

# Ten Year Performance Evaluation of a Field-Scale Zero-Valent Iron Permeable Reactive Barrier Installed to Remediate Trichloroethene Contaminated Groundwater

D. H. PHILLIPS,<sup>\*,†</sup> T. VAN NOOTEN,<sup>‡</sup>  
L. BASTIAENS,<sup>‡</sup> M. I. RUSSELL,<sup>†</sup>  
K. DICKSON,<sup>†,||</sup> S. PLANT,<sup>§,⊥</sup>  
J. M. E. AHAD,<sup>†,¶</sup> T. NEWTON,<sup>†,▽</sup>  
T. ELLIOT,<sup>†</sup> AND R. M. KALIN<sup>†,○</sup>

Environmental Engineering Research Centre, School of Planning, Architecture & Civil Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, U.K., Flemish Institute for Technological Research (VITO), Environmental and Process Technology, 200, 2400 Mol, Belgium, Centre for the Built Environment Research, School of Planning, Architecture & Civil Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, U.K., and Golder Associates (U.K.) Ltd., Landmere Lane, Edwattton, Nottingham, NG12 4DE, England, U.K.

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The Monkstown zero-valent iron permeable reactive barrier (ZVI PRB), Europe's oldest commercially-installed ZVI PRB, had been treating trichloroethene (TCE) contaminated groundwater for about 10 years on the Nortel Network site in Northern Ireland when cores from the reactive zone were collected in December, 2006. Groundwater data from 2001–2006 indicated that TCE is still being remediated to below detection limits as the contaminated groundwater flows through the PRB. Ca and Fe carbonates, crystalline and amorphous Fe sulfides, and Fe (hydr)oxides have precipitated in the granular ZVI material in the PRB. The greatest variety of minerals is associated with a ~1–2 cm thick, slightly cemented crust on top (up-gradient influent entrance) of the ZVI section of the PRB and also with the discontinuous cemented ZVI material (~23 cm thick) directly below it. The greatest presence of microbial communities also occurred in the up-gradient influent portion of the PRB compared to its down-gradient effluent section, with the latter possibly due to less favorable conditions (i.e., high pH, low oxygen) for microbial growth. The ZVI filings in the down-

gradient effluent section of the PRB have a projected life span of > 10 years compared with ZVI filings from the continuous to discontinuous cemented up-gradient ZVI section (upper ~25 cm) of the PRB, which may have a life span of only ~2–5 more years. Supporting Information from applied, multi-tracer testing indicated that restricted groundwater flow is occurring in the upper ~25 cm of the ZVI section and preferential pathways have also formed in this PRB over its 10 years of operation.

## Introduction

Zero-valent iron (ZVI or Fe<sup>0</sup>) remains the reactive medium that is most used in permeable reactive barriers (PRBs) (1–7). It is both durable and effective in treating a wide range of contaminants in groundwater, both organic (1, 3, 8–10) and inorganic (4, 5, 11, 12). Dense nonaqueous phase liquid (DNAPL) halogenated hydrocarbons, which include trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE), tetrachloroethylene (PCE), and vinyl chloride (VC), all have been successfully remediated by ZVI PRBs (3, 10). Electron transfer from the iron surface to the hydrocarbon generally results in reductive dehalogenation. During this process, hydrogen replaces halogen ions (i.e., Cl<sup>-</sup>) which eventually can yield ethene (C<sub>2</sub>H<sub>4</sub>) or ethane (C<sub>2</sub>H<sub>6</sub>) products which then can be fully mineralized via biodegradation (3, 8).

Mineralogical product variabilities within ZVI PRBs occur due to the different brands of reactive ZVI filings used, and site-specific groundwater geochemistries and contaminants. For example, in the Y-12 in-situ ZVI PRB that used Peerless ZVI to treat U and NO<sub>3</sub> in high carbonate and calcium groundwater environment, Phillips et al. (4–6) report deposits of carbonates (aragonite [CaCO<sub>3</sub>], calcite [CaCO<sub>3</sub>], siderite [FeCO<sub>3</sub>], carbonate green rusts [Fe<sub>4</sub><sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>(OH)<sub>12</sub>][CO<sub>3</sub>·2H<sub>2</sub>O]), Fe oxyhydroxides (goethite [α-FeOOH], lepidocrocite [γ-FeOOH], akaganeite [β-FeOOH]), and iron sulfides (mackinawite [(Fe, Ni)<sub>9</sub>S<sub>8</sub>], amorphous FeS, sulfate green rust [Fe<sub>4</sub><sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>(OH)<sub>12</sub>][SO<sub>4</sub><sup>2-</sup>·2H<sub>2</sub>O]). Jeen et al. (13) report that aragonite precipitation occurred more in the influent portion of Connelly granular ZVI columns, while ferrous hydroxy carbonate (FHC) [Fe<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>] occurred throughout the columns. This build-up of carbonate precipitates was found to exponentially decrease the reactivity of ZVI to treat TCE. In a column test of Gotthart Maier Metallpulver granular ZVI, Van Nooten et al. (14) found deposits of vivianite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O], siderite [FeCO<sub>3</sub>], FHC, carbonate green rust, amorphous FeS, and sparse magnetite [Fe<sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>O<sub>4</sub>]. However, despite the many studies which have been conducted on reaction product mineralogies of ZVI PRB systems, field observations generally are not available over a sufficient duration to show the potential precipitation characteristics of a ZVI PRB system over the extended periods for which they are supposed to operate (13). Of the few ZVI PRB field studies (2, 4, 5, 15–20), that do give some insight into longer term mineral precipitation, most are on barriers that have been operating for <5 years, excepting for the PRBs designed as treatment walls (as reported by Warner et al. (16) after 10 years operation to treat chlorinated solvents and Wilkin et al. (17) after 8 years operation to treat chromium).

Apart from mineralogical studies on PRB's, both phospholipid fatty acids (PLFA) analysis (21, 22) and DNA-analysis (22) have been used to show that specific microbial communities also develop in PRB's over time due to the specific conditions created by the strongly reducing environment in the ZVI reactive zone. Microbial activity can contribute to contaminant removal in a direct way by microbial degrada-

\* Corresponding author phone: +44 (0)28 9097 5590; e-mail: d.phillips@qub.ac.uk.

