TCE Plume Remediation via ISCR-Enhanced Bioremediation Utilizing EHC® and KB-1®

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Groundwater below an operating manufacturing facility in Portland, Oregon, was impacted by chlorinated volatile organic compounds (CVOCs), with concentrations indicative of a dense, nonaqueous-phase liquid (DNAPL) release. The downgradient plume stretched under the adjacent Willamette River, intersecting zones of legacy impacts from a former manufactured gas plant (MGP). An evaluation of source-area and downgradient plume treatment remedies identified in situ *bioremediation as most likely to be effective for the CVOC plume, while leaving the legacy impacts for other responsible parties. With multiple commercially available products to choose from, the team developed and implemented a bench test to identify the most appropriate technology, which was further evaluated in a field pilot study. The results of the testing demonstrated conclusively that bioremediation enhanced by* in situ *chemical reduction (ISCR) using EHC® and KB-1® was most appropriate for this site, providing outstanding results. The following describes the implementation and results of the tests. © 2008 Wiley Periodicals, Inc.*

INTRODUCTION

In situ chemical reduction (ISCR) and microbial degradation are recognized, well-established technologies for remediation of chlorinated solvent plumes, with many choices for amendments appropriate for a variety of sites. In some cases, clients/practitioners/regulators are faced with a surfeit of potential solutions, with no clear differentiating factors, requiring bench and pilot studies prior to full-scale implementation. This article summarizes the results of a comparative bench test that clearly identified the best combination of technologies for the site—EHC® and KB-1®.

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. KB-1 is a mixed consortium of anaerobic bacteria, including *Dehalococcoides ethenogenes* (*Dhc*). 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 trichloroethene (TCE) concentrations characteristic of the presence of nonaqueous-phase liquid (NAPL).

The article also updates the results of a subsequent field pilot test (initial results were reported in Peale et al., 2007), both in a source area and at the downgradient end of the

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plume, which confirmed the bench results. In short, the combination of ISCR using EHC and KB-1 resulted in rapid degradation of TCE and its degradation products.

SITE BACKGROUND

The site consists of an operating facility in Portland, Oregon, adjacent to the Willamette River. Operations at the facility began in 1980, after the site had been developed by filling during the 1970s. Prior to development, portions of the property were used for waste disposal from a manufactured gas plant (MGP). The MGP waste stream included petroleum hydrocarbon DNAPL (dense, nonaqueous-phase liquid), which was incorporated into the fill, along with spent oxide waste, dredged sediment, and quarry spoils.

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

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 in the early 1980s, 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.

Direct-push investigation in the source area showed that concentrations of TCE and *cis*-1,2-dichloroethene (DCE) ranged as high as 592,000 and 90,000 μg/L (respectively) at depths ranging from approximately 50 to 110 feet below ground surface (bgs). 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 have been estimated to be on the order of 0.1 to 0.2 feet/day.

Investigation at the riverbank showed that concentrations of TCE, DCE and vinyl chloride (VC) ranged as high as 2,000, 34,000, and 5,000 μg/L (respectively) at depths ranging from approximately 80 to 130 feet bgs. The soil in the zone impacted by TCE consists of alluvial sands, with occasional thin silt layers. Legacy impacts (petroleum hydrocarbon DNAPL) have been observed in riverbank wells screened from 109 to 124 feet bgs. Groundwater flow velocities at the riverbank have been estimated to be on the order of 1 to 10 feet/day.

The client team identified two aggressive but achievable objectives: TCE DNAPL remediation in the source area and attainment of highly conservative screening-level values (SLVs) at the riverbank.

AMENDMENT SELECTION

In 2005, a preliminary technology screen indicated that an *in situ* remedy, incorporating ISCR and/or biodegradation, would likely be successful. Faced with multiple choices for *in situ* remedies, a comparative bench test was proposed to determine the ability of

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Exhibit 1. Site map

treating TCE and daughter products using enhanced reductive dechlorination. Three commercially available *in situ* treatment technologies were evaluated: (1) emulsified soybean oil, (2) polylactate, and (3) EHC. The bench studies also generated design data to facilitate field applications.

The bench test consisted of adding the various amendments to columns packed with soil from the site. Groundwater from the site was spiked with TCE at concentrations comparable to site conditions at the downgradient extent of the plume (i.e., approximately 10,000 μg/L). (The groundwater was also spiked with MGP constituents benzene and naphthalene at representative concentrations.) The groundwater was circulated for four contact periods with periodic sampling and respiking. Groundwater was then circulated for three subsequent periods, with TCE feed concentrations increased to 240,000, 870,000, and 640,000 μg/L to evaluate the potential for source area remediation.

