Successful ISCR-Enhanced Bioremediation of a TCE DNAPL Source Utilizing EHC® and KB-1®

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Remediation of chlorinated solvent DNAPL sites often meets with mixed results. This can be attributed to the diametrically opposed nature of the impacts, where the disparate dissolved-phase plume is more manageable than the localized, high-concentration source area. A wide range of technologies are available for downgradient plume management, but the relative mass of contaminants in a DNAPL source area generally requires treatment for such technologies to be effective over the long term. In many cases, the characteristics of DNAPL source zones (e.g., depth, soil heterogeneity, structural limitations) limit the available options. The following describes the successful full-scale implementation of in situ *chemical reduction (ISCR) enhanced bioremediation of a TCE DNAPL source zone. In this demonstration, concentrations of TCE were rapidly reduced to below the maximum contaminant level (MCL) in less than six months following implementation. The results described herein suggest that ISCR-enhanced bioremediation is a viable remedial alternative for chlorinated solvent source zones. © 2010 Wiley Periodicals, Inc.*

INTRODUCTION

The case for remediation of dense, nonaqueous-phase liquid (DNAPL) source zones is an open question. In particular, treatment (as opposed to containment) of relatively deep chlorinated-solvent DNAPL sources is complicated by uncertainty related to physical, chemical, logistical, and economic factors. These uncertainties were highlighted in recent publications (Sale et al., 2008), and older references (Kavanaugh et al., 2003; NRC, 2004) question the viability and practicality of remediating DNAPL source zones. The consensus appears to be that *in situ* remediation of chlorinated-solvent DNAPL source zones achieves varying levels of success, but the benchmark of maximum contaminant levels (MCLs) established by the U.S. Environmental Protection Agency remains elusive, thereby often requiring alternative definitions of success.

Individually or in combination, *in situ* chemical reduction (ISCR) and enhanced anaerobic microbial degradation are recognized, well-established technologies for remediation of chlorinated-solvent plumes downgradient of source areas. Chlorinated-solvent DNAPL source areas are often treated with technologies that are resource-intensive (e.g., electric resistive heating), incompatible with operating facilities (e.g., removal), or unpredictable (e.g., surfactant flushing, neat or emulsified oil

Published online in Wiley Interscience (www.interscience.wiley.com). DOI: 10.1002/rem.20251

sequestration). Containment options for source areas are typically better suited to unoccupied facilities with generally accessible DNAPL sources. The subject property described in this article involved with a deep (40 to 110 feet below ground surface [bgs]) trichloroethene (TCE) DNAPL source area that effectively limited options to an *in situ* remedy that relied on reductive dechlorination.

EHC® is a hydrophilic carbon/zero-valent iron (ZVI) blend that promotes degradation of aliphatic hydrocarbons via microbial ("classic" sequential dechlorination) and abiotic (ZVI-induced hydrogenolysis) pathways. EHC is manufactured by Adventus Americas Inc. (Freeport, Illinois). KB-1® is a mixed consortium of anaerobic bacteria, including *Dehalococcoides* ethanogenes (*Dhc*), provided by SiREM of Guelph, Ontario, Canada. Prior to this project, injection of EHC had not been attempted at depths corresponding to those presented at this site. Similarly, EHC and KB-1 had not been field tested at sites with TCE concentrations characteristic of the presence of DNAPL.

Field data confirm successful installation and performance of the remedy and suggest that both abiotic and microbial pathways are effecting TCE DNAPL mass removal.

Previous reports have documented the progress for this site, from a comparative bench test of various technologies through field pilot testing of ISCR technology (Peale et al., 2008). This article describes the full-scale implementation of ISCR-enhanced bioremediation and describes data collected for the year following commencement of implementation. In short, the remedial action objective (RAO) for the source area (TCE concentrations below 1 percent of the solubility limit, or 11,000 μg/L) was achieved in less than 12 months following the initiation of the remedy, with several monitoring points demonstrating TCE concentrations below the US EPA MCL (5 μg/L). Field data confirm successful installation and performance of the remedy and suggest that both abiotic and microbial pathways are effecting TCE DNAPL mass removal. These results provide an alternative perspective to the documents referenced earlier—ISCR-enhanced bioremediation of deep chlorinated-solvent DNAPL is potentially practicable.

SITE BACKGROUND

The site is an operating facility in Portland, Oregon, adjacent to the Willamette River. Industrial operations at the facility began in 1980, after the site had been developed by filling during the 1970s. Prior to filling and development, portions of the property were used for waste disposal from a manufactured gas plant (MGP). The MGP waste stream included petroleum hydrocarbon DNAPL, which was incorporated into the fill, along with spent oxide waste, dredged sediment, and quarry spoils. The legacy MGP impacts will be addressed in the future and are not the subject of this article.

Industrial operations at the facility included the use of TCE from approximately 1980 to 1989. TCE and/or TCE-containing wastewater were released to the subsurface, roughly between 1980 and 1984, but the exact date and volumes are unknown. The releases likely occurred immediately upgradient of the primary manufacturing building, which covers most of the groundwater plume between the source area and the riverbank (Exhibit 1). Groundwater flows from the upland under the river, with a small portion of the impacted plume intersecting transition-zone water and surface water in the river.

Direct-push investigation in the source area showed that dissolved-phase concentrations of TCE and *cis*-1,2-dichloroethene (*cis*-DCE) ranged as high as 592,000 and 90,000 μg/L (respectively) at depths ranging from approximately 50 to 110 feet bgs.

Exhibit 1. Site map and approximate extent of TCE in groundwater

Concentrations of TCE and DCE in monitoring wells ranged as high as 259,000 μg/L and 142,000 μg/L, respectively. Concentrations of the other DCE isomers and vinyl chloride were orders of magnitude lower; the relatively high concentrations of *cis*-1,2-DCE suggested the presence of a native consortium capable of TCE transformation, but not complete sequential dechlorination and mineralization. TCE DNAPL was not encountered, but the concentrations and depth of the impacts suggested that DNAPL was or had been present (US EPA, 1993).

The soil in the source area consists of fill (from 0 to 25 feet bgs), underlain by silt (about 25 to 50 feet bgs), silty sand (to about 170 feet bgs), and gravels and cobbles (to about 200 feet bgs), underlain by basalt characteristic of the Columbia River Basalt deposits. Significant soil and groundwater legacy impacts, including petroleum hydrocarbon DNAPL, are present throughout the fill and alluvial units, and are being addressed by other responsible parties. Groundwater flow velocities in the source area are estimated to be on the order of 0.1 to 0.2 foot/day, and increase downgradient by a factor of approximately 10.

Exhibit 2. Pilot study results

Well ID	Group	Location	Date	TCE (μg/L)	*cis*-1,2-DCE (μg/L)	Vinyl Chloride (μg/L)
WS-19-101	1	PRB	6/27/2006	92,900	39,100	22.2
WS-19-101	1	PRB	11/14/2008	**0.59**	16.4	45.6
WS-19-71	1	PRB	6/27/2006	6,500	88,400	29.5
WS-19-71	1	PRB	11/14/2008	28.4	115	140
WS-18-101	2	DNG	6/28/2006	198,000	33,600	40.6
WS-18-101	2	DNG	11/14/2008	603	71,300	40,500
WS-18-71	2	DNG	6/27/2006	7,990	90,800	25.8
WS-18-71	2	DNG	11/14/2008	**0.81**	688	8,620

Bold indicates US EPA MCL achieved.

PRB—Injection Zone.

DNG—Downgradient.

AMENDMENT SELECTION

Unlike some abandoned or inactive Brownfield sites, the source area at this site is located in the middle of an operating silicon wafer fabrication facility. During the initial technology screening, a variety of remedial technologies were evaluated and eventually discarded due to incompatibility with facility operations, or the presence of legacy MGP-related impacts. For example, thermal technologies were found to be incompatible with temperature-sensitive subsurface piping. Source removal via excavation was precluded by the operating structures and the depth (approximately 100 feet below ground surface) of the source. *In situ* oxidation technologies were identified as likely compromised by the presence of MGP-related impacts. Surfactant-based approaches were complicated by the limited recovery footprint (including the fabrication building) and the potential liability associated with mobilizing DNAPL. The technology screening left ISCR as the most viable DNAPL source removal technology.

