Obtaining High-Resolution Data to Demonstrate BOS 100® Performance in a Large TCE Plume with Extensive DNAPL Present

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ABSTRACT: A high-resolution, quantitative-data approach was implemented at a large, urban industrial facility where trichloroethene (TCE) was used extensively as a cleaning solvent. The site was underlain by river deposits and sedimentary bedrock. Subtle facies changes resulted in solute concentrations that varied by orders of magnitude in distances of only centimeters (cm). This inherent complexity was the impetus for quantitative, high-resolution data to characterize site conditions and design, implement, and demonstrate the performance of the BOS 100® remedial program. Burgeoning technologies such as the Membrane Interface Probe (MIP) can be effective qualitative screening tools, but are ineffective for accurate injection design or performance monitoring, especially at sites where dense non-aqueous phase liquid (DNAPL) is present. At this site, the high-resolution program consisted of analyzing 1,291 continuous soil samples from 186 borings and 5,515 groundwater samples from 1,349 monitoring wells. Pre-treatment data were used to calculate mass flux and mass discharge to develop an accurate conceptual site model (CSM); evaluate source and plume strength; and calculate injectate loadings. The benefit of the high-resolution data was to identify zones which transmitted the bulk of the contaminant mass. This insight was necessary to design and implement an effective and economical remedy. Post-treatment data were used to evaluate injectate distribution and to confirm the effectiveness of the BOS 100® program.

INTRODUCTION

A large quantity of TCE was stored and used at a manufacturing facility located in a major metropolitan area. Decades of tankage spills and product-line releases resulted in an approximately 230 square meter (m^2) DNAPL plume and an approximately 6,200 m^2 dissolved-phase plume (Figure 1). TCE in soil was observed at concentrations up to 54,450,000 micrograms per kilogram (µg/kg) and TCE in groundwater was observed at concentrations up to 1,280,000 micrograms per liter (µg/L).

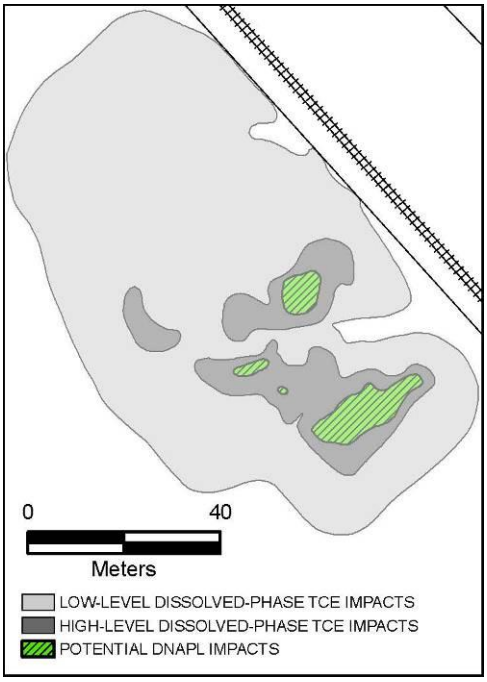

FIGURE 1. TCE plume.

An extensive technical feasibility review was conducted to select an appropriate remedy. Biotic methods were dismissed because there was very little if any apparent natural biodegradation in the subsurface. Conventional abiotic methods, e.g., chemical oxidation or chemical reduction, were dismissed because of inherent deficiencies, e.g., solute mobilization, reagent depletion, and insufficient residence time. Instead, a carbon-based technology (BOS 100®) was selected because typical deficiencies are not a factor and remediation is complete following a

single application. Retreatment is only necessary if slurry distribution is insufficient, not because of rebound, i.e., back diffusion.

In extremely heterogeneous settings such as this site quantitative, high-resolution data are needed to accurately characterize and map solute distribution in soil and groundwater. Data gathering does not stop at design, but is integral to the implementation phase as well. Successful injection programs need to be flexible and supported by robust performance monitoring that allows using "where you have been" to adjust for "where you need to go".

