

A Biotic/Abiotic Three-Phase In Situ Barrier System to Treat TCE in Groundwater

Robert W. Tossell (btossell@ch2m.com), Blair Greenly, and Brian Whiffin
(CH2M HILL, Waterloo, Ontario, Canada)
Josee Gagnon, (Dessau-Soprin, Montreal, Quebec)
Luc Arguin (Dessau-Soprin, Quebec City, Quebec)
Michael Duchene (EnviroMetal Technologies Inc., Waterloo, Ontario)
Mark Strong (CH2M HILL, Charlotte, North Carolina)
Steve Chen (ARS Technologies, New Brunswick, New Jersey)
Bernard Michaud (Department of National Defense, Quebec, Canada)

ABSTRACT: A groundwater remediation pilot test (PT) consisting of three (3) in series, in situ reactive barriers was designed to evaluate treatment of dissolved phase trichloroethene (TCE) at concentrations up to 650 µg/L and *cis*-1,2-dichloroethene (*cis*-DCE) concentrations up to 350 µg/L at the Canadian Department of National Defense (DND) site in Valcartier, Quebec, Canada. The layout of the pilot test cell provides for the testing of biotic/abiotic treatment approach consisting of a mixture of zero valent iron and an integrated ZVI-carbon product (EHC[®] from Adventus) (ZVI/EHC), hydrogen sparging, and air sparging. Geology at the PT cell consists of sand with fine sand seams from ground surface to 28 metres below ground surface (m bgs) (92 ft bgs). Depth to groundwater is 10 m bgs (33 ft bgs) and a bedrock confining unit is at 28 m bgs (92 ft bgs). The ZVI/EHC barrier was installed using a proprietary pneumatic injection method developed by ARS Technologies. A total of 44,000 kilograms (96,000 pounds) of ZVI/EHC were injected into 12 points at a ratio of 2.7 to 1 (ZVI/EHC). Hydrogen sparging is being used to supplement hydrogen concentrations needed for reductive dechlorination of TCE. Four (4) hydrogen sparging wells were installed to evaluate radius of influence and treatment benefits of hydrogen sparging. As a final treatment, air sparging/bioventing wells were installed downgradient of the hydrogen sparging wells in the event that vinyl chloride (VC) is produced and needs treatment. All barrier systems and monitoring wells were installed during July 2006 and post construction PT monitoring was initiated in August 2006. Results to date indicate that groundwater TCE and *cis*-DCE concentrations have declined by over 50%, primarily in the ZVI/EHC barrier. Very high flow velocities and colder than anticipated groundwater temperatures have resulted in a reduction in the rate at which in situ chemical and biological treatment occurs and has increased the acclimation period for biological degradation.

INTRODUCTION

This paper presents the early results of a pilot test (PT) that utilizes an innovative combination of technologies to form a multi-barrier approach for in situ treatment of trichloroethene (TCE) and *cis*-1,2-dichloroethene (*cis*-DCE) at the Valcariter Garrison in Valcartier, Quebec, Canada. Chlorinated solvents (TCE up to 650 µg/L and *cis*-DCE up to 350 µg/L) are present at the PT site. The Valcartier site is a challenge for traditional technologies such as pump and treat due to the highly permeable aquifer material and

very high groundwater velocities (reported to be 80 to 100 m/yr on average). In situ treatment with ZVI is possible even with the cold groundwater temperatures present at Valcartier (8 °C to 12°C), although at reduced rates (O'Hannesin et al., 2004). A lack of total dissolved solids (primarily chloride) that could increase iron corrosion needed for electron production (Gotpinger et al., 1999) is also absent. Site conditions indicate that biological degradation could occur with the use of a recently developed controlled-release carbon and micro-scale ZVI substrate (EHC; Mueller et. al., 2004; and Losi et al., 2006). The concept of using an integrated substrate to supplement fine-grained ZVI has not been studied thoroughly at this proportion and scale. Experience to date suggests that there is a positive synergistic effect on VOC degradation due to the abiotic degradation with the ZVI combined with the biotic degradation facilitated by the addition of the organic carbon. The layout of the PT provided for the testing of three technologies in series (Figure 1):

- Barrier 1 - ZVI/EHC barrier
- Barrier 2 - hydrogen sparging
- Barrier 3 - air sparging/bioventing

The benefit to operating the PT with this approach is that the effectiveness of ZVI/EHC, hydrogen sparging and air sparging can be evaluated independently as well as in combination with each other. Evaluating the effectiveness of the three reactive barriers individually and in combination will allow for an optimum full-scale system to be identified that has the lowest life-cycle cost.

