

## **In Situ Accelerated Anaerobic Biodegradation of a Chlorinated Source Area**

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**ABSTRACT:** In situ accelerated anaerobic biodegradation (AAB) is being successfully employed to treat chlorinated solvents that were historically released into soil and groundwater beneath Building 719, a mission-critical maintenance facility at Dover Air Force Base (DAFB), Delaware. Contaminants are attributed to engine cleaning activities conducted in the building and include trichloroethene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), and their degradation products. The AAB system was installed to remediate contaminated groundwater in the source area and minimize the continued contribution to the dissolved plume extending approximately one mile downgradient. The AAB system establishes hydraulic control in the source area by recirculating groundwater through injection and extraction wells located outside Building 719. A carbon substrate and metabolic nutrients are added to the recirculated groundwater as it is reinjected to enhance the natural microbial population at the site. This creates and maintains a reactive zone in the vicinity of the injection wells where contaminants are reductively dechlorinated via microbial metabolic processes. An estimated 130 pounds (59 kilograms [kg]) of TCE were degraded to ethene between May 2002 and October 2004. Additionally, during a period of elevated water table conditions (January 2003 to July 2003), an estimated 530 pounds (240 kg) of TCE were dissolved from the shallow soils and made available for biodegradation.

### **INTRODUCTION**

In situ accelerated anaerobic biodegradation (AAB) is being successfully employed to treat chlorinated solvents that were historically released into soil and groundwater beneath Building 719, a mission-critical maintenance facility at Dover Air Force Base (DAFB), Delaware. Contaminants are attributed to engine cleaning activities conducted in the building and include trichloroethene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), and their degradation products. An AAB system was installed to remediate contaminated groundwater in the source area and minimize the continued contribution to the dissolved plume extending approximately one mile downgradient. In addition, the enhanced biological activity creates an increase in surfactant compounds associated with metabolic processes in the source area. "Biosurfactants" have been demonstrated to promote solvent partitioning into groundwater from aquifer solids, thereby improving cleanup rates and efficiency (Jennings and Tanner, 2000).

Remediation and characterization of the source area at Building 719 are limited in part by the inaccessible location of source contaminants underneath the building foundation. Any remedial efforts undertaken must not disrupt operations at this critically active site. Thus, more intrusive remedial methods that might otherwise be appropriate were eliminated from consideration. The AAB system establishes hydraulic control in the

source area by recirculating groundwater through injection and extraction wells located outside Building 719. A carbon substrate (sodium lactate) and metabolic nutrients (dibasic ammonium phosphate [DAP]) are added to the recirculated groundwater as it is reinjected to enhance the natural microbial population at the site. This creates and maintains a reactive zone around the injection wells where contaminants are reductively dechlorinated via microbial metabolic processes.

The purpose of this paper is to demonstrate that AAB is a viable remediation technology for remediating groundwater in a chlorinated solvent source area where direct access to the source material is not feasible, as is the case at Building 719.

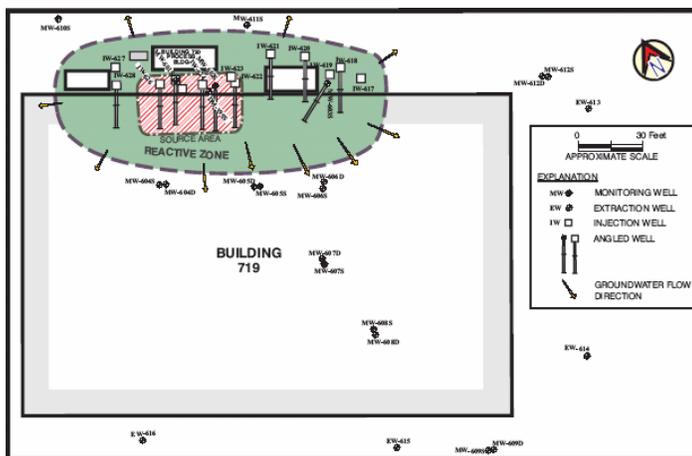
## SITE CONDITIONS

The surficial lithology at the site consists of 35 to 40 feet (ft) (11 to 12 meters [m]) of unconsolidated Pleistocene deposits of the Columbia Formation under Building 719. The Columbia Formation consists of silts and sandy silts to a depth of 6 to 8 ft (1.8 to 2.4 m) below ground surface (bgs), grading to medium- and coarse-grained sands to a depth of 35 to 40 ft (11 to 12 m) bgs with some minor clay lenses. Underlying the Columbia Formation is the upper clay and silt unit of the Calvert Formation, which acts as an aquitard to the downward migration of contaminants.