All three technologies showed reduction in TCE throughout the study. When inoculated with the *Dhc* microbial culture (KB-1), the EHC columns successfully

Exhibit 2. Rate data from bench test of EHC + KB-1

Duration of Circulation Period	TCE Spike Concentrations (μg/L)	Effluent Concentration (μg/L)	Rate (per Day)	Half-Life (Days)
14	11,000	250	0.3	2.6
21	10,000	66	0.2	2.9
28	9,400	5	0.3	2.6
14	11,000	3	0.6	1.2
21	240,000	13	0.5	1.5
21	870,000	200	0.4	1.7
42	640,000	16	0.3	2.7
		Mean Results	0.4	2.2

dechlorinated feed concentrations ranging as high as 870,000 μg/L of TCE, with minimal accumulation of DCE and VC. In summary:

- At the highest spike concentrations, the combination of EHC and KB-1 provided the best performance with respect to removal of not only TCE, but also its degradation products. These data suggest that EHC and KB-1 in combination can be used to remediate TCE NAPL zones.
- Absent amendment with the *Dhc* microbial culture, the EHC column showed the greatest removal of CVOCs. Complete dechlorination was confirmed in the EHC column by an increase in ethene.
- The addition of the *Dhc* microbial culture to the emulsified oil, lactate, and EHC columns enhanced the removal of TCE and daughter products.
- The EHC and emulsified oil treatments exhibited the best overall performance for TCE at lower concentrations.

Exhibit 2 summarizes the rate data for the EHC + KB-1 combinations. Half-life values for TCE ranged from 1.2 to 2.9 days, with a mean value of 2.2 days.

A combination of EHC + KB-1 was selected for the field pilot study. The emulsified soybean oil treatment was not selected due to significant accumulations of degradation products during the high-concentration runs—characteristic of DCE stall. Unresolved questions about potential sorption of VOCs (including aromatics) and polycyclic aromatic hydrocarbons (PAHs) from the groundwater into the emulsified soybean oil were an additional negative factor. The polylactate treatment was not selected based on the lack of TCE degradation and accumulation of intermediates.

PILOT STUDY

In May 2006, a total of 21 tons of EHC were injected to install a permeable reactive barrier (PRB) measuring 28 feet long by 21 feet wide by 40 feet thick (from 90 to 130 feet bgs) in the riverbank pilot test area (Exhibit 3). In June 2006, an additional 13.5 tons of EHC were injected into the suspected source area within an area measuring 20 feet long

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Exhibit 3. Riverbank pilot-study area

by 15 feet wide by 56 feet thick (from 50 to 106 feet bgs; see Exhibit 4). An application rate of 1 percent to soil mass was targeted for the riverbank PRB and 1.5 percent in the source area. EHC was injected as a 20 to 30 percent solids slurry (with potable water) using standard Geoprobe equipment (provided by Boart-Longyear E&I) and high-pressure pumps. A week after the EHC injections, approximately 84 L of KB-1 were added to the 20 riverbank PRB EHC injection points, and 60 L of KB-1 were added to the 12 source area EHC injection points (in both areas, the KB-1 injections were installed by redrilling through the previous EHC points).

At the riverbank pilot study area, monitoring wells were installed 25 feet upgradient (WS-21-112), within the PRB (WS-22-112), and 20 feet downgradient of the PRB (WS-20-112). The monitoring wells were screened from 96 to 111 feet bgs. An existing monitoring well (WS-11-125) was located 10 feet downgradient of the PRB, screened from 109 to 124 feet bgs. Pilot-study sampling commenced immediately after installation of the PRB (baseline sampling event May/June 2006) and then on a monthly schedule.

At the source-zone pilot-study area, monitoring well pairs were installed within the PRB (WS-19-71/101) and approximately 10 feet downgradient of the PRB