Site Description. The Site is located in the Laurentian Mountains of Quebec. The geology is comprised of unconsolidated weathered alluvial deposits interbedded with glacio-fluvial sediments. Weathered bedrock lies beneath the sand aquifer. The upper unit consists of unconsolidated sands and gravels are present within the first 28 to 30 meters (90 to 100 feet) below ground surface (m bgs). This unit is a shallow, unconfined aquifer. Groundwater is typically encountered at a depth of 10 m bgs. Bedrock is encountered at approximately 28 to 30 m bgs at the PT site but is found at greater than 40 m bgs at other portions of the site. Concentrations of TCE and *cis*-DCE ranged from the reporting limit of 0.5 µg/L to 650 µg/L near the PT location. TCE stratification occurs at the site, with the highest concentrations being present in the lower portion of the sand aquifer, just above the bedrock surface.

METHODS AND MATERIALS

The ZVI /EHC barrier was installed using a proprietary pneumatic injection method known as FeroxTM. This method was selected because it can achieve the depth limits required for installation (greater than 40 m bgs), and it can achieve the radius of influence required to provide treatment under the described site conditions. The process utilizes zero valent iron (ZVI) powder/EHC mixture (as a slurry), injected under high pressure (by fluidizing the aquifer for optimal mixing) into the subsurface, to create a permeable reaction zone. Nitrogen is used as the carrier gas to delay premature iron oxidation. It is also readily available, relatively inexpensive, and there are minimal health and safety issues with its storage and handling. Injection was done one boring at a time in 1.1 m (3-5-foot [ft]) packered intervals across the entire saturated thickness zone of the shallow, unconfined aquifer; from just above the competent bedrock at 28 m bgs to 10 m bgs.

During, injections the casing were retracted at the individual injection borehole to prevent borehole collapse during injections. A total of 44,000 kg or 96,000 lbs of ZVI/EHC were required for the barrier. ZVI was 45 to 600 micron supplied by Quebec Metal Powders Ltd. of Sorel-Tracy, Quebec. EHC is a fibrous controlled-release carbon with micro-scale ZVI (10 to 15 micron) supplied by Adventus Remediation Technologies Inc. of Mississauga, Ontario.

Reductive dechlorination (biotic process) utilizes hydrogen as an electron donor. In the event that ZVI/EHC barrier did not treat all of the target compounds, hydrogen sparging wells were installed to supplement the hydrogen concentration in the aquifer to promote the continued reductive dechlorination of residual TCE and *cis*-DCE.

Four (4) hydrogen sparge wells were installed, each equipped with two inch diameter wells, and 18 inch long sparge points (Figure 1).