As described previously (Peale et al., 2008), a comparative bench test demonstrated that the combination of EHC and KB-1 was more effective and appropriate for meeting the project objectives than two other commerically available electron donors (EOS® and HRC®). An extensive field pilot test confirmed the effectiveness of the sequential *in situ* installation in the TCE DNAPL source zone. During the field pilot, TCE concentrations were reduced from concentrations indicative of DNAPL (approximately 11,000 to 100,000 μg/L) to concentrations approaching or below the MCL (1 to 10 μg/L) (Exhibit 2). These results indicated that ISCR-enhanced bioremediation of TCE DNAPL to MCL levels is a rapid, effective, and practical alternative.

IMPLEMENTATION

The initial design of the full-scale implementation considered a single permeable reactive barrier (PRB) with performance assessed through the use of 11 performance monitoring

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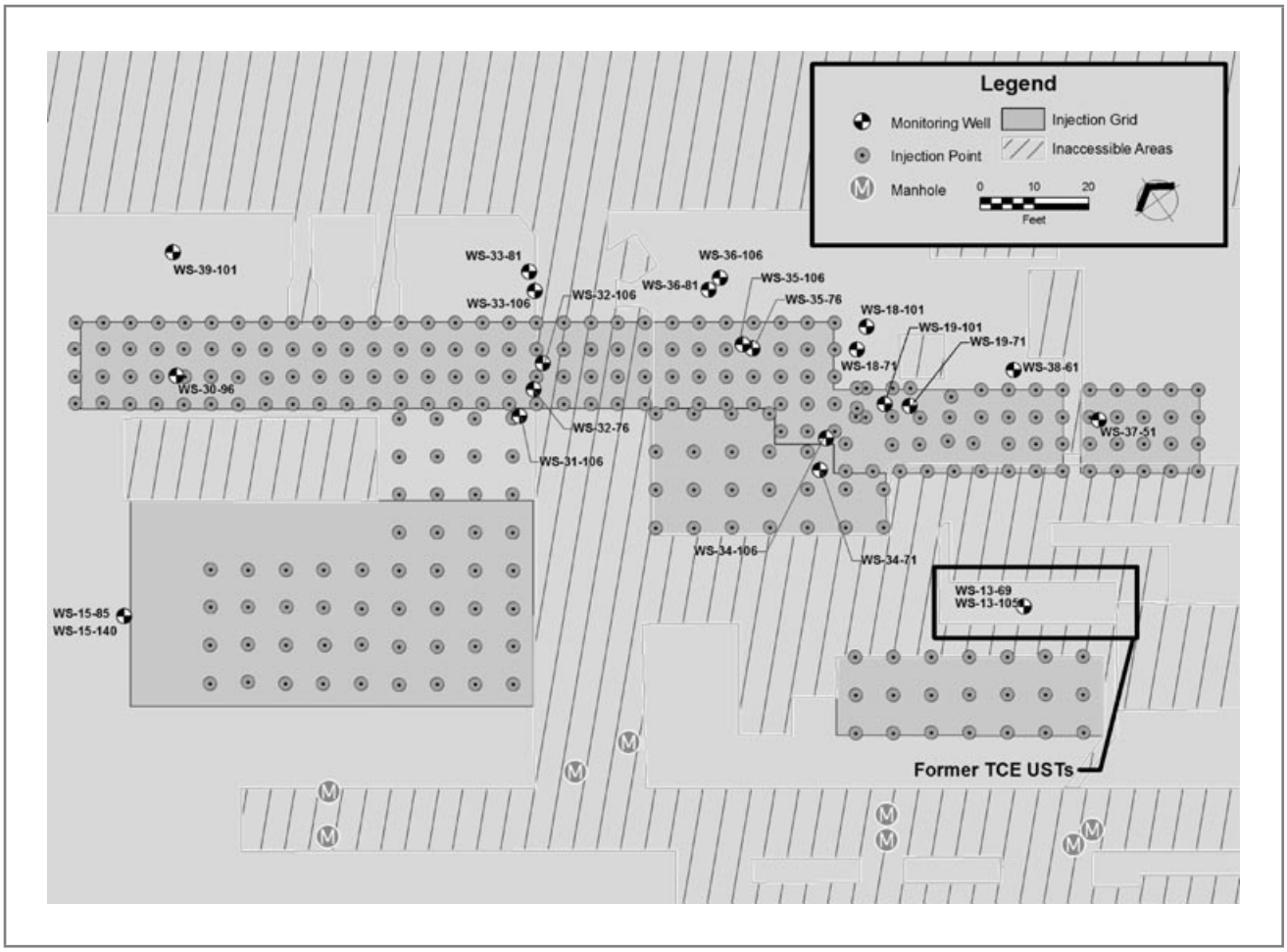

Exhibit 3. Source area, PMWs, proposed PRB alignment

wells (PMWs). Regulatory considerations resulted in additional source treatment upgradient of the PRB, and additional PMWs (23 total). Exhibit 3 shows the source area, PMWs, and the proposed PRB created via sequential EHC and KB-1 injections. The estimated baseline extent of the TCE source area over the injection threshold (11,000 μg/L) was based upon PMW and direct-push data collected prior to injection. Exhibit 3 also shows the areas where drilling could not occur, due to the presence of subsurface or overhead utilities.

Implementation consisted of an approximately 150-foot-long PRB containing EHC and KB-1, installed at depths ranging from approximately 40 to 112 feet bgs using direct-push technology. Supplemental injections were completed upgradient of the PRB to treat additional source areas. EHC was injected first, followed later (usually 7 to 14 days) by KB-1 injections. The EHC was injected at four-foot vertical intervals, with two-foot offsets between injection rows to enhance the vertical coverage.

Injections commenced in January 2009 and were completed in June 2009 (Cascade Drilling of Portland, Oregon). Approximately 200 injection points were completed, as shown in Exhibit 4. Exhibit 4 also shows how the proposed injection locations required relocation due to the presence of subsurface utilities. Each location required clearing for

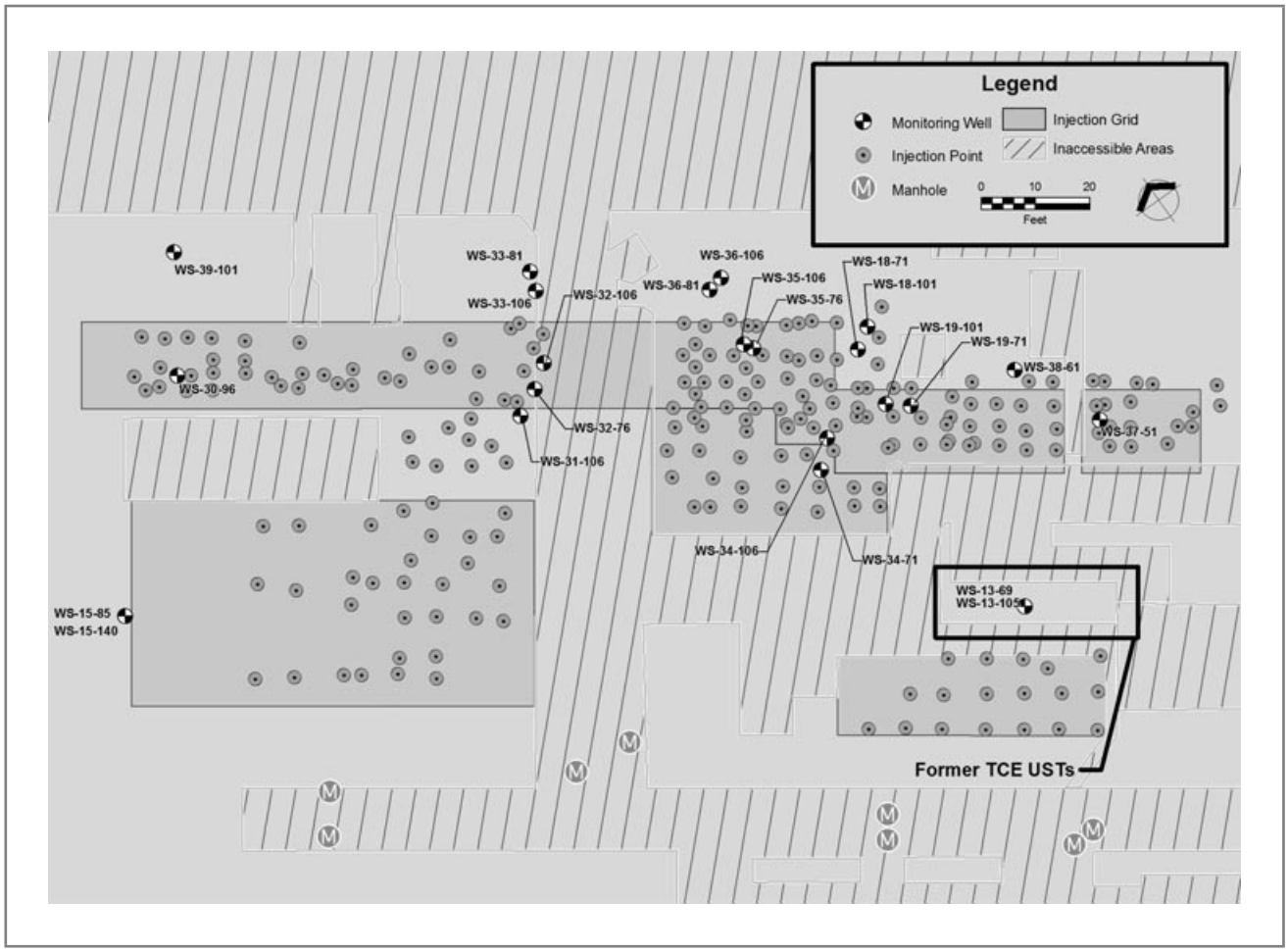

Exhibit 4. Completed injection points

subsurface utilities to a depth of 10 feet bgs using a vacuum truck. Several locations were installed as angled borings due to the overhead pipe rack.

