Paper L-67, in: G.B. Wickramanayake and H.V. Rectanus (Chairs), *In Situ and On-Site Bioremediation—2009.* Tenth International In Situ and On-Site Bioremediation Symposium (Baltimore, MD; May 5–8, 2009). ISBN 978-0-9819730-1-2. Publisher: Battelle Memorial Institute, Columbus, OH. **www.battelle.org/biosymp**

In Situ Bioremediation of Chlorinated Ethenes Using Liquid Atomized Injection

Brendan J. Lazar, P.E. (blazar@trcsolutions.com) and Nidal M. Rabah, PhD, P.E., PMP
(TRC Environmental Corporation, Millburn, New Jersey, USA)

ABSTRACT: Liquid atomized injection (LAI) was used to optimize the amendment delivery and increase the extent of influence for enhanced in situ bioremediation of a source zone within a chlorinated ethene-impacted, shallow unconfined aquifer at an industrial site in Middlesex County, New Jersey. The source zone had PCE and TCE impacts in ground water and soil within both the saturated and unsaturated zones at relatively elevated levels. EHC®, a patented combination of controlled-release carbon and zero valent iron, was selected as the bioremediation amendment due to the high contaminant concentrations and amenable site conditions. A field-pilot test was designed and implemented to comparatively evaluate the spatial distribution of EHC® via conventional hydraulic injection and enhanced injection with LAI.

Six hydraulic and four LAI injection points were used to inject 8,500 pounds of EHC® as a 30% slurry over the source zone area of 2,400 square feet. Pressure influence, change of geochemical conditions and visual observations at nearby ground water monitoring wells were used to evaluate the spatial distribution and extent of influence of both delivery techniques. Pressure influence was consistently observed 25 feet away from the LAI injection points. The results confirmed that the LAI technique enhanced the amendment distribution and increased the extent of influence significantly compared to hydraulic injection. LAI pressures had to be occasionally reduced or conventional hydraulic injection incorporated to mitigate potential blow-by or surface overflow of the injection slurry for shallower injection intervals near subsurface utilities, former test borings, and unpaved areas. The use of LAI resulted in significant cost savings for the remedial program, while effectively delivering the amendment within the impacted zone.

Post-injection groundwater monitoring demonstrated the effectiveness of the LAI amendment delivery and enhanced bioremediation as evidenced by post-injection ground water monitoring results which included:

- Rapid establishment of favorable geochemical conditions including decreased dissolved oxygen, decreased Redox potential, increased turbidity, and stable pH;
- Increased TOC, alkalinity, dissolved iron, and dissolved manganese in both zones (shallow and deep) of the treatment zone monitoring well;
- Increased dissolved gases including methane, ethane, and carbon dioxide with stable levels of ethene;
- Reduction of PCE and TCE along with the evolution and reduction of daughter products including cis- and trans-1,2-DCE, 1,1-DCE, and VC;

The amendment delivery was optimized through the use of LAI and initial post-injection results demonstrate multiple lines of evidence for the biological reduction of chlorinated

ethenes at this site. Longer term post-injection groundwater monitoring results will be presented along with implications for optimizing full-scale design and implementation.

INTRODUCTION

The remedial professional tasked with selecting and designing an in situ remedy must account for a number of potentially competing factors. At a minimum, these include client goals; regulatory requirements; project budget and schedule; site conditions and constraints; hydrogeology; types and concentrations of contaminants,; geochemistry; and electron donors and acceptors. A conceptual site model is developed from this information to assist in the selection of the appropriate in situ remedial strategy which encompasses the type of amendment(s) and injection technology. The ability to effectively and efficiently introduce and distribute the amendments into the subsurface is of growing importance for successful in situ remediation programs.

This study focuses on the use of an advanced injection technology, LAI, in combination with hydraulic injection (HI) in a shallow aquifer to distribute a combined organic-inorganic amendment (EHC®) into the formation. A pilot-test study was initiated during May 2008 to assess the effectiveness of treating chlorinated ethene contamination in groundwater and soil with EHC®. Initial results indicate that the combination of LAI and hydraulic injection effectively distributed the amendment, which induced anaerobic and reducing conditions and the reduction of chloroethene concentrations.