Site Description. The site was underlain by river deposits and sedimentary bedrock (Figure 2). Impacted alluvium included approximately 5 meters (m) of interbedded granular and fine-grained deposits. Beneath the source area was approximately 15 m of well-graded sands and gravels underlain by an aquitard of silt and silty clay where DNAPL pooled at the interface. Impacts did not extend into the underlying claystone bedrock. Solute transport was dictated primarily by physical properties of the DNAPL, (e.g., density) and by aquifer characteristics.

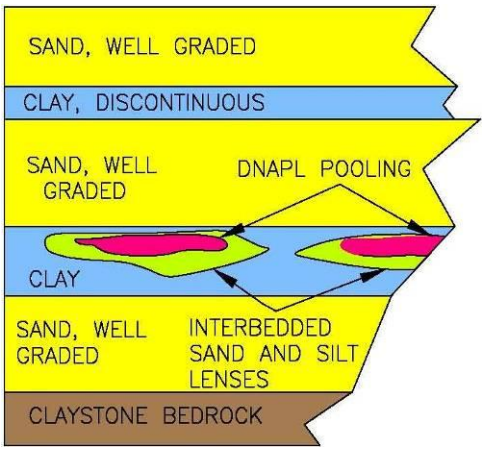

FIGURE 2. Matrix column.

Aquifer characteristics which had the biggest impact on site remediation were the anisotropy and heterogeneity caused by the variance in matrix density and grain size in the alluvial sands. Other challenges were caused by a very small gradient that resulted in solute distribution and flow direction being less predictable. Over the course of history, it did not take much to "tip the table one way or the other", so flow direction, hence, distribution patterns changed frequently.

Remedial Technology. The selected remedy was *in-situ* treatment using an immiscible, activated carbon solid injectate, BOS 100®. Each carbon grain is impregnated with elemental iron (Figure 3) such that carbon adsorption properties are coupled with the dechlorination process of iron (a stepwise function that produces a variety of byproducts, i.e., "daughters"). Based on applicable half-cell reactions and associated Gibbs Free Energy of Reaction, the elemental iron serves as an electron donor (being oxidized in the process) and the aliphatic chloroethenes/chloroethanes serve as the principal electron acceptors. The final step is the generation of end-product hydrocarbons (ethene or ethane) which, due to very high vapor pressures and discretionary London dispersion forces, escape the matrix and allow for "fresh" contaminant to be adsorbed by the carbon catalyst.

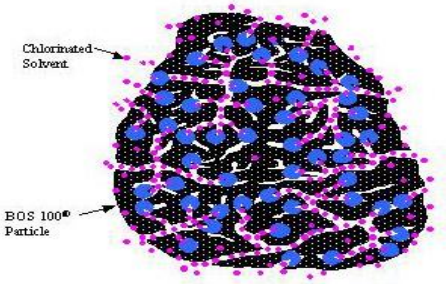

FIGURE 3. BOS 100® particle.

Deficiencies such as slow or incomplete treatment due to insufficient residence time are avoided in that the initial contaminant is sequestered in the BOS 100® (as are

kinetically-generated derivatives) during the cleanup cycle. The resident solutes are then reduced to innocuous end products via adequate contact with the impregnated iron.

Initial Challenges. Initial treatment was only marginally successful because of data gaps inherent to using standard site-characterization procedures. The conventional practice of collecting only a few soil samples and basing treatment strategy on a limited network of monitoring wells did not provide the detail necessary to generate an accurate CSM. In addition to needing higher-resolution data in the source area, it was imperative to shift the design focus to (saturated) soil impacts rather than basing injection loadings on dissolved-phase groundwater concentrations only.

Another challenge (apparent as more-focused data was obtained) was the fact that most of the dissolved-phase plume was contained within granular alluvium. Remedy delivery is less of a problem when the slurry is a miscible fluid. In this case, however, the remedy is a solid that is mixed in water as a slurry. The well-graded matrix of the native formation tended to strain out the granular BOS 100® thereby leaving large globular masses of injectate, rather than a more lenticular distribution. Ostensibly, a sand unit cannot be fractured so it was difficult to propagate the remedy outward via hyrdrofracturing. These distribution woes were overcome by using a high-pressure (14 E 10^6 Pascals), high-flow-rate [up to 16 liters per seconds (l/s)] pump to "jet" the granular carbon-based slurry into the formation. Mechanical mixing was achieved by "fluidizing" the sandy matrix (Figure 4).

