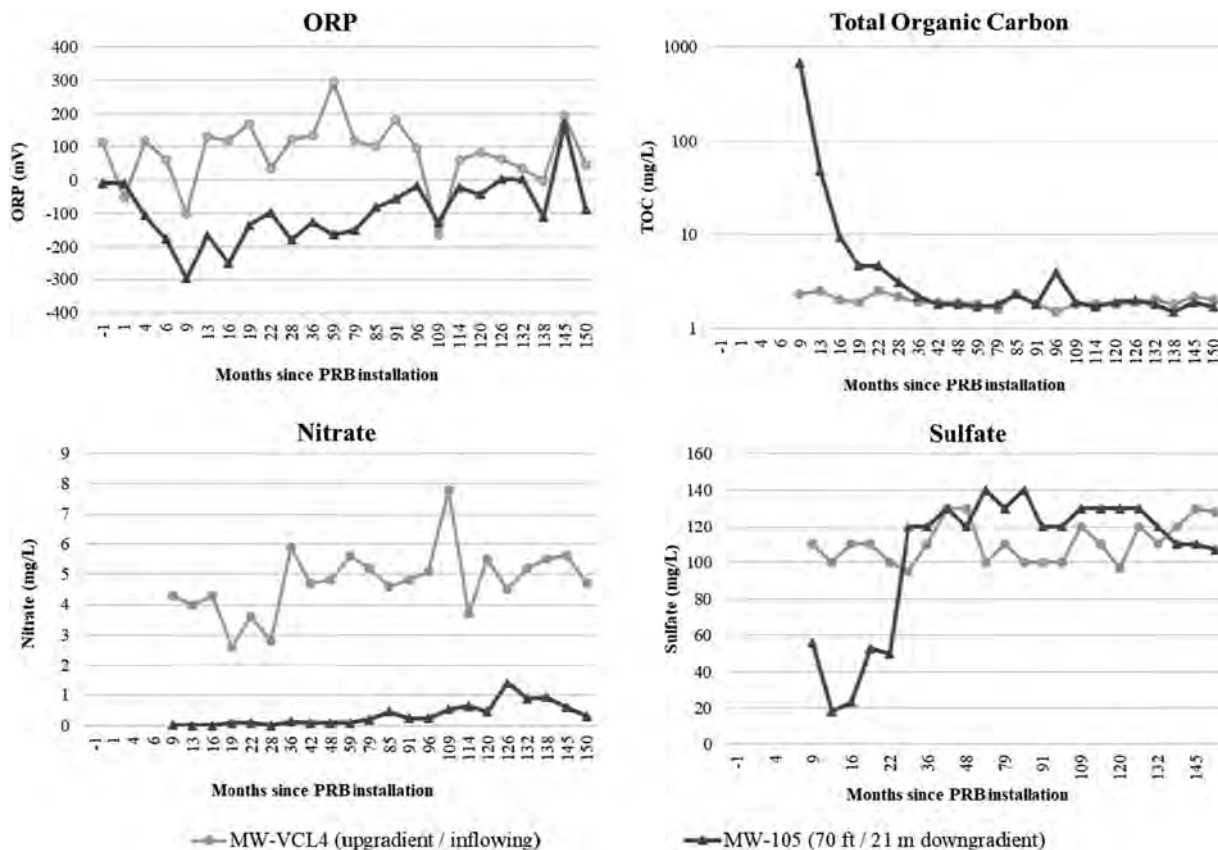
EXHIBIT 12 Effect on geochemistry downgradient from EHC PRB shown relative to inflowing concentrations over time. ORP, oxidation–reduction; PRB, permeable reactive barrier

reacting stoichiometrically with inflowing TEAs, resulting in an estimated ZVI longevity of only 3.7 years. However, the majority of the theoretical demand stems from inflowing sulfate and geochemical data suggested that ZVI alone was not supporting significant sulfate reduction. Sulfate reduction was observed initially, but after TOC concentrations returned closer to background (after ~2–3 years), little to no change in sulfate concentrations were observed downgradient of the PRB. Therefore, sulfate reduction appears to be biologically mediated. Accordingly, in removing sulfate reduction from the calculation, the annual ZVI consumption rate is then instead estimated at 3%, resulting in an estimated longevity of 33 years before being depleted. The calculations are conservative in that they assume that ZVI is the only electron donor and do not account for the impact of the organic carbon substrate. However, it should be noted that these calculations do not consider the potential for passivation, distribution, or the kinetics of these reactions, but is intended to provide an estimate of the potential timeframe before the ZVI is fully consumed. The observed reactive life is typically less than the predicted lifespan of the ZVI.