Site Description. The 32-acre industrial facility is located in Middlesex County, New Jersey, in a mixed residential, commercial, and light industrial area. The site is bisected by a small tributary stream, which separates the northern (undeveloped) and the southern (developed) areas of the site which included the study area. Historical industrial use of the site dates back to 1900 including power generating operations as well as alkaline battery and printhead manufacturing. Past operations resulted in soil and groundwater, contamination with chlorinated ethenes, specifically, tetrachloroethene (PCE), trichloroethene (TCE), and *cis*-1,2 dichloroethene (c-DCE). The contaminated groundwater and soil are mostly limited to the overburden aquifer. The site is currently an active industrial park mainly used for office and warehouse space.

Geology and Hydrogeology. The site is underlain by the Plainfield outwash deposits, which consist of glaciofluvial silty sand with little gravel. At the developed portions of the site, a 2 to 6 foot thick layer of artificial fill consisting of debris in a matrix of sand, silt, and clay overlies the natural deposits. The outwash deposits extend to a depth of approximately 20 to 22 feet below surface grade (bsg) where the bedrock interface is located. Ground water occurs within the overburden between 3 and 7 feet bsg and is shallower near the stream. The lateral groundwater flow direction in the overburden is northerly to northwesterly at an average hydraulic gradient of 0.004 ft/ft. A relatively impermeable layer of silty clay derived from weathered bedrock is present at the bedrock interface and retards vertical migration of ground water from the overburden to the bedrock. The bedrock formation below the overburden is the Passaic Formation of the Newark Supergroup, which consists of reddish-brown shale, siltstone and mudstone.

MATERIALS AND METHODS

Amendment. EHC® was selected for the in situ amendment, which is a controlled-release, integrated carbon (fibrous organic material) and ferrous sulfate material produced by Adventus LLC. The amount of material for the pilot test was designed to be approximately 0.2% of the soil mass in the treatment zone based on site specific parameters (contaminant concentrations, electron acceptors, geochemistry, and hydrogeology). Approximately 8,500 pounds (lbs) of EHC were used in the pilot test. EHC was mixed with water in a hopper via a recirculating pump to make a 30% to 35% slurry.

Treatment Zone. The pilot test targeted the chlorinated volatile organic compound (CVOC) source zone at the site. Shallow soil with high CVOC concentrations (PCE = 5,800 mg/kg, TCE = 1,080 mg/kg, *cis*-1,2-DCE = 440 mg/kg) was excavated to a depth of approximately 6 feet bsg in December 2007 in advance of the pilot test. The pilot test was designed to encompass the source zone and target the groundwater and residual soil impacts. The treatment area had dimensions of approximately 60 feet in length by 40 feet in width. The treatment zone extended from the top of the water table (~4 to 5 feet bsg) to the bottom of the overburden formation (~20 to 22 feet bsg) for an average thickness of approximately 14 feet.

Amendment Injection. ARS Technologies, Inc.. of New Brunswick, New Jersey. was retained for drilling and injection services. Four injection points (LAI-1 through LAI-4) were completed with the LAI technology utilizing compressed nitrogen as the carrier gas. Hydraulic injection (HI) was also performed at six injection points (HI-1 through HI-7). Hydraulic injection was mainly used on shallow intervals between 7 and 13 feet bsg to prevent “daylighting” and pavement upheaval. The drilling and injection equipment included a tow-behind air compressor, mixing trailer with a hopper and recirculating centrifugal trash pump, compressed nitrogen trailer, LAI pressure control manifold, 6,300 gallon water tanker, and Geoprobe 7720DT track-mounted direct-push rig. A photoionization detector was used to monitor the air quality during injection.

Groundwater Monitoring. Two monitoring wells were installed to monitor the effectiveness of the pilot test, which were both screened from approximately 4 feet to 22 feet bsg. MW-20 is located within the treatment zone slightly downgradient of the source area. MW-21 is located approximately 24-feet downgradient of MW-20 and outside of the treatment zone. A monitoring well (MW-3) located approximately 200 feet upgradient was utilized as the background well to characterize upgradient groundwater conditions. During the injection, water level and water quality parameters were collected before and after each injection point to monitor any shifts in geochemistry or prolonged groundwater mounding.