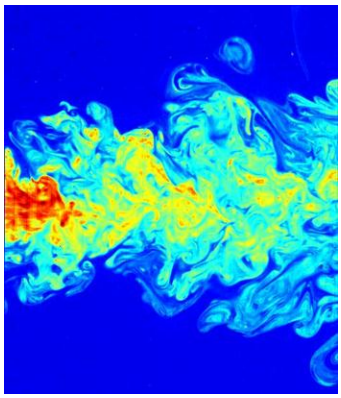

FIGURE 4.
Mechanical mixing.

CHARACTERIZATION APPROACH AND METHODS

As the project advanced, more data was gathered to the point where a "high resolution" image of the site evolved that was used to generate a detailed and accurate CSM. Abundant soil and groundwater samples were collected in the DNAPL areas and throughout the dissolved-phase plume.

In the DNAPL areas, soil data were used to characterize the sorbed and dissolved-phase impacts in saturated samples and the groundwater data were used to characterize the

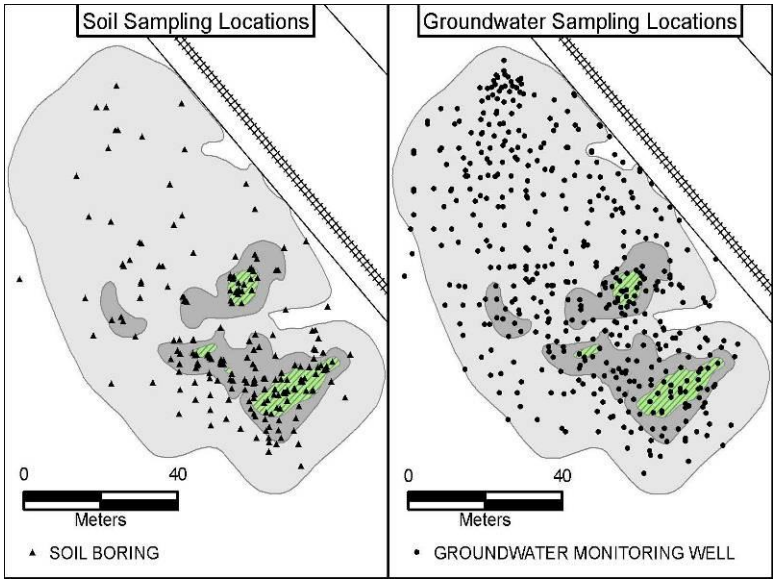

FIGURE 5. High-resolution data obtained from soil boring and groundwater well locations.

extent of desorptive partitioning. Care was taken to prevent vertical migration during probing/drilling.

Within the dissolved-phase plume, groundwater data were used to evaluate plume strength and solute distribution due to advective and dispersive transport. In all cases, soil and groundwater concentrations were used to design appropriate slurry loadings for treatment.

Continuous Soil Sampling. Direct-push technology (DPT) was used to complete 186 soil borings throughout the DNAPL and dissolved-phase plume areas (Figure 5). Continuous soil samples were collected and analyzed to generate vertical profiles of pre-treatment solute distribution and post-treatment BOS 100® distribution.

Detailed boring logs were kept to document lithology, color, relative moisture content, and visual and/or olfactory evidence of volatile organic compounds (VOCs). In fine-grained deposits, fracture patterns and/or other pathways were noted which might affect leakage, and hence, solute fate and transport. Soil samples were field screened at approximate 15 cm intervals with a photo-ionization detector using ambient temperature headspace analysis methods to aid in determining potential zones of impact.

Soil samples were collected from all zones of apparent impact or from intervals of approximately 30 cm (1,291 samples in all) and analyzed for VOCs using US Environmental Protection Agency (EPA) Method 8260B. As listed in Table 1, TCE concentrations could vary 5 orders of magnitude in 46 cm, indicating that preferential pathways steered solute circuitously through the matrices, but with apparent precision.