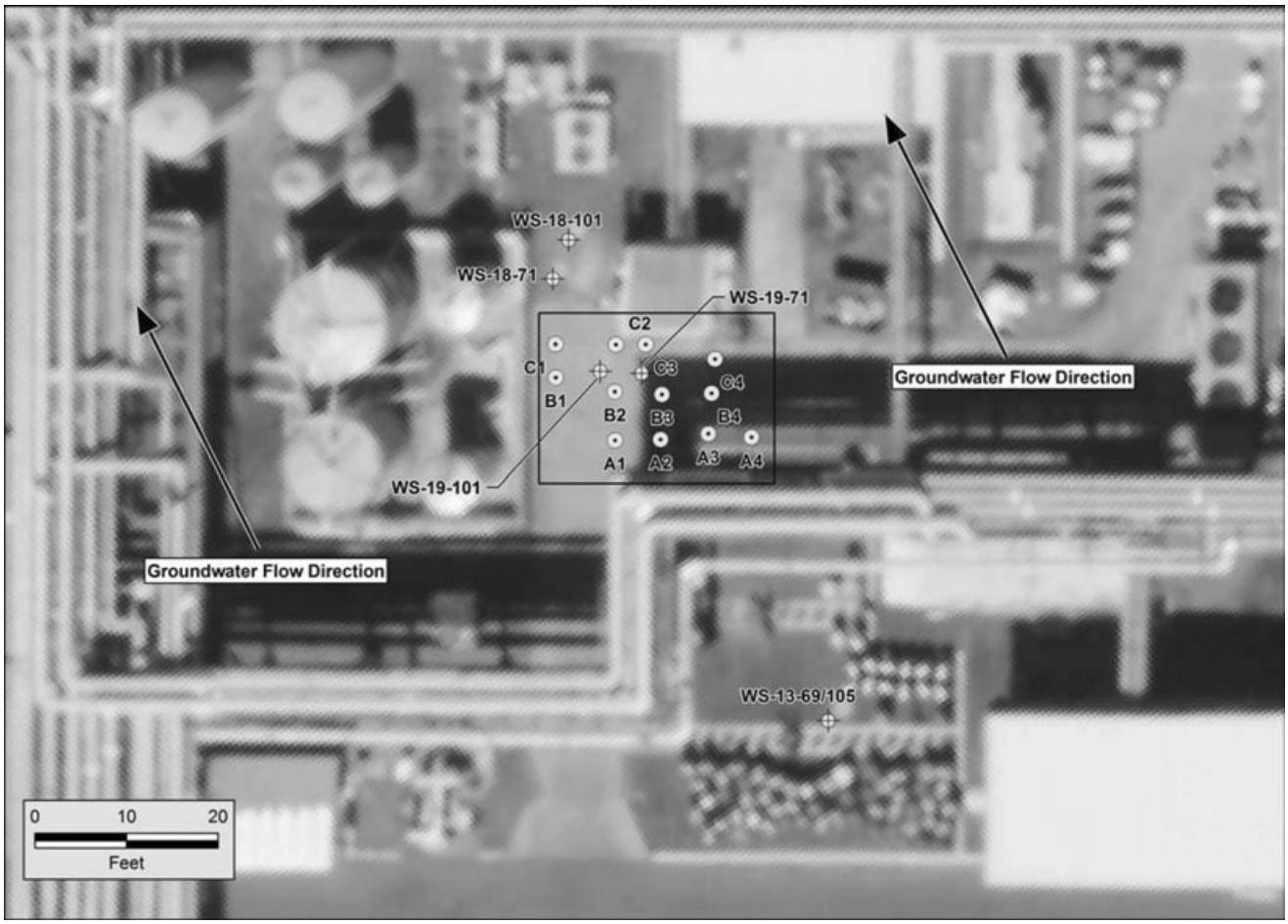

Exhibit 4. Source-area pilot-study area

(WS-18-71/101). Each pair was screened from 60 to 70 and 90 to 100 feet bgs. An existing well pair (WS-13-69/105) is located approximately 20 feet upgradient of the PRB, with screens from 53 to 68 and 89 to 104 feet bgs. Pilot-study sampling in the source area was initiated prior to installation of the PRB (baseline sampling event June 2006) and continued on a monthly schedule.

All monitoring wells were installed by Boart-Longyear E&I using a limited-access rotosonic rig. Groundwater samples from the wells in both areas were collected using dedicated bladder pumps and low-flow/parameter stabilization techniques. The groundwater samples were analyzed by Specialty Analytical (SA) of Tualatin, Oregon. The analytical schedule included VOCs (US EPA Method 8260), PAHs (US EPA Method 8270), metals (US EPA Method 6010), volatile fatty acids, fixed gases, total organic carbon, and other performance indicators. Groundwater samples were also quantitatively analyzed for *Dhc* by SiREM in Mississauga, Ontario, Canada.