The EHC material was delivered to the site as a fine powder and mixed into a 30 percent slurry with potable water. The slurry was delivered to the subsurface using twin trailer-mounted ChemGrout 600 pumps powered by compressed air. Two pump trailers were operating simultaneously throughout most of the injection program, with an average rate of four injection points per day. EHC injections proceeded in a top-down fashion, using GeoProbe's pressure-activated injection tips. Initial pumping pressures were high (approximately 400 to 600 pounds per square inch [psi]) until modification to the pressure-activated injection tips reduced the required pressure.

The KB-1 consortium was injected using a peristaltic pump and standard GeoProbe sampling screen. The consortium was pumped from anaerobic delivery vessels in 500- to 700-mL aliquots and followed by 2 L of anaerobic chase water. The anaerobic chase water was prepared by adding EHC to a 500-gallon poly tote of potable water. KB-1 injections were completed in a bottom-up fashion, using the same borings from the EHC injections.

In total, approximately 594,000 pounds of EHC and 1,831 liters of KB-1 (at a cell density of 1×10^{11} cells/L) were injected into the subsurface. The injection amounts were based on the successful field pilot test; however, based on the data presented later,

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these amounts may have been conservatively high and fewer materials could have been injected yielding similar results. Nevertheless, it is estimated that the longevity of the iron component of the EHC material will range from 14 to 21 years. This time frame provides a conservative level of protection for the risk-averse project team and is similar to the time elapsed since the release.

Lessons Learned During Implementation

Several challenges were identified and mitigated during implementation:

- Daylighting of EHC initially occurred and caused concerns about adequate subsurface distribution. The injection crew effectively mitigated daylighting after injection by leaving approximately 10 feet of capped direct-push rod in the injection boring after the injections were completed. Interestingly, daylighting occasionally occurred at significant distances (approximately 20 feet) from the operating injection point, suggesting effective lateral distribution of EHC.
- Subsurface utilities were identified in facility plans provided. Substantial additional subsurface piping was discovered as boreholes were cleared using the vacuum truck. A color-coded surface marking system was used to identify proposed, obstructed, and completed points. While the vacuum truck added expense, the downside risk of facility shutdown due to pipe breakage was unacceptable.
- Overhead piping restricted installation in portions of the planned PRB alignment. Borings were installed at shallow angles (10 to 15 degrees from vertical) to ensure installation under the piping, without risking damage to the facility infrastructure. However, the angled borings proved difficult to complete, and tooling loss due to breakage occurred more frequently than expected. This approach is not recommended for future deep injections.

PERFORMANCE MONITORING

Groundwater data were collected from 23 PMWs located upgradient, within, and downgradient of the PRB (Exhibit 4). Eight PMWs predated installation; the remaining wells were newly constructed per the request of the Oregon Department of Environmental Quality (DEQ). Data collection included an extensive suite of parameters to identify degradation rates and pathways. Target analytes included TCE and its degradation products, including ethene, ethane, and chloride. Secondary analytes that confirmed distribution and/or migration of the injected materials included iron, total organic carbon, ketones, and Gene-Trac© analysis for KB-1 bacteria by SiREM. Tertiary analytes that confirmed reducing conditions and abiotic pathways included sulfate, methane, and chloroalkanes. Other analytes included metals and volatile fatty acids.

Samples were collected from the wells using dedicated bladder pumps and low-flow parameter stabilization techniques. The samples were analyzed by Specialty Analytical (SA) of Tualatin, Oregon. Groundwater samples were also quantitatively analyzed for *Dhc* by SiREM in Mississauga, Ontario, Canada.

Baseline samples were collected from the new PMWs located downgradient of the PRB prior to injection implementation (with one potential exception). Monitoring commenced in February 2009 and continued on a bimonthly basis starting in May 2009.

Data collection included an extensive suite of parameters to identify degradation rates and pathways. Target analytes included TCE and its degradation products, including ethene, ethane, and chloride.

Additional baseline data from four pre-injection (existing wells) dating back to 2003 were used for evaluating the performance. The data evaluation considers the entire data set collected between January/February 2009 and December 2009, but for the sake of brevity focuses on the target and secondary analytes.

RESULTS

The project team, working with the state regulatory authority (Oregon DEQ), identified the primary Remedial Action Objective (RAO) for full-scale implementation to be the reduction of TCE in groundwater to below 1 percent of its aqueous solubility, the threshold for the likely presence of TCE DNAPL. Achieving this RAO would demonstrate the effectiveness of ISCR-enhanced bioremediation for TCE DNAPL source zones. Additional considerations important for the monitoring program included the generation of daughter products (*cis*-1,2-DCE, vinyl chloride, and dechlorinated alkenes/alkanes), downgradient distribution of beneficial effects (i.e., treatment of source material in inaccessible areas downgradient of the injection zone), and evaluation of TCE half-lives.

TCE concentrations were reduced to below the injection threshold in most of the PMWs within six months of commencing injections, and the RAO was achieved in all of the wells within five months of injection completion.

Discussion of the data is divided into two groups—Group 1 PMWs are generally located within the PRB or supplemental injection zones and were intended to provide data regarding direct effects of the injections. Group 2 PMWs are located downgradient of the PRB injection zones and were intended to provide data about the indirect effects (i.e., groundwater-mediated) of the injections. The benefits observed in the Group 2 PMWs would presumably extend to inaccessible source materials, such as those suspected to be present under the adjacent building.

Target Analyte Results—TCE, cis-1,2-DCE, and Vinyl Chloride

The TCE results are summarized in Exhibit 5 and confirm the unique effectiveness of ISCR-enhanced bioremediation: namely, TCE concentrations were reduced to below the injection threshold in most of the PMWs within six months of commencing injections, and the RAO was achieved in all of the wells within five months of injection completion. The average preinjection concentration of TCE in the Group 1 PMWs initially above the injection threshold was reduced from 82,933 μg/L to 1,238 μg/L in December 2009. The average preinjection concentration of TCE in Group 2 PMWs initially above the injection threshold was reduced from 21,733 μg/L to 2,638 μg/L.

The percent mass reduction in all of the Group 1 PMWs increased from 91.2 percent in July 2009 (completion of injections) to 99.1 percent in December 2009, and the percent mass reduction in all of the Group 2 PMWs increased from 81.7 percent to 98.6 percent during the same time frame. The TCE MCL was achieved in 9 of the 21 PMWs located within or downgradient of the injection zones.

