Enhanced Anaerobic Bioremediation Shuts Down a TCE Plume Groundwater Treatment System

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ABSTRACT: At a manufacturing facility, rows of injection wells were used to gravity feed 60% sodium lactate solution into the shallow sand aquifer in order to promote enhanced anaerobic bioremediation (EAB) of trichloroethylene (TCE). Concentrations of TCE were as high as 20,000 μg/L, and bioremediation successfully treated them to less than 50 μg/L during four years of active treatment. Intermediate daughter products cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC) did temporarily accumulate and sub slab depressurization was required to mitigate indoor air risks. The complete dechlorination daughter product, ethene, was also generated steadily throughout the process. The site groundwater cleanup goals established by the State of Connecticut were drinking water criteria for offsite groundwater. Monitored natural attenuation is expected to reduce residual contamination levels to meet drinking water criteria within the next several years. A predictive plume model was developed from historical data. The model demonstrated that the chloroethenes attenuated naturally, although slowly, and their concentrations decreased with distance downgradient from the source. The model results were also used to negotiate alternative on-site cleanup goals that were calculated to be protective of human health at downgradient off-site receptors. These higher cleanup standards were acceptable to the regulatory agency as the endpoint for active remediation and the start of monitored natural attenuation.

INTRODUCTION

At a manufacturing operation in Connecticut, chlorinated ethene solvents were found in the shallow aquifer mostly beneath the facility building. The contaminants were predominantly TCE with historical groundwater concentrations as high as 50,000 μg/L in the source area. Tetrachloroethene (PCE) was also a source chemical, although present at lower concentrations up to 600 μg/L. Historically total 1,2-DCE concentrations were as high as 23,000 μg/L, and although usually below detection limits, VC concentrations have been as high as 600 μg/L when observed. Redox conditions in the affected groundwater ranged from moderately reducing in the source area to aerobic farther downgradient.

Hydrogeology. The shallow aquifer starts at approximately 4 ft (1.2 m) below ground surface (bgs) and is composed of sand that is underlain by varved clay at approximately 14 ft (4.3 m) bgs as shown in the cross-section in Figure 1. The chloroethene plume is approximately 10 ft (3.0 m) thick, 500 ft (150 m) long in the direction of groundwater flow, and 140 ft (43 m) wide. Pumping test data indicated a horizontal hydraulic conductivity of 50 ft/day (15 m/day), from which we estimated a natural groundwater velocity of 0.8 ft/day (0.2 m/day) to the west.