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FIELD OBSERVATIONS

Direct-push injection of EHC had not been previously attempted at these depths. As such, significant challenges were encountered during installation in the riverbank area. First, the required injection pressure was higher than usual (in order to overcome the hydrostatic pressure). An air-powered piston pump was not effective in delivering the slurry. After trial and error, a hydraulic-powered Bean pump generating a maximum of 600 psi was found to be satisfactory. Secondly, hydrostatic pressure and resulting heave required water loading for monitoring well installation. Since KB-1 is redox-sensitive, a 500-gallon poly tank of water treated with lactate and sodium sulfite (to reduce the oxidation-reduction potential to –75 mV) was prepared and employed for downhole drilling fluids. Finally, significant MGP legacy impacts (i.e., aromatic and PAHs) were present in the overlying fill unit (approximately 0 to 35 feet bgs) in the riverbank area. In order to prevent dragdown of the legacy impacts, the upper 35 feet had to be cased off before advancing the injection tooling to depth. Initially, this was attempted by using a secondary direct-push rig to install conductor casing. However, the resulting lack of lateral support caused shearing of the direct-push rods within the casing. After trial and error, it was found that pilot holes filled with hydrated bentonite chips prevented shearing; while unconfirmed, it is thought that the bentonite provided the necessary lateral support.

Employing the lessons learned in the riverbank area, installation in the source area went quite smoothly, notwithstanding extremely limited access (including overhead pipe racks, secondary containment structures, and buildings). Although the legacy impacts were more significant, hydrostatic pressures were less, and the injection depths were shallower. In both areas, injection pressures ranged from approximately 300 to 400 psi. In both areas, daylighting of injected material was minor and not considered to result in a significant reduction in injection effectiveness.

After trial and error, a hydraulic-powered Bean pump generating a maximum of 600 psi was found to be satisfactory.

RESULTS

As noted above, monitoring consisted of monthly groundwater sampling (through May 2007) for the target analytes (chlorinated volatile organic compounds [CVOCs], and ethene and other gases). Quarterly sampling continued through February 2008. Monitoring also includes sampling for performance indicators such as sulfate (a redox indicator), acetylenes (abiotic degradation parameters), volatile fatty acids (VFAs, as indicators of microbial activity and fermentation), and metals related to legacy impacts at the site. This section describes the results for the target analytes and the KB-1 bacteria.

Target Analyte Results

The CVOC results are summarized in Exhibit 5. The results confirmed that the combined approach was successful—extremely conservative regulatory screening levels were achieved at the riverbank. The screening levels shown are comparable to or lower than US EPA maximum contaminant levels (MCLs) for drinking water. Although drinking water is not a recognized beneficial use for this aquifer, state regulators have set these screening levels as a conservative target for source control. Exhibit 5 also demonstrates the success of

Exhibit 5. Summary of pilot-study results

Riverbank Area		Concentration (μg/L)				Percent Reduction
Well	**Date**	**TCE**	**DCE**	**VC**	**CVOCs**	**Total CVOC**
Regulatory Screening Level		*3*	*70*	*2.4*	–	
WS-22-112	Jun-06	584	3,074	474	4,132	–
(within PRB)	Feb-08	ND	ND	ND	ND	99.99%
WS-11-125	May-06	22.9	10,557	2,490	13,069	–
(downgradient, with MGP DNAPL)	Feb-08	ND	80	16.4	96.4	99.30%
WS-20-112	Jun-06	1,100	10,067	1,610	12,777	–
(downgradient)	Feb-08	ND	0.73	ND	0.73	99.99%
Source Area		**Concentration (μg/L)**				**Percent Reduction**
Well	**Date**	**TCE**	**DCE**	**VC**	**CVOCs**	**Total CVOC**
WS-19-71	Jun-06	6,500	89,010	30	95,540	–
(within PRB)	May-08	ND	135	436	571	99.40%
WS-19-101	Jun-06	92,900	39,497	22	132,419	–
(within PRB)	May-08	ND	77.5	200	278	99.80%
WS-18-71	Jun-06	7,990	91,624	26	99,640	–
(downgradient)	May-08	227	1,780	4,350	6,130	93.85%
WS-18-101	Jun-06	198,000	34,133	41	232,174	–
(downgradient)	May-08	2,070	10,600	45,200	55,800	75.97%

the combined approach in a potential TCE DNAPL source area—very high concentrations of TCE were reduced to nearly nondetect, and mass removal was as high as 99 percent.

