

# *In Situ* Remediation of PCE at a Site With Clayey Lithology and a Significant Smear Zone

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Groundwater at the former Serry's Dry Cleaning site in Corvallis, Oregon, was impacted by chlorinated volatile organic compounds (CVOCs). The primary CVOCs impacting the site include tetrachloroethene, trichloroethene, dichloroethene, and vinyl chloride, which were detected at concentrations up to 22,000, 1,700, 3,100, and 7 µg/L, respectively, prior to treatment. Large seasonal fluctuations in groundwater CVOc concentrations indicated that a significant fraction of the CVOc mass was present in the smear zone. Field-scale pilot tests were performed for the Oregon Department of Environmental Quality's Dry Cleaner Program to evaluate the performance of EHC<sup>®</sup> in situ chemical reduction (ISCR) technology. The pilot study involved evaluating field performance and physical distribution into low-permeability soil using basic Geoprobe<sup>®</sup> injection tooling. The testing results confirmed that bioremediation enhanced by ISCR supported long-term treatment at the site. This article describes the implementation and results of the tests. Performance data are available from a three-year period following the injections, allowing for a discussion about sustained performance and reagent longevity. © 2010 Wiley Periodicals, Inc.

## INTRODUCTION

EHC<sup>®</sup> combines controlled-release, hydrophilic organic carbon with micro-scale zero-valent iron (ZVI) for *in situ* chemical reduction (ISCR) of chlorinated compounds in groundwater. Following the placement of EHC into the subsurface, various physical, chemical, and microbiological processes combine to create strongly reducing conditions that stimulate rapid dechlorination of many oxidized compounds, such as chlorinated ethenes, ethanes, and other chlorinated solvents. This typically yields safe, rapid, and effective destruction of targeted contaminants without the accumulation of conventional, dead-end intermediates. EHC degrades chlorinated ethenes through a combination of both biotic and abiotic pathways, including dehalogenation, beta-elimination, and hydrogenation.

*In situ* remediation of low-permeability soils using EHC or any other reagent is often complicated by at least two factors: (1) clayey formations generally contain a higher proportion of constituents sorbed to the soil matrix, and (2) it is often difficult to achieve effective distribution of remedial reagents in tight soils. As a result, contaminant destruction is often limited and concentration rebounds are commonly observed. Use of rapid-releasing and short-lived reagents under these conditions can further exacerbate

these challenges. Once the reagent has been consumed, further desorption of chlorinated volatile organic compounds (CVOCs) still present in the soil will predictably recontaminate the groundwater. Because degradation reactions are aqueous-based, removal kinetics are ultimately limited by desorption rates, and total removal rates are hence largely governed by the longevity of the remediation reagent. Data from the Serry's site confirm an effective EHC lifespan of at least three years. Hence, successful long-term treatment of the site's clayey formation was achieved despite what could be viewed as "non-uniform, non-homogenous" distribution.

Long-term monitoring suggests that diffusion, advection, and dispersion serve to enhance the effective distribution of reagent constituents in the subsurface and provide treatment well beyond these fractures.

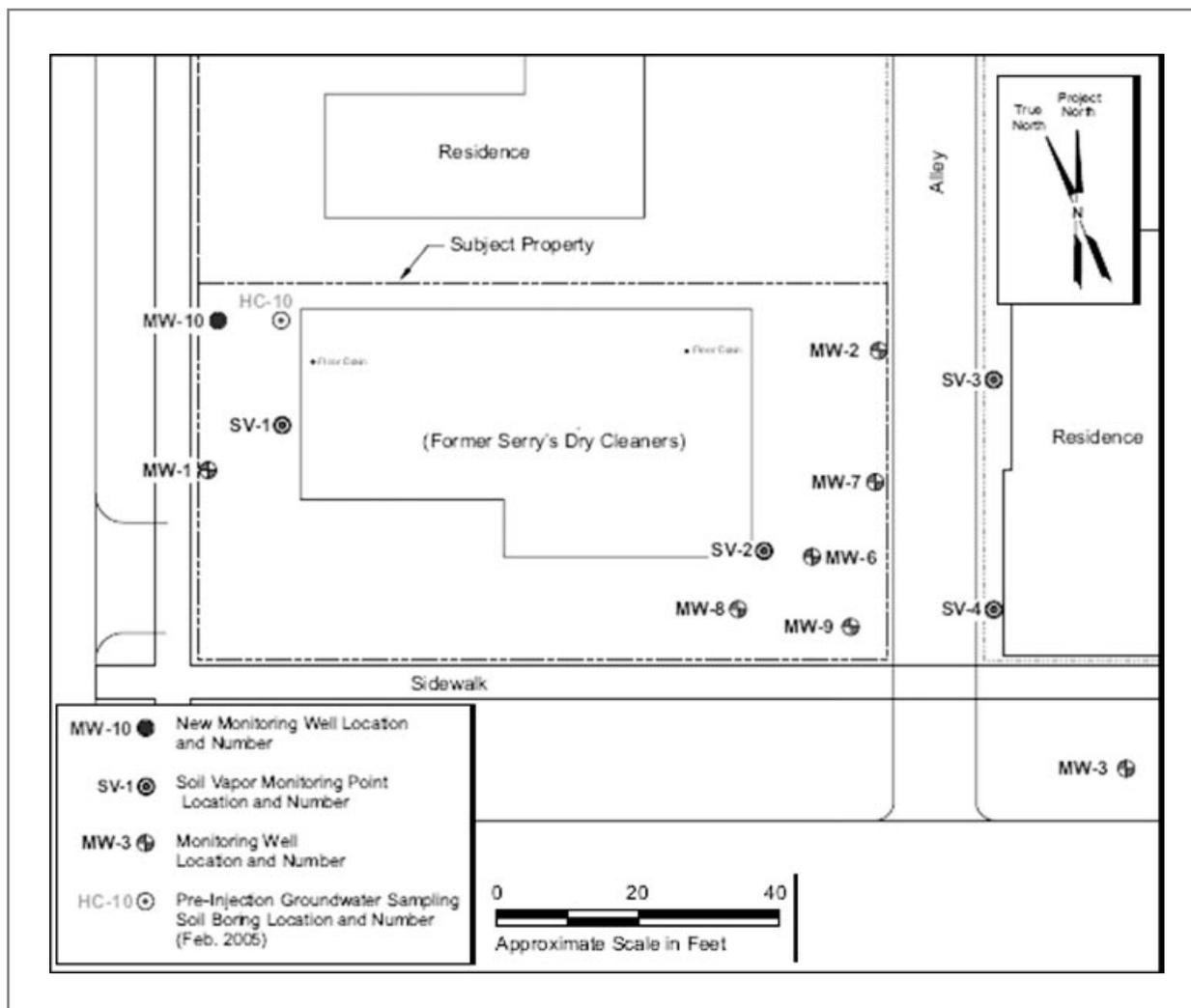
When injected under high pressure, EHC slurry has been observed to displace into discrete fractures in the soil matrix. Long-term monitoring suggests that diffusion, advection, and dispersion serve to enhance the effective distribution of reagent constituents in the subsurface and provide treatment well beyond these fractures. These same processes, and others, transport CVOCs to the reactive sites. As a result, homogenous distribution of EHC into the soil matrix is not required for effective treatment, as may be required for other reagents.