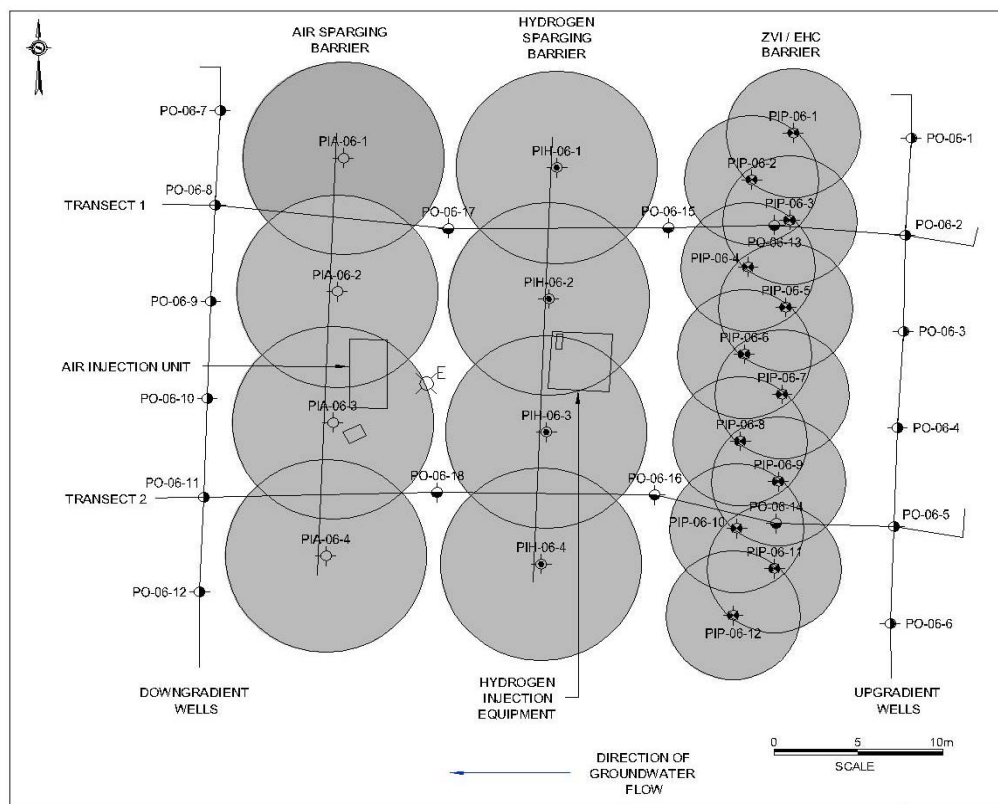


FIGURE 1. Pilot test layout.

At each location, one sparge well was installed at approximately 27 m bgs (96 ft bgs). Compressed hydrogen gas was sparged into the wells using pressurized canisters at 6 cubic feet per minute (cfm) and 50 pounds per square inch (psi) once per week. Flow rates were regulated using an in-line pressure regulator. Compressed hydrogen gas canisters were replaced weekly by a licensed contractor.

The third PRB in the multi-barrier approach is air sparging/bioventing. The air sparging/bioventing PRB consists of four (4) sparging locations and eight (8) sparge points (two points per location at 27 m bgs and 18 m bgs). In the event that complete

dechlorination does not occur in the first two reactive barriers, both *cis*-DCE and VC can be treated under aerobic conditions within the air sparging barrier. The air sparging system is operated continuously at 15 cfm per point (120 cfm total) at pressures ranging from 25 to 35 psi.

Monitoring wells were installed as a row of nested pairs upgradient of the PT and downgradient of the PT as prescribed in the project's original Request for Proposal by DND. A total of twelve (12) dual completion monitoring wells (with specified well screen depths), six installed upgradient (PO-06-1 to PO-06-6 A [deep] and B [shallow]) and six downgradient (PO-06-7 to PO-06-12 A [deep] and B [shallow]) of the three reactive barriers are being used to monitoring performance over the 10 months of monitoring. Six additional monitoring wells (PO-06-13 to PO-06-18) were installed to evaluate performance between barriers and within the ZVI/EHC barrier. These locations are were screened between 20 and 26 m bgs (see Figure 1). All monitoring wells were installed using the air rotary technique.

The upgradient/downgradient wells and barrier monitoring wells were aligned to create two transects of monitoring wells to evaluate each barrier independently (Figure 1). Groundwater samples were collected weekly for volatile organic compound (VOC) characterization and monthly for geochemical parameters including oxidation reduction potential (ORP), dissolved oxygen (DO), chloride, sulfate, nitrate, total organic carbon (TOC), dissolved hydrocarbon gasses (methane, ethene and ethane), pH, and dissolved iron and manganese.

Bromide was injected into upgradient monitoring wells PO-06-2A&B and PO-06-5A&B as a conservative tracer to allow for groundwater velocity to be estimated. A bromide specific probe and samples were collected periodically to monitoring for bromide ion concentrations in groundwater samples. The data was used to develop breakthrough curves which were used to estimate groundwater velocities.

Samples were obtained from four monitoring well locations and analyzed for the presence of microorganisms associated with reductive dechlorination: *dehalococcoides*, *dehalobacter* and *desulfuromonas*. The purpose of this sampling was to assess if the naturally occurring microorganism associated with reductive dechlorination are present and if the populations are large enough to suggest that reductive dechlorination is possible. Further, since *dehalococcoides* is the only known microorganism that degrades TCE to *cis*-DCE to VC, evaluating its presence will allow the investigators to determine if the aquifer has the potential to degrade TCE past *cis*-DCE.