As noted earlier, significant concentrations of *cis*-1,2-DCE prior to active remediation suggested that a native population of bacteria capable of TCE degradation was present, but relatively low vinyl chloride concentrations (combined preinjection average of approximately 800 μg/L) suggested that complete dechlorination was not supported at significant rates. The presence of significant concentrations of *cis*-1,2-DCE (preinjection) complicated evaluation of the effectiveness of the remedy, which relied in part upon sequential dechlorination. The mass of TCE, *cis*-1,2-DCE, and vinyl chloride was estimated along three transects oriented transverse to the groundwater flow direction and

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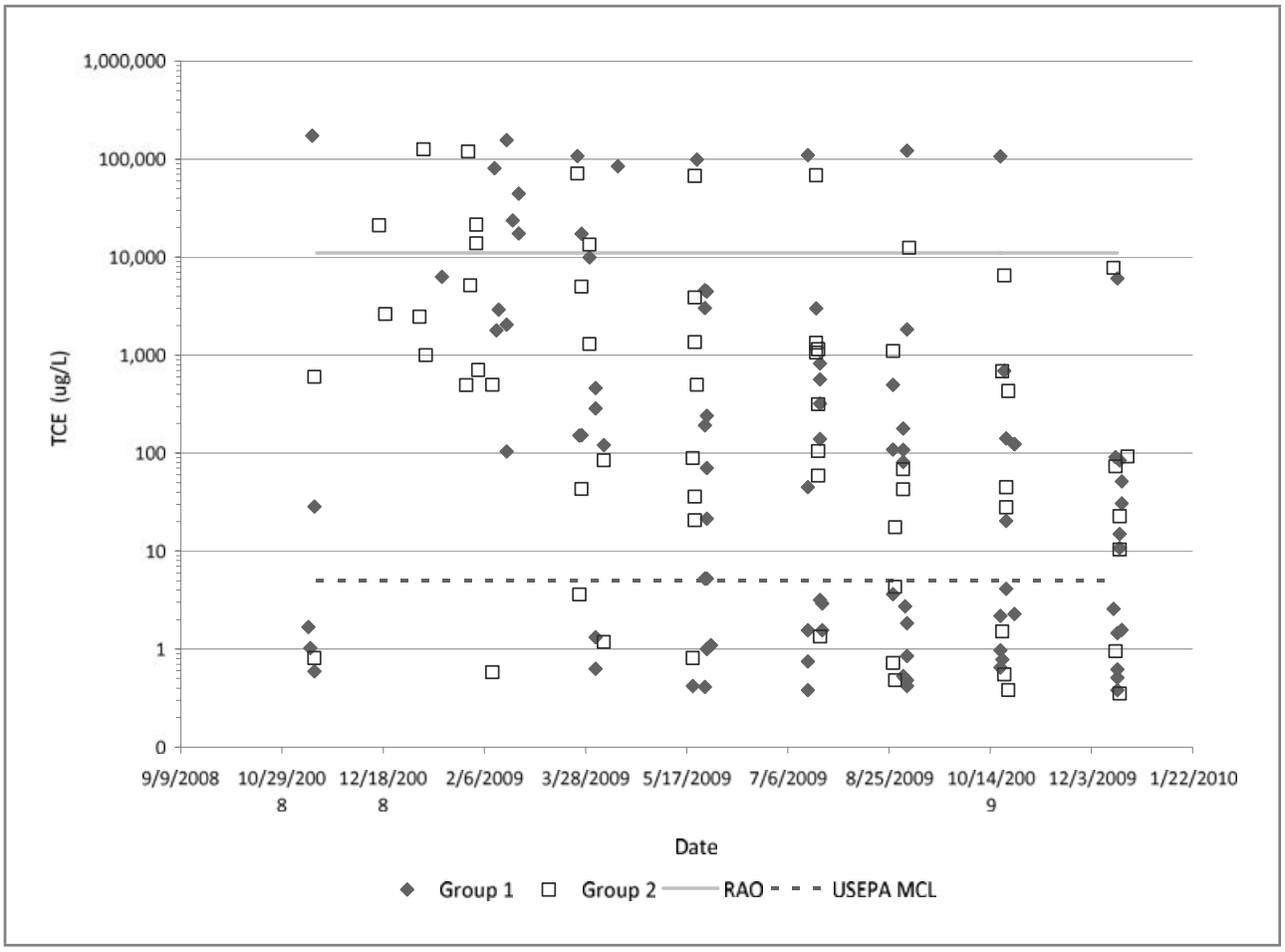

Exhibit 5. Log scatter plot of TCE (ug/L) in groundwater

within the estimated extents of the source area (Exhibit 6) using the geostatistical estimating routines in the Environmental Visualization System (EVS) software program (developed by C-Tech; Laie, HI).

Exhibit 7 summarizes the TCE molar mass (M) along the transects and within the larger estimated extent of the source area itself. As shown in the exhibit, approximately 1,870 M of TCE were destroyed and a net combined 918 M of daughter products (*cis*-1,2-DCE and vinyl chloride) were created within the estimated source extent. For the sum of the transects, approximately 93 M of TCE were destroyed, and a net combined 76 M of daughter products were created.

At the downgradient transect (T3), approximately 11 M of TCE were destroyed and a net combined 31 M of daughter products were destroyed (−31 M "created"). Exhibit 8 compares DCE molar mass along the three transects, and shows that while DCE mass was created within the treatment zones, these impacts did not extend to downgradient wells.

The following observations are made from the target analyte data set:

1. These data confirm the effectiveness of ISCR-enhanced *in situ* bioremediation of a TCE DNAPL source zone.

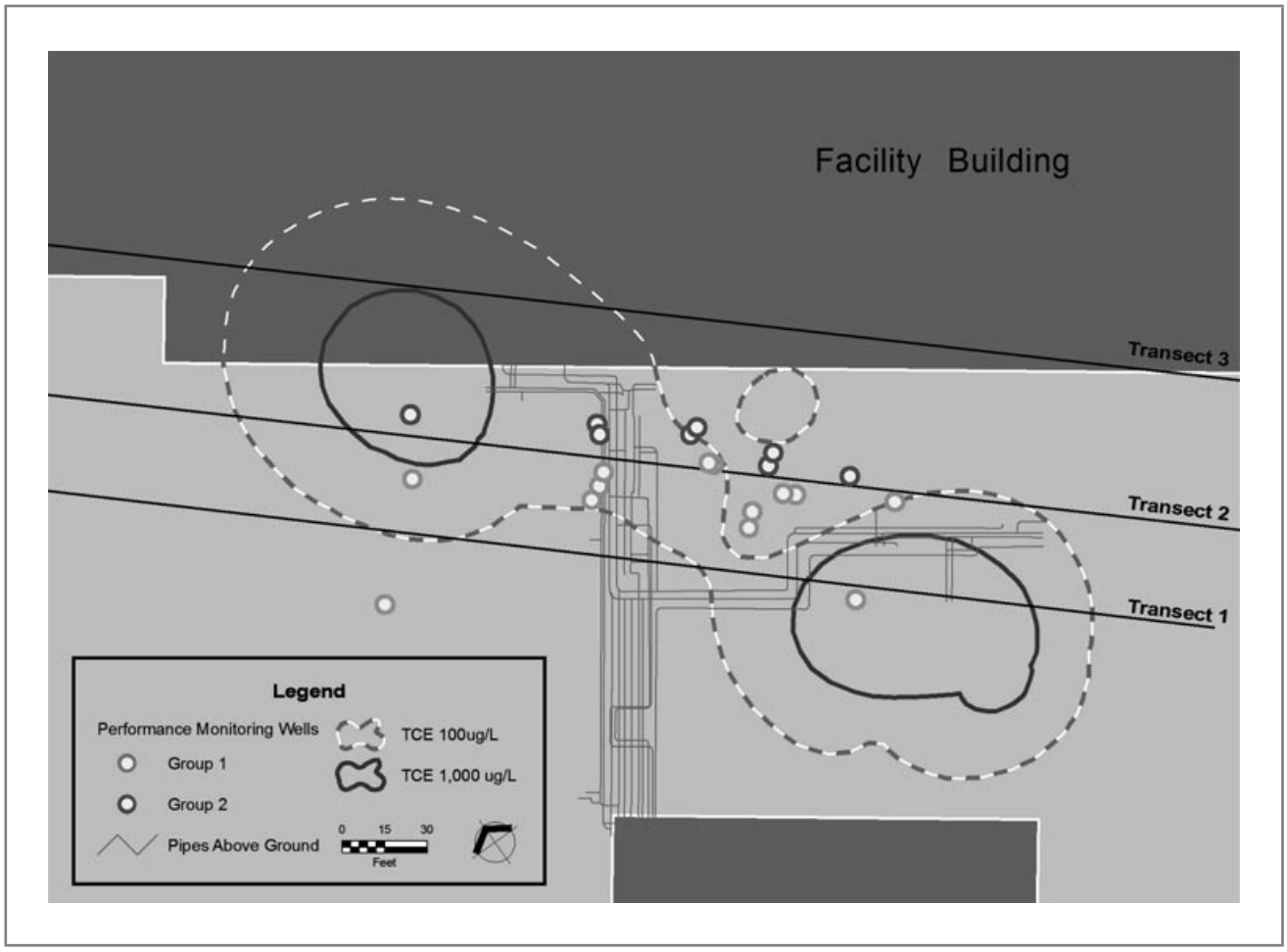

Exhibit 6. Transect locations and estimated TCE source extent above 100 μg/L (six months post-injection)