Field-scale pilot tests were performed for the Oregon Department of Environmental Quality's (DEQ's) Dry Cleaner Program to evaluate the performance of EHC. The pilot study involved evaluating field performance and physical distribution into low-permeability soil using basic Geoprobe® injection tooling. The primary goal of the pilot-scale treatment was to reduce the concentration of CVOCs in soil and groundwater around a suspected hotspot. This hotspot may have historically contributed to indoor air vapor intrusion at the site and adjacent residences.

## SITE BACKGROUND

The former Serry's Dry Cleaning site is located in Corvallis, Oregon. Serry's Dry Cleaning operated from 1978 until 2001. The building is now occupied by a commercial vendor. The primary CVOCs found at the site prior to treatment included tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC) at concentrations up to 22,000, 1,700, 3,100, and 7 µg/L, respectively. The Serry's site was accepted into the DEQ's Dry Cleaner Environmental Response program in July 2001.

The groundwater table fluctuates heavily in the study area, and the groundwater flow direction at the site changes with seasonal conditions; however, it primarily flows toward the southeast during the summer and to the northwest during the rainy season. The groundwater table ranges from approximately 7 feet (2.1 meters) below ground surface (bgs) during the rainy season to as low as 15 feet (4.6 meters) bgs during the summer. The groundwater flow velocity is unknown but assumed to be low due to the type of soils at the site and the shallow hydraulic gradients measured. The lithology at the targeted depth interval at the site is composed of interbedded layers of sandy silt and silty clay. There is no confirmed source of PCE at the site. However, groundwater concentrations suggest two hotspots: (1) the northwest corner (proximal to HC-10; Exhibit 1), and (2) the southeast corner of the building (proximal to MW-6). Large seasonal fluctuations in groundwater CVOC concentrations suggest that high levels of CVOCs are sorbed to the smear zone within the study area. For discussion purposes, project north has been set parallel to an adjacent street. As the building is currently occupied, access is difficult to



**Exhibit 1.** Site plan with monitoring locations

obtain. Therefore, groundwater, soil, or soil gas monitoring has not been conducted below the building, and the possibility of a source area under the building could therefore not be excluded.

