

Persistence of Chloroethane During Full-Scale Enhanced In Situ Bioremediation of Chlorinated Ethanes

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ABSTRACT: Groundwater at a former site has been impacted by the release of chlorinated aliphatic hydrocarbons (CAHs), including 1,1,1-trichloroethane (1,1,1-TCA) and related degradation products including 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE), and chloroethane (CA). A pilot test of enhanced in situ bioremediation (EISB) using emulsified vegetable oil (EVO) was conducted between March 2004 and November 2005. Based on results of the pilot test, a full-scale injection was implemented from December 2005 to January 2006. The full-scale injection used a combination of readily-degradable sodium lactate and slow-release EVO to sustain the reaction zone. Both injections were intended to stimulate anaerobic degradation of CAHs in groundwater.

Semi-annual groundwater monitoring performed after the 2005/2006 full-scale injection indicated that EISB was effective in reducing concentrations of 1,1,1-TCA, 1,1-DCA, and 1,1-DCE in groundwater. Concentrations of CA increased following the injections as a result of the sequential dechlorination of 1,1,1-TCA to 1,1-DCA to CA. Concentrations of CA generally declined after 1,1,1-TCA and 1,1-DCA were depleted. However, monitoring results for April 2008 (28 months after the full-scale injection) indicated that degradation of CA had slowed, and concentrations of CA remained elevated above clean-up criteria throughout the treatment zone. Geochemical data suggested that conditions suitable for the anaerobic degradation of CA were diminishing, and/or a residual source of CAHs may exist in the vadose zone or capillary fringe in the source area.

A second full-scale injection was performed in September and October 2008 to further enhance anaerobic degradation of CA. Concentrations of 1,1,1-TCA, 1,1-DCA, and 1,1-DCE remained below detection limits or below clean-up goals. At 2 months after the second full-scale injection, CA concentrations had increased in a portion of the source area, but decreased in the majority of the treated area of the plume. In the period from 2 to 7 months after the second full-scale injection, CA concentrations decreased at all locations but still remained above clean-up goals.

To the authors' knowledge, significant accumulation and persistence of CA has not been reported at sites where 1,1,1-TCA is being remediated by EISB. The persistence of CA at this site is attributed to possible residual sources of parent compounds and a relatively slower degradation rate for CA compared to 1,1,1-TCA and 1,1-DCA. It is anticipated that CA concentrations will continue to decrease over time as there is evidence that the second full-scale injection further remediated residual CAH parent compounds in the source area. Monitoring data is presented to illustrate the ultimate fate of CA at the site.

INTRODUCTION

The primary performance objective of EISB at the site is to restore groundwater quality to below clean-up goals for all contaminants of concern (COCs) to achieve site closure as quickly as possible. Initial injections of organic substrate were effective in enhancing anaerobic biodegradation of 1,1,1-TCA, 1,1-DCA, and 1,1-DCE at the site. For a short period after each injection event, concentrations of CA increased as a result of the sequential dechlorination of 1,1,1-TCA to 1,1-DCA to CA. Following each post-injection increase, concentrations of CA generally declined after 1,1,1-TCA and 1,1-DCA were depleted. However, concentrations of CA did not decrease to below clean-up goals, and additional injections have been required in an attempt to meet clean-up goals for CA.

TECHNICAL APPROACH

Each substrate injection event (pilot test, first and second full-scale) utilized a mixed substrate of sodium lactate and EVO. The EVO product was composed of approximately 46 percent soybean oil and 4 percent sodium lactate by weight. The mean droplet size of oil in the product is reported to be less than 1.0 micron. Approximately 3,500 gallons (13,265 liters (L)) of the substrate mixture was injected during the pilot test into four injection wells located in the source area of the CAH plume. The substrate was injected over a 10-foot (ft) (3-meter (m)) interval from approximately 6 to 16 feet (2 to 5 m) below grade. Figure 1 depicts the source area and treatment zone relative to site features.