Exhibit 7. Molar mass (*M*) of TCE, cis-1,2-DCE and VC in source area

	TCE Destroyed (*Created*)	DCE and VC Generated (*Destroyed*)	TCE Destroyed (*Created*)	DCE and VC Generated (*Destroyed*)	TCE Destroyed (*Created*)	DCE and VC Generated (*Destroyed*)
	Source Extents		Sum of Transects		Transect 3 (downgradient)	
Apr-09	1,214	2,509	59	80	8	31
Jun-09	378	315	21	32	2	1
Jul-09	*(41)*	3,482	1	156	*(2)*	30
Sep-09	161	*(814)*	5	*(45)*	3	*(45)*
Oct-09	67	*(1,953)*	2	*(70)*	0	*(7)*
Dec-09	91	*(2,621)*	5	*(76)*	0	*(42)*
Totals	1,870	918	93	76	11	*(31)*

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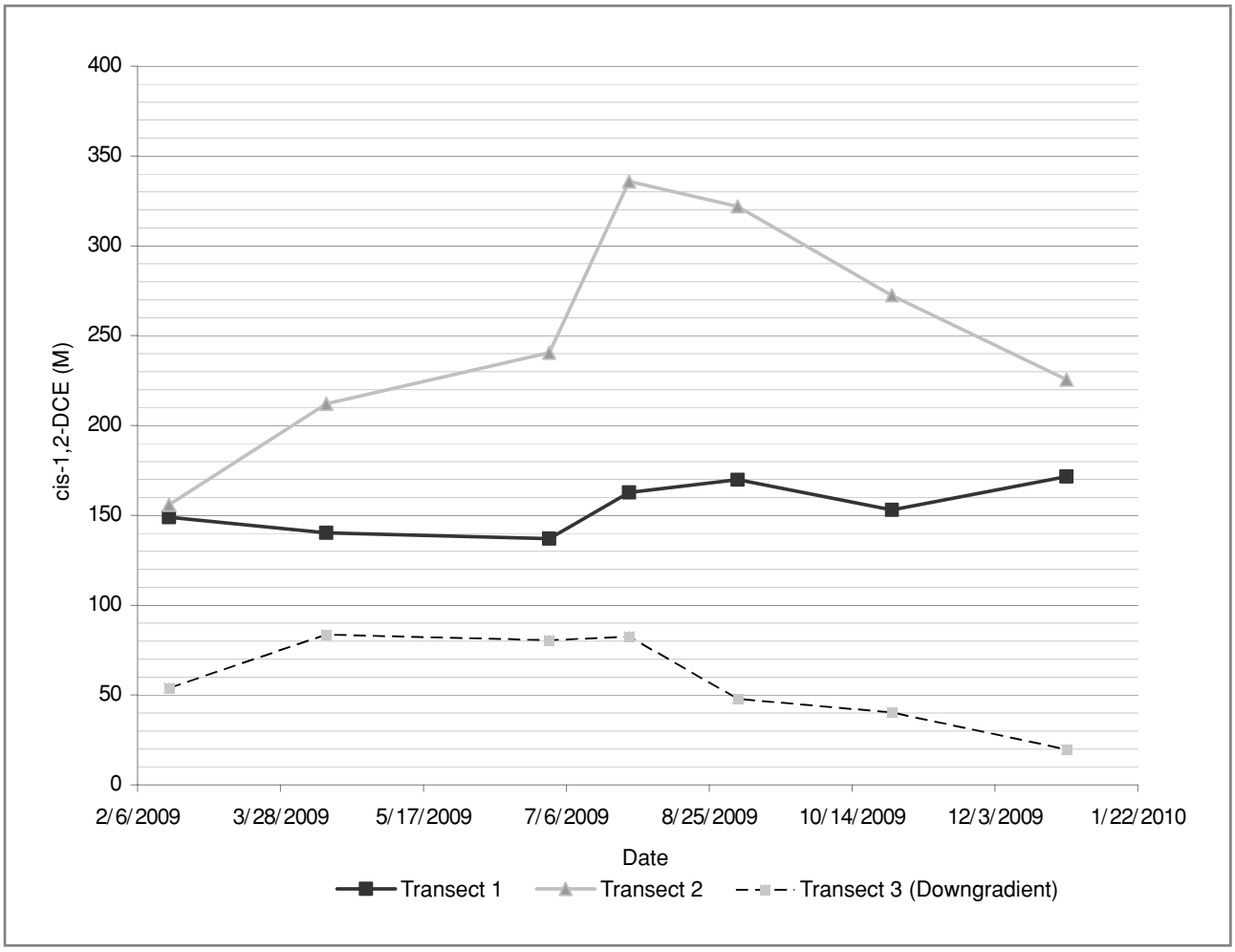

Exhibit 8. Comparison of cis-1,2-DCE molar mass (*M*) along transects

2. The molar mass calculations suggest that the generation of DCE and vinyl chloride is not stoichiometric, as is characteristic of microbially mediated sequential dechlorination. As such, mass reduction may also be occurring via an abiotic pathway (e.g., beta-elimination).
3. The generation of daughter products via the selected approach was transient and did not result in accumulation at downgradient points (i.e., along transect 3). While DCE mass increased within the treatment zone, the mass was significantly decreased (i.e., by a factor of 3 to 11) by the time groundwater reached the downgradient transect.

Target Primary Analytes—Ethene, Ethane

Groundwater samples were also analyzed for fixed gases (ethene and ethane) representing the fully dechlorinated end products characteristic of both microbially mediated and abiotic pathways. Ethene was detected at a frequency of about three times that of ethane.

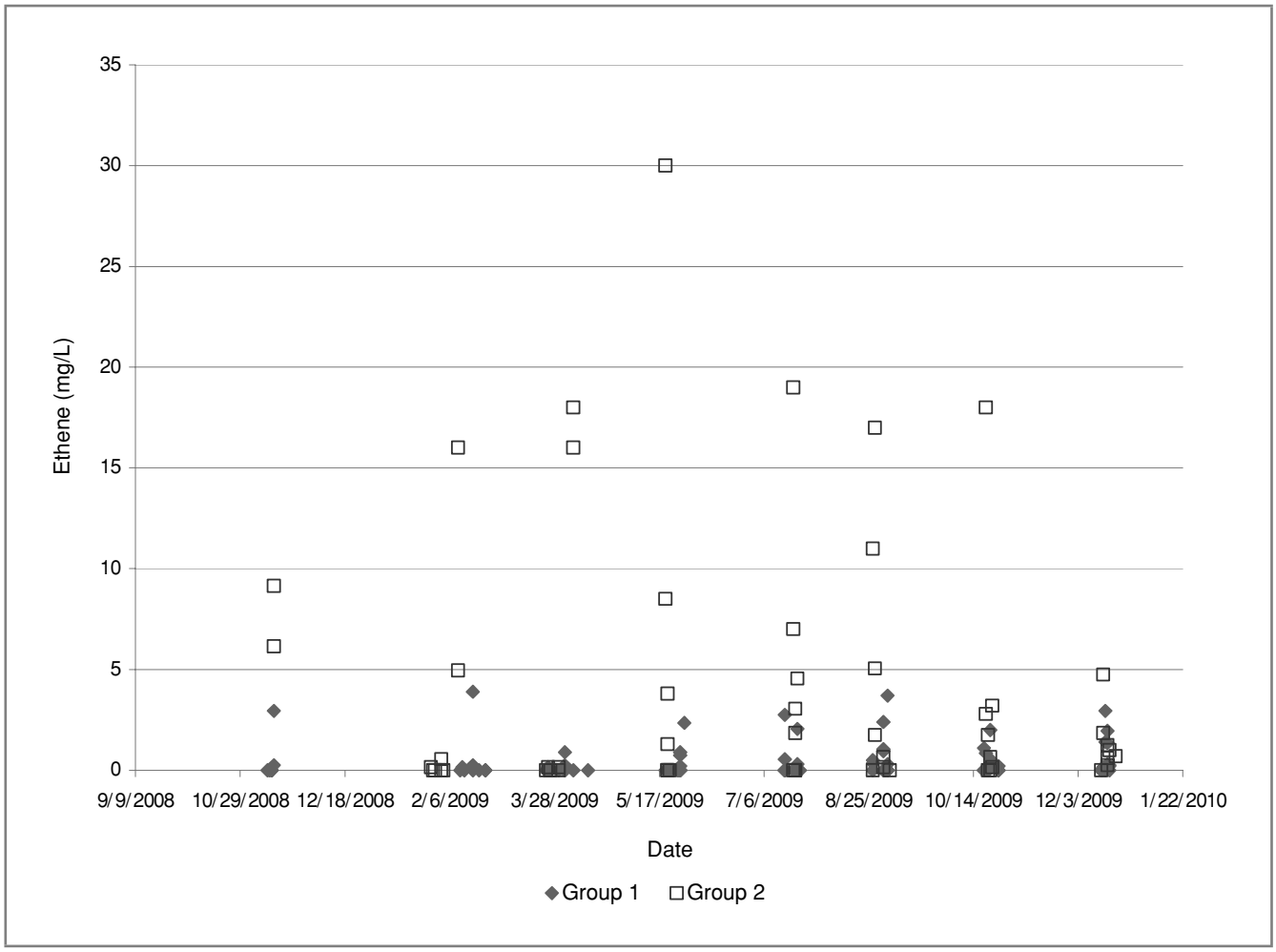

Exhibit 9. Increased ethene (mg/L) in groundwater confirming complete dechlorination

The concentrations ranged as high as 3.9 mg/L in the Group 1 PMWs, and as high as 30 mg/L in the Group 2 PMWs (Exhibit 9).