6.2 | Organic carbon consumption

The EHC organic carbon component is fine-grained plant fiber that is rich in cellulose and hemicellulose. Carbon consumption (decay) in the subsurface is often assumed to follow a first-order model. A first-order carbon decay constant (K) of 1.6×10^{-3} per day was obtained in cellulose columns used to promote denitrification exposed to a nitrate flux of about 70–75 milligrams (mg/L) nitrate-N at room temperature (Vogan, 1993). This equates to a 50% loss of cellulose in about 300 days or 10 months. Lower rates of degradation (K of 5×10^{-4} per day) were obtained in sawdust columns exposed to the same flux. Sawdust contains a relatively higher proportion of hemicellulose and lignin. In-situ sawdust-based denitrifying systems have operated for 15 years at field temperatures (Robertson, Vogan, & Lombardo, 2008). Decay rates are temperature dependent and would be expected to be lower at colder groundwater temperatures. On the basis of these data, it has been estimated that the organic carbon substrate in EHC would last somewhere between 2 and 5 years under typical groundwater temperatures, also depending on the dose rate used and influx of TEAs.

Field data measured downgradient from the PRB showed a decrease in background TOC concentrations after 2 years. It would, therefore, appear that much of the more readily degradable organic carbon fraction (cellulose) had been consumed after approximately 2 years which is in the lower end of the estimated range. This may be explained by high groundwater flow rates and inflowing concentrations of sulfate.

Beyond the predicted lifespan of TOC supplied by the EHC, microbial biomass generated from injection of degradable carbon has been demonstrated to act as an extended source of TOC via

EXHIBIT 13 Theoretical calculations of ZVI consumption and longevity

PRB vertical interface (m²)	PRB width (m)	ZVI dose rate (% wt/wt)	ZVI mass (kg)	GW seepage velocity (m/day)	Effective porosity	Flux through PRB (L/year)
251	4.6	0.4%	8,709	0.55	15%	7,534,688

|	Influent (mg/L)	Mass flux (kg/year)	Mass flux (mol/year)	ZVI used (mol/yr)	ZVI used (kg/year)	ZVI used (%/year)
Water corrosion	–	–	–	–	142	1.6
DO	0.4	3	94	126	7	0.1
CT	1	8	49	98	5	0.1
CF	0.1	0.8	6	6	0.4	0.004
NO$_3$	4	30	486	1,944	108	1.2
SO$_4$	120	904	9,418	37,673	2,102	24.1
Estimated total % ZVI consumed per year						
% Consumed if reacting stoichiometrically with inflowing sulfate						**27.2**
% Consumed if not reacting with inflowing sulfate						**3.0**
Estimated ZVI longevity, year						
Estimated longevity if reacting stoichiometrically with inflowing sulfate						**3.7**
Estimated longevity if not reacting with inflowing sulfate						**33.1**

Abbreviations: DO, dissolved oxygen; CF, chloroform; CT, carbon tetrachloride; PRB, permeable reactive barrier; ZVI, zero-valent iron.

endogenous decay of the microbial biomass, which could potentially extend the lifespan of the TOC beyond the predicted time (Suthersan, Nelson, Schnobrich, Kalve, & McCaughey, 2013).

7 | COMPARING EHC PRB EFFLUENTS TO SIMULATED VALUES FOR ZVI

The ZVI in EHC is expected to last for decades based on the above theoretical calculations while TOC concentrations were below what would be considered optimal levels for reductive dechlorination after