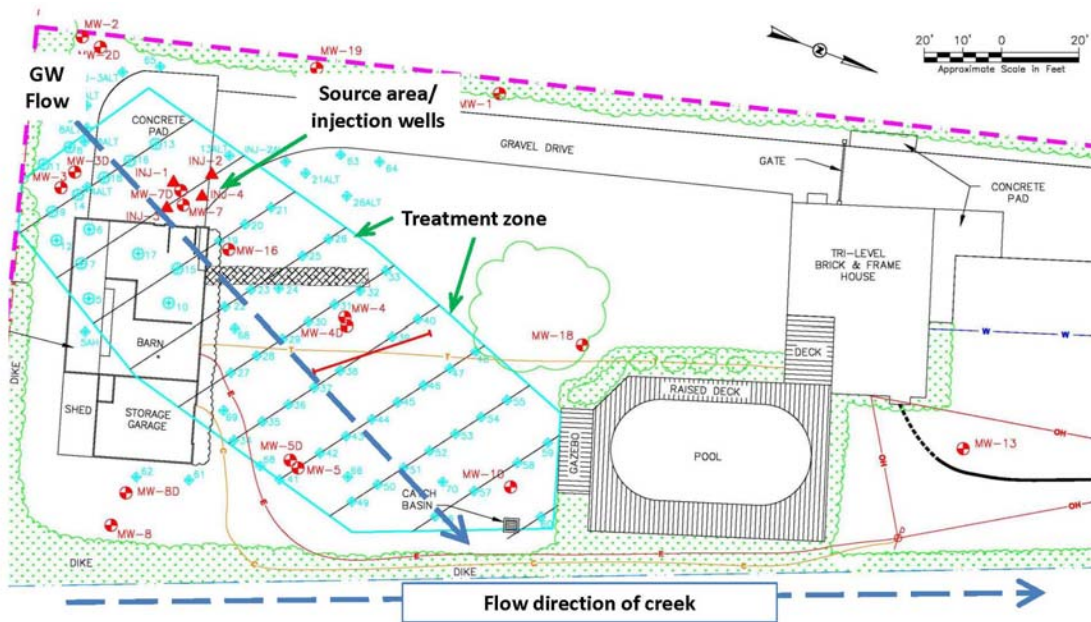


FIGURE 1. Site plan showing source area, injection wells, and treatment zone.

During each full-scale injection event, substrate mixture was injected into the four injection wells located in the source area, into 15 injection points in and up-gradient of the source area, and into 50 locations down-gradient of the pilot test injection area. Approximately 40,000 gallons (151,600 L) of substrate mixture was injected during each of the two full-scale events. The down-gradient injection points were installed on 8-ft

(2.5-m) spacing perpendicular to the groundwater flow direction to provide overlapping coverage, and on 15-ft (4.6m) spacing parallel to the groundwater flow direction.

Sufficient substrate was applied in the pilot and first full-scale application to achieve an overall oil saturation of 1.2 to 1.5 percent of the subsurface pore space. The effective oil percentage was increased to 2.0 to 2.2 percent for the second full-scale injection event, primarily to sustain biodegradation at sulfate reducing to methanogenic conditions for a longer period of time.

During the pilot test and first full-scale injection, lowering of injection rates and pressures resulted in a more uniform distribution of substrate, with the pilot test injection taking five days and first full-scale injection lasting more than 25 days. The injection procedure was modified for the 2008 injection by using a longer injection screen (42-inch) instead of an injection tool with focused lateral injection (two holes at same vertical position). During the second full-scale injection event, the Wavefront Technology Solutions Inc. (Wavefront) Primawave™ Process Tool ('Hornet' tool) was used in an attempt to increase the injection flow rate, minimize day-lighting, and to reduce field time. The 'Hornet' tool induces a pressure wave into the flow of substrate that is intended to trigger elastic expansion of the pore spaces within the formation and increase the rate of injection. The maximum practical injection rate was approximately 1 gallon (3.79 L) per minute (gpm) during the first full-scale injection due to significant day-lighting. The average flow rate achieved during the second full-scale injection was between 2 and 3 gpm (7.6 and 11.4 liters per minute) without significant day-lighting.

RESULTS

The pilot test was successful based on reductions in concentrations of 1,1,1-TCA, 1,1-DCA and 1,1-DCE (Ferris et al., 2006). Concentrations of CA increased overall, but exhibited a decrease in areas where 1,1,1-TCA and 1,1-DCA were depleted. The results of the pilot test confirmed the efficacy of the treatment technology and supported the plan for a full-scale injection.