The ethane and ethene data confirmed that TCE and its degradation products were completely dechlorinated, likely by a combination of abiotic and microbially mediated pathways. Ethene production commenced prior to injection of KB-1 in some Group 2 PMWs, indirectly confirming the abiotic pathway. As shown in Exhibit 9, ethene concentrations were generally higher in the Group 2 PMWs, confirming downgradient advection of ethene, and downgradient distribution of EHC and/or KB-1.

Production of ethene continued in some wells long after chlorinated VOCs were reduced to low concentrations, suggesting that ethene migration from other active dechlorinating areas is occurring, or that desorption of chlorinated VOCs from the soil is occurring at similar rates as the degradation.

Secondary Analyte Results—Iron, Ketones, and KB-1 Counts

Secondary analytes that confirmed distribution and/or migration of the injected materials included iron, ketones, and Gene-Trac analysis for *Dhc* bacteria characteristic of KB-1.

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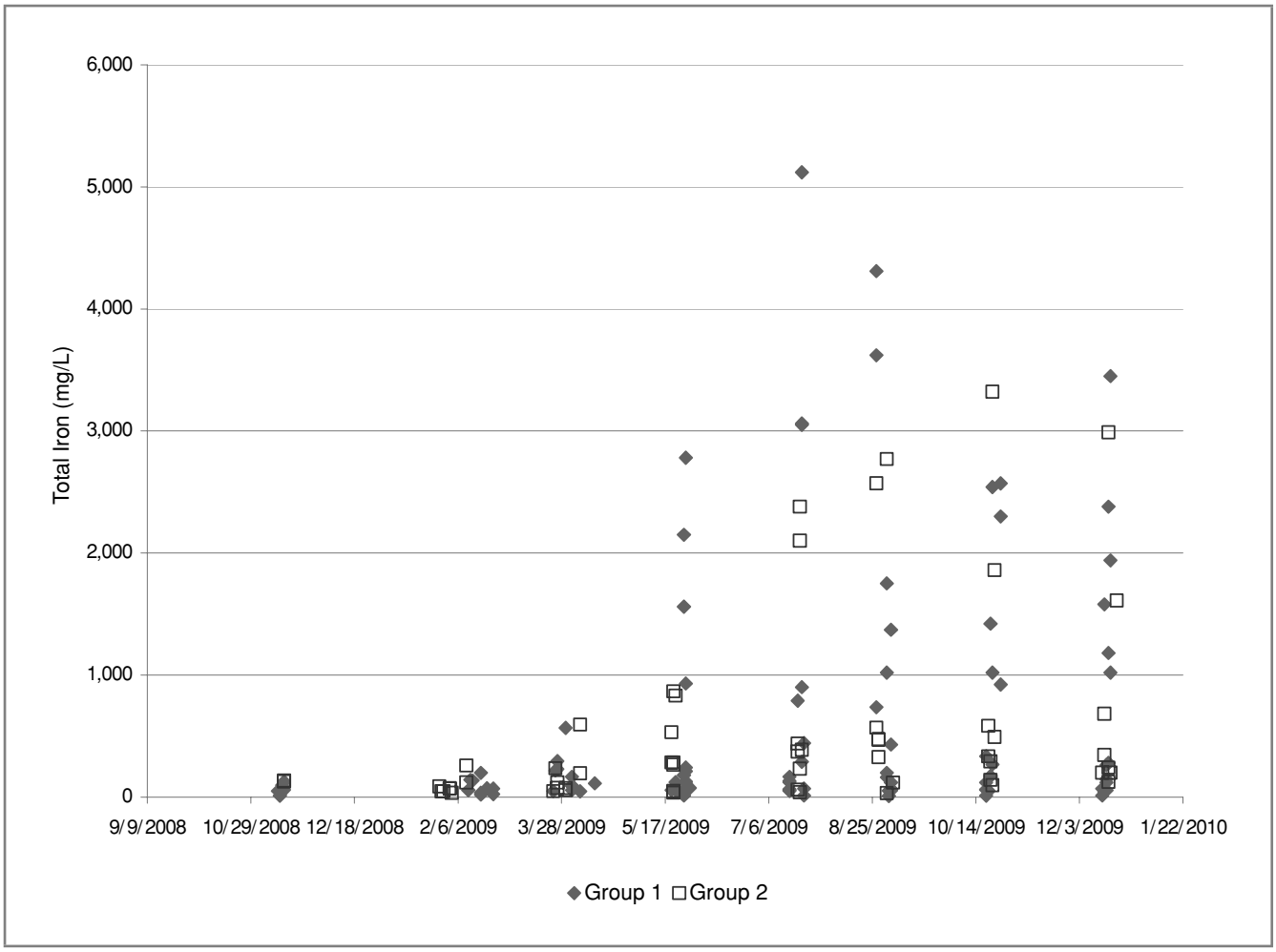

Exhibit 10. Total iron (mg/L) in groundwater confirming distribution of EHC

The groundwater samples were analyzed for total and dissolved iron. The total iron concentrations in the Group 1 and 2 PMWs are shown in Exhibit 10. The preinjection concentrations (November 2008) ranged as high as 134 mg/L (due in part to the pilot injections from 2006). Shortly after injections commenced, iron concentrations increased by orders of magnitude, reaching over 5,000 mg/L in Group 1 and over 3,000 mg/L in Group 2. The Group 2 data confirm distribution of iron downgradient of the injection zones, suggesting that the EHC component of the remedy will be effective on inaccessible source material under the adjacent building.

The VOC analysis included analysis of ketones (acetone, 2-butanone) produced by organic carbon fermentation reactions resulting from EHC injections. The acetone and 2-butanone data were strongly correlated; Exhibit 11 summarizes the 2-butanone data from Group 1 and 2. As shown in the exhibit, the average 2-butanone concentration in Group 2 (1,277 mg/L) was greater than the average concentration from Group 1 (1,066 mg/L). These data confirm generation of ketones downgradient of the injection zones, further indicating downgradient distribution of the organic carbon component of the EHC. The data also suggest that the biological component of the remedy will be effective on inaccessible source material under the adjacent building.