† Environmental Engineering Research Centre.

‡ VITO.

§ Centre for the Built Environment Research.

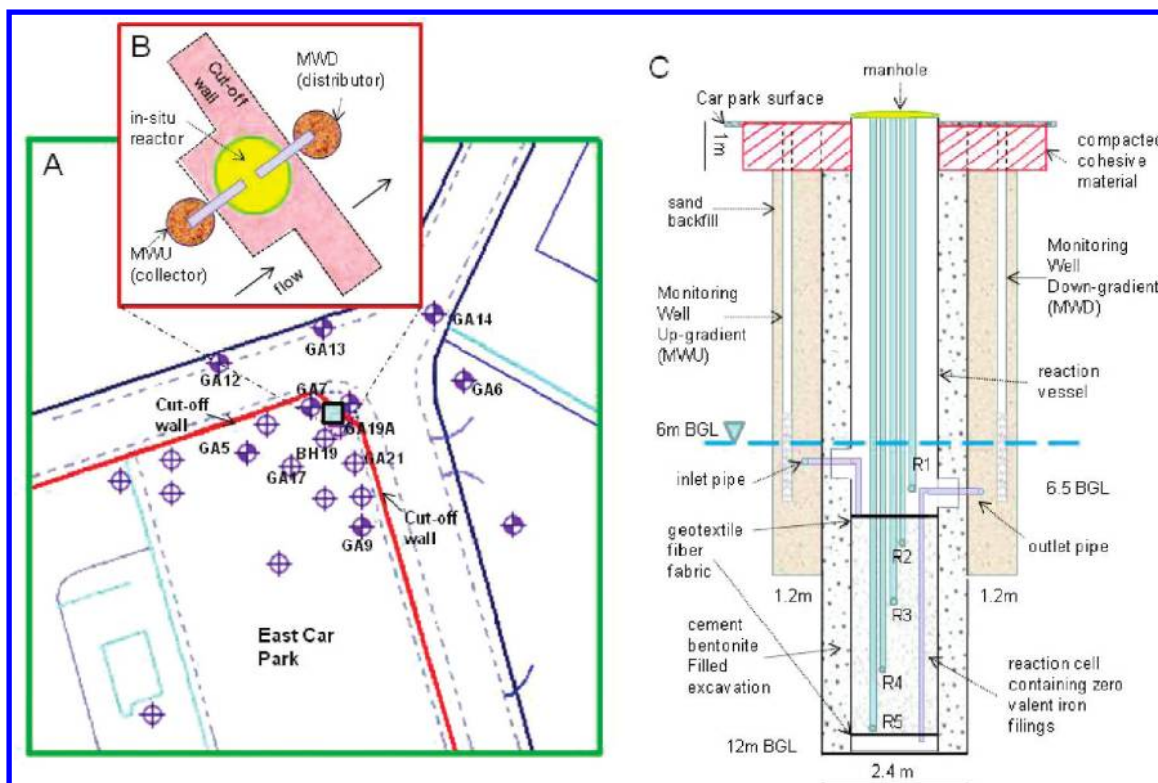
⊥ Golder Associates (U.K.) Ltd.

|| Current address: EBA Engineering Consultants Ltd., Canada.

¶ Current address: Geological Survey of Canada, third floor, 490, rue de la Couronne, Quebec City, Quebec, G1K 9A9, Canada.

▽ Current address: New Mexico Bureau of Geology & Mineral Resources, New Mexico Tech, 801 Leroy Place, Socorro, New Mexico 87801.

○ Current address: University of Strathclyde, David Livingstone Centre for Sustainability, Level 6, Graham Hills Building, 50 Richmond Street, Glasgow, G1 1XN, Scotland, U.K.



**FIGURE 1.** Diagrams of the (A) Nortel East car park showing borehole and PRB locations, (B) aerial view of the funnel-and-gate PRB (cutoff wall acts as the funnel and PRB acts as the gate), and (C) vertical view of the PRB (not to scale). BGL = below ground level.

tion (23, 24), but also in an indirect way by promoting the formation of highly reactive iron minerals (14, 25–27).

The Monkstown ZVI PRB is one of the oldest field-scale PRBs in the world. The first 5 years of operation (1996–2000) was reported by Beck et al. (28). The current paper examines the subsequent longer-term performance of the Monkstown PRB through its second 5 years of operation (2001–2006) by investigating (1) the geochemistry of the groundwater in the PRB (to determine if TCE is being dehalogenated); (2) the condition of the ZVI filings medium (especially corrosion, mineral precipitates and coatings, and cementation); and, (3) the microbial communities within the PRB and their potential impact on the mineralogy and TCE remediation.

## Materials and Methods

**Barrier Installation and Design.** In December 1995, Keller Ground Engineering, Ltd. and Golder Associates completed construction of a “funnel-and-gate” ZVI PRB at the Nortel Networks facility in Monkstown, Newtownabbey (northeast of Belfast), Northern Ireland (Figure 1). The in-situ PRB comprises a steel circular column reaction vessel filled with commercial grade Master Builders (0.57–2 mm diam.) ZVI filings (EnviroMetals Technologies, Inc., ETI). The PRB was installed vertically in the ground to a depth of 12.2 m specifically to treat a small, shallow, highly concentrated (~390 mg/L) plume of dissolved TCE and related breakdown products. The circular reaction vessel is 1.2 m in diameter and is divided into three compartments. The lower compartment, which contains the granular ZVI reactive medium, is 7.3 m long. This section has a steel door to maintain anaerobic conditions for effective dehalogenation. The rest of the vessel (middle and upper sections) is empty. Access into the vessel is through a manhole at the surface, and gases are vented from the PRB via a modified street lamp. Groundwater is directed to the top inlet of the reaction vessel by two 30.5 m long × 0.6 m wide × 12 m deep bentonite cement cutoff slurry walls, which act as the “funnel” portion for the PRB. Groundwater then moves vertically by gravity

through the ZVI reactive section “gate” to be discharged through a piped outlet to the down-gradient side of the slurry wall. The depth of the barrier was chosen to toe into a zone of low hydraulic permeability at a depth of c.10 m, consisting of a continuous stiff clayey layer beneath the coarser gravel lenses which acts as an aquitard to groundwater flow. The water table at the site is ~6.1 m below ground level, with an underlying aquifer at ~12.2 m in depth (29). The PRB was placed at the boundary of the East Car Park (Figure 1) based on field characterization and modeling (29). Further information on PRB design, site hydrology, and the multi-tracer test is given in the Supporting Information (SI).