The riverbank area data show nearly simultaneous reduction of TCE, DCE, and VC (Exhibit 6). In the PRB well (WS-22-112) and farthest downgradient well (WS-20-112), the degradation rates were faster than in the intermediate well, WS-11-125. The difference in rates is likely due to the presence of additional legacy impacts (MGP DNAPL) in the deeper well—for example, desorption of the CVOCs from the MGP DNAPL into the aqueous phase could offset the mass removal rate. Regardless, the simultaneous reduction of the parent and daughter products suggests that mass reduction is occurring via an abiotic pathway, consistent with conclusions reached by others (Brown et al., 2007).

The source-area data reveal a difference in the initial relative concentrations between the shallow wells and the deep wells, with a larger fraction of TCE at depth. Following the injections, the TCE (as measured in the PRB wells, WS-19-71/101) was quickly reduced, resulting in the accumulation of DCE. The concentrations of DCE have continued to degrade to VC, and the accumulation of VC slowed and then reversed as DCE was depleted. Concentrations of ethene in the PRB wells ranged as high as 7,300 and 5,150 μg/L in the shallow and deep zones, respectively.

As shown in Exhibit 7, the data from the source-area PRB wells are more characteristic of the classical sequential degradation (i.e., microbial) pathway. However,

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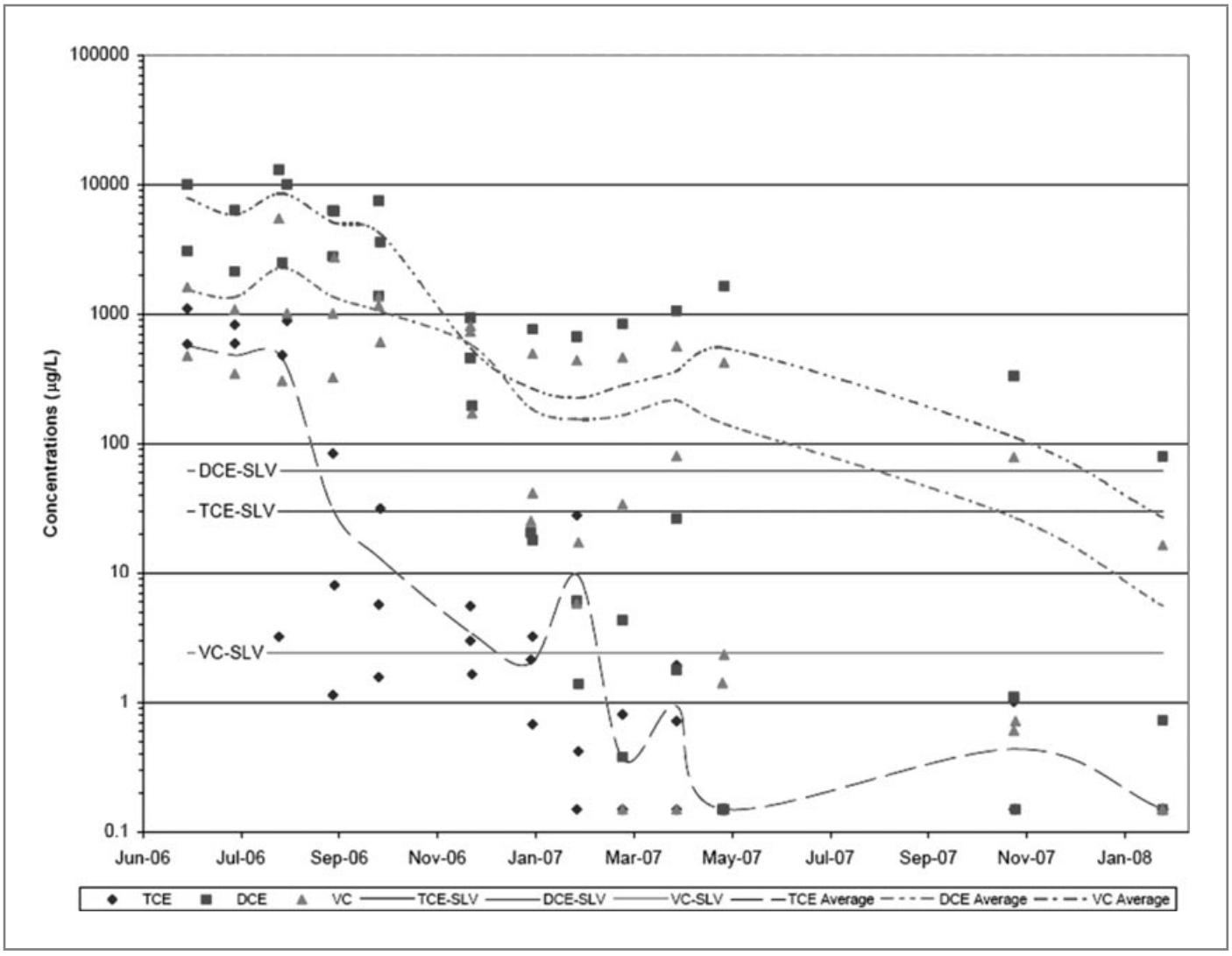