## PILOT STUDY

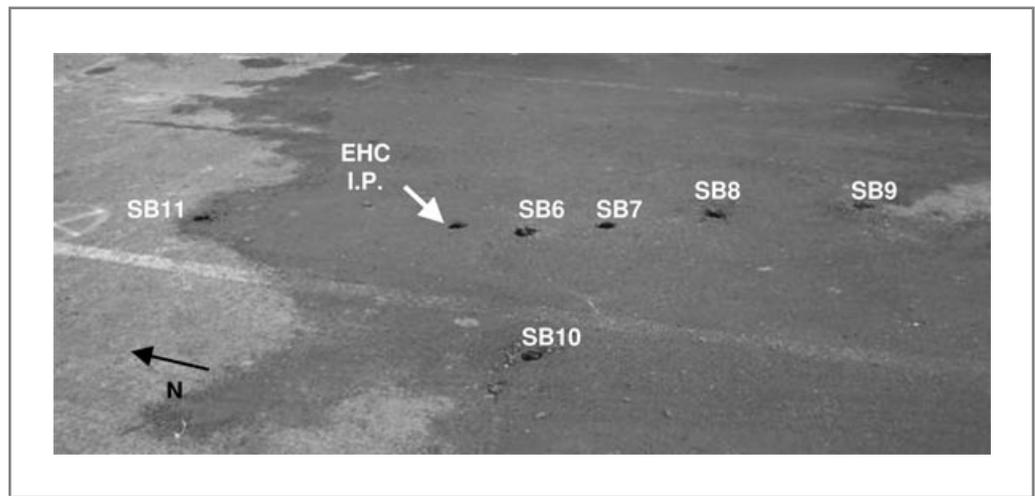
A small test injection was conducted in December 2005 to evaluate the effectiveness of direct-push methods in distributing EHC in the low-permeability soils. The larger-scale field implementation was conducted in August 2006.

### *Test Injection*

A total of 450 lbs (204 kg) of EHC was injected from 13 to 25 feet (4.0 to 7.6 meters) bgs as a 30 percent slurry. The EHC slurry was injected into four discrete layers spaced 4 feet (1.2 meters) apart using GeoProbe's pressure-activated injection tip, with 38 gallons



**Exhibit 2.** Injection tip

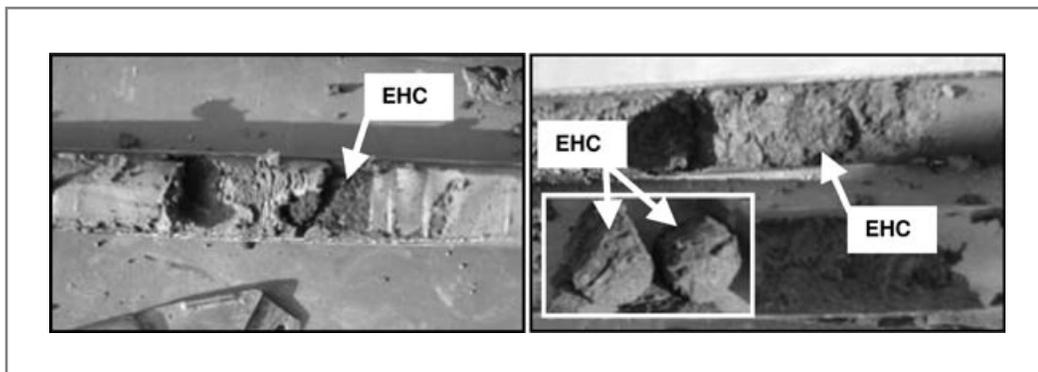


**Exhibit 3.** Soil sampling locations around EHC injection point

(144 liters) of slurry injected into each layer (total injection volume of 152 gallons [575 liters]). This injection tip has four openings at the sides, which serve to direct the slurry horizontally (Exhibit 2). Furthermore, the injections were conducted in a top-down fashion to ensure vertical distribution. A high-pressure pneumatic grout mixing and pumping system was used to mix and pump the EHC to the injection tip. Six soil cores were obtained around the injection point (from 0.5 to 5 feet [0.15 to 1.5 meters]) from the injection point to assess the radius of influence of the injection (Exhibit 3). EHC fractures were found at the farthest sampling points indicating that the radius of influence was up to at least 5 feet (1.5 meters). Both horizontal and vertical fractures were observed in the soil cores, suggesting that the slurry penetrated horizontally a certain distance but will eventually rise toward the surface. This rise ultimately limits the radius of influence around each point and the volume that could be injected into each point before surfacing of the slurry occurs. Exhibit 4 shows some of the EHC bands or fractures observed in the soil cores.

The following lithology was observed from the soil sampling:

- brown sandy, clayey silt from 8 to 20 feet (2.4 to 6.1 meters) bgs;
- stiff brown silty clay from 20 to 22 feet (6.1 to 6.7 meters) bgs;