The first full-scale injection was implemented between November 2005 and January 2006. Monitoring results indicated the full-scale application was also effective in reducing concentrations of 1,1,1-TCA, 1,1-DCA, and 1,1-DCE. Similar to the pilot test, concentrations of CA increased due to the sequential dechlorination of 1,1,1-TCA to 1,1-DCA and CA; and concentrations of CA generally decreased in areas where 1,1,1-TCA and 1,1-DCA were depleted. The concentrations of 1,1,1-TCA decreased to below the clean-up goals by October 2006 (10 months after first full-scale injection) and concentrations have remained low.

Figure 2 shows 1,1,1-TCA concentrations just prior to the pilot test injection and at 10 months after the first full-scale injection, respectively. Red triangles depict the injection wells, while contour intervals are based on remedial clean-up goals. Shaded areas represent clean-up goal exceedances, and areas of progressively darker shading indicate order of magnitude exceedances above the clean-up goal. After March 2006, there were no 1,1,1-TCA concentrations above clean-up goals. By April 2008, groundwater monitoring indicated that the degradation of CA had slowed, and concentrations of CA remained above clean-up goals throughout the treatment area suggesting that (1) conditions suitable for the anaerobic degradation of CA were diminishing, and/or (2) a residual source of

CAHs may exist. To further enhance the in situ anaerobic degradation of CA, a second full-scale injection was implemented between September and October 2008.

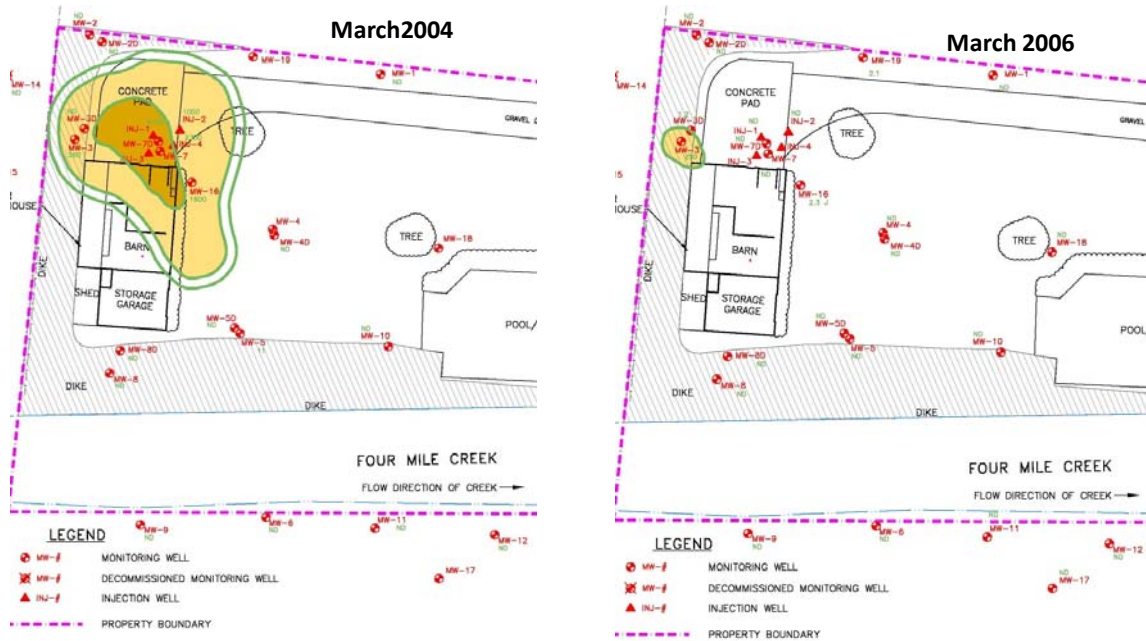


FIGURE 2. 1,1,1-TCA plume in March 2004 (pre-pilot test injection) and in March 2006, 3 months after first full-scale injection.