Exhibit 6. Riverbank pilot-study area results showing individual data, averages, and screening-level values (SLVs)

initial rates of TCE degradation match VC production, indicating that DCE is being degraded at least as fast as it is being produced. Later data show subparallel trends for TCE, DCE, and VC, suggesting an increased amount of mass removal via a nonsequential pathway.

The data for the downgradient well pairs exhibit similar trends, as shown in Exhibit 8. Complete dechlorination is occurring, with ethene concentrations ranging as high as 4,650 and 15,000 µg/L in the deep and shallow zones (respectively).

Initial half-life values (during significant reductions in TCE concentrations) for the PRB well were 4 and 6.7 days for the deep and shallow zones (respectively). These values are consistent with the bench-test data and support the value of bench testing for design of field application. Mean half-life values were 23 and 64 days for the deep and shallow zones (respectively) and suggest slowing reduction as concentrations decreased.

In general, these results exceeded expectations with respect to the rate and amount of mass removal.

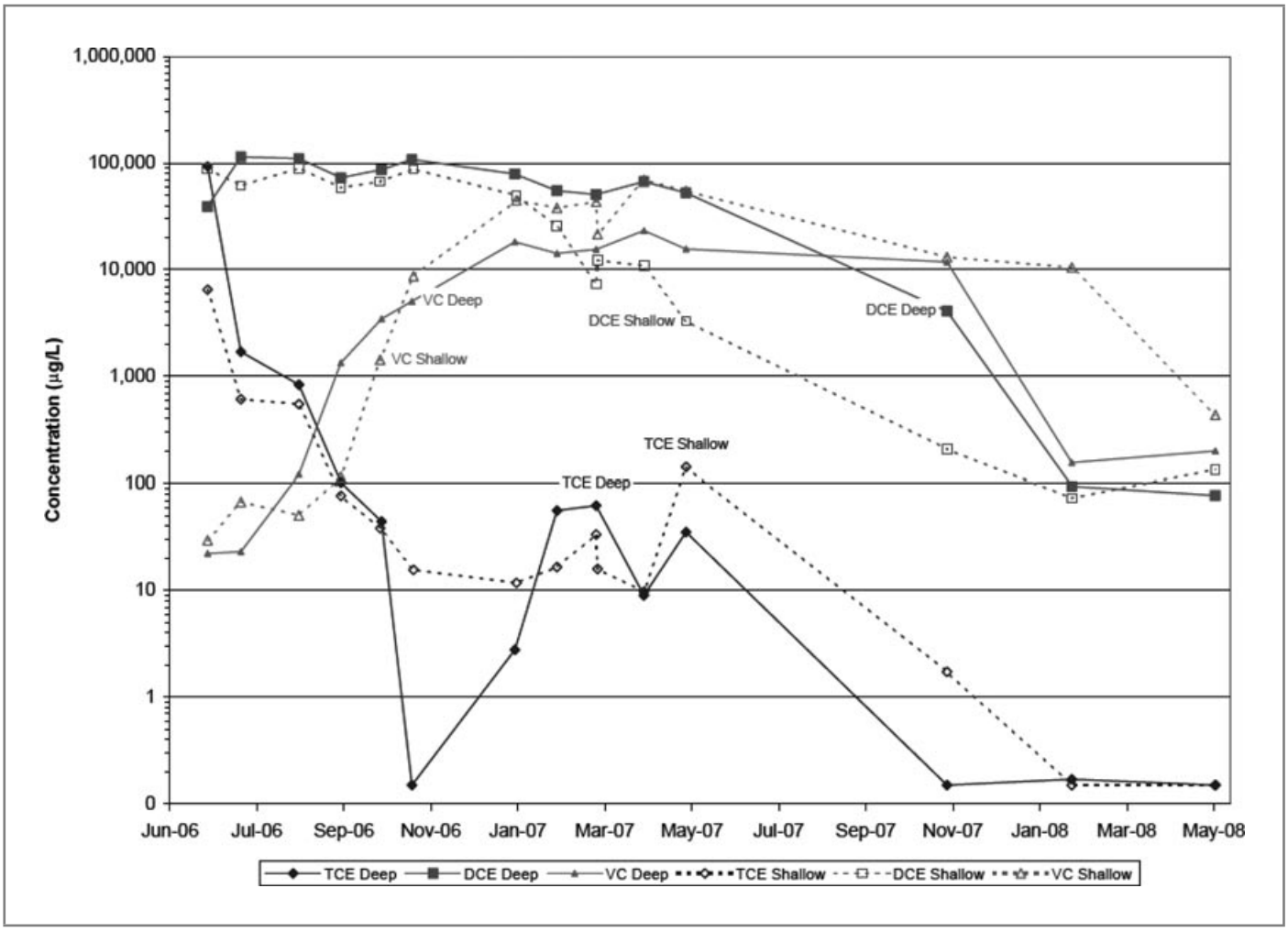