<2 years. Simulations were performed using the laboratory determined degradation rates for ZVI to evaluate whether the ZVI component alone would provide the continued level of treatment observed. Simulations were performed using the maximum and most recent inflowing groundwater data and effluent concentrations were simulated using the laboratory determined half-life data of 0.4 and 9.6 hr for CT and CF, respectively (Exhibit 14). In either scenario, a residence time of ~2 hr would be required to achieve the goal of reducing CT by 95%. At a groundwater flow velocity of 1.8 ft/day (0.55 m/day), this requisite flow through thickness of 0.15 ft (4.6 cm) of 100% ZVI. However, significantly longer residence times would be
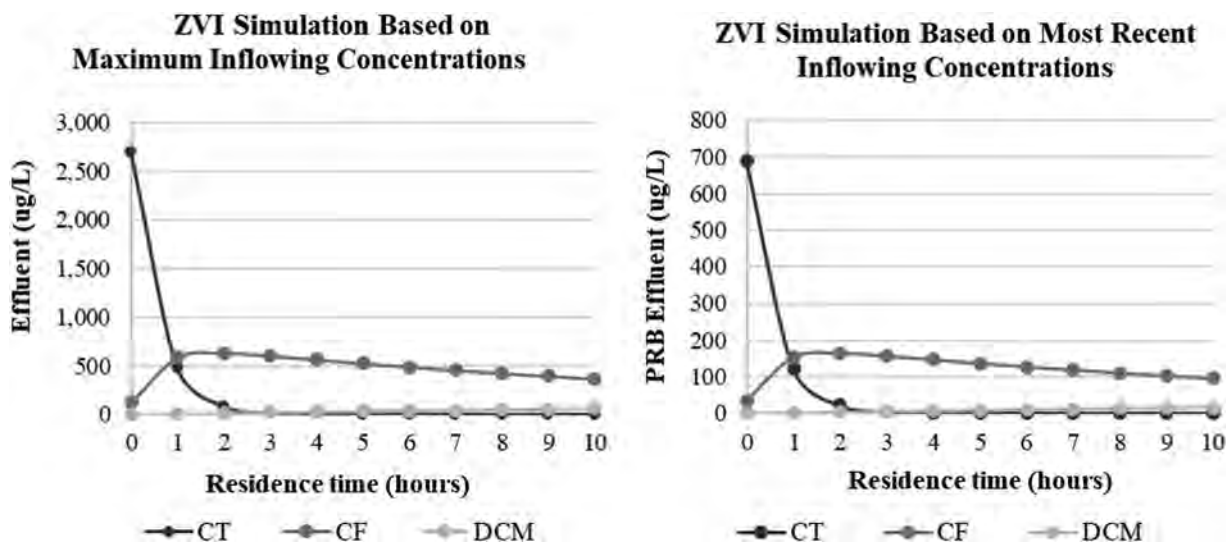
EXHIBIT 14 Simulated effluent concentrations in contact with 100% ZVI. CF, chloroform; CT, carbon tetrachloride; DCM, dichloromethane; PRB, permeable reactive barrier; ZVI, zero-valent iron

EXHIBIT 15 Comparison of simulated vs. actual PRB effluent concentrations following ~1 hr of residence time

	Feb 2007 (maximum inflowing concentrations)	Oct 2017 (most recent data)
Influent concentrations		
CT (µg/L)	2,700	689
CF (µg/L)	120	34
DCM (µg/L)	ND (<5)	ND (<5)
Simulated effluent concentrations		
CT (µg/L)	477	122
CF (µg/L)	589	154
DCM (µg/L)	5	1
Actual effluent concentrations		
CT (µg/L)	33	44
CF (µg/L)	8	8
DCM (µg/L)	ND (<5)	ND (<5)

Abbreviations: CF, chloroform; CT, carbon tetrachloride; DCM, dichloromethane.

needed to degrade the CF being produced. After 2 hr of residence time, the effluent would contain an estimated ~160–630 µg/L of CF at the estimated molar conversion.

The EHC PRB contained an equivalent of 1.8 cm of 100% ZVI at a dose rate of 1% EHC (containing 40% ZVI) distributed over a 15 ft (4.6 m) PRB width. At a groundwater flow velocity of 1.8 ft/day (0.55 m/day), this equates to a residence time of <1 hr. On the basis of the above simulations, this is theoretically inadequate to facilitate the level of CT treatment observed after the organic carbon component had been consumed and would result in CF generation. Exhibit 15 shows the predicted effluent concentrations after 1 hr of residence time using the maximum and most recent inflowing concentration data. Actual effluent concentrations measured downgradient from the PRB are also presented for the same time points. Actual data are showing that a higher degree of CT treatment is achieved relative to the predicted values for ZVI alone with significantly less CF being accumulated. Therefore, in theory, the ZVI component alone would not be expected to support the level of treatment observed.

8 | DISCUSSION OF POTENTIAL MECHANISMS FOR PRB LONGEVITY

Since direct abiotic degradation with ZVI would not be expected to provide the level of treatment observed, this raises the question of what other mechanisms may be contributing to the continued treatment performance. Two possible contributing factors include recycling of biomass and the contribution from biogenic iron sulfide minerals.

8.1 | Recycling of biomass

Bioremediation strategies that involve the addition of electron donors have been demonstrated to generate increased levels of biomass through stimulation of the existing microbial community. When the initial supply of electron donor is consumed, the endogenous decay of that biomass can act as a potentially long-term

supplemental source of electron donor through several rounds of microbial turnover (Suthersan et al., 2013; Adamson & Newell, 2009). Even at low concentrations, that supplemental supply of electron donor could be sufficient to sustain the moderately reducing conditions required for biodegradation of CT.