TABLE 1. TCE concentrations in soil.

Boring ID: B108	
Depth (meters)	**TCE Results (µg/kg)**
9.26-9.32	8,067
9.57-9.63	115
9.87-9.93	55
10.18-10.24	93
10.6-10.63	512
10.78-10.85	97
11.09-11.15	428
11.43-11.49	53,760
11.55-11.61	25,477,000
11.67-11.73	915,300
12-12.07	193
12.31-12.37	180,190
12.55-12.61	42,367
12.92-12.98	23,210
13.35-13.47	428

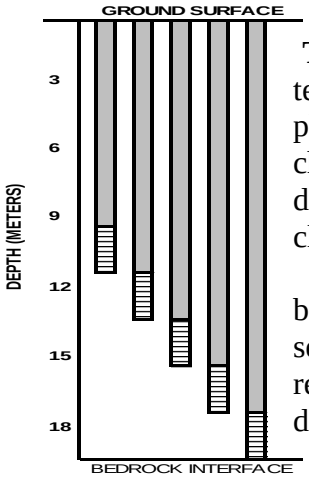

FIGURE 6. Nested wells.

Temporary Well Installation. DPT was used to install 1,349 temporary monitoring wells throughout the DNAPL and dissolved-phase plume areas (Figure 5). The purpose of the wells was to characterize impacted regions, evaluate treatment performance during remedy implementation, and provide confirmation that target cleanup levels had been achieved.

A primary "take away" from the detailed logs of the continuous borings was that aquifer architecture was complex. Subsequently, selecting appropriate well-screen locations was critical in representing aquifer heterogeneity that resulted in the complex distribution of solute.

The wells were constructed using 2.54 cm diameter, flush-threaded polyvinyl chloride pipe and 10-slot screen. During the characterization phase, as many as five nested wells (Figure 6)

were installed at a single location in the DNAPL area to generate a vertical profile and to determine the "basement" of impact. These, and all other wells, were later used to obtain high-resolution data during implementation and closure phases of the project.

A total of 5,515 groundwater samples were collected from site wells using dedicated bailers and/or low-flow methods and analyzed for VOCs using EPA Method 8260B. Similar to soil profiles, facies changes in the native geologic units resulted in TCE concentrations in groundwater that could vary 3 orders of magnitude between adjacent screened intervals.

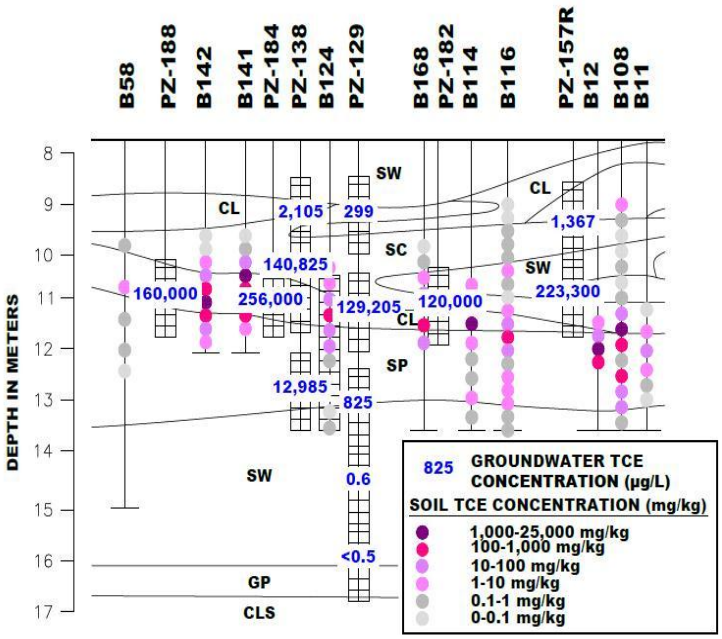

FIGURE 7. Typical cross section/transect.