**Exhibit 4.** Soil cores showing horizontal (left) and vertical (right) EHC fractures (darker material)

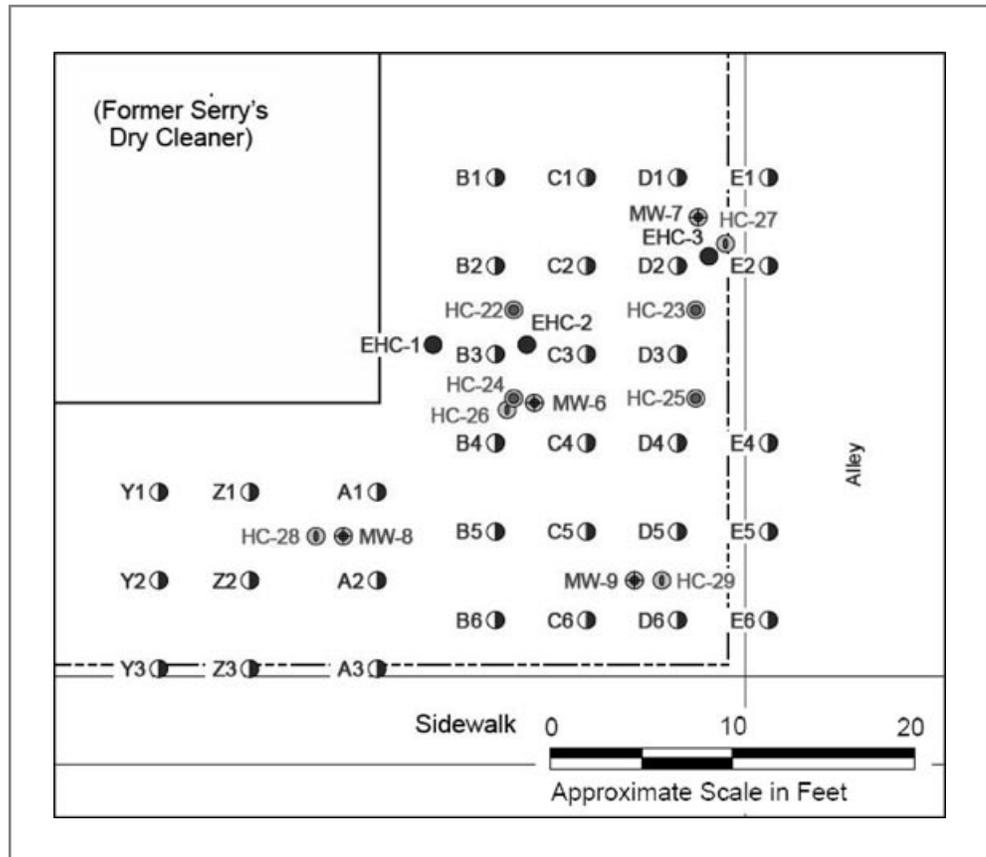


**Exhibit 5.** Grout mixing unit CG-500

- stiff gray clay below 22 feet (6.7 meters) bgs; and
- water-bearing and loose sand layers were encountered at approximately 26 feet (7.9 meters) bgs.

### ***Full-Scale Implementation***

In August 2006, a total of 10,250 lbs (4,649 kg) of EHC was injected into an area measuring approximately 825 square feet by 20 feet deep (from 10 to 30 feet bgs) (77 square meters by 6.1 meters deep [from 3.0 to 9.1 m bgs]), which resulted in an average application rate of 0.6 percent to soil mass and a product cost of approximately \$1.24 per cubic foot (\$44 per cubic meter) of treated soil. The EHC was supplied as a dry powder in 50-lb (22.7-kg) bags and mixed with water onsite into slurry containing about 29 percent solids (Exhibit 5). Using conventional direct-push technology, the EHC slurry was injected at 3 to 6 gallons per minute (GPM) (11 to 23 liters per min [L/min]) at a pressure of approximately 200 to 400 pounds per square inch (psi) (14 to 28 bar). The depth interval targeted was from the groundwater table (approximately 10 feet [3.0 meters] bgs) to approximately 30 feet (9.1 meters) bgs, where a less permeable layer was encountered. The EHC was injected in discrete layers using the Geoprobe pressure-activated injection tip and high-pressure grout mixing unit.



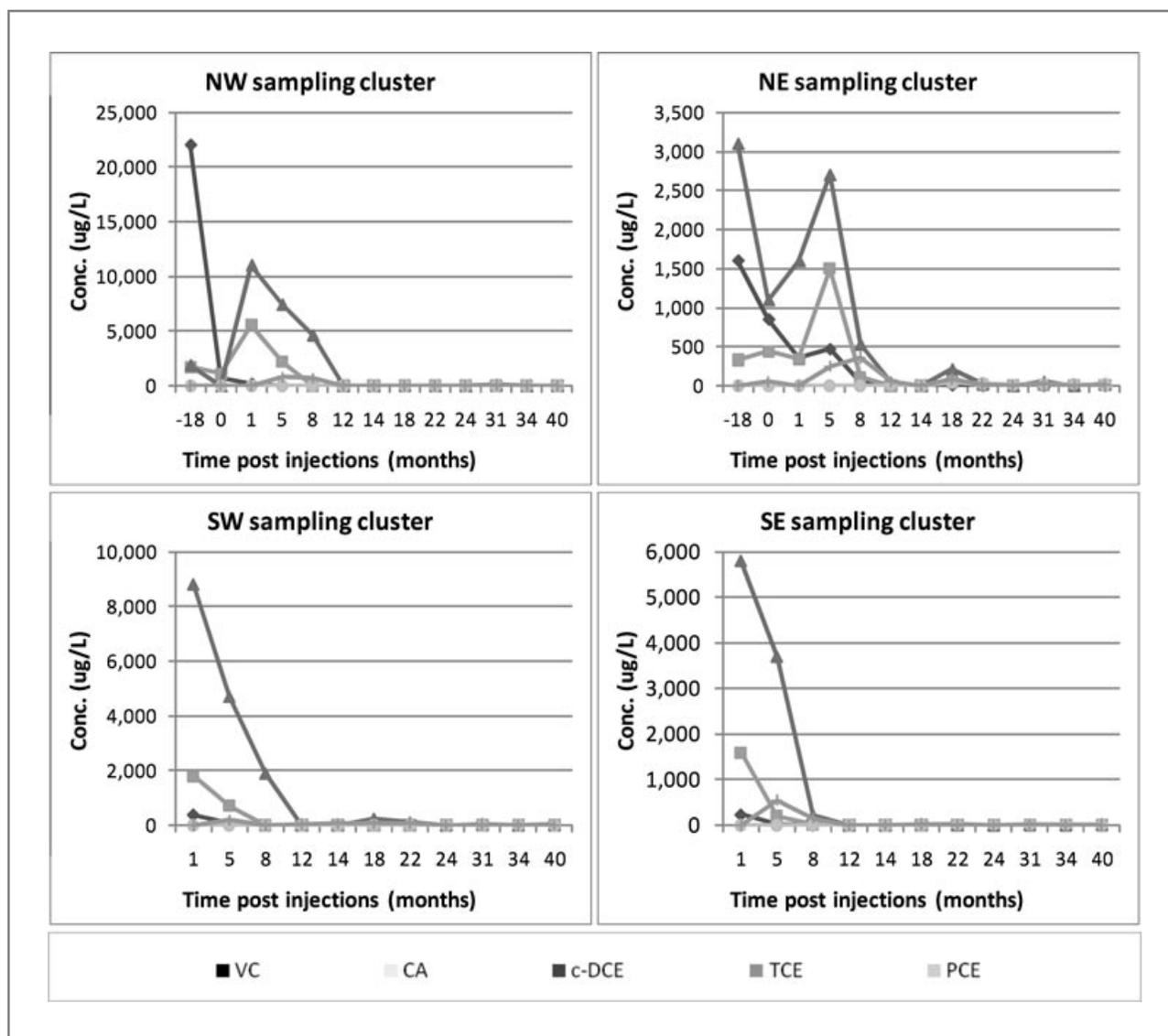
**Exhibit 6.** EHC injection locations, groundwater sampling locations, and monitoring wells