Low-flow groundwater sampling was conducted for five sampling events: pre-injection, 1-month post-injection, 3-months post-injection, 6-months post-injection, and 9-months post-injection. In each event, MW-3, MW-20, and MW-21 were sampled for VOCs and a suite of nutrients, electron acceptors, total organic carbon, and dissolved gases. Ground water samples were collected from two depth intervals at MW-20 and MW-21. MW-20-1 and MW-21-1 samples were collected from 8 feet bsg representing the shallow zone, while MW-20-2 and MW-21-2 were collected from 20 feet bsg representing the deep zone.

Two Bio-Trap® samplers were also deployed in MW-20 for 35 days prior to the final post-injection sampling round at 273 days post-injection. Assessment of the microbial community was conducted via quantitative polymerase chain reaction (qPCR) targeting *Dehalococcoides* spp. (DHC), *Desulfuromonas* spp. (DSM), *Dehalobacter* spp. (DHB), *Desulfitobacterium* spp. (DSB), Total Eubacteria (EBAC), Iron and Sulfate Reducing bacteria (ISR), Methanogens (MGN), and dechlorinating functional genes (tceA, bvcA, vcrA).

RESULTS

Amendment Injection. The HI and LAI injection techniques were compared throughout the pilot test. A summary of the treatment thickness and the amendment mass per injection location is provided in Table 1 below.

TABLE 1. Summary of liquid atomized injection and hydraulic injection of EHC®.

LAI Injection Point	**LAI-1**	**LAI-2**	**LAI-3**	**LAI-4**			**LAI Average**
Bottom of Injection (ft bsg)	21	20	22	21			21
Top of Injection (ft bsg)	9	6	10	7			8
Thickness (ft)	12	14	12	14			13
EHC Mass (lbs)	1980	1925	1320	1540			1691
Hydraulic Injection Point	**HI-1**	**HI-2**	**HI-4**	**HI-5**	**HI-6**	**HI-7**	**HI Average**
Bottom of Injection (ft bsg)	20	19	13	13	13	13	15
Top of Injection (ft bsg)	5	9	7	7	7	7	7
Thickness (ft)	15	10	6	6	6	6	8
EHC Mass (lbs)	495	438	186	186	186	269	293

Prior to utilizing LAI, injection at HI-1 was completed to assess the effectiveness of distributing EHC due to conventional hydraulic injection. Continuous post-injection soil coring throughout the treatment interval at two test borings located 3 feet away from the injection point did not reveal any discernable evidence of the amendment in the soil. The uncertainty in visually detecting the amendment in the soil core may be attributed to ineffective distribution or to the reddish-brown color of the soil matrix interfering with visual observation of the amendment. Thus, no definite determination of hydraulic injection radius of influence (ROI) could be made based on visual observations.

LAI was utilized effectively to inject approximately 80% of the designed amendment mass into the treatment zone as shown in Table 1. The carrier gas (compressed nitrogen) was pulsed during injection of the amendment to aid in controlling the amendment distribution and injection rate. Figure 1 shows an example of the carrier gas pulsing based on the pressure readings at the LAI pressure control manifold for the interval between 15 and 17 feet bsg at LAI-1. The technology proved effective in the deeper zones between 13 and 22 feet bsg with pressure influence observed consistently between 20 and 25 feet from the injection point. The pulsing of the carrier gas in the shallower regions proved to be problematic. Most of the intervals between 7 and 13 feet bsg were completed with hydraulic injection due to suspected pavement upheaval and/or amendment "daylighting" at adjacent locations of poorly abandoned soil borings or nearby utility trenches.