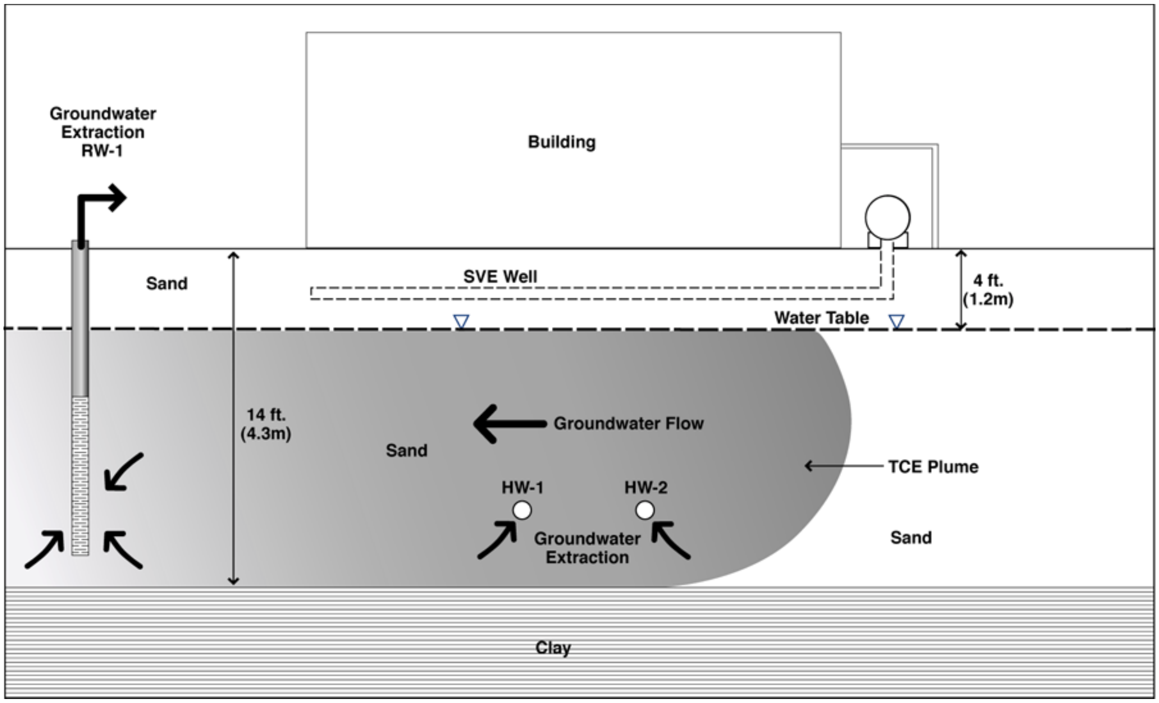

FIGURE 1. Schematic Site Cross Section Showing the Shallow Aquifer Stratigraphy.

Remediation History. Chloroethenes in the vadose zone, between the water table below and the building slab above, were removed through horizontal soil vapor extraction (SVE) wells that were run from July 1997 through September 1999. Groundwater contamination was pumped from below the building and treated using air stripping and activated carbon. The groundwater was extracted through two horizontal wells oriented perpendicularly to the direction of groundwater flow, one in the farthest upgradient part of the source area and the second approximately 120 ft (35 m) downgradient. A third vertical extraction well is located farther downgradient, beyond the building footprint at the property boundary (see Figure 1). Under the influence of groundwater pumping, the horizontal hydraulic gradient approximately doubled, resulting in an estimated enhanced groundwater velocity of approximately 1.6 ft/day (0.5 m/day).

Operation of the groundwater pump and treat system began in May 1997, and by 2001 annual chloroethene mass removal had leveled off to approximately 3 lb/yr (1.4 kg/yr). Starting in July 2004, anaerobic bioremediation was gradually phased in, while simultaneously phasing out groundwater pump and treat in the source zone. Recently, the downgradient vertical extraction well and treatment system was shutdown and active treatment suspended. The bioremediation system is described in detail below.

IN SITU BIOREMEDIATION SYSTEM DETAILS

Anaerobic bioremediation was initiated through the addition of 60% (w/w) aqueous sodium lactate solution, directly into the chloroethene plume. Sufficient lactate was supplied to provide a dissolved organic carbon (DOC) groundwater concentration of approximately 2,000 mg/L in the biotreatment zone. The lactate solution was gravity fed directly into 2-inch (5.1 cm) diameter injection wells, arranged in rows oriented perpendicularly to the direction of groundwater flow and starting upgradient in the most contaminated portion of the source area (Figure 2). The injection wells were screened from 1 ft (0.3 m) below the water table to the top of the underlying clay layer.