The EHC was added to a total of 32 injection points (Exhibit 6), including nine additional points south of the building. The additional points were added due to issues with surfacing: it was not possible to achieve the originally planned application rate of 1 percent to soil mass in the tight soil formation at the targeted flow rate of approximately 5 GPM (19 L/min) due to pressure buildup in the subsurface. The treatment area was therefore increased, resulting in a lower application rate of 0.6 percent to soil mass within the treatment area. In addition, a relatively tight injection spacing of 5 feet (1.5 meters) was used for the EHC injections based on the results from the test injection. Approximately 18 lbs (8.2 kg) of EHC were added per vertical foot on average. The injection work was completed in five days.

Exhibit 6 also shows the locations of four new monitoring wells (MW-6 to MW-9) installed in January 2007, four months following full pilot injections. Previous monitoring performed in February 2005 and August and September 2006 was conducted via direct-push probe exploration locations (HC-22 to HC-29). Nearby direct-push borings are therefore used as baselines for the data evaluation presented in the next section.

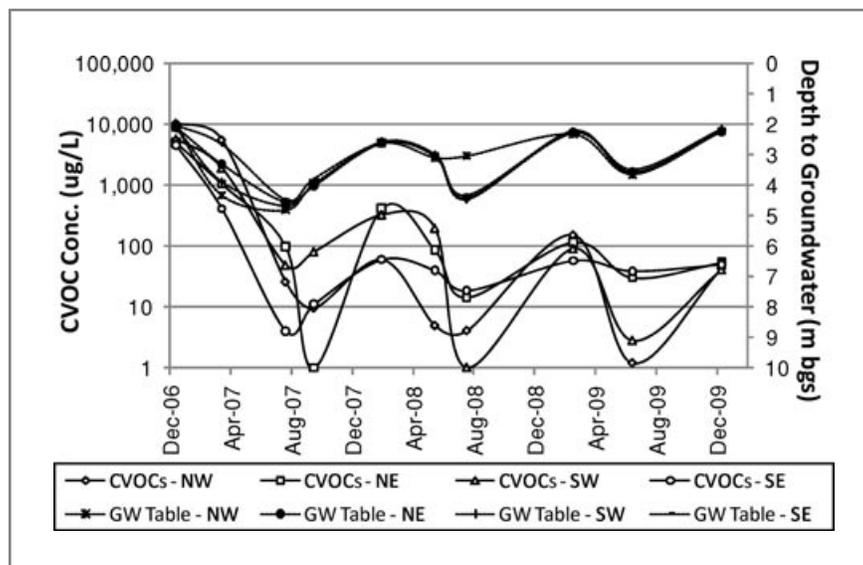
## PILOT STUDY RESULTS

Following injection of EHC into a suspected source area, PCE was decreased to below the detection limit of 1 µg/L and total CVOCs decreased from a maximum of 25,606 µg/L