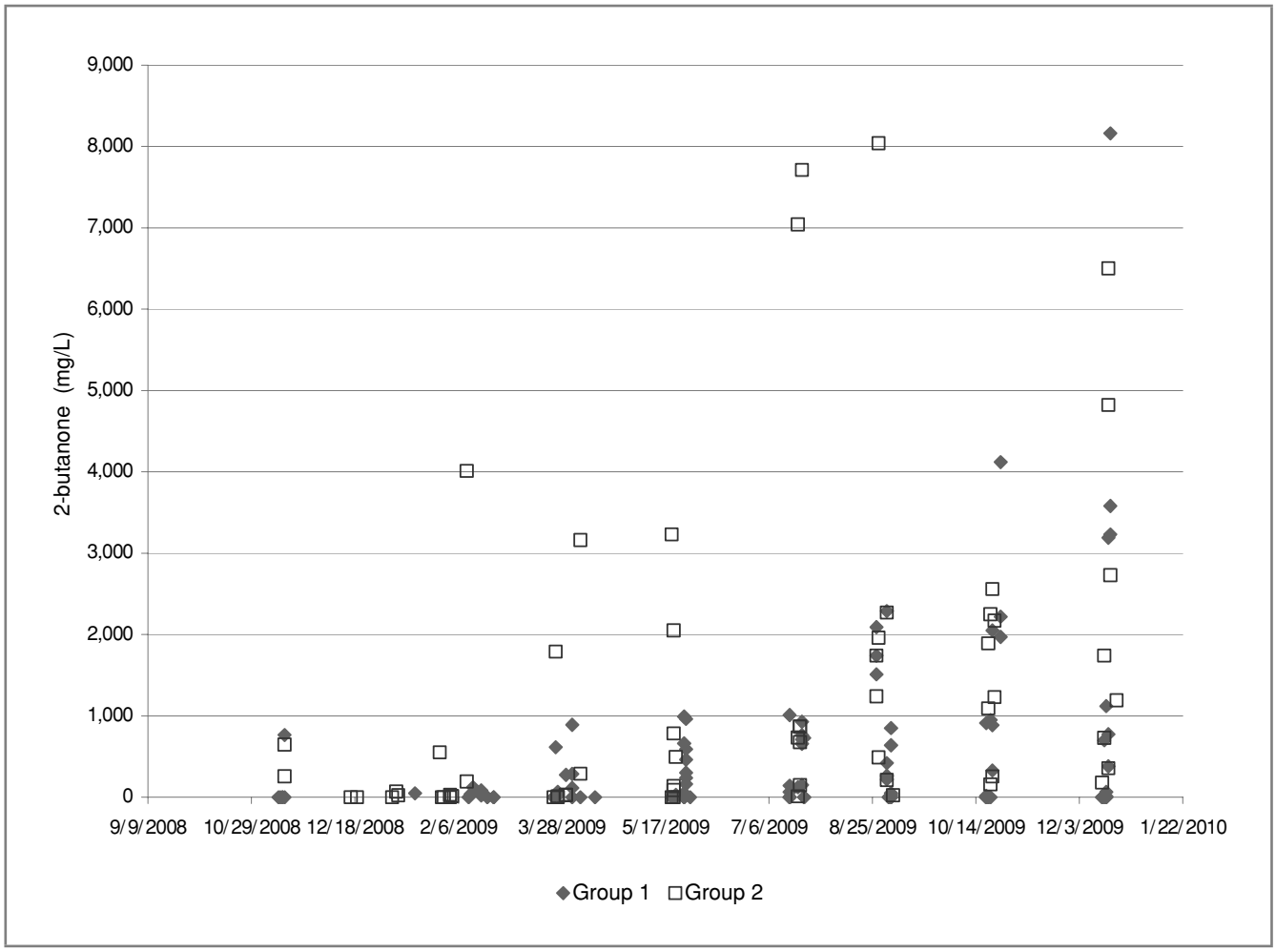

Exhibit 11. 2-butanone (mg/L) in groundwater confirming distribution of EHC

SiRem provided analytical data for *Dhc* bacteria and *Dhc* bacteria containing the vinyl chloride reductase gene (vcrA). The geometric means of the Groups 1 and 2 data from 2007 (preinjection data) and February, July, and October 2009 are included in Exhibit 12. The counts (cells/L) and relative amounts (percent) increased in both Groups 1 and 2 but were greater in the Group 2 PMWs than the Group 1 PMWs. Maximum counts for *Dhc* and vcrA-containing bacteria were detected in the Group 2 PMWs and were as high as 2×10^9 and 3×10^8 cells/L, respectively. These data confirm distribution and growth of dechlorinating bacteria downgradient of the injection zones, and suggest that the KB-1 component of the remedy will be effective on inaccessible source material under the adjacent building.

Tertiary Analytes—Sulfate, Methane, and Chloroalkanes

Tertiary analytes included sulfate, methane, and chloroalkanes. The sulfate and methane data were collected to confirm that reducing conditions were operating in the desired oxidation-reduction potential (ORP) range for the KB-1 bacteria (i.e., lower than −100 mV). Sulfate is reduced to sulfide at an ORP of around −217 mV, so the

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Exhibit 12. *Dhc* and *vcrA* data in groundwater confirming distribution of KB-1

	Geometric Means			
	% DHC	DHC Count (cells/L)	% VCR Bacteria	vcr Gene (cells/L)
Baseline (Select Group 1-2007)	0.33	6.E+04	NA	NA
Group 1 Feb 09	NA	NA	0.01	9.E+04
Group 1 Oct 09	0.30	1.E+06	0.15	9.E+05
Group 2 Jul 09	6.51	9.E+07	0.24	6.E+06
Group 2 Oct 09	11.25	2.E+08	4.30	4.E+07
	Max Data			
	% DHC	DHC Count (cells/L)	% VCR Bacteria	vcr Gene (cells/L)
Baseline (Select Group 1-2007)	27	4.E+07	NA	NA
Group 1 Feb 09	NA	NA	0.05	2.E+05
Group 1 Oct 09	48	6.E+08	19	1.E+08
Group 2 Jul 09	78	2.E+09	3	3.E+08
Group 2 Oct 09	61	9.E+08	19	2.E+08

Note: NA means not analyzed.

disappearance of sulfate is a more reliable indicator of reducing conditions than field measurements of ORP. Exhibit 13 is a scatter plot of sulfate data from the Group 1 and 2 PMWs, confirming that while initial concentrations of sulfate were elevated, concentrations dropped significantly. These data indicate that reducing conditions (ORP of approximately −217 mV) were established, and the initial high concentrations of sulfate did not inhibit growth of the KB-1 consortium.

Redox conditions can also be inferred from methane data, as CO_2 is oxidized to methane at an ORP of approximately −238 mV. Methane production also confirms an excess amount of fermentable carbon (as a result of the EHC injections). Exhibit 14 is a scatter plot of methane data and confirms that favorable redox conditions and EHC fermentation reactions are well established, with concentrations in both groups exceeding the solubility limit.

Chloroalkane production via hydrogenation has been identified as a potential abiotic degradation pathway for TCE and its degradation products (Brown et al., 2009). 1,1,2-trichlorethane (1,1,2-TCA) was observed in Group 1 PMW WS13-69 prior to the PRB installation, suggesting that some hydrogenation of TCE was occurring. Following the PRB installation, other chloroalkanes, specifically 1,1- and 1,2-dichloroethane (DCA) and chloroethane (CA), were observed at relatively low, but steady concentrations. The DCA isomers were infrequently detected and at low concentrations (average of approximately 1 μg/L for both). CA was detected most frequently and at the highest average concentration of 17 μg/L. 1,1,2-TCA was often detected in the same wells where CA was detected but at lower average concentration (approximately 3 μg/L),