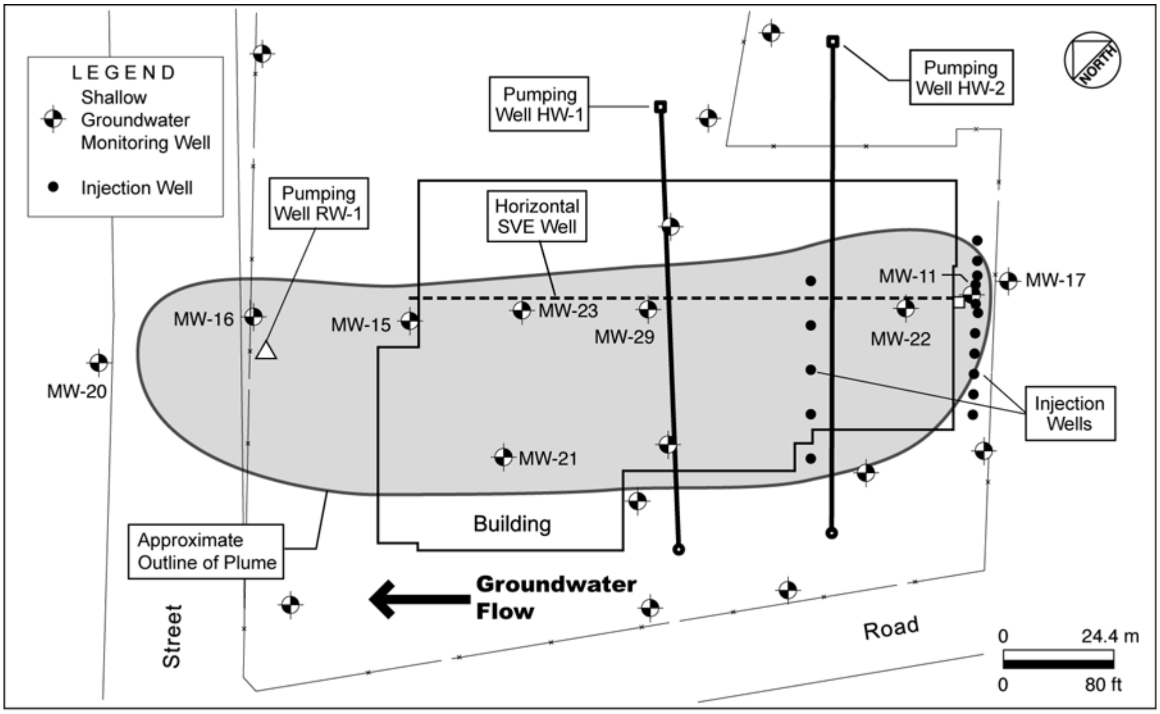

FIGURE 2. Site Plan Showing the Locations of Groundwater Extraction Wells, Organic Carbon Injection Wells, and Monitoring Wells.

In July 2004, the first lactate addition was performed utilizing the farthest upgradient row of injection wells (Row 1). Groundwater pumping from the nearest downgradient extraction well HW-2 helped to distribute this first addition of DOC throughout the treatment zone. Within two months, DOC was detected in groundwater sampled from HW-2, so its pumping was stopped to prevent further removal of the added lactate. Subsequent lactate injections involved both Row 1 and Row 2, located approximately 120 ft (35 m) down gradient from Row 1. The second injection was begun in April 2005, and two months later groundwater extraction from HW-1, farther downgradient, was stopped as well. Thus, as noted above, only the vertical extraction well RW-1 continued to operate to mitigate potential off-site chloroethene migration until recently. Additional lactate injections were conducted in June 2006 and October 2006. The injection system was expanded by one additional, farther downgradient row of injection wells just west of HW-1. Two additional lactate injections were conducted in August 2007 and February 2008.

Periodically, groundwater samples are collected from monitoring wells within the biotreatment zone and tested for pH, redox potential, dissolved oxygen (D.O.), nitrate, ferrous iron, sulfate, methane, ethane, ethene, DOC, metabolic acids, and halogenated volatile organic compounds (HVOCs) to follow the progress of bioremediation and the relevant groundwater geochemistry. Approximately five months after each lactate injection, most of the added carbon has been depleted as observed by DOC concentrations falling below 100 mg/L, and further addition of lactate is required to continue the anaerobic dechlorination process. Lactate metabolism appears to follow a pseudo-first order decay model, with a half life of approximately one month.

BIOREMEDIATION RESULTS

Within one month of the second lactate injection in May 2005, methanogenic redox conditions were established and maintained thereafter in the biotreatment zone, with methane groundwater concentrations ranging from 3,000 to 23,000 µg/L, and sulfate groundwater concentrations staying below 10 mg/L. At the same time, the groundwater redox potential was in the -100 to -220 mV range, and pH held steady between 6.5 and 7.

Almost one year into the biotreatment, after the second lactate injection, TCE concentrations had increased from approximately 5,000 to 20,000 µg/L. This was likely due to increased solubilization of the high concentration organic carbon source (Bioavailability Enhancement Technology™, U.S. patent no. 6,783,678). Dechlorination daughter product cDCE, VC, and ethene concentrations increased even more sharply at the same time. Thus, even as more TCE dissolved into the groundwater, complete dechlorination of the parent compounds all the way to ethene was occurring.