**Exhibit 7.** Concentration of CVOCs measured at the four sampling clusters within the pilot study area

to below 100  $\mu\text{g/L}$  at all locations within 12 months (Exhibit 7). The PCE degradation resulted in an initial buildup of TCE, DCE (primarily *cis*-1,2-DCE), and VC, indicating that sequential dehalogenation was occurring (biological pathway). However, conversion rates were less than stoichiometric, and concentrations of all constituents appeared to decrease simultaneously, suggesting that abiotic treatment mechanisms also occurred at significant rates. Observed generation of VC was limited, indicating that abiotic beta-elimination was a significant pathway for *cis*-1,2-DCE degradation. A smaller concentration of chloroethane (CA) was also observed (maximum concentration of 44  $\mu\text{g/L}$  measured in February 2008—18-month data), suggesting that hydrogenation might also be occurring, although not likely at a rate significant for overall chloroalkene removal at the site. The pathway of CA formation is hypothesized to be hydrogenation of VC to form CA (i.e., addition of two hydrogen atoms and converting the carbon double



**Exhibit 8.** Total CVOCs and depth to groundwater

bond to a single bond). No 1,2-dichloroethane (DCA) or any other more highly chlorinated alkanes have been detected in samples from any of the site wells.

Historically, CVOC concentrations in groundwater fluctuate heavily with the seasons in the study area. Exhibit 8 shows the groundwater elevation and total CVOC concentrations (PCE plus daughter products including CA) measured since the well installations. Transient rebound was observed during the rainy season (18-month data), presumably due to the introduction of CVOCs from the smear zone as a result of a six- to seven-foot (1.8- to 2.1-meter) increase in the groundwater table. While the groundwater table remained high through June 2008 (22-month data), total CVOC concentrations decreased, suggesting continued treatment via resident, active EHC. By August 2008 (dry season), PCE and TCE both decreased to below the detection limit of 1 µg/L at all locations. The rebound observed during the following wet seasons has become smaller with each year following the EHC injection, suggesting that seasonal treatment of the smear zone is also being achieved. As desorption is promoted during the high groundwater table, the CVOCs become available for degradation. During the March 2009 sampling event, total dissolved CVOC concentrations decreased by 64 percent from the previous wet season (a maximum of 150.9 µg/L was measured in March 2009, as compared to a maximum of 417.5 µg/L measured in February 2008). In the latest sampling event conducted in December 2009 (high groundwater table), total dissolved CVOCs were measured at a maximum concentration of 63.1 µg/L, which represents an additional 58 percent decrease from the March 2009 data.

The distribution of CVOCs has shifted over time, with *cis*-1,2-DCE followed by CA and VC currently being the dominating constituents. CA was measured at a maximum concentration of 15.7 µg/L during the most recent sampling event and now comprises approximately 25 percent of total CVOCs, suggesting that abiotic hydrogenation has become a significant degradation pathway for VC removal. Acetylene was included in the March 2009 sampling schedule to verify the occurrence of abiotic beta-elimination. However, due to the transient nature of acetylenes, it was not detected above the

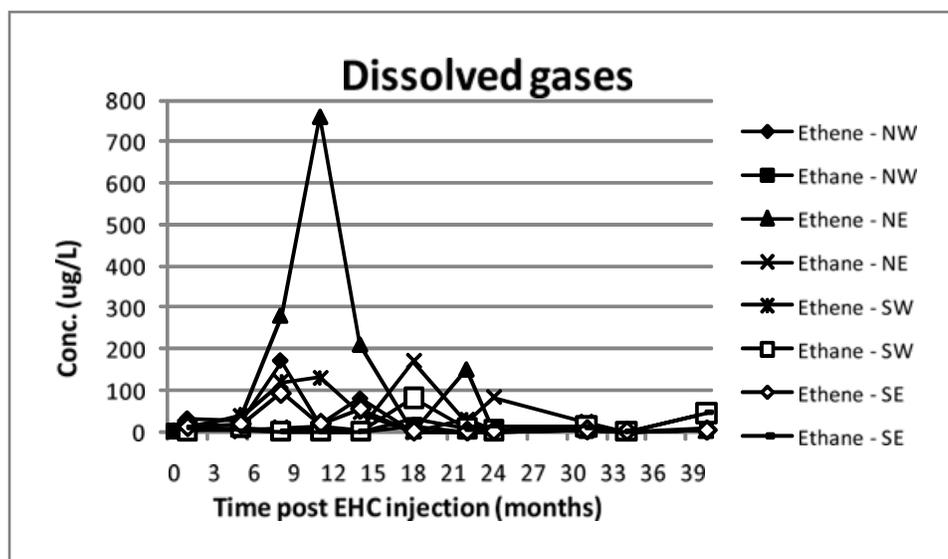


Exhibit 9. End products

detection limit of 10  $\mu\text{g/L}$  in any of the wells. It has therefore not been possible to directly quantify the proportion of CVOCs undergoing abiotic beta-elimination.

### Dehalogenation End Products

An increase in ethene and ethane levels confirms that complete dehalogenation is occurring at the site without any microbial addition (Exhibit 9). Ethene levels of up to 760  $\mu\text{g/L}$  were measured in July 2007 (11-month data), which constitutes an increase of 96 percent compared with the maximum concentrations measured in August 2006. As total dissolved concentrations of chlorinated ethenes decreased within the treatment zone, the concentration of dissolved ethene and ethane has also decreased. However, concentrations of ethane have generally remained above baseline levels, suggesting that a small mass of adsorbed CVOCs remain and that degradation is still ongoing. A spike in ethane concentrations was observed during the rainy seasons (18-month and 40-month data), as CVOCs sorbed to the smear zone entered the system and became available for dehalogenation. During the 2009 dry season (34-month data), ethene and ethane were below the detection limit of 0.5  $\mu\text{g/L}$  in all wells, which is consistent with the very low CVOC concentration measured in groundwater during this time. A correlation has been observed between total CVOC concentrations and ethene plus ethane measured in groundwater, following an initial acclimatization period of seven months.