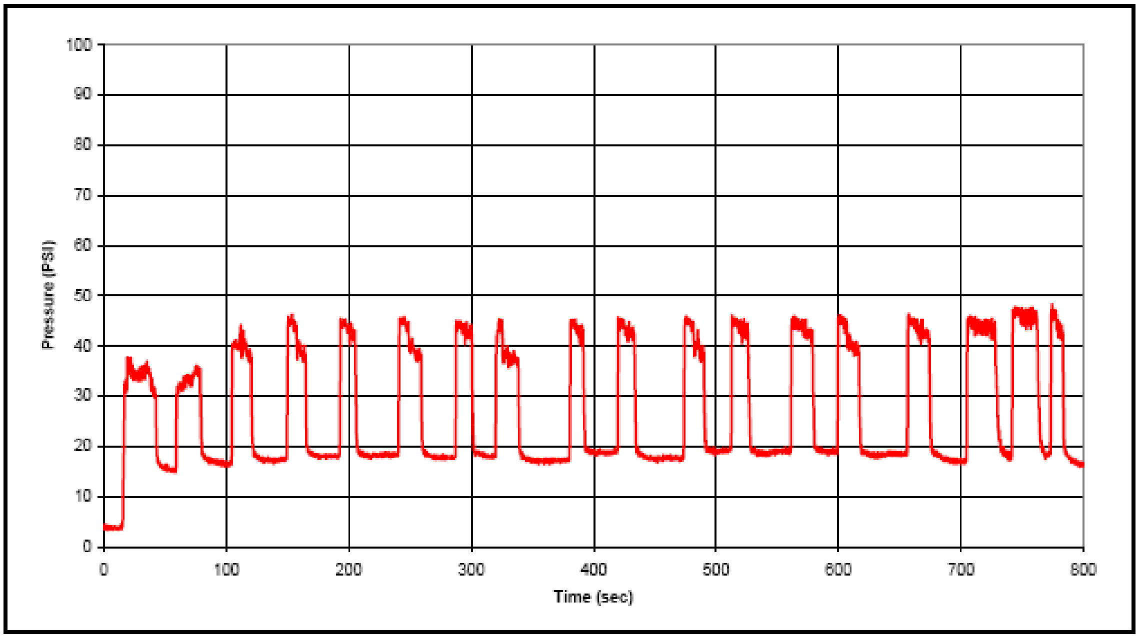

FIGURE 1. Pressure graph of LAI carrier gas pulsing—injection point LAI-1 (15-17 ft)

The ROI for LAI was estimated to vary preferentially between approximately 15 and 25 feet, while the hydraulic injection ROI was estimated to be less than 6 feet. The radii were estimated based on geochemical and pressure measurements in the target monitoring well (MW-20) and for LAI in the downgradient monitoring well (MW-21) as well. These radii were utilized to determine the approximate amount of amendment loaded per pound of soil (Table 1) for LAI and HI injection points, which were on average 0.17% and 0.29%, respectively. These estimates support that EHC was effectively distributed into the treatment zone at approximately the designed loading rate of 0.20% lbs EHC® per lb of soil in the treatment zone. The actual amendment dosage at overlapping injection zones was estimated to exceed 0.5% of the soil mass.

Geochemical and Analytical Results. The injection of the amendment resulted in a geochemical shift to anaerobic and reducing conditions in the treatment monitoring well (MW-20) as well as in the downgradient monitoring well (MW-21). Slight differences were observed between shallow and deep zones, but both zones generally followed the same trends for all measurements and analyses. The pH and dissolved oxygen measurements for MW-20 is presented in Figure 2. The pH remained relatively constant in both zones within an amenable range between 6.4 and 7.4 for biotic and abiotic reduction of chloroethenes. The dissolved oxygen (DO) in the treatment well (MW-20) immediately decreased to anaerobic conditions and remained low throughout the post-injection monitoring in both the shallow and deep zones.

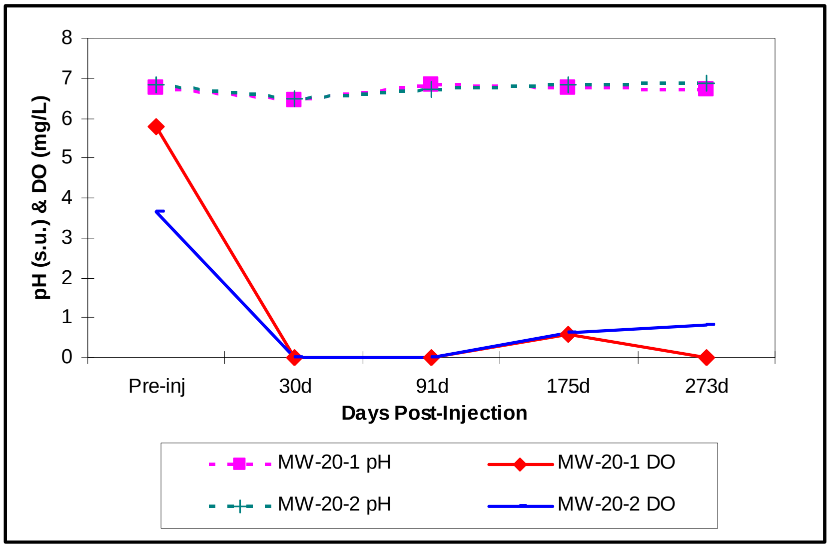

FIGURE 2. Dissolved oxygen (DO) and pH levels at shallow and deep intervals in source monitoring well.