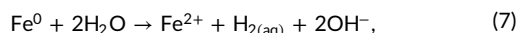## 8.2 | Sulfate reduction and indirect effects from biogenic minerals

A more probable explanation for the continued reducing conditions and extended PRB life is the contribution from a reduced iron sulfide mineral-based reactive zone formed downgradient of the PRB during the initial sulfate reduction phase. Once formed, reduced iron sulfide minerals may act as an electron reservoir aiding to maintain reducing conditions. These minerals also provide additional reactive surface area for abiotic dechlorination reactions.

Sulfate reduction by sulfate-reducing bacteria (SRBs) is expressed by Equation (6). Iron corrosion will result in the release of ferrous iron and hydrogen (Equation (7)), which can combine with sulfide to form mackinawite (Equation (8)).
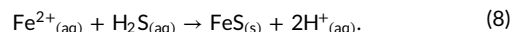
Sulfate reduction by SRBs as follows:

$$2CH_2O_{(s)} + SO_4^{2-} + 2H^+_{(aq)} \rightarrow H_2S + 2CO_{2(aq)} + 2H_2O, \quad (6)$$
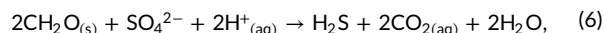
Ferrous iron produced from iron corrosion:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_{2(aq)} + 2OH^-, \quad (7)$$

Precipitation of ferrous iron with sulfide:

$$Fe^{2+}_{(aq)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + 2H^+_{(aq)}. \quad (8)$$

Mackinawite can, in turn, be oxidized by CT, resulting in its reductive dechlorination (Lan & Butler, 2016; Matheson & Tratnyek, 1994). Since abiotic reduction in contact with either reduced minerals or ZVI particles is a surface reaction requiring direct contact, a potential key aspect of these indirect iron effects would be an enhanced surface area for abiotic dechlorination reactions, noting that the EHC reagent itself was found to distribute into discrete seams upon injection. Another study showed that each 1.0 L of groundwater with sulfate at 3,000 mg/L generated about 1.2 ft^2 (0.11 m^2) of very reactive iron sulfide mineral surface area following the application of organic carbon substrate and ferrous iron to a high sulfate aquifer (Leigh & Owen, 2015). This represents up to an order of magnitude more surface area compared to estimated values for microscale ZVI on a weight basis. Furthermore, the iron sulfide minerals were found to precipitate and coat the soil particles along preferential pathways, thereby extending the reactive zone beyond the reagent seams.

Abiotic degradation in contact with iron sulfide minerals is a redox reaction where ferrous iron (Fe^{+2}) is oxidized to its ferric form (Fe^{+3}) and the chlorinated organic compound is reduced. This reactive mineral zone may also be continuously rejuvenated by low
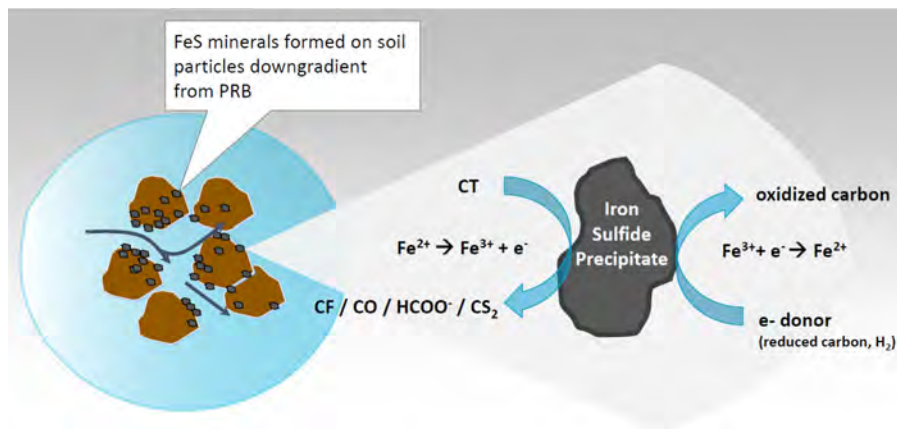
EXHIBIT 16 Regeneration of iron sulfide minerals following oxidation by CT. CF, chloroform; CT, carbon tetrachloride; PRB, permeable reactive barrier

levels of TOC present in inflowing groundwater (~2 mg/L), from the cycling of TOC through the generation of biomass, and from hydrogen produced by ongoing ZVI corrosion (Exhibit 16).