By May 2009, monitoring data showed CA concentrations continued to decrease, suggesting that there is no longer a residual source of CAH parent compounds. Concentrations over time for CA for the entire plume are presented on Figure 3. The isopleths in Figure 3 illustrate the changes in concentrations and lateral extent before and after various injection events.

Figure 4 shows the total molar and molar concentration of each CAH with time for groundwater samples for the monitoring location MW-7, central to the injection area. The total molar concentration of CAHs in MW-7 spiked after the pilot test injection. This was likely the result of contaminants sorbed to the soil matrix being mobilized by substrate injection, with vegetable oil acting as a surfactant. Concentrations of 1,1,1-TCA were significantly reduced within 3 months, followed by a reduction in 1,1-DCA within 6 months. By 9 months after the pilot test injection, CA represented nearly 100% of the total molar concentration. With the depletion of parent compounds, CA concentrations have decreased and show a continued reduction, with occasional spikes due to seasonal influences. These changes indicate that sequential dechlorination of 1,1,1-TCA and 1,1-DCA to CA was stimulated, but that the rate at which CA was degraded was lower than the rate at which it was produced.

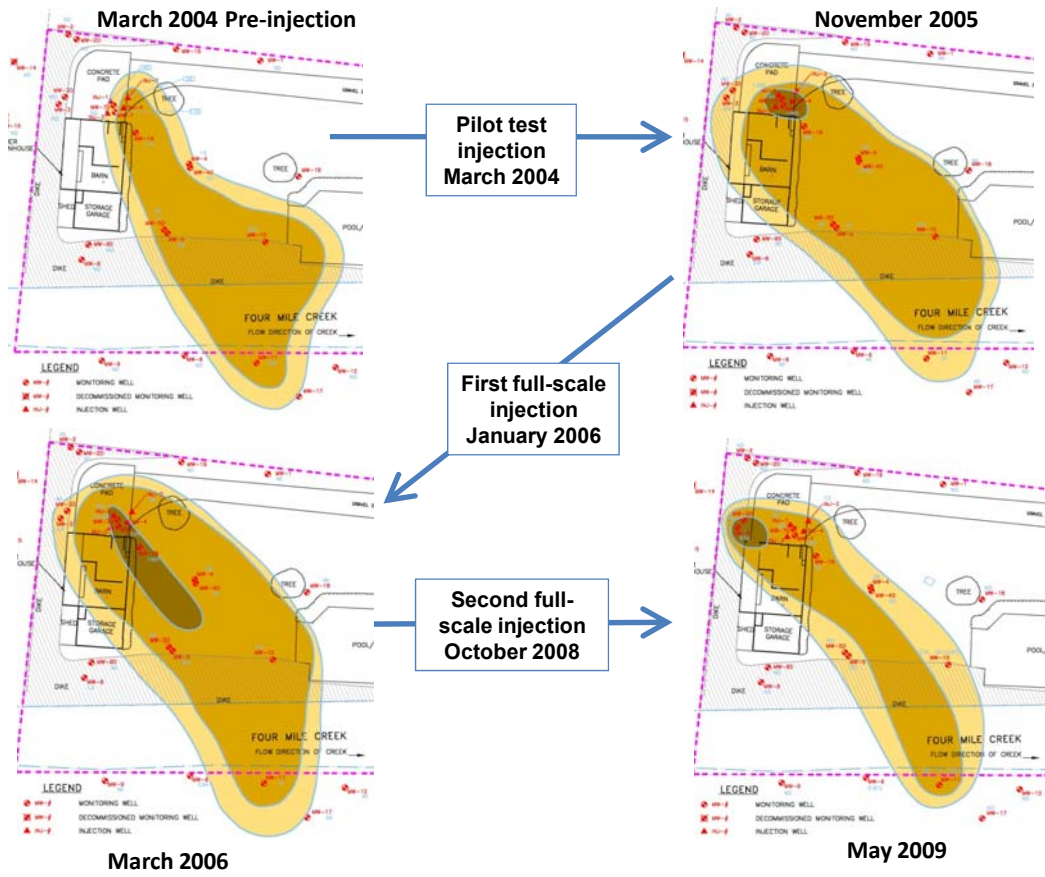


FIGURE 3. Chloroethane in groundwater.