Figure 3 presents the oxidation reduction potential (ORP) for source area monitoring well MW-20. ORP exhibited a rapid shift toward reducing conditions immediately following injection that was sustained between -140 millivolts (mV) and -240 mV in MW-20 from 30 days through 175 days post-injection. The upward trend towards anoxic conditions observed after 91 days post-injection may be indicative of the consumption of the amendment and potential need for repeated injection or increased loading.

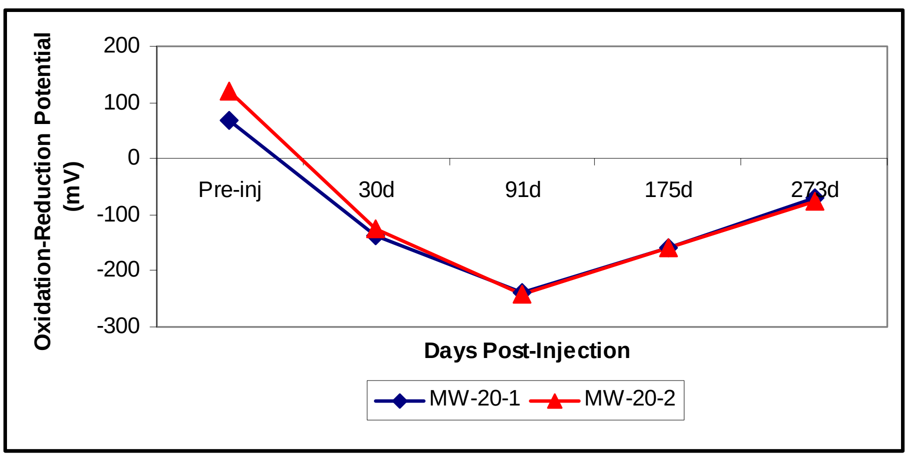

FIGURE 3. ORP at shallow and deep intervals in source area monitoring well.

Figure 4 depicts the total organic carbon (TOC) and sulfate concentrations at source area monitoring well MW-20 and upgradient monitoring well MW-3. TOC rapidly increased 30 days post-injection compared to the pre-injection results in MW-20, but available TOC appears to have been rapidly consumed within 91 days post-injection. The sulfate concentrations in MW-20 ranged between 18 and 48 milligrams per liter. Slight, but un-sustainable, reduction of sulfate was observed at 30 days post-injection.

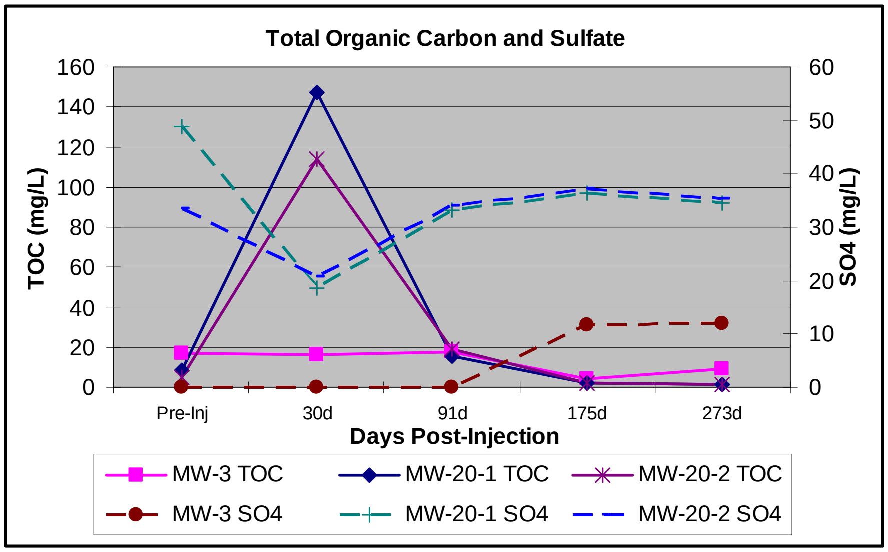

FIGURE 4. TOC and Sulfate concentrations at source area well MW-20 (shallow and deep intervals) and upgradient monitoring well MW-3

The analytical results confirmed the reduction of CVOC concentrations, albeit at a relatively slow degradation rate and mass loss. Figure 4 presents the results for deep interval at source area monitoring well MW-20-2. Total chlorinated ethene concentrations decreased by 53% over 273 days. PCE, TCE, *cis*-1,2-DCE, and VC concentrations decreased by approximately 63%, 35%, 48%, and 63%, respectively.