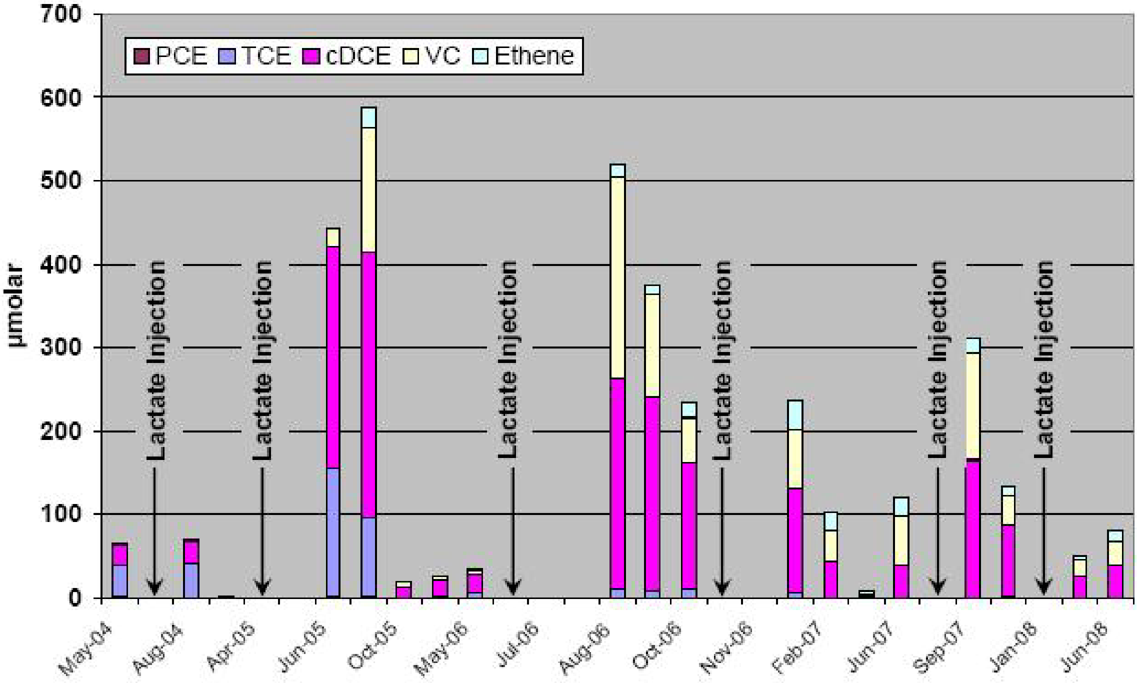

FIGURE 3. Chloroethene Transformations in Molar Units Observed at MW-22 during Biotreatment, where the Arrows Indicate Lactate Injection Events.

Starting in June 2005, TCE groundwater concentrations began to decrease steadily, while cDCE, VC, and ethene groundwater concentrations rose. Still later, around August 2006, the concentrations of cDCE and VC peaked and then began to fall, while ethene concentrations continued to increase slowly. Due to the increased VC concentrations, a portion of the SVE system was temporarily reactivated under the building. By February 2007, TCE groundwater concentrations were less than 50 µg/L in the source area and ethene was as high as 990 µg/L. PCE, originally present at much lower levels than TCE, decreased from approximately 200 µg/L to less than 5 µg/L during the same treatment period. The chloroethene transformations at the most contaminated source area well, MW-22, are shown in molar units in the bar chart in Figure 3. The concentration increases attributed to Bioavailability Enhancement Technology™ decreased in magnitude at MW-22 with each lactate injections. This suggests that the source mass is being successfully depleted using this technology. Similar results were observed at the other treatment zone wells.

In August 2006, groundwater samples from the source area biotreatment zone were collected for analysis by quantitative polymerase chain reaction (QPCR). The results indicated 5.5×10^5 copies per mL of *Dehalococcoides spp.* (DHC) 16S rRNA gene and 2.1×10^5 copies per mL of the vinyl chloride reductase functional gene, vcrA, at monitoring well MW-22. Thus, abundant dechlorinating bacteria are present in the biotreatment zone with the appropriate gene functionality to dechlorinate PCE and TCE completely. Bioaugmentation with a commercially available DHC-containing culture was not applied to the site, as it was not expected to further increase chloroethene biodegradation activity.