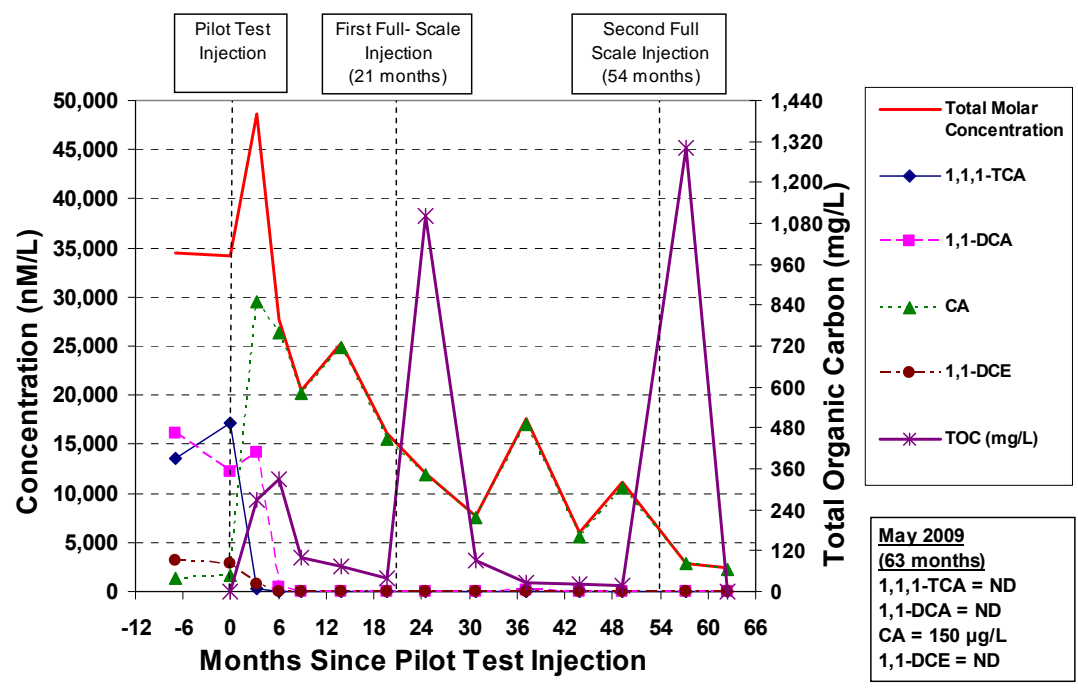


FIGURE 4. Changes in MW-7 molar concentrations.

Concentrations of total organic carbon (TOC) spiked after each injection event, but significantly decreased approximately six months after each injection event. This information indicates that multiple full-scale applications are necessary to allow sufficient treatment time (i.e., longer design life) for reduction of chloroethane to reach target levels. Similar trends are observed in MW-16, which is located at the down-gradient edge of the source area and is also within the treatment zone. Although the pre-injection 1,1,1-TCA concentrations were lower in down-gradient monitoring well MW-5, there was a spike in chloroethane after each injection event, as shown on Figure 5.