RESULTS AND DISCUSSIONS

The following sections present the results of the monitoring and characterization completed to date. Given the level of data collection, only a portion of the data can be presented herein. Results from September 2006 and February 2007 were used for technology evaluation. These dates represent 10 weeks and 33 weeks following technology implementation/start-up. The discussions focus primarily on the deeper aquifer zone, where higher concentrations of TCE and *cis*-DCE are present.

Tracer and General Chemistry. Bromide tracer data indicate an ambient groundwater velocity on the order of 150 to 170 m/yr (500 to 550 ft/yr). The original design was based on (ZVI/EHC barrier) on a much lower anticipated flow rate of 80 to 100 m/yr. In

addition, groundwater monitoring from August to February indicated that groundwater temperatures ranged between 5°C to 8°C. This temperature range is much lower the temperature 8°C to 12°C provided at the time of PT design. The colder groundwater temperature reduces the kinetics of in situ chemical and biological treatment, and likely also increases the acclimation period for biological degradation.

Geochemical monitoring for ORP and DO show that geochemical conditions within the aquifer remain unchanged from upgradient to downgradient of each of the ZVI/EHC and hydrogen sparging reactive barriers and are predominantly aerobic (ORP typically 100 mV and DO ranging from 4 to 6 mg/L). Groundwater pH within the ZVI/EHC barrier was initially quite high (averaging 8.0 to 8.5) following injection of ZVI-EHC, but has decreased over time to near neutral pH of 6.5 to 7.5.

Microorganisms. Groundwater samples analyzed for the presence of microorganisms were obtained from PO-06-6A (deep), PO-06-11A (deep), PO-06-13 and PO-06-14 (see Figure 1). A significant population of *dehalobacter spp.* was detected at two of the four monitoring well locations (PO-06-6A and PO-06-14). This suggests biotic reductive dechlorination is possible at the site. However, because the chlorinated solvent degrading microorganisms populations are quite variable, continuous and consistent reductive dechlorination is not occurring. *Dehalococcoides spp.*, and *desulfuromonas spp.* were either not detected or not detected in significant quantities at any of the four (4) monitoring well locations. The absence of *Dehalococcoides spp.* indicates that a microorganism population is not present at the site that would allow for reductive dechlorination past *cis*-DCE.

Background (Upgradient) Monitoring Well Locations. The TCE concentrations at the deep, upgradient monitoring well locations PO-06-1A through PO-06-6A, while exhibiting some variability, have indicated conditions upgradient of PT cell have been reasonably consistent. TCE concentrations are generally higher at the south end of the PT cell, with TCE concentrations averaging ~150 µg/L at PO-06-1A (north end) and ~450 µg/L at PO-06-6A (south end) (Figure 2). Similar, but lower concentrations of *cis*-DCE, are detected at the upgradient monitoring well locations, with the ratio of TCE to *cis*-DCE averaging about 3. No VC was detected above the method detection limit of 0.05 µg/L. This indicates that degradation of TCE has stalled at *cis*-DCE upgradient of the PT cell.

Interior Monitoring Well Locations. The six interior monitoring wells form portions of Transects 1 and 2. Transect 1 is on the north side of the PT and Transect 2 is on the south site of the PT (Figure 1 and Figure 2). Concentrations of TCE exhibited a high degree of variability, but generally exhibited a decreasing trend over time. Between weeks 10 to week 33, the % TCE concentration reduction at the interior monitoring well locations ranged from 22% to 87% (Figure 2). The TCE reduction (based on September 2006 to February 2007) at the individual locations are as follows:

Transect 1 (North):

within ZVI/EHC barrier	PO-06-13: 61%	(150 µg/L to 59 µg/L)
downgradient of ZVI/EHC barrier	PO-06-15: 87%	(110 µg/L to 14 µg/L)
downgradient of H ₂ barrier	PO-06-17: 59%	(270 µg/L to 110 µg/L)