In June 2008, TCE groundwater concentrations continued to decrease steadily, while cDCE, VC, and ethene groundwater concentrations leveled off. Still later, around August 2008, the concentrations of cDCE and VC peaked and then began to fall, while ethene concentrations continued to increase slowly.

DEVELOPMENT OF ALTERNATIVE CLEANUP LEVELS

The site is located within the Connecticut River watershed and the state-mandated groundwater cleanup goals were set to drinking water criteria (known in Connecticut as the Groundwater Protection Criteria – GWPC) as follows: PCE = 5 µg/L, TCE = 5 µg/L, cDCE = 70 µg/L, and VC = 2 µg/L. As described above, the anaerobic bioremediation program has initiated complete dechlorination of the parent compounds all the way to ethene. However, site groundwater chloroethene concentrations are not expected to reach GWPC within a remediation timeframe within four years of active remediation. Therefore, we collaborated with the Connecticut Department of Environmental Protection (CT DEP) to develop alternative cleanup levels (ACLs), protective of public health but higher than drinking water standards. Active remediation of the plume would end once ACLs are reached, and a long term monitoring program would begin, as long as natural attenuation would be capable of eventually attaining GWPC.

The nearest residences are located approximately 150 ft (45 m) down gradient of the western boundary of the site. CT DEP required that intermediate cleanup standards protect against health risks posed by HVOC volatilization into the basements or first floors of these houses. It would not be necessary to meet the stricter drinking water standards in the shallow aquifer there, since potential drinking water wells at these homes would be screened in a deeper aquifer beneath the clay layer and therefore not in communication with the chloroethene plume. The relevant standards would be the Connecticut Residential Volatilization Criteria (RVC): PCE = 340 µg/L, TCE = 27 µg/L, cDCE = 830 µg/L, and VC = 1.6 µg/L. GWPC remain the ultimate remediation goals to allow final site close-out. The strategy of ending active remediation after higher RVC-based ACLs are attained would be acceptable to CT DEP only if we could demonstrate that natural attenuation processes are viable and would continue to shrink the HVOC plume going forward.

Natural Attenuation Model The historical groundwater monitoring data illustrated the behavior of the undisturbed plume under natural conditions that would again be in effect after active remediation was ended. The data reviewed was composed of chloroethene concentrations in groundwater samples from seven wells located along the centerline of the plume, starting in the upgradient source area and continuing downgradient beyond the site boundary: MW-11, MW-22, MW-29, MW-23, MW-15, MW-16, and MW-20 (see Figure 2). They were collected over the seven-year period from 1990 through 1996, during quarterly monitoring rounds, producing up to 24 data points per well depending on the wells original installation. During this time PCE, TCE, and DCE were observed at each well. During the seven-year period, each chloroethene concentration at each well fluctuated, but showed no temporally increasing or decreasing trends. The plume appeared to be in a steady state, and concentrations decreased with increasing distance downgradient from the source area.

Natural background conditions for the shallow aquifer appeared to be aerobic prior to lactate injections, as indicated by recent monitoring data at background wells, where D.O. levels ranged between 5 and 8 mg/L. It is likely that the processes responsible for plume attenuation with distance are aerobic biodegradation for TCE, DCE, and VC, as well as dispersion for all of the chloroethenes.

Because the pre-remediation plume was stable, we calculated average concentrations over the seven-year period for the chloroethenes at each of the centerline wells. For each compound, separate plots of the natural logarithm of the time-averaged concentration at each monitoring well versus distance downgradient showed linear behavior, indicating first order decay with distance. The slopes and correlation coefficients determined from each log plot are shown in Table 1. These slopes are distance decay constants that allow the calculation of chloroethene concentrations at any point along the plume centerline, based on concentrations observed at a monitoring well by the following formula:

$$C_1 = C_2 \times \exp[m(x_1 - x_2)]$$

where C_1 and C_2 are specific chloroethene compound concentrations at locations x_1 and x_2, and m is the compound-specific distance decay constant. Multiplying the calculated distance decay slopes by the estimated groundwater velocity (0.77 ft/day) converts distance to travel time and yields approximate natural attenuation decay rates. These rates are also listed in Table 1 along with calculated natural attenuation half lives.