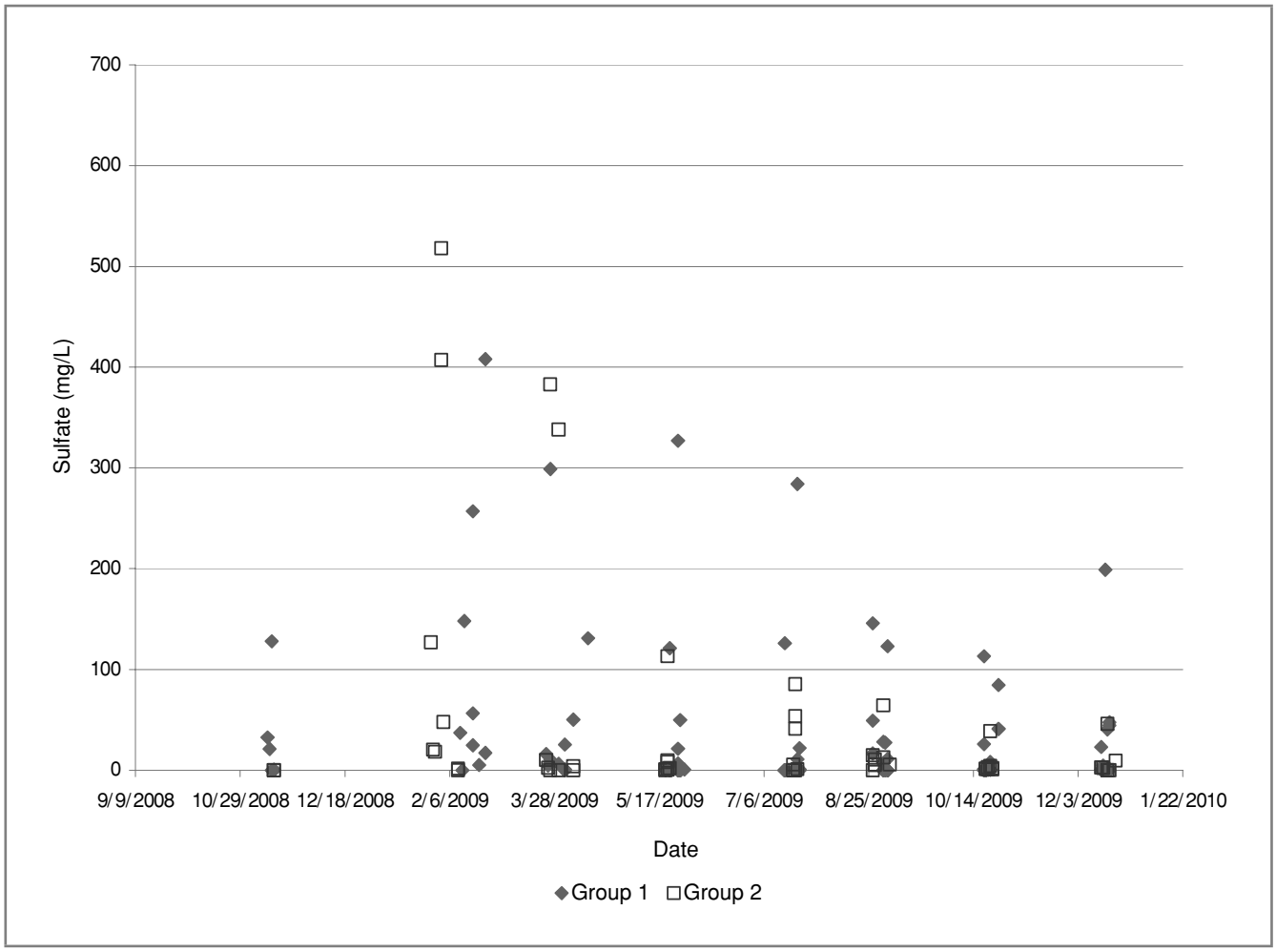

Exhibit 13. Reduction of sulfate (mg/L) in groundwater confirming reducing conditions

suggesting that the hydrogenation pathway was producing both compounds, or that the sequential conversion of TCE to DCA and DCA to CA occurred at a relatively higher rate compared to the final conversion of CA to ethane. The low concentrations confirm that hydrogenation is occurring but is not likely an important contributor to chloroalkane removal.

DISCUSSION

Several available documents identify significant or insurmountable challenges preventing implementation of *in situ* bioremediation of chlorinated-solvent DNAPL sites. One document begs the question in its title: *The DNAPL Remediation Challenge: Is There a Case for Source Depletion?* (Kavanaugh et al., 2003) Another document states that, regardless of method:

> The technical difficulties involved in characterizing and remediating source zones and the potential costs are so significant that there have been no reported cases of large DNAPL sites where remediation has restored the site to drinking water standards. (NRC, 2004)

Remediation DOI: 10.1002/rem

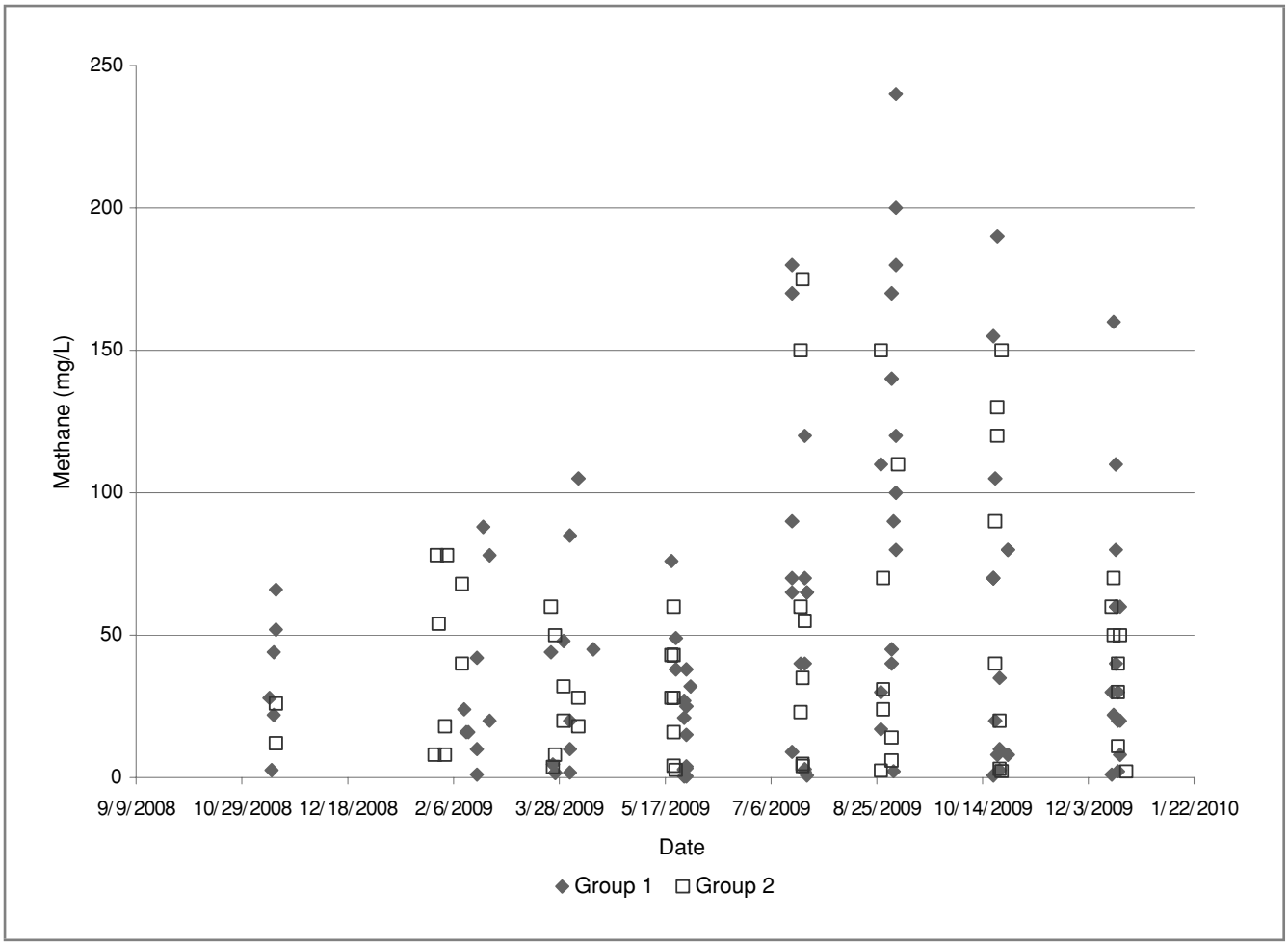

Exhibit 14. Increased methan (mg/L) in groundwater confirming reducing conditions and EHC fermentation reactions

A third provides general discussion ("frequently asked questions") regarding DNAPL source-zone remediation, and suggests that alternative goals, such as partial mass removal, may be the only practicable outcome from most of the available treatment technologies (Sale et al., 2008). A fourth reference concluded that *in situ* bioremediation is indeed a "viable, credible and effective technology for remediation of DNAPL source zones and provides several advantages over traditional source zone remediation technologies" (Interstate Technology & Regulatory Council, 2007). The relative dates of these documents demonstrate how the perspective on this technology has changed over a relatively short time frame.

The initial results and conclusions discussed in this article support the emerging view that, in some cases, ISCR can represent a potentially effective DNAPL management tool. It is recognized that additional studies could be performed to further identify pathways and rates, but the data presented herein provide sufficient evidence that ISCR-enhanced *in situ* bioremediation is an effective approach for achieving the benchmark of US EPA MCLs in chlorinated-solvent DNAPL zones.

CONCLUSIONS

TCE concentrations in samples collected from the site monitoring wells and direct-push sampling ranged as high as 259,000 and 592,000 μg/L, respectively. These concentrations suggested a high probability of the presence of TCE DNAPL, likely associated with a release in the early 1980s. The project team identified an achievable RAO of reducing TCE concentrations to below the 1 percent of TCE solubility threshold (i.e., 11,000 μg/L).

Five months following completion of a PRB and supplemental treatment zones composed of EHC and KB-1, the RAO was met in all 23 of the monitoring points. Furthermore, the US EPA MCL for TCE (5 μg/L) was achieved in 9 of the 23 mointoring points. The TCE percent mass reduction ranged as high as 99.1 percent in the injection zone, and 98.6 percent downgradient of the injection zone. Other data confirmed that the injected amendments are advecting downgradient and treating potential DNAPL mass located in inaccessible areas under the adjacent building. Removal of TCE and its degradation products is occurring by both abiotic and microbially mediated pathways.

A weight-of-evidence approach to data assessment confirms that ISCR is a potentially effective remedial technique for chlorinated-solvent DNAPL source zones in relatively deep, heterogeneous aquifers.

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