**Groundwater Analysis.** Groundwater was sampled bi-annually from 2001 to 2006 from sampling wells both around and within the PRB. Sampling points (R1–R5) are set at depth sequentially within the PRB reactive vessel and are accessed by covers outside of the vessel (Figure 1). Up-gradient (MWU) and down-gradient (MWD) manhole well sampling points are located in the flow collection and discharge zones, respectively, adjacent to the PRB. Additional up-gradient and down-gradient groundwater monitoring boreholes (BH) also were installed around the PRB along with other background wells (GA). The current paper focuses specifically on monitoring results from the directly up-gradient wells GA7, GA19(A), MWU, GA9, GA5, BH19, GA17, GA21, and down-gradient wells GA13, GA12, GA6, MWD, and GA14 (Figure 1). VOCs in the groundwater samples were analyzed by purge-and-trap GC-MS. Ca, Mg, Na, K, Fe, and Mn were determined by inductively coupled plasma spectrometry (ICPS), whereas  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were measured by ion chromatography. Nitrate was measured colorimetrically, and alkalinity was titrated. An ion selective electrode was used to measure pH.

NETPATH v.2.13 calculations (30) were made using selected geochemical parameters within the PRB on water samples from the reactive vessel (R1–R5). Samples had been taken quarterly during 1996 (started 18/04/1996) then

annually during the following four years of initial operation (up to 18/07/2000) (see SI).

**Core Material Analysis.** Some 10 years after the initial PRB installation, cores of the reactive material were collected in polyurethane tubes (118 cm long  $\times$  5.1 cm wide). After excess water was removed (by pumping in-situ), the cores were exhumed vertically from the center of the PRB using a Geoprobe corer. Because of spillage, only partial retrieval ( $\sim$ 91.4 cm) of the cores from the top ( $\sim$ 6.5–7.10 m) and bottom ( $\sim$ 9.6–10.5 m) of the ZVI zone was obtained. Retrieval of the mid-section of the PRB was not possible. Handling, preparation, X-ray diffraction (XRD), and scanning electron microscope (SEM) analysis of the sampled core material were carried-out according to Phillips et al. (5, 6). Immediately after they were removed from the PRB, the ends were capped and the cores were placed in airtight cylinders which were purged with Ar gas. The sealed cylinders subsequently were kept in cold storage at 4 °C until the cores were prepared for analysis. During preparation, the cores were removed from the cylinders and immediately placed in an anaerobic chamber. The ZVI PRB material from each core was separated into four segments (usually  $\sim$ 15.2 cm long), prepared according to Phillips et al (6) and immediately analyzed with a PANalytical X-ray diffractometer equipped with PANalytical's X'Pert Highscore software. The XRD used a Ni-filtered CuK $\alpha$  radiation operated at 40 kV and 40 mA with a 2 theta range of 10–60. Undisturbed and polished sections of both loose and cemented ZVI PRB material also were carbon coated with an Agar Auto carbon coater and analyzed immediately using a Philips SEM equipped with an Oxford Instruments backscatter electron (BSE) analyzer and energy dispersive (EDS) and wavelength dispersive (WDS) spectrometers.

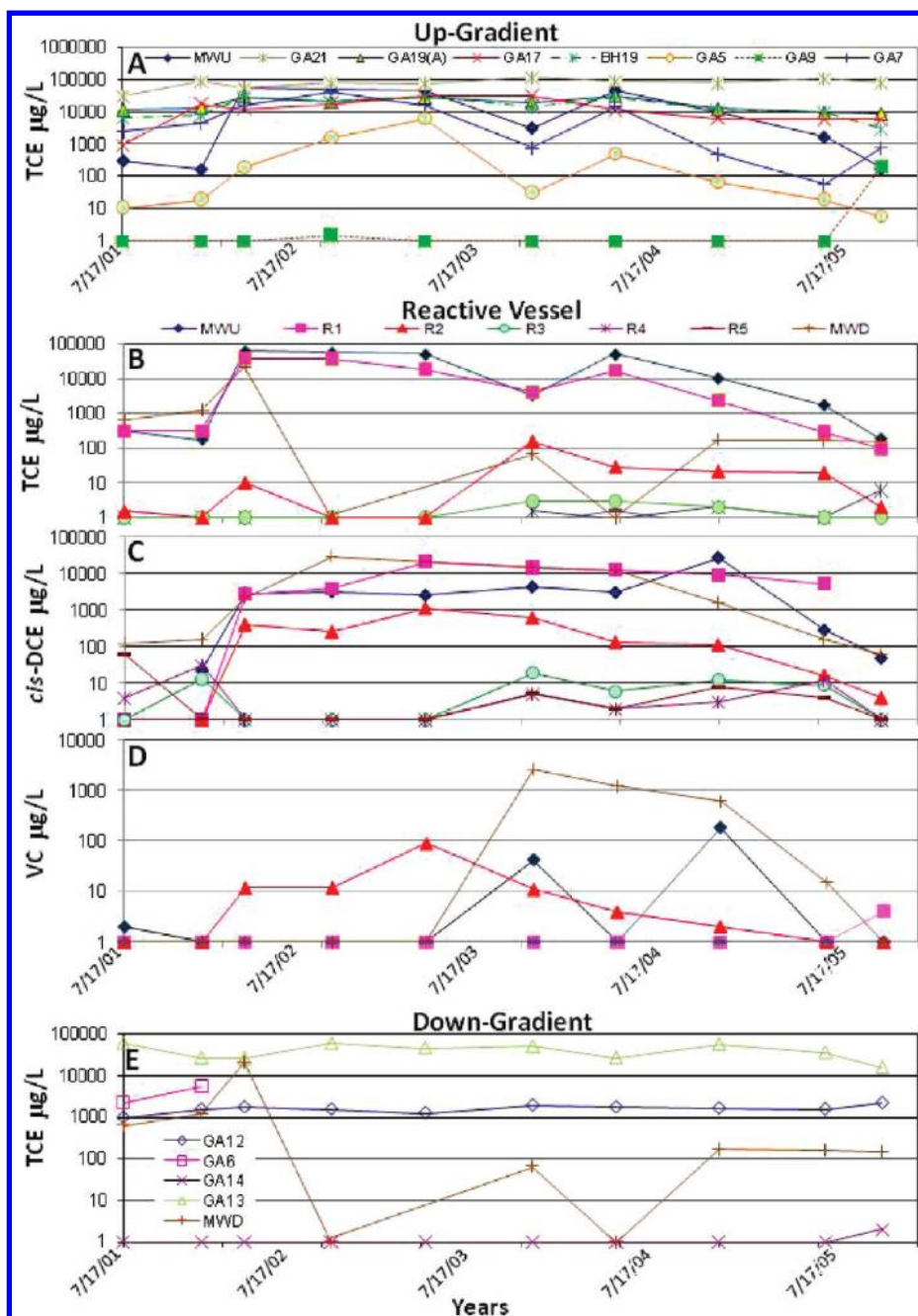
**Microbial Community Analysis.** ZVI filings samples (2 g) were collected and prepared in an anaerobic chamber for microbial analysis in duplicate at three different core lengths from the up-gradient influent and down-gradient effluent sections of the ZVI zone. These samples were stored at 4 °C in aluminum bags flushed with nitrogen to ensure anaerobic conditions. Groundwater samples (1 L) also were collected in duplicate from sampling points R1–R5 and the up-gradient (MWU) and down-gradient (MWD) manhole wells. DNA was extracted both from the cores and groundwater samples as described by Hendrickx et al. (31). Groundwater samples were first filtered on a 0.45  $\mu$ m filter (Millipore) and filtrates were transferred to a Tris-glycerol (10 mM –15%) buffer for DNA-extraction. The microbial diversity of the samples was evaluated by PCR-DGGE using different group specific primer sets targeting *Eubacteria* (32), *Archaea* (33), iron reducing bacteria (IRB, *Geobacteraceae*, and *Geothrix*) (34, 35), sulfate reducing bacteria (SRB) (36), denitrifying bacteria (37), and methanogens (38). The primer sets used are summarized in Figure 4A. PCR-DGGE conditions are described elsewhere (14).