### EHC Indicator Parameters

To assess whether the wells are in fact under the EHC zone of influence, the groundwater was sampled for total dissolved organic carbon (TOC) and ferrous iron (Fe(II)). A significant increase was observed at all sampling locations, confirming that successful product placement and sufficient distribution had been achieved. TOC and Fe(II) have been detected at maximum concentrations of 2,800 and 130 mg/L, respectively.

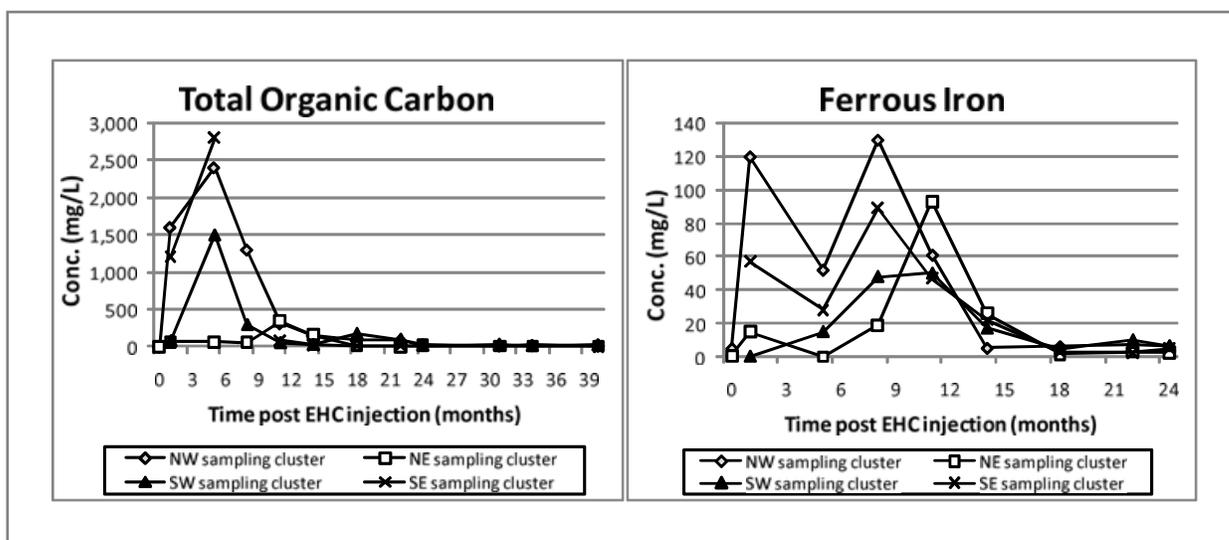


Exhibit 10. EHC breakdown products

Dissolved concentrations have gradually decreased over time and returned closer to background levels (Exhibit 10). However, TOC levels appear to have stabilized slightly above the baseline range of less than 0.8 to 1.8 mg/L; by the latest sampling event conducted 40 months after installation, TOC was measured at concentrations ranging from 3.3 to 18.6 mg/L. Fe(II) has not been included in the monitoring schedule after 24 months.

### Redox Indicator Parameters

Following the EHC injections, the oxidation-reduction potential (ORP) decreased within the injection zone. Sulfate concentrations decreased from a baseline concentration range of 7 to 34 mg/L to below the detection limit of 0.1 mg/L, suggesting that sulfate-reducing conditions were established within the injection zone. Furthermore, a concurrent increase in methane suggests methanogenic conditions were achieved, and dissolved hydrogen gas was available for complete biotic dehalogenation (Exhibit 11). The fluctuations observed in ORP indicate that the redox conditions may also be affected by the shifts in the groundwater table, hydraulic gradients, and infiltration of seasonal precipitation.

During high-precipitation periods, water levels rise and gradients become steeper across the site. This results in an interesting pattern of data at the site, including simultaneous reductions in methane concentration, increases in PCE and TCE concentrations, and declines in ORP. This seemingly contradictory set of data is likely the result of a system temporarily out of homeostasis. Changing groundwater gradients and infiltration of precipitation introduce competing electron acceptors, such as dissolved oxygen, nitrate, and sulfate, which consume available dissolved hydrogen, resulting in methanogenesis stall. Some combination of methane oxidation and migration reduce methane concentrations. Concurrently, rising water levels contact residual vadose-zone CVOCs and corroding ZVI, resulting in an increase in dissolved CVOC levels and a decrease in ORP.