Transect 2 (South):

within ZVI/EHC barrier	PO-06-14: 22%	(180 µg/L to 140 µg/L)
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downgradient of ZVI/EHC barrier PO-06-16: 43% (350 µg/L to 200 µg/L)
downgradient of H₂ barrier PO-06-18; 54% (370 µg/L to 170 µg/L)

Similar reductions were noted for *cis*-DCE (see Figure 2). These data would indicate that both beta-elimination (in the presence of ZVI) and reductive dechlorination may be occurring simultaneously. However, given the decreases of both TCE and *cis*-DCE, the abiotic pathway (beta elimination) appears to be more substantial. VC was not detected above the method detection limit of 0.05 µg/L, indicating that degradation of TCE, if proceeding via reductive dechlorination, had stalled at *cis*-DCE.

Downgradient Monitoring Well Locations. The trend in TCE concentrations at the deep, downgradient monitoring well locations PO-06-7A through PO-06-12A were highly variable over the monitoring period. Generally, concentrations on the north side of the PT cell (PO-06-7A to PO-06-9A) show a decreasing trend from September 2006 to February 2007. Monitoring wells on the south side (PO-06-10A to PO-06-12A), tend to have higher concentrations compared to the north monitoring wells and either decrease or increased over the September 2006 to February 2007 monitoring period (Figure 2).

The distance from the ZVI/EHC barrier to the downgradient monitoring wells is approximately 30 m. With groundwater velocity estimated to be between 100 m/yr to 150 m/yr, groundwater originating at the ZVI/EHC barrier would take 10 to 15 weeks to reach the downgradient monitoring well locations. The change from high variability in TCE concentration at around week 12 to week 14 (data not shown) correlates well to when groundwater from the ZVI/EHC barrier would be anticipated at the downgradient monitoring wells. The general downward trend in TCE concentration observed between week 13 and week 23 could be indicative of groundwater that has migrated through the ZVI/EHC barrier now being detected at the downgradient monitoring well locations.

Following week 25, the concentration of TCE increases at two downgradient monitoring wells located at the south portion of the PT cell (PO-06-11A and PO-06-12A) (Figure 2). An evaluation of groundwater elevation data has shown that the direction of groundwater flow has shifted slightly from almost true east-to-west, to a slightly southeast-to-northwest direction. This may be a seasonal phenomenon. As noted for the upgradient monitoring wells, the highest TCE concentration is observed at the south portion of the PT cell. Therefore, the slight shift in groundwater flow direction is introducing TCE impacted groundwater that has not migrated through the treatment zone(s) in to the southwestern corner of the PT cell. If the TCE concentration data for PO-06A and PO-06-12A is removed from the concentration versus time graph, it becomes evident that there is less variability in the TCE concentration data and that a decreasing trend is evident at locations PO-06-7A and PO-06-9A starting from approximately week 10 (December 2006) and continuing to week 33 (February 2007) (Figure 2).

Hydrogen sparging was conducted for over three months. Performance monitoring downgradient of the hydrogen sparging barrier indicated a transient drop in ORP but no appreciable decrease in TCE or *cis*-DCE concentrations. Due to lack of dissolved organic carbon in the aquifer to support the hydrogen sparging effectiveness, hydrogen sparging was discontinued in December 2006. Given the distribution of transect wells and the variation in groundwater flow direction, it is difficult to discern the effectiveness of the hydrogen sparging system. Due to lack of performance the system was shut down.