## Results and Discussion

**Contaminant Distribution in Groundwater. Up-Gradient Wells.** TCE concentrations in the source zone before PRB installation were as high as 390 mg/L (29). Concentrations of TCE in up-gradient wells from 2001 to 2006 (Figure 2A) were similar to the concentrations from 1995 to 2001. TCE concentrations in Well GA9 furthest away from the up-gradient entrance of the PRB remained below detection. Removal of the highly contaminated aquifer material source initially from of the trench during installation of the PRB and cutoff walls resulted in a rapid decrease in TCE concentrations in some of the up-gradient wells closest to the PRB. However, residual contaminated material remains in the subsurface. During the first 5 years (1996–2001), most monitoring wells up-gradient of the PRB showed a trend toward decreasing

concentrations of TCE over time (28). However, the lowest concentrations of TCE in the up-gradient portion of the site to the PRB have remained significantly higher than the design criteria for remediation ( $\sim$ 10  $\mu$ g/L), except at GA9. For example, the TCE concentration in BH19 initially was 250 mg/L in March 1994, but decreased to  $\sim$ 4 mg/L in February 2001. An exception to the trend occurred in GA17 which had 360  $\mu$ g/L TCE in April 1998, but increased to 730  $\mu$ g/L TCE in July 2000 and then decreased to 50  $\mu$ g/L TCE in February 2001. From April 1996 to July 2000 the TCE concentration in MWU also fluctuated from 510  $\mu$ g/L to 79 mg/L. From 1994 to 2001, *cis*-DCE, concentrations ranged from below detection to 62 mg/L, and VC was detected only once (530  $\mu$ g/L in well MWU in April 1998). 1,1 DCE and 1,2 *trans*-DCE were not detected in the up-gradient wells. The highest concentration of TCE was in GA21, where it fluctuates from 32 mg/L in July 2001 to 120 mg/L in October 2003. At the entrance to the PRB, MWU had TCE concentrations of 170  $\mu$ g/L in December 2001 fluctuating to 60 mg/L in March 2002.

**Reaction Vessel.** Contaminant concentrations in the reaction vessel fluctuated over the 10-year period of operation, perhaps due to release of trapped sections of TCE (created by construction activities during installation) into the groundwater plume moving through the reaction vessel, and/or the fluctuations in the up-gradient wells. The contaminant chemistry indicates that TCE is being dehalogenated in the PRB (Figure 2A–D). From 1994 to 2001, TCE ranged from 38 mg/L in April 1996 to 450  $\mu$ g/L in Feb 2001, reflecting the trend of decreasing concentrations over time as also shown in the up-gradient wells in the first 5 years of operation (28). From 2001–2006, TCE and *cis*-DCE concentrations in R1 (Figure 2B–C) follow the same trends as those in the MWU up-gradient collection well indicating that these concentrations follow TCE and *cis*-DCE concentrations in the contaminated water entering the PRB from up-gradient. Indeed, the R1 sampling point is right at the entrance to the reactive vessel where there are no ZVI filings present. The concentrations of TCE in R2, located in the ZVI section of the PRB, however, are dramatically lower and do not follow the same TCE trends in comparison to R1 and MWU wells indicating that TCE is being remediated where the ZVI, its by-products and perhaps microbes all contribute to reductive dehalogenation. *cis*-DCE concentrations at R2 show a similar trend to TCE concentrations from R1, indicating still some influence from the *cis*-DCE entering the PRB from the up-gradient, but are lower in concentration and also show a more rapid reduction in peak concentrations. The concentrations of both TCE and *cis*-DCE in R3 to R5 are dramatically lower than their concentrations in R2, whereas *cis*-DCE concentrations are generally higher than TCE concentrations indicating dehalogenation of TCE. There appears also to be some lag in the increase of concentrations of TCE and *cis*-DCE as seen in the period before October 2003 which could reflect an increase in residence time in the upper portion of the ZVI reactive material due to a decrease in void space from the build-up of mineral precipitates. TCE is present in the MWD well indicating either residual contaminations from PRB installation or a preferential pathway that has transferred some TCE through the ZVI section of the PRB. However, *cis*-DCE is notably higher compared to TCE in this well, indicating reductive dehalogenation. VC also was detected at the R2 sampling point (Figure 2D), while absent from both MWU and R1. VC dramatically decreases from 2600 mg/L in October 2003 to 15 mg/L in May 2005 in the MWD well as it decreases at R2. Spikes in VC concentrations are observed in October 2003 at 42  $\mu$ g/L and in October 2004 at 180  $\mu$ g/L in the MWU well during the same time frame as the increase in VC in the MWD well. However, the MWD down-gradient well showed higher concentrations than up-gradient inputs implicating the presence of degradation products.