9 | CONCLUSIONS

PRB installation at the project site has served to significantly reduce the plume size and downgradient chloromethane concentrations. Groundwater sampling results have shown up to 99.5% decline in CT concentrations without the accumulation of catabolites measured 16 months after the PRB installation. Two years after installation, the CT removal rate decreased to approximately 95% removal and appears to have stabilized at that level for the 12 years after injection for which data are available. However, geochemical data downgradient of the PRB indicate that the PRB may be nearing the end of its reactive life with redox conditions approaching inflowing concentrations.

TOC concentration data suggest that the more readily degradable organic carbon fraction of EHC reagent was consumed within 2 years of installation. Theoretical ZVI consumption calculations suggest the microscale ZVI may last for about 33 years before being fully consumed. However, ZVI alone is not expected to support the level of treatment observed given the dose rate, reagent distribution, and residence time of the PRB.

Sulfate reduction was observed initially, but after TOC concentrations returned closer to background after ~2–3 years, little to no change in sulfate concentrations was observed downgradient of the PRB. This indicates that the sulfate reduction was biologically mediated and that ZVI alone did not react significantly with inflowing sulfate.

Notably, conditions downgradient of the PRB remained reducing for several years after TOC concentrations returned closer to background levels. Furthermore, CT degradation continued to exceed what could be expected from the ZVI component alone. We hypothesize that the formation of a reduced iron sulfide mineral zone during the initial sulfate reduction phase may account for the sustained reducing conditions and continued chloromethane treatment.

The EHC PRB has provided an effective and cost-efficient remedial solution for plume management at this site. Using an estimated linear groundwater flow velocity of 1.8 ft/day (0.55 m/day) and an estimated effective porosity of 15%, the PRB has treated an estimated total of 3,000,000 ft^3 (90,000 m^3) of groundwater since its installation. The PRB constitutes a green solution (no on-going energy requirements); with limited maintenance costs related to groundwater performance monitoring over the life of the PRB.

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Josephine Molin is a senior engineer at PeroxyChem Environmental Solutions with over 15 years of experience in the application of PeroxyChem's portfolio of in situ remediation technologies. Ms. Molin specializes in the application of ISCR reagents and her recent work has concentrated on the development and application of substrates promoting biogeochemical degradation of chlorinated organics. She received a Master's degree in Environmental Engineering from Uppsala University in Sweden in 2003, during which she published her work on using surfactant-modified zeolites for adsorption of viruses and bacteria in groundwater.

John Valkenburg is a University of Illinois graduate (BS in Dietetics and MS in Environmental Engineering). Mr. Valkenburg worked for 5 years as a research chemist with the Illinois State Geological Survey, publishing work on chlorinated VOC sampling in low recharge environments as well as on pesticide migration in sensitive hydrologic environments. He worked in environmental consulting engineering for 16 years and is a licensed professional engineer in Michigan. John specializes in developing conceptual remediation design approaches, with emphasis on in situ reagent applications.

Alan Seech, Ph.D., is a soil chemist and microbiologist with 29 years of experience in environmental remediation. His early research on biodegradation of chlorinated pesticides and nitroaromatics in soil resulted in the discovery of a treatment that combined metallic reducing agents and biodegradable organic matter to sharply increase degradation of these recalcitrant contaminants. The discovery yielded several patents and resulted in the start of a soil remediation business known as Grace Bioremediation Technologies (1996–2002), which was sold to a group of investors in 2002. The business continued as the Adventus group of companies for 10 years with Dr. Seech as CEO. The Adventus business was acquired in 2011 and is now part of PeroxyChem Environmental Solutions. The three main environmental remediation products developed from Dr. Seech's work, DARAMEND® for soil, EHC® for groundwater, and MetaFix® for heavy metals have been successfully applied at more than 1,000 sites in Canada, the United States, Europe, South America, and Asia.

Ryan Oesterreich received a Bachelor of Science degree in Geological Engineering as well as Geology and Geophysics from the University of Wisconsin—Madison in 2004 and a Master of Science degree in Environmental Engineering from the Colorado School of Mines in 2008. He has been with Arcadis since 2008 working primarily on in situ remedial strategy development, implementation, and optimization for sites with a variety of groundwater contaminants. He currently leads the In Situ Reactive Zone Practice Area within Arcadis' Technical Knowledge and Innovation network and is a licensed professional engineer and professional geologist in Minnesota.

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