The water table is typically encountered approximately 8 ft (2.4 m) bgs, but varies with precipitation and has ranged from 4 to 11 ft (1.2 to 3.4 m) bgs since the system was installed. The thickness of the saturated zone at the Building 719 system is approximately 24 to 36 ft (7 to 11 m). The direction of groundwater flow under non-pumping conditions is generally to the southwest in the vicinity of Building 719, but can vary slightly depending on water table conditions.

Site delineation sampling identified residual contamination in the shallow portion of the aquifer beneath a parts cleaning room located along the northern side of Building 719 (Figure 1). The major contaminants of concern were TCE and 1,1,1-TCA and their degradation products cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride (VC), 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE), and chloroethane. TCE concentrations as high as 280,000  $\mu\text{g}/\text{kg}$  in the shallow soils and 21,000  $\mu\text{g}/\text{L}$  in the shallow groundwater were detected at the site.

Solvent concentrations decreased rapidly with depth, confirming that the source area is confined to the shallow silty soils between 4 and 8 ft bgs under the building. Significant concentrations of degradation products, primarily cis-1,2-DCE and 1,1-DCA, were also present, suggesting that anaerobic degradation was occurring locally in the source area.



**FIGURE 1. Building 719, Dover Air Force Base, DE.**

## **SYSTEM DESIGN AND OPERATION**

The AAB system is modeled after a successful pilot demonstration downgradient of the site conducted by the Remediation Technology Development Forum (RTDF, 2000). The major components of the AAB system include four groundwater extraction wells located on the downgradient side of Building 719, 12 injection wells located along the northern wall of the building adjacent to the cleaning room, 20 monitoring wells installed around and inside the building, and a process building to house the system controls and amendments (Figure 1). Seven of the 12 injection wells and three monitoring wells were installed at 45 degree angles to get as close to the source area as possible. Groundwater is extracted from the lower portion of the aquifer on the downgradient side of the building and reinjected into the upper portion of the aquifer upgradient of the source area, creating a downward flowing recirculating cell beneath the building. Monitoring wells were installed into both the shallower (10 to 20 ft [3 to 6 m] bgs) and deeper (25 to 30 ft [7 to 9 m] bgs) portions of the aquifer to monitor contaminant and degradation product concentrations, geochemical conditions, water table elevations, and substrate and nutrient distribution.

The system was activated and groundwater began recirculating through the injection wells in February 2002. Sodium lactate and DAP are pulsed into the system one day per week, rather than continuously, to minimize biofouling in the system components. Injection flow rates were determined by the water levels in the injection wells, and usually varied between 10 and 15 gallons (38 to 57 liters [L]) per minute (gpm). In July 2003, the injection wells were converted to a pressure injection system to overcome high water table conditions and biofouling problems that were reducing injection rates. Pressure injection and pulsing of the substrate and nutrient has been very effective in limiting biofouling of the injection wells. An anaerobic biocide (Tolcide PS200) and hydrogen peroxide were used occasionally to rehabilitate the wells when they became excessively biofouled.