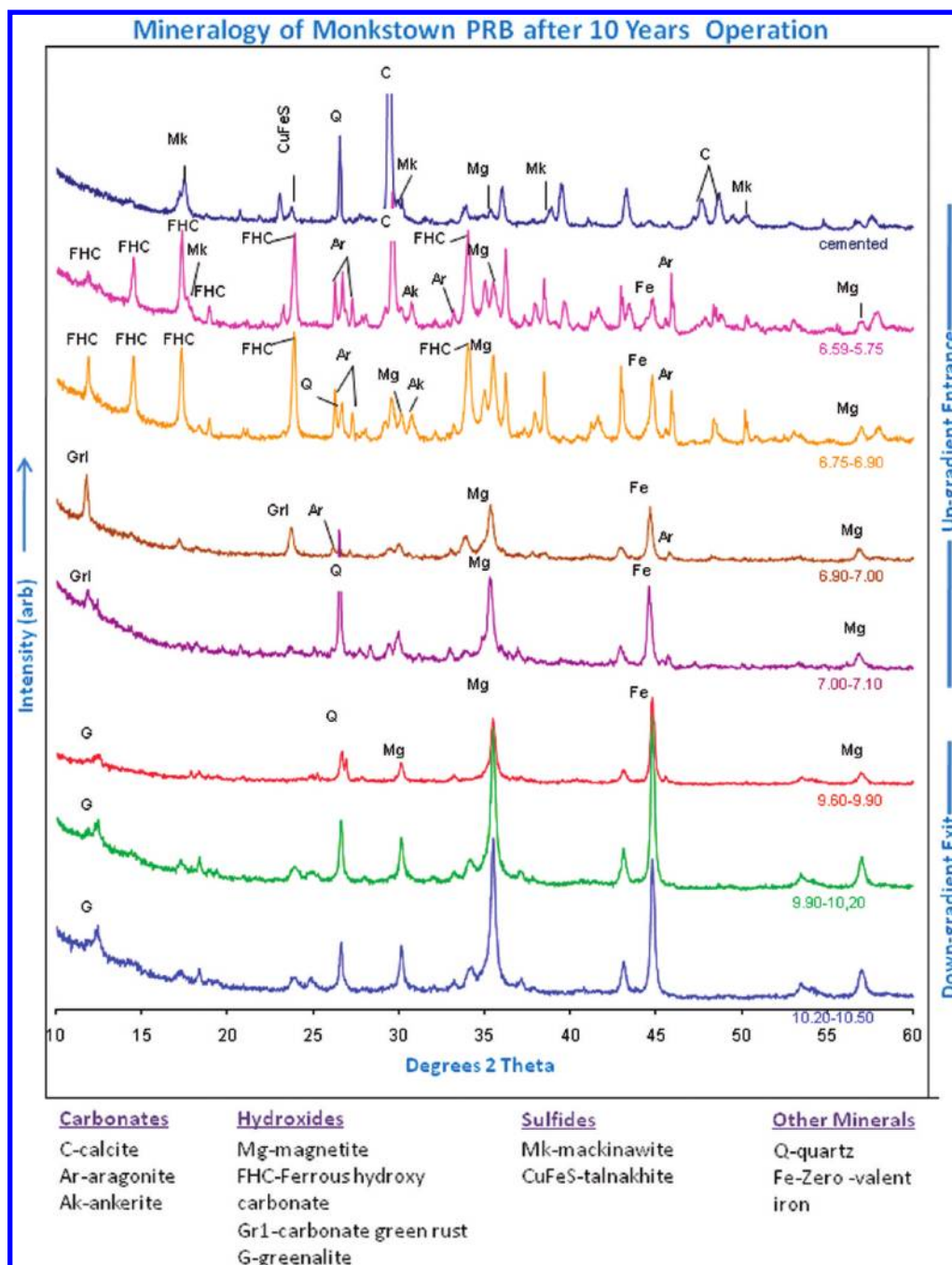


**FIGURE 2.** TCE concentrations from 2001 to 2006 in (A) up-gradient wells, (B) reactive vessel, and (E) down-gradient wells; (C) *cis*-DCE concentrations within the reactive vessel; and (D) VC within the reactive vessel.

1,2 *trans*-DCE was detected only in the MWU well in October 2003 at 17  $\mu\text{g/L}$ , whereas 1,1-DCE was detected in MWD from October 2004 at 50  $\mu\text{g/L}$  to 13  $\mu\text{g/L}$  in May 2005. These trends suggest that the TCE dehalogenation pathway within the PRB reactive medium reflects predominantly TCE degradation to *cis*-DCE (with minor amounts of 1,1-DCE) to VC (39). However, although chlorinated ethene was not measured in the PRB, separation of the three tracers in the breakthrough curves at R2 (data not shown) in a supporting tracer test suggested the possible presence of a gas phase (e.g., bubbles) within the system at the inlet of the PRB, which is consistent with some full degradation and breakdown products.