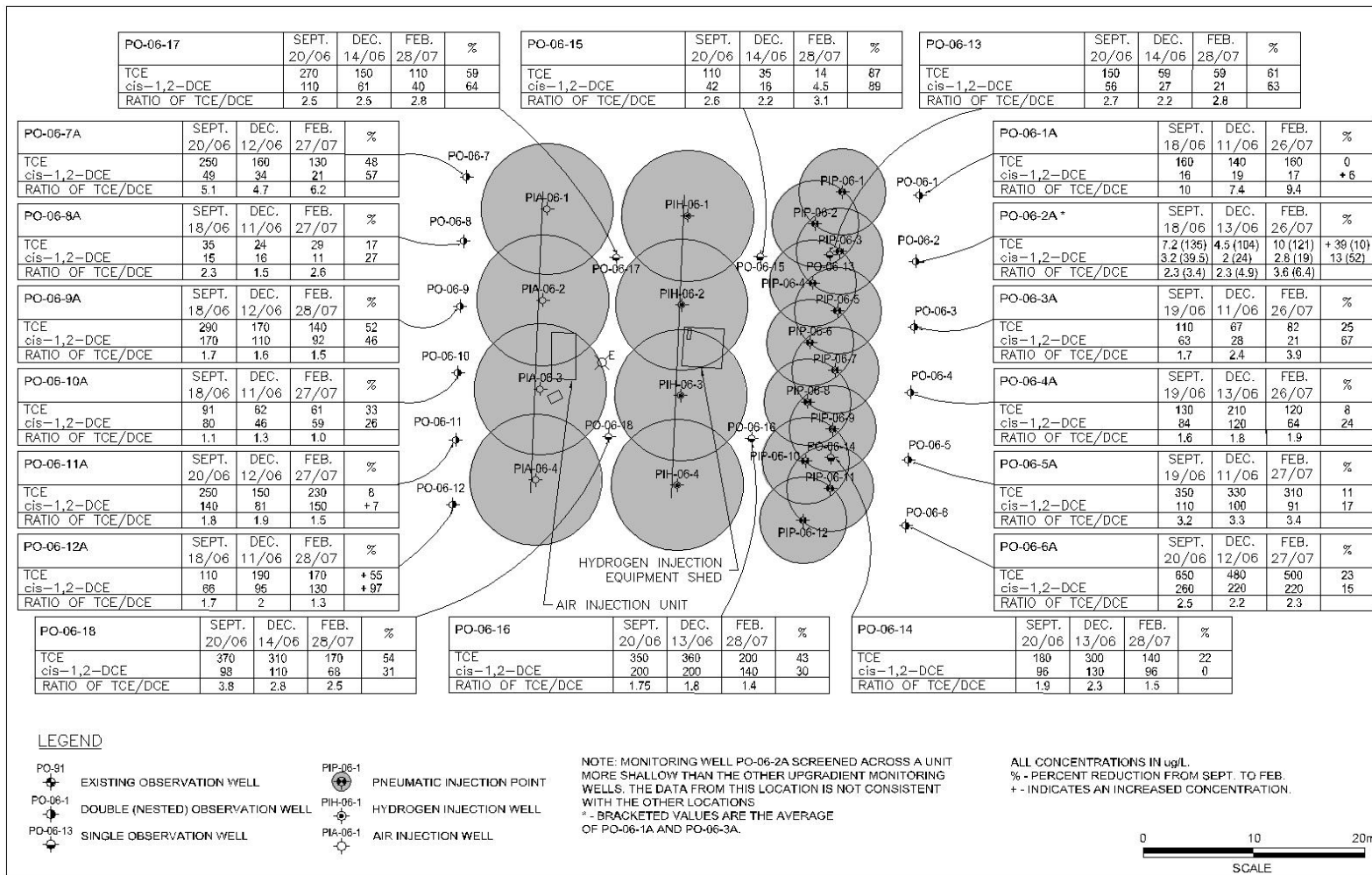


FIGURE 2. Concentrations of TCE and cis-DCE in September 2006 and February 2007.

Monitoring of the air sparging system appeared to be effective for increasing DO concentrations as downgradient wells were quite high (DO = 8 to 10 mg/L) and concentrations of TCE and *cis*-DCE appear lower in some downgradient monitoring wells compared with upgradient transect wells. This would indicate that air sparging is producing a non-uniform pattern, but maybe effective in decreasing TCE and *cis*-DCE concentrations.

CONCLUSIONS

Pilot test performance monitoring results have shown that in situ treatment with the multi-barrier approach has the capability of treating TCE and *cis*-DCE at rapid groundwater velocities and low groundwater temperatures provided sufficient mass of ZVI and EHC are available. The lower than anticipated groundwater temperature of 5°C to 8°C has resulted in a reduction in the that rate at which in situ chemical and biological treatment occurs and an increase in the acclimation period for biological degradation and higher groundwater velocities has resulted in less contaminant removal than expected. It is anticipated that concentrations will continue to decline slowly over time as microbial populations continue to grow and populate the EHC carbon source even at these low temperatures.

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