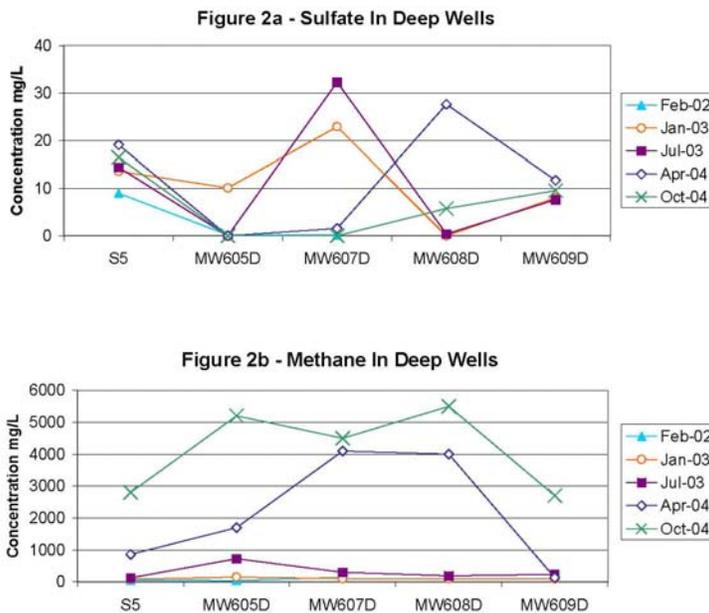
## **REDUCTIVE DECHLORINATION PROCESS**

The mineralization of chlorinated solvents to non-toxic end products occurs through the process of reductive dechlorination. Reductive dechlorination is a step-wise process of chlorine atom replacement with hydrogen via oxidation-reduction (redox) reactions. Thus, tetrachloroethene (PCE) degrades to TCE, which degrades to DCE, which degrades to VC, which degrades to ethane. The reductive dechlorination process is described in detail in several published documents (AFCEE, 2004; US EPA, 1998; Matthews, 1994; ITRC, 1998). Redox reactions yield energy, which is used by naturally occurring microbes that mediate the reactions for metabolic processes. Reductive dechlorination redox reactions involve organic carbon sources that serve as electron donors and solvents that act as electron acceptors. While some contaminated sites contain organic carbon sources, most sites require the addition of a substrate to create and maintain the desired anaerobic conditions for degradation.

Common anthropogenic and naturally occurring compounds compete with chlorinated solvents as electron acceptors. Some compounds that microbes reduce more readily than chlorinated solvents include nitrate, manganese, ferrous iron, and sulfate. It is generally understood that these compounds must be consumed before chlorinated solvents will be utilized and thereby biodegraded. In terms of potential energy yielded, TCE is a less favorable electron acceptor than sulfate and more favorable than carbon

dioxide. Therefore, evidence of sulfate reduction and methanogenesis (i.e., utilization of carbon dioxide as an electron acceptor) at a site suggests ideal redox conditions for TCE reductive dechlorination.

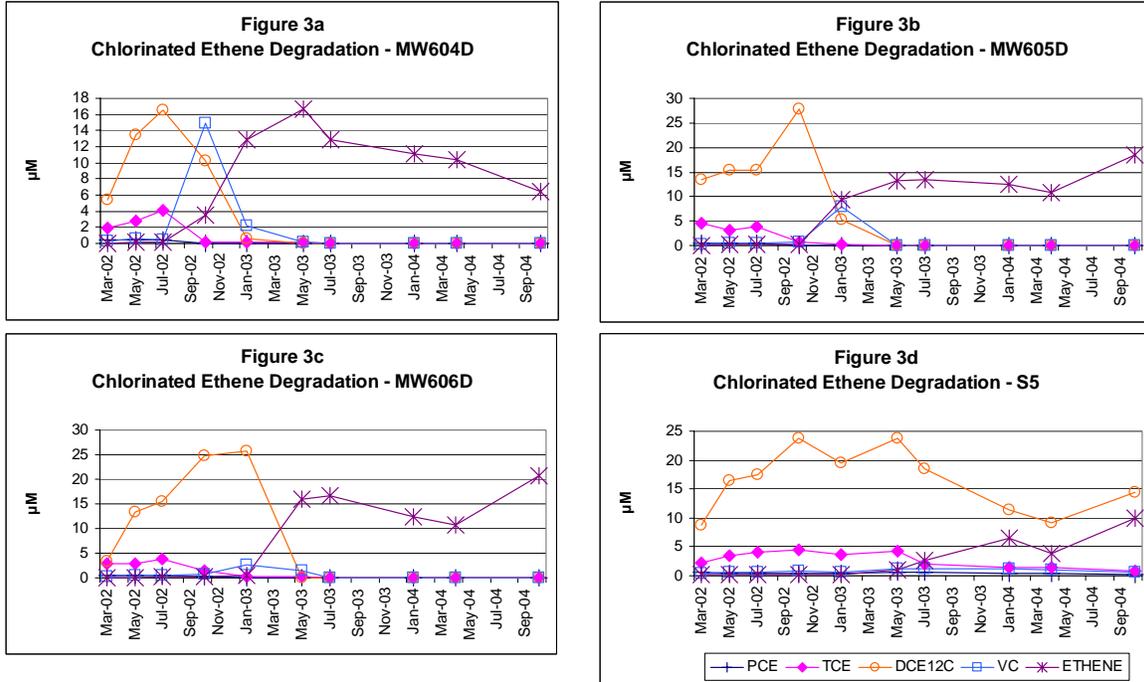
At Building 719, negligible concentrations of sulfate and elevated methane (the end product of methanogenesis) measured downgradient of the injection well field in well MW605D reflect the development of redox conditions in the reactive zone ideal for utilization of TCE as an electron acceptor by microbes (Figures 2a and 2b).