Cross Sections and Transects. Detailed geologic cross sections were generated from the boring logs and annotated with TCE concentrations from the extensive array of soil and groundwater samples (Figure 7). These quantitative data were preferred over qualitative data that might otherwise have been obtained from a standard MIP survey.

In the early stages of the project, the cross sections were used to identify data gaps in understanding the complex geologic setting. Additional soil borings/wells were installed and/or additional sampling activities were conducted, accordingly.

Once site characterization was considered complete, cross sections orthogonal to groundwater flow were used as transects to quantify source-zone and plume strength. Plume stability was of less concern since the project objective was to conduct thorough, plume-wide treatment to achieve rapid site closure. Given the age of the plume, it was assumed to be stable to contracting.

Calculating Mass Flux and Mass Discharge. To better understand plume behavior, a site should not just be evaluated based on solute concentrations at discrete locations. The static nature of such an approach can be misleading. A mass-flux/mass-discharge approach factors in groundwater velocity to better evaluate solute fate and transport. In essence, even if solute concentrations are high but groundwater velocity is very low (or even stagnant), then the mass flux is very low; hence, solute mobility is very low, ergo so is risk.

Assessing the risk of impact to downgradient receptors is a common application of mass-flux/mass-discharge measurements. For this site, treatment was conducted plume wide and there was no evidence of off-site impacts; therefore, there was very little risk to third parties. The purpose of a mass-flux/mass-discharge analysis in this case was twofold. First, mass flux was used to identify the variability in solute concentrations and

the transmissive zones through which the bulk of the mass moved. Second, mass-discharge measurements over time were used to ensure that targeted levels (5 µg/L of TCE) were being met at the downgradient property boundary, even though a higher, risk-based concentration of TCE was allowed within the (on-site portion of the) plume. In other words, the property boundary needed to be the "zero flux line".

It was important to understand plume architecture (solute distribution dictated by heterogeneity) and plume strength (contaminant mass moving in groundwater per unit time – The Interstate Technology & Regulatory Council, 2010) to develop an appropriate treatment design. These metrics were evaluated by calculating mass flux within solute-bearing horizons along cross-sectional transects.

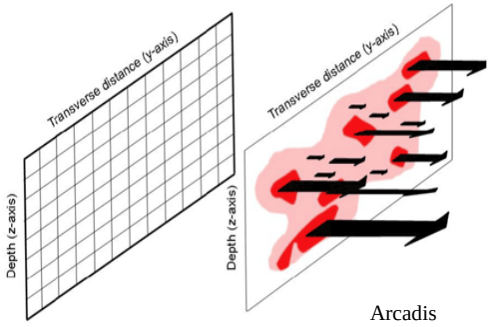

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FIGURE 8. Different solute strengths moving through the subsurface.

Mass flux is the mass rate per unit area (grams/day/square meter) at a discrete location in a plume (Figure 8) and mass discharge is the total mass per unit time (grams per day, i.e., g/d) that flows through an entire cross section of a plume. The transect method was used to calculate mass flux and mass discharge in and just downgradient of the source area and along other transects throughout the plume to evaluate remedy performance. Seepage velocities were estimated at individual wells along transects using equilibrium flow rates established during low-flow sampling activities. Corresponding TCE concentrations in groundwater from those wells were used to calculate mass flux and mass discharge, as follows:

$$\text{Mass Flux (J)} = q_0 \cdot C = -K \cdot i \cdot C$$

Where:
q_0 = groundwater flux, $L^3/L^2/t$ (e.g., volume/area/d)
K = saturated hydraulic conductivity, L/t, (e.g., m/d)
i = hydraulic gradient, dimensionless (e.g., m/m)
C = contaminant concentration, M/L^3 (e.g., mg/volume)

Mass discharge is the integration of the mass fluxes across a selected transect:

$$\text{Mass Discharge } (M_d) = \int_A J dA$$

Where:
A = area of the transect, L^2 (e.g., m^2)
J = spatially variable mass flux
(The Interstate Technology & Regulatory Council, 2010)

Note that mass flux (J) varies both spatially and temporally across transects and these variations may be significant. Spatial and temporal variations in mass flux are caused by variations in both contaminant concentrations and groundwater-flow magnitude and direction, which typically vary widely for most dissolved plumes (Guilbeault, Parker, and Cherry, 2005). In contrast, mass discharge (M_d) can vary only over time at transects since

there is only a single value for an entire transect (The Interstate Technology & Regulatory Council, 2010).