**Down-Gradient Wells.** Major ion chemistry in the down-gradient wells generally shows a range of different water facies types, from bicarbonate-rich to chloride-rich (28, 29). Contaminant chemistry potentially shows impact of the PRB on wells closest to the reactive cell, with little or no impact

on more distant wells. MWD, which is the outlet closest to the reactive cell, shows a decrease in concentration of TCE from 12 mg/L in March and July 1996 to 440  $\mu\text{g/L}$  in July 2000 over the first five years (28). Subsequently, from 2001–2006 in MWD, TCE fluctuated between 0  $\mu\text{g/L}$  in September 2002 and March 2004 to 21 mg/L in March 2002 (Figure 2E). *cis*-DCE concentrations fluctuated from 102  $\mu\text{g}$  in July 2001 to 28 mg/L in September 2002. The elevated levels of TCE and *cis*-DCE in MWD during September 2002 reflect the generally low hydraulic gradient conditions and possibly residual levels of TCE in the subsurface material down-gradient of the PRB. The decrease of contaminant concentrations in down-gradient wells generally reflects a similar trend to the up-gradient wells. GA6, GA10, and GA12 showed a decreasing trend in TCE from 1994 to 2001 (28). However, from 2001 to 2006 there have been fluctuations. *cis*-DCE was detected in most down-gradient wells with a maximum concentration of 9.5 mg/L in GA6 in August 1997. The elevated TCE



**FIGURE 3.** X-ray diffractogram identification of the minerals and their distribution in the ZVI section of the PRB.

concentrations in GA6, GA12, and GA13 are due to TCE contamination prior to the installation of the PRB. Also, the contaminated groundwater from GA13 is pumped over to the up-gradient portion of the site to be treated by the PRB. 1,1-DCE was not detected in any of the down-gradient wells, however, 1,2 *trans*-DCE was detected in small amounts in GA5 at 0.8  $\mu\text{g/L}$  to 3  $\mu\text{g/L}$  from March 2001 to September 2006 and in GA7 at 2  $\mu\text{g/L}$  to 4  $\mu\text{g/L}$  from October 2003 to May 2005.

**Condition of the ZVI Reactive Materials.** *NETPATH Modeling.* The major ion chemistry (including Fe and Mn) of waters within the reactive vessel (R1-R5 sampling ports) were monitored only over the first 5 years of operation of the Monkstown PRB, but geochemical speciation using a thermodynamic minerals database embedded within the NETPATH code (30) generally support the interpretation of certain mineral saturation and precipitation occurring within this reactive vessel (see SI).

*Mineral Precipitates in the PRB.* On opening the cores, the material was found to consist mainly of loose, individual black ZVI grains/filings, apart from a thin crust of cementation at the up-gradient interface of the ZVI material in the reactive vessel. A combination of XRD, SEM-EDS, and SEM-WDS mapping analysis showed mineral precipitates ranging from Fe (hydr)oxides, Ca and Fe carbonate, carbonate green rusts, and Fe sulfides (Figure 3). Quartz, which was washed into the system, was also detected by XRD throughout the ZVI material. ZVI was detected throughout the PRB, except in the cemented crust on the top of the reactive zone where groundwater first enters the ZVI portion of the PRB. The mineralogy of the intermediate, unsampled section (from 7.1–9.6 m) is thought to be similar to core material collected directly above and below it, because XRD analysis show little difference in mineralogy of samples collected at 7.0–7.1 m and 9.6–9.9 m. However, over the 6.75–6.9 m depth just below the crust layer at the top of the ZVI section of the PRB

there is an increase in X-ray diffractogram peak size and frequency indicating a greater amount of minerals and greater oxidation.

**Iron (Hydr)oxides.** Fe oxides were present in cores throughout the reactive material. Magnetite [Fe<sub>3</sub>O<sub>4</sub>] was the major mineral, and was detected by XRD throughout the ZVI portion of the Monkstown PRB. Kohn et al. (40) reported magnetite, maghemite, FHC, fayalite [Fe<sub>2</sub>SiO<sub>4</sub>], and wüstite [FeO] in their column study using Master Builder ZVI. Although fayalite was absent from Monkstown PRB material, a very similar mineral, greenalite [Fe<sub>2-3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>], was detected in the down-gradient effluent section (9.6–10.5 m) of the PRB (Figure 3). Greenalite may also be present from 7.00–7.10 m.

**Carbonates.** Groundwater passing through the reactive vessel changes from 'calcium bicarbonate' water facies, which was the predominant groundwater type up-gradient to the PRB, to a 'magnesium/sodium sulphate/chloride' type indicating loss of calcium and bicarbonate due to carbonate mineral precipitation and dehalogenation of TCE (28). This groundwater geochemistry was in agreement with the mineralogy of the ZVI material. Aragonite (detected from 6.59 to 7.00 m) and calcite (detected from 6.59 to 6.9 m) were present in the cemented layer where groundwater first enters the ZVI reactive zone (SI, Figure S1A). FHC is observed by SEM as square-shaped plates that exfoliate into florettes (SI, Figure S2A and B). Kukkadapu et al. (41) report that FHC forms from the reduction of magnetite which can be an abiotic or biotic process. Biotic processes accelerate its precipitation. Kohn et al. (40) also detected FHC in the presence of magnetite on Master Builder ZVI. Clusters of acicular-shaped crystals of aragonite [CaCO<sub>3</sub>] were observed on the ZVI filings in the Monkstown PRB, sometimes coated with Fe (hydr)oxides and FeS. Ankerite (Fe-rich CaCO<sub>3</sub> with a large amount of Mg and Mn substitution) [Ca(Fe, Mg, Mn)(CO<sub>3</sub>)<sub>2</sub>] was detected by XRD and observed by SEM from 6.59 to 6.9 m (SI Figure S1B) where groundwater first enters the up-gradient portion of the ZVI material of the PRB. Ankerite, an euhedral, rhombohedral-shaped mineral, formed as twinned and clusters of crystals on the surface of the ZVI filings. Carbonate green rust was detected by XRD from 6.9 to 7.1 m and observed by SEM as sparse, euhedral hexagonal mineral grains associated with FHC (SI Figure S1C).