**FIGURE 2. Sulfate and methane in deep wells.**

### REDUCTIVE DECHLORINATION IN THE DEEP PORTION OF THE REACTIVE ZONE

Data collected from three monitoring well pairs are used to assess the prevailing geochemical conditions and contaminant/daughter product concentrations within the reactive zone that has been established around the injection wells (Figure 1). MW604SD, MW605SD, and MW606SD are located directly downgradient of the injection well field and the source area. The data collected from these wells represent groundwater as it migrates out of the reactive zone. These data suggest differentiation between the shallow and deep portions of the surficial aquifer in the reactive zone. In general, pH and oxidation-reduction potential (ORP) have remained relatively stable over time in the deep part of the reactive zone, with a pH near 7 and ORP measurements between -100 and -200 millivolts (mv). Also distinctive to the deep zone is clear evidence of nearly stoichiometric degradation of TCE to ethene, which is associated with the step-wise process of reductive dechlorination. Molar concentration graphs of PCE, TCE, cis-1,2-DCE, VC, and ethene in the three deep monitoring wells downgradient of the reactive zone (Figures 3a-c) show that by May 2003 nearly all chlorinated ethenes reinjected into the system (represented by S5 concentrations Figure 3d) were converted to ethene. High ethene and low chlorinated ethane concentrations after June 2003 show that complete destruction of parent/daughter compounds continued through October 2004.



**FIGURE 3a-3d. Chlorinated ethene degradation in deep wells.**

To demonstrate how effectively solvents are destroyed as recirculated groundwater passes through the reactive zone, chlorinated ethene concentrations in the groundwater prior to injection (S5) are compared to those in the three well pairs directly downgradient of the reactive zone (Table 1). As of May 2003, more than 98 percent of the PCE, TCE, cis-1,2-DCE, and VC passing through the deep portion of the reactive zone was degraded to ethene. Conservative estimates from calculations based on molar concentrations of ethene detected in the three deep downgradient wells and assumed groundwater velocity indicate that at least 130 pounds (59 kg) of TCE were degraded to ethene between May 2002 and October 2004.

**TABLE 1. Percent destruction - deep monitoring wells.**

	S5	MW604D		MW605D		MW606D	
	Chlorinated Ethenes (µg/L)	Chlorinated Ethenes (µg/L)	% Destruction	Chlorinated Ethenes (µg/L)	% Destruction	Chlorinated Ethenes (µg/L)	% Destruction
<b>Mar-02</b>	1248	862	30.93%	2023	-62.10%	783	37.26%
<b>May-02</b>	2168	1755	19.05%	2018	6.92%	1781	17.85%
<b>Jul-02</b>	2344	2231	4.82%	2106	10.15%	2105	10.20%
<b>Oct-02</b>	2993	1951	34.81%	2842	5.05%	2655	11.29%
<b>Jan-03</b>	2476	227.1	90.83%	1035.5	58.18%	2691	-8.68%
<b>May-03</b>	3038	34.4	98.87%	14.18	99.53%	111.8	96.32%
<b>Jul-03</b>	2235	8.45	99.62%	6.59	99.71%	12.87	99.42%
<b>Jan-04</b>	1422	5.55	99.61%	1.1	99.92%	19.8	98.61%
<b>Apr-04</b>	1202	6.62	99.45%	15.76	98.69%	15	98.75%
<b>Jul-04</b>	1475	8.8	99.40%	12.8	99.13%	26.6	98.20%
<b>Oct-04</b>	1585	3.74	99.76%	10.5	99.34%	10.22	99.36%

chlorinated ethenes = PCE, TCE, cis-1,2-DCE, and vinyl chloride

## PARTITIONING OF CHLORINATED SOLVENTS INTO SHALLOW GROUNDWATER

Conditions in the shallow portion of the reactive zone differ from those observed in the deep portion. For example, field measurements of ORP in the shallow wells have fluctuated significantly over time from 0 to -100 mv, while measurements in the deep wells have been consistently more negative. This difference is attributed in part to the influence on groundwater chemistry by chlorinated solvents desorbing from the source area soils between injection wells and MW604, MW605, and MW606 (Figure 1). The high desorbed solvent concentrations may mask the degradation in the shallow portion of the aquifer.