TABLE 1. Distance Decay Constants for the Chloroethenes Calculated from Pre-Remediation Groundwater Monitoring Data.

Compound	**Slope (1/ft)**	**Corr. Coeff. (r^2)**	**Decay Rate (1/day)**	**Half Life (yr)**
PCE	-0.0025	0.7384	-0.0019	2.0
TCE	-0.0040	0.8189	-0.0031	0.97
cDCE	-0.0039	0.9012	-0.0030	0.99
VC	-0.0043	0.5016	-0.0033	0.90

Regulatory Agreement. The nearest house is approximately 670 ft (205 m) downgradient from the source area. By regulatory agreement, the RVC must be met in the shallow groundwater beneath this residence and beneath all locations farther downgradient. We used the above distance decay equation to back-calculate groundwater concentrations at site monitoring wells that would result in compliance with the RVC at this nearest residence. Furthermore, CT DEP directed us to add an extra level of caution around VC since it poses the greatest volatilization hazard. During anaerobic bioremediation, DCE acts as a source of VC via the dechlorination pathway. During the initial stages of biotreatment, the average VC to DCE concentration ratio was approximately 0.15. Thus, we conservatively set the DCE intermediate limits equal to the VC values calculated as above divided by the 0.15 VC/DCE concentration ratio. Finally the intermediate concentration goal for PCE was set at the RVC at all locations rather than values calculated by the distance attenuation model, since the RVC (340 μg/L) is relatively high and already attained throughout the plume. See Table 2 for a summary of the final mandated cleanup goals (GWPC), the volatilization criteria (RVC), and the negotiated ACLs to be met at the downgradient property boundary and within the source area in order to end active groundwater remediation.

TABLE 2. Summary of Final Cleanup Goals and Negotiated Alternative Cleanup Levels to End Active Groundwater Remediation.

Criterion	**Point of Compliance**	**PCE (μg/L)**	**TCE (μg/L)**	**cDCE (μg/L)**	**VC (μg/L)**
GWPC	Everywhere	5	5	70	2
RVC	Off-site residential	340	27	830	1.6
ACL	Downgradient property boundary	340	50	19	2.9
ACL	Source area	340	309	119	18

Based on the calculations described above, CT DEP agreed to the following groundwater quality dependent timeline for phasing out remediation and eventually closing the site. When the ACLs are met at the downgradient property boundary (locations MW-16 and RW-1), plume migration control will no longer be necessary and the groundwater pump and treat system will be shut down. When the ACLs are met in the source area (locations MW-11, MW-22, and MW-29), volatilization risks at downgradient residences are no longer a concern and active bioremediation will be ended. At this point the remedy becomes natural attenuation with semi-annual groundwater monitoring. After two years of semi-annual results that meet the ACLs, the monitoring frequency will be decreased to biannual until the GWPC are reached and site closeout can be arranged.

CONCLUSIONS

In situ biostimulation with 60% sodium lactate solution effectively promoted anaerobic dechlorination of PCE and TCE within one year of initial lactate addition. At first, intermediate daughter product DCE and VC groundwater concentrations increased significantly, and only began to decrease after TCE parent compound concentrations were depleted. Throughout the bioremediation process, ethene concentrations gradually increased, indicating that complete dechlorination was occurring. Bioaugmentation with a DHC-containing bacterial culture was not necessary to achieve complete dechlorination at this site.

Anaerobic bioremediation is successful and is expected to reduce chloroethene concentrations by several orders of magnitude within approximately two to four years of treatment initiation, which is an improvement over the pump and treat system whose performance would likely continue for more than ten years. However, the state-mandated cleanup goals are very low and still not easily attainable by bioremediation. The model developed from pre-remediation groundwater data showed that under normal aerobic conditions, natural attenuation was occurring, with chloroethene concentrations decreasing exponentially with distance downgradient. The model results were used to develop intermediate cleanup goals for the on-site plume that would result in protection of human health at downgradient off-site residential receptors. These ACLs formed a rational and attainable goal to end active groundwater treatment that was economically acceptable to the responsible party and environmentally acceptable to the regulator. This approach can serve as a model to advance a remediation project while balancing reasonable expectations of treatment performance with practical cleanup goals that protect human health and the environment.