**Sulfides.** Mackinawite [(Fe,Ni)<sub>9</sub>S<sub>8</sub>] was detected by XRD where groundwater first enters the up-gradient portion of the ZVI material in the cemented crust down to 6.75 m (Figure 3). Iron sulfide minerals, including amorphous FeS, were observed by SEM as thin coatings on ZVI filings and mineral surfaces throughout the ZVI section of the PRB, particularly in the cemented crust (SI Figures S3–S5). The amorphous FeS more than likely crystallized into mackinawite (5). Talnakhite [Cu<sub>9</sub>(Fe,Ni)<sub>8</sub>S<sub>16</sub>] was detected by XRD in the cemented crust. Therefore, it appears that, along with Ca carbonate minerals, Fe sulfide minerals (talnakhite, amorphous FeS, and mackinawite) are the main precipitates in the cemented crust on top (up-gradient influent entrance) of the ZVI section of the PRB.

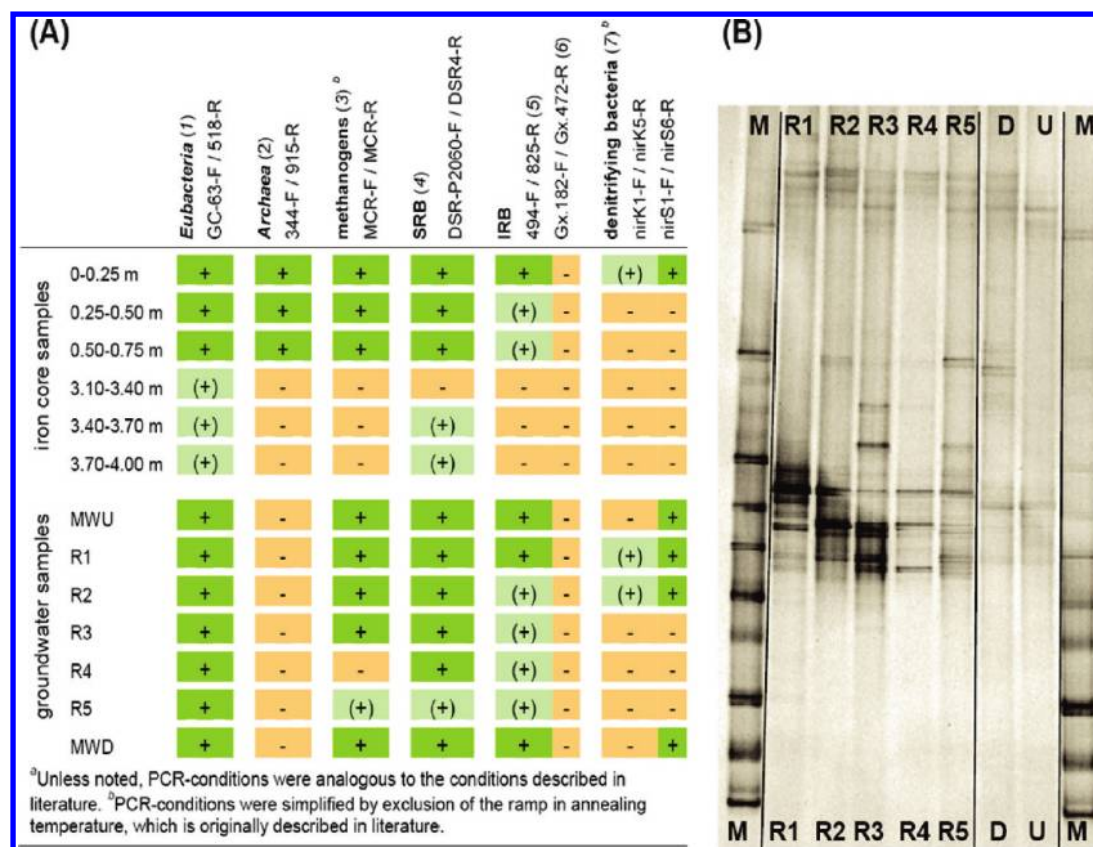
#### **Depletion and Cementation of the ZVI Reactive Material.**

SEM observations of polished sections of ZVI material from the Monkstown PRB reveal that in the up-gradient section (upper ~25 cm) of the PRB, there has been notable corrosion over the 10 years of operation, (SI, Figures S4, S5). Almost 35% of the ZVI filings have corroded into smaller fragments in the up-gradient section (upper 25 cm) of the ZVI portion of the PRB. Fe (hydr)oxide rinds have replaced about 40 to 80% of the ZVI filings in the thin (1–2 cm) cemented crust layer where the rinds are 25 to 200 μm thick. Also, some ZVI filings are completely corroded in this cemented crust layer where groundwater first enters the ZVI reactive zone. However, with depth the ZVI filings show less corrosion,

particularly in the down-gradient effluent section of the PRB where corrosion rinds ranged from about 5 to 75 μm in thickness. Similar corrosion patterns have been reported by Phillips et al. (4, 5) for the Y-12 barrier. The rinds on the ZVI filings were composed mainly of Fe hydroxides and Fe oxides with continuous layers of FHC platelets, patches of CaCO<sub>3</sub> and smooth coatings of amorphous FeS (SI Figures S1–S5). In the oxidized, cemented layer, the ZVI may last only a further 2–5 years; however, this is a very thin zone of about 1–2 cm in thickness. In the deeper sections of the PRB, the ZVI filings appeared to be more intact and thicker, although caution must be exercised as these observations are based on the visual examination of the corrosion rinds in polished sections. Gu et al (42) report similar 10 to 20 μm thick oxyhydroxide rinds on ZVI filings where HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were flushed through a column. After 10 years of operation, ZVI filings in the Monkstown PRB appeared to be in better condition compared to ZVI from other PRBs (4, 5), especially with depth, even though the ZVI filings have been continually immersed in water. This may be due to the encapsulated columnar reactive vessel design which has decreased oxygen contact with the ZVI filings.

The thin (1–2 cm) crust layer of continuous cementation where groundwater first enters the ZVI section of the PRB was easily broken by hand. Beck et al. (28) reported a 5 cm thick cemented zone that was broken and removed from the PRB when it was opened for sampling in 2000. Therefore, only a 6–7 cm thick layer of continuous cementation developed over the 10 years of operation of the PRB. Some zonation of precipitates occurred in the cemented layer where, iron sulfide predominates in places, and CaCO<sub>3</sub> dominates other sections (SI, Figures S3, S5), perhaps from colonization of microbial communities. Directly below the cemented layer, there was a less continuous cementation (2 mm to 2 cm chunks mixed with individual Fe<sup>0</sup> grains) ~23 cm in thickness. This layer has FHC, aragonite, calcite, mackinawite, amorphous FeS, and the appearance of magnetite and green rust that were not detected in the overlying cemented zone. A recent multi-tracer test (see SI) in the Monkstown PRB indicated that flow has become quite constricted and effective porosity appeared to have been reduced, more than likely by structure formation from mineral precipitation and ZVI filings clumping together through cementation in the upper ~25 cm. The tracer test also suggested the potential development of some preferential pathways in the medium over the 10 years of PRB operation. However, this upper section of the PRB remains the most reactive part of the system.