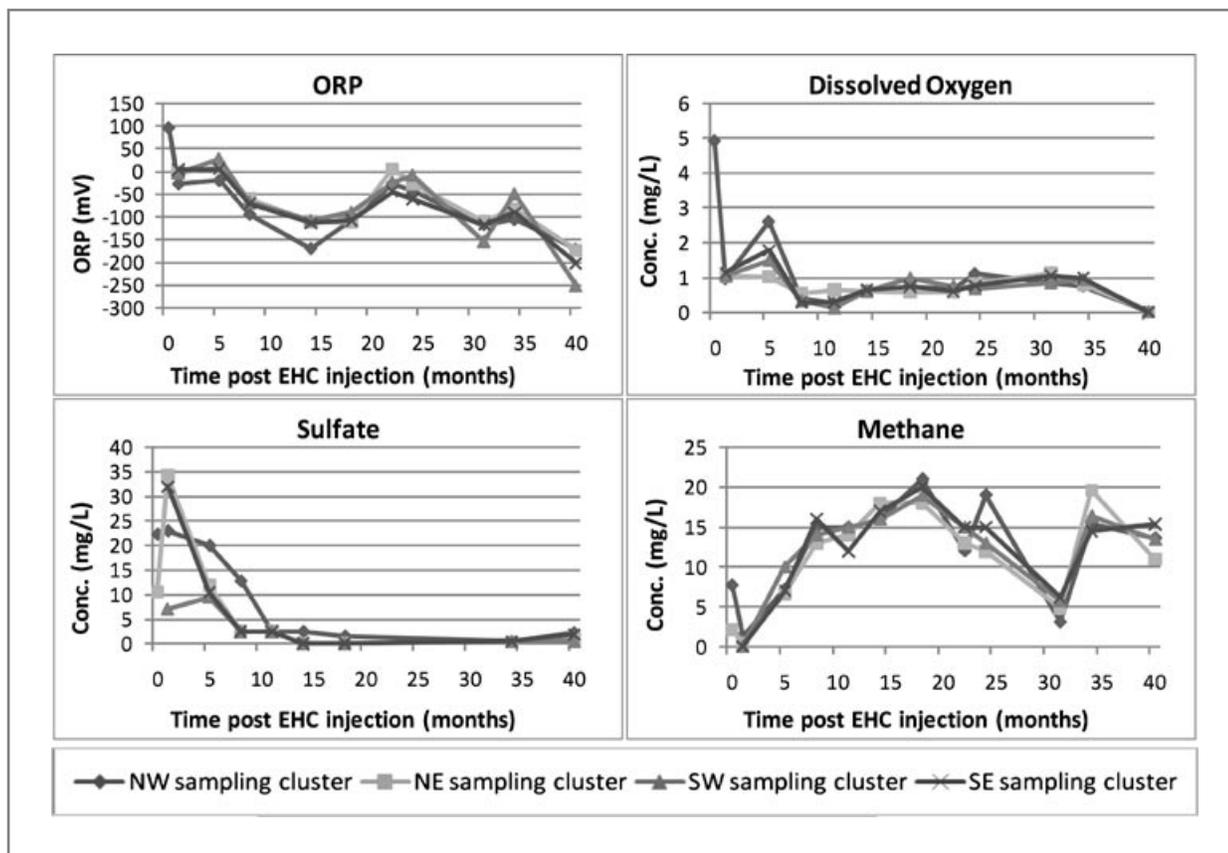


Exhibit 11. Effect on redox indicator parameters

## DISCUSSION AND CONCLUSIONS

EHC was successfully injected into the low-permeability formation using a high-pressure grout pump and conventional direct-push equipment. Via physical evaluation, it was confirmed that the slurry displaced into discrete fractures in the subsurface. Observed removal efficiency exceeded 99 percent of total CVOCs, confirming that sufficient and effective distribution was achieved. Diffusion is expected to be the primary hydrogeological factor supporting distribution, considering the low-permeability formation and expected slow groundwater velocity.

Over three years following the injections, redox indicator parameters suggests that reducing conditions are being maintained within the injection zone; ORP, DO, and sulfate are still significantly below baseline, and methane concentrations remain elevated.

Although dissolved concentrations of EHC breakdown products (TOC and Fe(II)) have gradually decreased over time and are now close to background levels, it appears that CVOC degradation is still ongoing, as evidenced by elevated levels of degradation end-products during the rainy season. Furthermore, the transient rebound observed during the latest wet season was generally much smaller than the previous years, suggesting that treatment of the smear zone is being achieved as desorption is being promoted.

The distribution of CVOCs has shifted, with *cis*-1,2-DCE, CA, and VC currently being the dominating dissolved fractions. The distribution of degradation products

suggests that abiotic hydrogenation is becoming a more significant degradation pathway as TOC levels are declining. The presence of *cis*-1,2-DCE and VC indicates that sequential reductive dehalogenation of PCE and TCE is also occurring but at a relatively lower rate than initially.

In conclusion, the EHC injections have promoted long-term treatment at the site in both saturated and seasonally saturated intervals. This treatment is the result of several CVOC destruction pathways that continue to remain active three years after the initial injections. As a result, despite large seasonal variations in groundwater elevation, significant rebound has been avoided.

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**Troy Fowler** (troy.fowler@hartcrowser.com) received his BS in biochemistry from the University of Kansas in 1999. He has eight years of experience designing, implementing, and interpreting performance of various bioremediation projects. He has assisted both private and governmental interests with dozens of projects that have effectively applied a broad range of innovative technologies. He specializes in remediation of chlorinated solvents based on site- and project-specific considerations.

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