Table 2. Mass flux and mass discharge.

Average Seepage Velocity (v) of Fine-Grained Alluvium	2.35E-07 cm/sec
Average Seepage Velocity (v) of Coarse-Grained Alluvium	2.19E-06 cm/sec
Average Hydraulic Gradient	0.0035 (unitless)
Average Mass Flux From Source Area (Pre-Treatment)	682,185 mg/m^2/year
TCE Mass Discharge From Source Area (Pre-Treatment)	138 kg/year
Average Mass Flux From Source Area (Post-Treatment)	31,984 mg/m^2/year
TCE Mass Discharge From Source Area (Post-Treatment)	6 kg/year
Mass Flux Percent Reduction	**95.31 %**

Mass-flux calculations along the transect shown on Figure 7 are presented in Table 2. The estimated pre-treatment mass discharge was 138 kilograms per year (kg/y), based on a cross-sectional area of approximately 165 m^2. The estimated post-treatment mass discharge was 6 kg/y, a mass reduction of over 95 percent as a result of the BOS 100® treatment.

TREATMENT DESIGN, IMPLEMENTATION, AND MONITORING

Obtaining quantitative, high-resolution data to fully characterize the site and prepare an accurate CSM also resulted in a remedial design that was extremely successful. It is essential for *in-situ* treatment to know where the solute "is" and where it "isn't". To be effective, especially "cost effective", in a complex setting such as this site, the design needs to be pin-point accurate and the implementation needs to be surgical or the vagaries and nuances of solute occurrence can cause solute persistence and result in project failure.

The design of the BOS 100® remedy was based on carbon adsorption (Freundlich isotherms) and iron demand of VOCs. Slurry loading is a volumetric calculation based on

ASSESSMENT SOIL BORING

PID Reading (ppm)	TCE Analytical Result (ug/kg)	Depth (meters)	Sample Run	Recovery	Soil/Rock Type
1	512				CL
ND	97	11.0			
1	---				ML
333	428	11.3			
9	---			60"	CL
9,999+	**25,477,000**	11.6			ML
390	**915,300**				
124	---	11.9			CL
4	193				
9	---	12.2			ML
109	180,190				
110	---	12.5			
761	42,367				
455	---	12.8			SP
57	23,210				
22	---	13.1		60"	
13	---				
40	428	13.4			
13	---				ML
2	---	13.7			

INJECTION INTERVALS

Depth (meters)	BOS-100® Injectate Loading (kg)
10.85	18.2
11.00	18.2
11.15	18.2
11.30	25
11.45	181.8
11.60	**181.8**
11.75	**181.8**
11.90	36.4
12.05	18.2
12.20	25
12.35	36.4
12.50	18.2
12.65	---
12.80	---
12.95	18.2
13.10	18.2
13.25	18.2
13.40	---
13.55	---
13.70	18.2

POST-INJECTION BORING

Depth (meters)	BOS-100® Observations
10.85	BOS-100® Observed
11.00	BOS-100® Observed
11.15	---
11.30	BOS-100® Observed
11.45	BOS-100® Observed
11.60	BOS-100® Observed
11.75	BOS-100® Observed
11.90	BOS-100® Observed
12.05	BOS-100® Observed
12.20	---
12.35	---
12.50	BOS-100® Observed
12.65	---
12.80	---
12.95	---
13.10	BOS-100® Observed
13.25	BOS-100® Observed
13.40	---
13.55	---
13.70	BOS-100® Observed

FIGURE 9. Proper implementation of design results in accurate placement of slurry.

grid dimension and solute concentration. Detailed cross sections and high-resolution soil and groundwater data were used to select target injection locations.