**Associated Microbial Communities.** Microbial community analysis focused on the detection of general as well as functional groups of bacteria which may affect ZVI PRB performance. PCR data show that *Eubacteria*, *Archaea*, denitrifying bacteria, IRB (*Geobacteraceae*), SRB, and methanogens, were present in reactive material in the reaction vessel, whereas iron(III) reducing *Geothrix* species were absent (Figure 4A). All these microbial groups were detected in the material collected near the inlet of the reactive zone, while only *Eubacteria* and SRB were detected in material collected more down-gradient in the vessel. This higher microbial population at the inlet corresponds also to constricted water flow due to structure development in the ZVI filings and drastic decrease in TCE concentration. Perhaps the constricted flow enhanced residence time for reductive dehalogenation of TCE and provided favorable conditions for greater microbial communities. The detection of less microbial groups downstream in the vessel might be related to the findings of Wilkin et al (21) who reported highest biomass levels in the aquifer iron interface up-gradient and a biomass decrease along the flow path of a field-scale ZVI PRB, most likely due to the generation of less favorable pH



**FIGURE 4.** Results of (A) PCR analysis with different primer sets<sup>a</sup> applied on DNA extracted from ZVI core and groundwater samples, and (B) DGGE analysis of eubacterial 16S rRNA gene sequences obtained from groundwater samples. Strong, weak, and negative PCR-signals are indicated with +, (+), and -, respectively. Lanes: M, DGGE marker; R1–R5, sampling points along the flow path of the vessel; D, down-gradient monitoring well; U, up-gradient monitoring well.

and redox conditions along the flow path. The pH ranged from ~7.5 in MWU, increasing with depth in the reactive vessel from ~8.2 to 8.5 in R1, 9.2 from R2-R4 and to ~9.8 in R5 and MWD during the first 5 years of operation (28). In contrast to the core samples, no *Archaea* were detected in the groundwater samples. Similar microbial groups were present along the flow path of the reactive vessel and in the up-gradient and down-gradient monitoring wells, except for denitrifying bacteria which were only detected in samples collected more up-gradient in the vessel. A stronger PCR detection in the up-gradient groundwater samples is in accordance with the results obtained from the core samples. PCR analysis was also used by Gu et al. (22) to target SRB, denitrifying bacteria and methanogens within a field-scale ZVI PRB and in the surrounding areas of the PRB after ~15 months of operation. Similarly, Gu et al. (22) detected all these groups of bacteria, although methanogens to a lesser extent, within the ZVI PRB and both up- and down-gradient from barrier. This study, however, targets more microbial functional groups and couples PCR results to DGGE fingerprint analysis to study the microbial diversity in more detail. DGGE fingerprints of eubacterial 16S rRNA gene sequences exhibited several common bands for the different sampling heights in the reaction vessel, whereas some other bands were clearly different (Figure 4B). Fingerprints of the samples originating from the up-gradient and down-gradient monitoring wells were similar to each other, but differed significantly from the samples originating from the reaction vessel, indicating that the microbial community in the reaction vessel differs significantly from the microbial community up- and down-gradient from the PRB. Significant microbial community shifts between ZVI material and up- and down-gradient aquifer material were earlier reported in laboratory-scale (14) and pilot-scale (43) iron barriers.

The targeted microbial groups may affect ZVI barrier performance, particularly indirectly. Sulfate reducing bacteria (SRB) can reduce sulphate present in groundwater to sulfides which subsequently react with available iron species. The formation of FeS coatings can significantly increase the reactivity of ZVI PRBs toward chlorinated ethenes (14). IRB may also be beneficial to the reactivity of the iron, as they can reduce iron (oxyhydr)oxides into iron minerals such as green rust (27), which has a high reactivity toward TCE (44). The presence of these microbial groups and the associated reactive minerals at the influent section of the Monkstown PRB may therefore have contributed to the rapid dehalogenation of TCE as it first enters the reactive vessel. Denitrifying bacteria and methanogens have been reported to cause heterogeneity in column-scale PRBs by the biological production of, respectively, nitrogen and methane gas (45, 46). As gases were not monitored in this study, it is not clear to what extent microbial gas production has contributed to the observed short-circuiting in the reactive vessel. Halorespiring bacteria such as *Dehalococcoides* species were not targeted in this study although they can contribute directly to contaminant removal by dechlorinating chlorinated aliphatic hydrocarbons as respiratory electron acceptors (47).

**Implications for PRB Design.** Cementation, corrosion, and mineral precipitation are common performance issues with field-scale ZVI PRBs, especially over the long-term, particularly in up-gradient sections of PRBs; nevertheless, the design of the Monkstown PRB likely has helped reduce the build-up of precipitates after 10 years of operation. The encapsulated columnar design of the PRB is probably responsible for the prolonged life-span of the reactive material, particularly at the effluent end because it prevents oxygen from entering the PRB to this depth. However, supporting information from multi-tracer testing has indi-

cated that a reduction in effective porosity has occurred in the upper ~25 cm of the ZVI medium, where the thin continuous cemented layer and underlying discontinuous cemented zone were present, and that preferential pathways may have formed in this PRB over the 10 years of operation. Nevertheless, the influent section of the PRB remains active in treating TCE. TCE has been progressively removed as groundwater flows down through the PRB. The presence of amorphous FeS and green rusts, likely related to the presence of specific microbial groups, may have contributed to TCE degradation in this part of the PRB.

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### Supporting Information Available

Details of geological material, site hydrology, PRB design, hydrogeochemistry in the reactive zone, multi-tracer test, and five figures of photomicrographs of mineral precipitates, ZVI corrosion and cementation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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