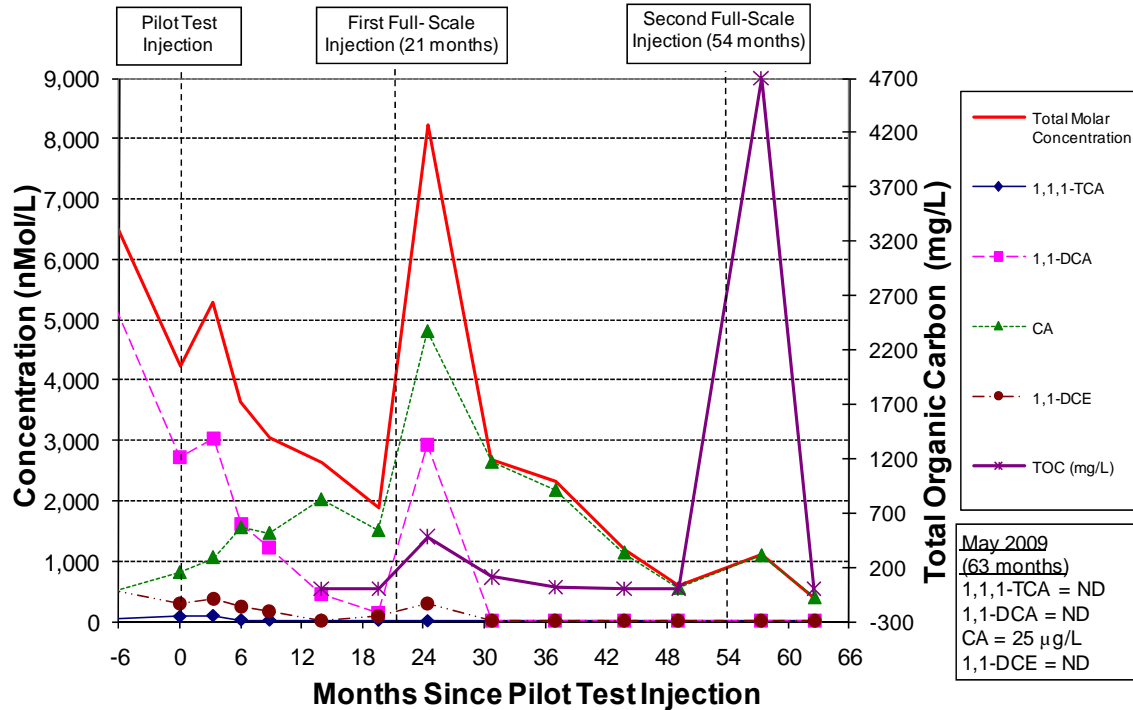


FIGURE 5. Changes in MW-5 molar concentrations.

Background concentrations of TOC in Site groundwater prior to injection were less than 3.0 mg/L. After injection in July 2004, TOC was elevated to 270 mg/L within the injection zone and to 17 mg/L in a monitoring well located 13 ft (4.0 m) down-gradient (Figure 6). Concentrations of TOC greater than 20 mg/L were sustained within the immediate injection zone for at least 20 months post injection (November 2005). In September 2004, the concentration of TOC peaked at the down-gradient monitoring well at a concentration of 69 mg/L. This suggests that the reactive zone expanded over time as a result of migration of the soluble component (lactate) of the substrate mixture. In October 2006 and May 2009, elevated levels of TOC have been observed at the downgradient edge of the treatment area, confirming expansion of the reaction zone. Elevated levels of TOC have not been observed at more distant monitoring locations.