Exhibit 7. Source-area pilot-study results—PRB wells

Gene-Trac Results

Periodic sampling for biological analysis was performed at each of the wells in the pilot-study areas. Samples were analyzed for total cell counts and *Dhc* fraction (using polymerase chain reaction [PCR] test methods). PCR testing identifies the number of copies of a *Dhc*-specific ribosomal ribonucleic acid present in the sample. The results provide an estimate of the number of *Dhc* present in the sample (expressed as cells per liter), as well as the fraction of the total microbial cell counts representing *Dhc*.

Exhibit 9 summarizes the increase in KB-1 in PRB and downgradient wells relative to the upgradient wells. The data suggest that the KB-1 may be advected downgradient of the injection zone by groundwater. An alternative explanation is that installation of the PRB rapidly improves conditions for DHC growth downgradient. The net result is the same, to the extent that bacteria capable of fully dechlorinating vinyl chloride and producing ethene are increased, by as much as four to five orders of magnitude, downgradient of the PRB.

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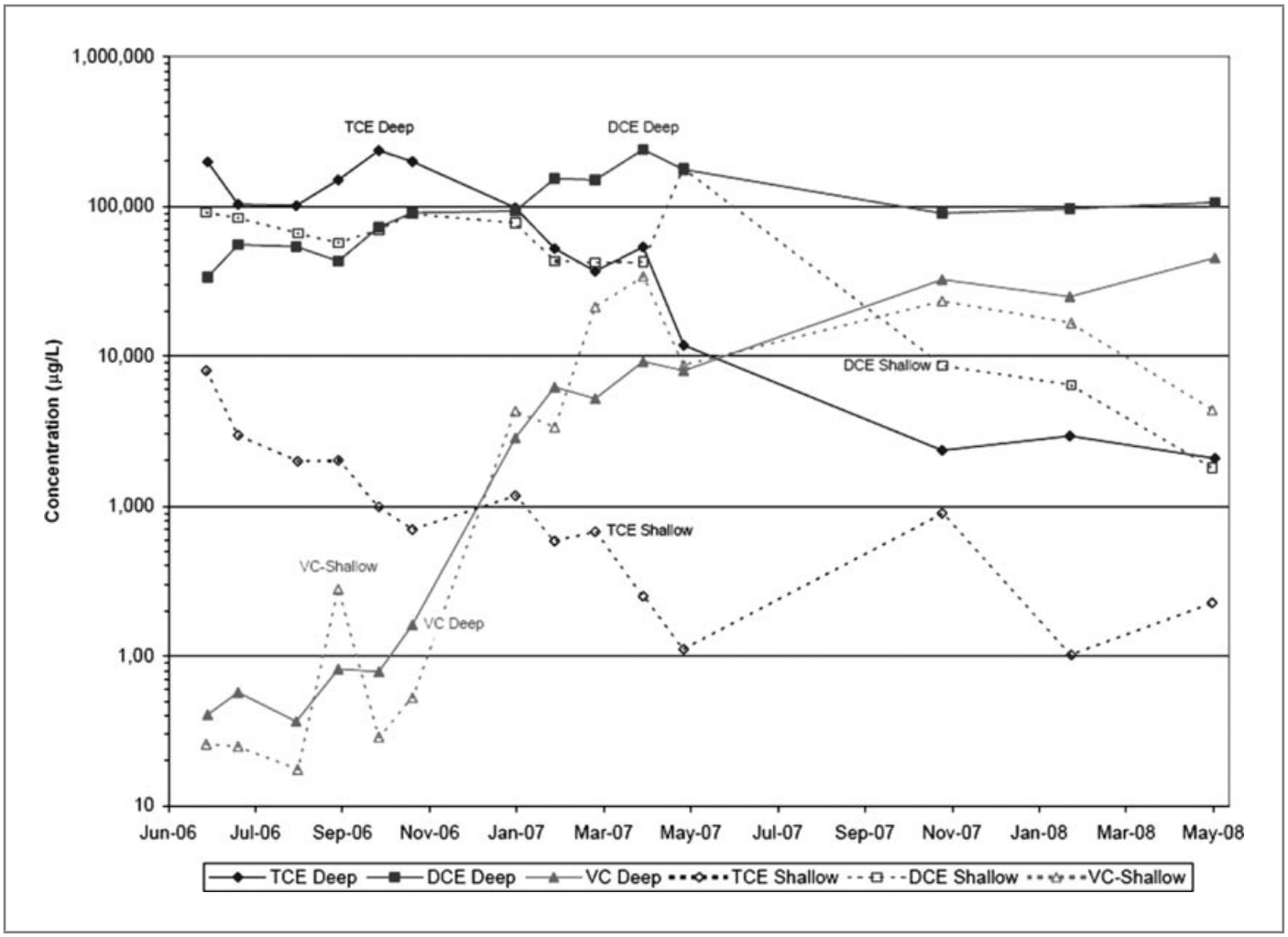