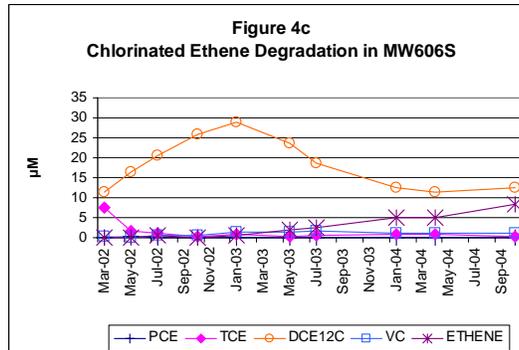
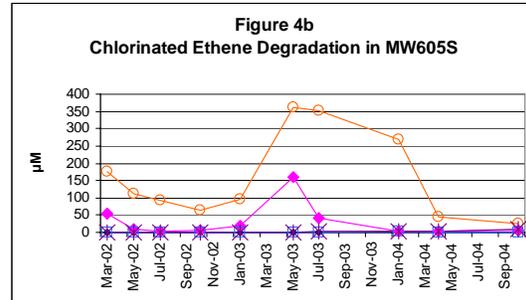
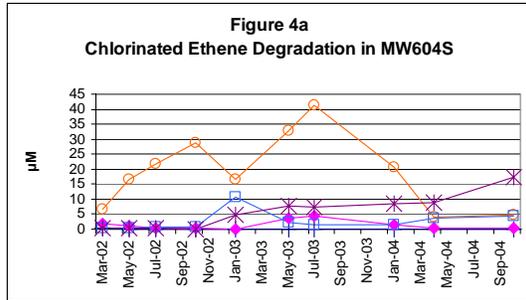
Because cis-1,2-DCE concentrations are high in the shallow groundwater, complete destruction in the shallow zone is not demonstrated as well as in the deep zone. Destruction percentages are less than 50 percent and are consistently negative in MW605S, indicating that continued desorption from source materials is taking place (Table 2).

**TABLE 2. Percent destruction - shallow wells.**

	S5	MW604S		MW605S		MW606S	
	chlorinated ethenes (µg/L)	chlorinated ethenes (µg/L)	% destruction	chlorinated ethenes (µg/L)	% destruction	chlorinated ethenes (µg/L)	% destruction
Mar-02	1248	990	20.67%	24300	-1847.12%	2103	-68.51%
May-02	2168	1780	17.90%	12167	-461.21%	1858	14.30%
Jul-02	2344	2214	5.55%	9692	-313.48%	2198	6.23%
Oct-02	2993	2881.7	3.72%	7272	-142.97%	2575.7	13.94%
Jan-03	2476	2284.4	7.74%	12051	-386.71%	3008.2	-21.49%
May-03	3038	3832.5	-26.15%	56122	-1747.33%	2442.8	19.59%
Jul-03	2235	4684.2	-109.58%	39689	-1675.79%	1973.1	11.72%
Jan-04	1422	2311.4	-62.55%	26340	-1752.32%	1374.4	3.35%
Apr-04	1202	698.99	41.85%	4613.8	-283.84%	1279.4	-6.44%
Jul-04	1475	1572.7	-6.62%	3619	-145.36%	1115.9	24.35%
Oct-04	1585	803.4	49.31%	3292	-107.70%	1323.1	16.52%

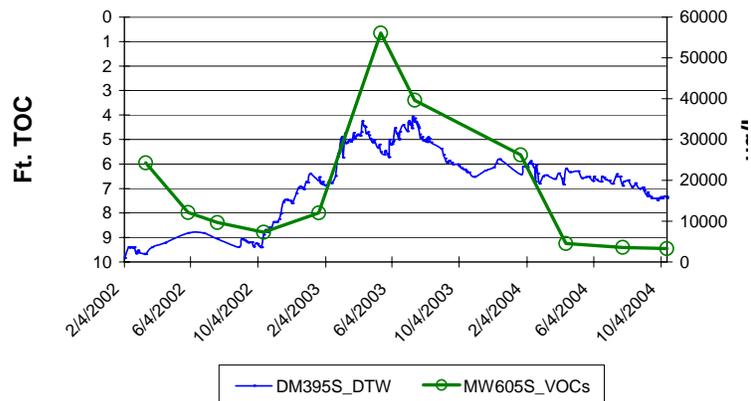
chlorinated ethenes = PCE, TCE, cis-1,2-DCE, and vinyl chloride