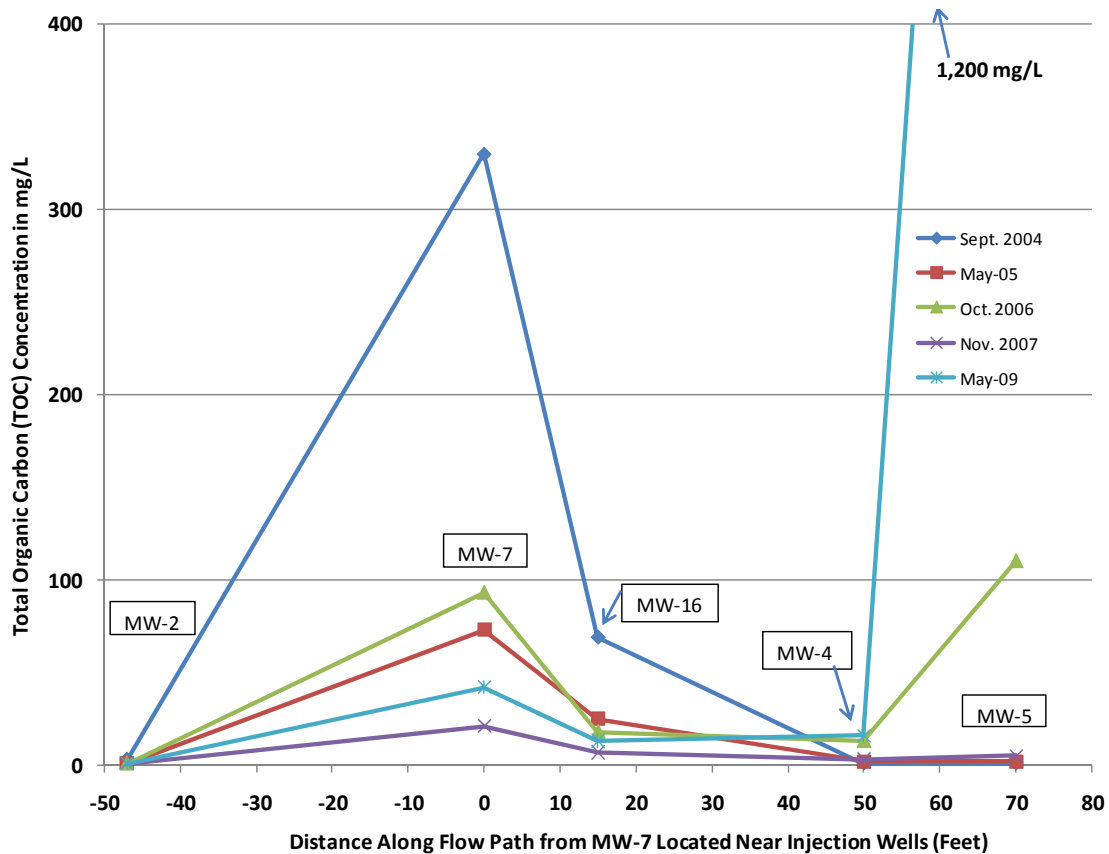


FIGURE 6. Total organic carbon over distance for select monitoring events.

Sulfate is the most significant competing electron acceptor at the site. Background concentrations of sulfate vary between 46 mg/L and 200 mg/L, but have been reduced to below 12 mg/L within the reaction zone. These low sulfate concentrations are indicative of sustained sulfate reducing conditions. Methanogenesis also consumes a large proportion of substrate, but does not appear to inhibit anaerobic dechlorination processes.

SUCCESS OF MULTIPLE INJECTIONS

The pilot test successfully stimulated anaerobic dechlorination resulting in the total reduction of 1,1,1-TCA in groundwater to clean-up goals across the entire site. Reductions in the concentrations of 1,1-DCA and 1,1-DCE, and increases in the concentrations of CA and ethane were also observed during the first 15 months of the pilot test. A subsequent decline in the concentrations of CA and an increase in ethane within the treatment zone (indicating CA is degrading to ethane), coupled with a decline in concentrations of TOC and a rebound in concentrations of sulfate, triggered a full-scale application that was implemented after monitoring in November 2005, approximately 20 months after the original pilot test injection.

The first of two full-scale injections of remedial substrate was conducted in late November 2005 through January 2006. The second full-scale injection was conducted in early September through late October 2008. Subsequent semi-annual groundwater monitoring events performed after the completion of the full-scale injections indicate that the

applications of EISB at the site have been highly effective in reducing concentrations of 1,1,1-TCA, 1,1-DCA, and 1,1-DCE in groundwater. CA has been produced as a result of the sequential dechlorination of 1,1,1-TCA to 1,1-DCA to CA. Concentrations of CA generally declined after 1,1,1-TCA and 1,1-DCA were depleted. Groundwater monitoring in December 2008 and May 2009 confirm that there has been no rebound of 1,1,1-TCA and intermediate daughter product 1,1-DCA, and that CA concentrations continue to decrease.

In October 2009, the regulatory agency adopted the use of current clean-up goals and CA concentrations in groundwater no longer exceed the current clean-up goals. An additional target area was identified as a result of changes to the applicable clean-up goals for 1,1-DCA. Investigation activities were conducted in that area to delineate the extent of CAHs, and substrate was injected in that area. Additional substrate injection (third full-scale) was implemented in the original source area with the intent to continue the sequential dechlorination of potential residual CAHs so that concentrations remain below the new clean-up goals. This work is anticipated to achieve all clean-up goals for the site.

REFERENCE

Ferris, S., B. Henry, C. Coker, and R. Lantzy. 2006. "Pilot Test Evaluation for Enhanced Anaerobic Bioremediation of Chlorinated Ethanes." *Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. Monterey, California, May 2006. Paper B-25. Battelle Press, Columbus, Ohio (CD format).