Implementing Sophisticated Remedy Design. A variety of implementation challenges were overcome because high-resolution data were available. As previously discussed, a complex system of preferential pathways resulted in very thin or narrow seams which carried extremely-high solute concentrations surrounded by deposits with little to no apparent impact. This high-resolution data allowed for precision placement of the remedy (Figure 9). In situations where DNAPL was present and very high loadings were required, guar (and a de-linking agent) was added to increase slurry density, i.e., approximately double the amount of BOS 100® could be suspended and injected into the formation.

Slurry distribution was occasionally inadequate due to preferential flow steering slurry away from a targeted area or because a very flat hydraulic gradient (4.88 E 10^{-4} m/m) within much of the treatment area caused unpredictable solute distribution. Radial injection grids were often used for re-treatment in lieu of Cartesian grids to overcome these challenges.

FIGURE 10. Evidence (black striping) of thorough BOS 100® distribution.

As previously discussed, other distribution challenges were overcome by using a high-pressure, high-flow-rate pump. An assortment of specialized injection tips were used to manage the flow from the pump. A typical slurry volume of from 120 to 190 liters was injected at rates ranging from approximately 10 to 16 l/s. Injection durations ranged from approximately 10 to 15 seconds. The injectate exited the tips at velocities that ranged from 60 to over 100 meters per second and was directed at select locations with precision. The effectiveness of this injection technique to distribute the BOS 100® slurry is shown in Figure 10.

TABLE 3. TCE concentrations in groundwater.

Well ID	Historical Maximum TCE Result (µg/L)	Recent TCE Result (µg/L)	Percent Reduction
PZ-039	10,100	10	99.90
PZ-040	52,244	98	99.81
PZ-052	106,250	6	99.99
PZ-055	1,280,000	4	100.00
PZ-125R	30,695	55	99.82
PZ-127	149,260	84	99.94
PZ-138	140,825	39	99.97
PZ-154	589,870	78	99.99
PZ-156R	594,125	6	100.00
PZ-157R2	210,000	62	99.97
PZ-165R	27,000	14	99.95
PZ-175	59,520	40	99.93
PZ-182	120,000	58	99.95
PZ-184	256,000	27	99.99

Performance Monitoring Methodologies. There were a number of performance-monitoring methods used during the implementation and closure phases of the project. Groundwater samples were collected frequently before, during, and after slurry injections to monitor remedy performance. It is important to be "nimble"

while in the field and next-day laboratory results for the samples allowed for design revisions to be implemented quickly. Mass discharge was periodically calculated along selected transects (Table 2) to monitor mass reduction, i.e., diminished plume strength, over time and to ensure that "zero" mass flux was maintained at the property boundary. Continuous soil borings were also completed and sampled after treatment in DNAPL areas to confirm that solute mass was significantly reduced/eliminated, when compared to data obtained from collocated, pre-treatment borings. When slurry distribution appeared inadequate (based on well response, i.e., no apparent reductions in TCE concentrations), forensic drilling was conducted to observe if seams of BOS 100® were present in the formation in the vicinity of nearby wells. Soil characteristics were noted during drilling for heterogeneities that might have caused slurry flow to deviate away from targeted areas.

Performance monitoring continued at designated on-site and point-of-compliance wells during the closure phase of the project. Typical "before" (pre-treatment) and "after" (post-treatment) monitoring results are shown in Table 3.

CONCLUSIONS

Obtaining high-resolution data was essential in characterizing and remediating this complex site, given such highly variable anisotropy and heterogeneity. The project was a success because the quantity and quality of data was used to generate an accurate CSM, optimize the placement of the very effective BOS 100®, and monitor the performance of the remedy. The DNAPL portion of the plume was reduced from percent-level concentrations (up to 54,770,000 micrograms per kilogram TCE in soil and 1,280,000 micrograms per liter TCE in groundwater) to closure levels. The dissolved-phase plume was also mitigated and site-closure monitoring began in 2011. A Request for No Action Determination has been submitted and closure of the site is expected in 2014.

ACKNOWLEGMENTS

This project was completed by LT Environmental, Inc. (LTE) of Arvada, Colorado, USA, for a confidential client. Though the name of the client is not disclosed, permission by the client was granted to LTE to present the project details contained herein.

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