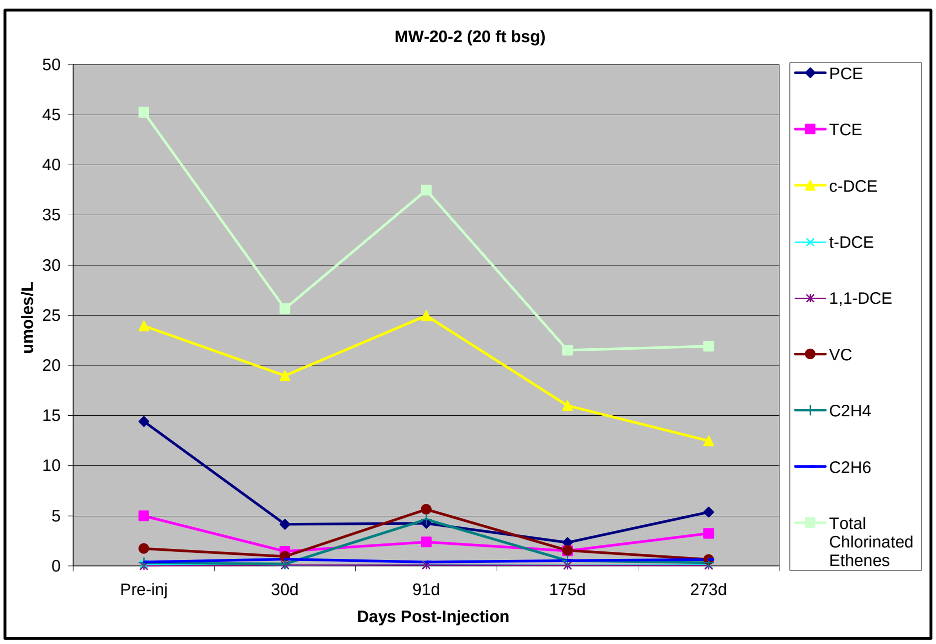

FIGURE 5. Chlorinated ethene trend for MW-20 at deep interval.

PCE=Tetrachloroethene, TCE=Trichloroethene, c-DCE=cis-1,2-Dichloroethene, t-DCE=trans-1,2-Dichloroethene, 1,1-DCE=1,1-Dichloroethene, VC=Vinyl Chloride, C_2H_4=Ethene, C_2H_6=Ethane]

Similar degradation trends were observed in the shallow zone with slightly lesser degradation rates. The rebound and tailing in the reduction of CVOC concentrations may be attributed to dissolution of sorbed contaminant mass and limited amendment dosage. Longer term monitoring will assist in evaluating the treatment and downgradient zones for effective remediation.

CONCLUSIONS

The pilot test proved to be successful in terms of injection strategy and distribution as well as resulting in conditions ideal for degradation of the chlorinated ethenes. LAI was an effective injection technique to distribute large quantities of EHC at a relatively quick rate and larger radius of influence. LAI is susceptible to short-circuiting and daylighting associated with preferential flow pathways and zones including poorly sealed soil borings and wells, utility trenches and unpaved shallow treatment zones. Such preferential pathways along with pressure gradients induced due to LAI may potentially result in contaminant mobilization. Continuous monitoring of the air quality near the ground surface and unpaved excavation area did not indicate that volatilization of contaminants was an issue. Although longer-term monitoring is necessary, several lines of evidence indicate that geochemical conditions favorable to degradation of chlorinated ethenes were established and the results indicate reduction of chlorinated ethene concentrations in the treatment zone. Geochemical measurements, rapid consumption of TOC, and slow contaminant degradation rates indicate that increased amendment loading rates may be required. Furthermore, preliminary evaluation of the microbial community indicates that sustained microbial reductive dechlorination may be limited and bioaugmentation may also be necessary.