Exhibit 8. Source-area pilot-study results—Downgradient wells

CONCLUSIONS

The data from this pilot study support the following general conclusions:

- TCE source zones can be remediated using an integrated technologies approach such as EHC + KB-1. TCE concentrations representative of NAPL were reduced to nondetect or very low levels, without a net accumulation of degradation products.
- The value of bench-testing potential amendments with site soil and groundwater should not be underestimated. Significant differences in bench-scale performance of the amendments helped clarify the selection process for the pilot study and informed the design of the pilot-study PRBs.
- Installation of ISCR-enhanced bioremediation PRBs via deep injection of EHC and KB-1 in alluvial aquifers can be practicable and should be considered for deep plumes of contaminants.
- Microbial cultures of KB-1 can be distributed downgradient of an injection zone.

Exhibit 9. Gene-Trac sampling results

Source Zone			
Well	**Date**	**%*Dhc***	***Dhc* count**
WS-13-69	Oct-06	0.3%	3E + 04
(upgradient)	Jan-07	0.002%	1E + 03J
WS-13-105	Oct-06	26%	4E + 07
(upgradient)	Jan-07	27%	5E + 06
WS-19-71	Oct-06	24%	4E + 07
(within PRB)	Jan-07	100%	4E + 09
WS-19-101	Oct-06	64%	4E + 08
(within PRB)	Jan-07	80%	4E + 08
WS-18-71	Oct-06	0.03%	6E + 04
(downgradient)	Jan-07	34%	7E + 07
WS-18-101	Oct-06	0.2%	7E + 05
(downgradient)	Jan-07	5%	1E + 07
Riverbank Area			
Well	**Date**	**%*Dhc***	***Dhc* count**
WS-21-112	Sep-06	ND	ND
(upgradient)	Dec-06	0.002%	1E + 03J
WS-22-112	Sep-06	1%	2E + 06
(within PRB)	Dec-06	33%	4E + 09
WS-11-125	Sep-06	10%	6E + 07
(downgradient)	Dec-06	9%	8E + 07
WS-20-112	Oct-06	68%	2E + 09
(downgradient)	Dec-06	43%	1E + 09

To date, the local regulatory agency has agreed that the pilot study was very successful and that the combined approach should be implemented in the source area. Accordingly, design of a PRB based upon the pilot-study design is in progress. At the riverbank, the agency has determined that the MGP impacts are a higher priority and that source control decisions will be driven by remedies to address these legacy impacts.

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Dr. **Fayaz Lakhwala** is the director of remedial design and engineering services at Adventus Americas, Inc., an environmental company that specializes in soil, sediment, and groundwater treatment technologies. Before joining Adventus in 2004, he was department head at URS Corp. in New Jersey where he managed the remediation engineering group. Dr. Lakhwala has over 17 years of experience in the area of site remediation and has worked on projects in the United States, Europe, and Asia. His expertise is in the areas of groundwater circulation wells, enhanced anaerobic bioremediation, advanced oxidation, *in situ* chemical oxidation, multiphase extraction, and bioreactor design and engineering. Dr. Lakhwala has a BE in chemical engineering from India and an MS and PhD in chemical engineering from the New Jersey Institute of Technology, Newark, New Jersey.

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