Although TCE is the parent compound in the source area, shallow wells contain higher concentrations of cis-1,2-DCE than TCE. As TCE is desorbed, it spontaneously degrades to the more soluble cis-1,2-DCE. This cis-1,2-DCE does not in turn spontaneously degrade, as evidenced by high DCE concentrations relative to VC and ethene (Figures 4a-c). Instead, cis-1,2-DCE persists in the shallow groundwater until it is recaptured by the extraction wells and reinjected into the reactive zone. Increasing ethene concentrations in MW604S and MW605S (Figures 4a and b) as well as several other shallow monitoring wells indicate that destruction of chlorinated ethenes occurs in the shallow part of the reactive zone and is increasing with time.



**FIGURE 4a-4c. Chlorinated ethene degradation in shallow wells.**

Although continual desorption of significant source mass may limit contaminant destruction in the shallow zone, this occurrence is beneficial in the long-term. Chlorinated solvents are only available for reductive dechlorination in the aqueous phase. In order for the AAB system to effectively remediate the Building 719 source area, the source mass must be partitioned into the groundwater, which only



**FIGURE 5. Source desorption - DTW and chlorinated ethenes in MW605S**

occurs when groundwater contacts contaminated soils during high water table conditions. Figure 5 shows the water table elevation measured in a monitoring well located in the injection well field from February 2002 to October 2004. High water table conditions prevailed for all of 2003, with the highest period from March through September 2003, at which time the water table was 4 to 5.5 ft (1.2 to 1.7 m) bgs. The dramatic increase in chlorinated ethene concentrations in MW605S during this period of high water table conditions suggests that source contaminants were actively desorbing into groundwater. The estimated mass of TCE that partitioned out of the soil and into the groundwater during 2003 was 870 pounds (395 kg). This estimate is based on dissolved phase concentrations measured in the three shallow monitoring wells and an average

groundwater velocity. An estimated total of approximately 1,200 pounds (544 kg) of TCE was desorbed between May 2002 and October 2004.

The effectiveness of the source desorption is demonstrated in the 2004 data on Figure 5. Total chlorinated ethene concentrations are less than those for 2002, when the water table was approximately 9 ft (3 m) bgs. At a minimum, the source zone from 6.5 to 9 ft (2.0 to 2.7 m) bgs has been significantly reduced. While the water table was high, sodium lactate injection was increased to as much as four times the original weekly injection volume. This was done to increase biological activity in the reactive zone to accommodate the increased mass of chlorinated ethenes in the shallow groundwater. Also, an increase in biosurfactants associated with biological activity should have improved the partitioning rate of the source contaminants and maximized source desorption while the water table was high. The effects that the high water table had on the shallower soils above 6 ft (1.8 m) bgs may be determined the next time the water table reaches similar levels.

## **CONCLUSIONS**

Data collected during the first three years of system operation of the Building 719 AAB system demonstrate that the system is effectively remediating the source area of chlorinated solvents beneath the building. Addition of sodium lactate and DAP to the subsurface have established redox conditions around the injection wells favorable for the use of TCE as an electron acceptor. Stoichiometric degradation of TCE to ethene in the deep portion of the reactive zone provides evidence that complete reductive dechlorination is occurring. Comparison of chlorinated ethene concentrations for groundwater entering the reactive zone to groundwater passing out of the deep part of the reactive zone shows destruction rates above 98 percent.

Assessment of TCE destruction in the shallow part of the reactive zone/aquifer is complicated by high concentrations of cis-1,2-DCE, which result from the breakdown of TCE as it desorbs from the source area into shallow groundwater. There is evidence that complete dechlorination will progress as cis-1,2-DCE concentrations decrease with lower water table elevations and/or reduction of the source mass. However, the partitioning of significant source mass into groundwater is crucial to the ultimate goal of remediating the source area. An estimated 1,200 pounds (544 kg) of TCE were desorbed from shallow soils during 2003 alone, when high water table conditions resulted in extended contact with the source contaminants.

After three years of operation, the Building 719 AAB system has proven to be an effective remediation remedy for the shallow chlorinated solvent source area while causing very little disruption to the critical activities at the site.

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