

Accelerated Anaerobic Bioremediation of a Solvent Source Area Using Direct Injection, Dover AFB, DE

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ABSTRACT: A solvent source area consisting primarily of tetrachloroethene (PCE) and trichloroethene (TCE) was located adjacent to the hazardous waste storage building (Site SS07) at Dover Air Force Base (DAFB), Delaware. The selected treatment for the site focuses on the source area using accelerated anaerobic biodegradation (AAB) by direct-push injection methods to distribute substrate and nutrients and natural attenuation for the downgradient dissolved plume. In March 2006, nearly 102,000 gallons (386,000 liters) of amended water (a mixture of water, sodium lactate, emulsified vegetable oil [EVO], and nutrients) were injected into 53 locations at multiple depths. Monitoring data indicate that aquifer conditions rapidly became more reducing and favorable to anaerobic biodegradation. Dissolved iron and methane concentrations increased and sulfate and dissolved oxygen (DO) levels declined. Increases in *cis*-1,2-dichloroethene (*cis*-1,2-DCE) and vinyl chloride (VC) concentrations were observed as early as three months after the injection, indicating parent contaminant degradation. Decreasing PCE and TCE concentrations and the detection of ethene in several wells provides further evidence that complete anaerobic degradation is occurring at the site. These trends continue to be seen nine months after injection.

Introduction. Oak Ridge National Laboratory (ORNL) and URS have successfully implemented in situ AAB to treat chlorinated solvents within the shallow water table near an old release site at DAFB. Although no solvent spill or leak was ever recorded at the hazardous waste storage building (#1306), delineation data indicated that PCE, and to a lesser degree TCE, most likely entered the soil off of one edge of the asphalt pavement surrounding the building. The release is probably very old since no soil source area was ever identified. The resulting contaminant plume extends at least 2,800 feet (ft) (853 meters [m]) to the Base boundary (Figure 1). Site data also indicated that reductive dechlorination of solvents was occurring at a rate insufficient to prevent off-site migration. Studies at similar sites at DAFB, however, indicated that biodegradation could be enhanced with the addition of organic carbon and nutrients (Remediation Technologies Development Forum [RTDF], 2000; and URS, 2007).

AAB using direct-push injection of amendments was the selected remedy based on assessment of the extent of contamination and aquifer hydraulic testing (U.S. Army Corps of Engineers [USACE], 2005; and ORNL, 2006a,b). A relatively small area of elevated PCE and TCE (total concentration greater than 500 micrograms per liter [$\mu\text{g/L}$]) was delineated by direct-push groundwater sampling (Figure 1). This was the area targeted for AAB treatment. Original plans called for installing injection and extraction wells to circulate amended groundwater across the area using a mobile treatment trailer designed for this purpose. However, an aquifer pump test indicated that the hydraulic properties of the aquifer were not favorable for circulation between permanently installed wells. Thus, direct injection was selected as the method of application.



FIGURE 1. SS07 source area and plume map.

This paper describes the implementation of AAB in a shallow groundwater source area and presents data demonstrating the initial success of the remedy.

SITE SETTING AND INITIAL CONDITIONS

The surficial lithology at the site consists of unconsolidated Pleistocene deposits of the Columbia Formation. This formation comprises silts and clays to about 10 ft below ground surface (bgs) (3 m) and becomes sandier (fine to coarse) with depth. The formation is approximately 55 to 60 ft (17 to 18 m) thick. 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 10 to 16 ft (3 to 5 m) bgs, but varies with precipitation. The horizontal gradient calculated during the initial investigation of this site was 0.0006 in the Columbia Aquifer. Groundwater flow is generally to the southwest towards the Base boundary. (Figure 1)

Site delineation sampling identified elevated ($>500 \mu\text{g/L}$) combined PCE and TCE concentrations in shallow groundwater in an irregularly shaped area that likely reflects localized preferential groundwater flow patterns. PCE and TCE were detected at concentrations as high as 32,000 and 2,220 $\mu\text{g/L}$, respectively, near the suspected release point. Concentrations downgradient are much lower and found deeper within the aquifer. The SS07 dissolved plume is defined by the 5 $\mu\text{g/L}$ total chlorinated solvent contour line. The decrease in concentrations is attributed mainly to dilution, although evidence of degradation is observed in the downgradient portion of the plume.

During delineation sampling in early 2006, four wells inside the treatment zone were sampled to assess conditions prior to treatment. The data in Table 1 indicate that the

source area was highly aerobic and that little or no degradation was occurring prior to the injection of amendments.

TABLE 1. Initial and ideal aquifer and plume conditions.

Parameter	Prior to Injection	Ideal Conditions for AAB*
DO, milligrams/liter (mg/L)	2 to 7	<0.5
Oxidation reduction potential (ORP), millivolts (mV)	75 to 275	negative
Total organic carbon (TOC) (mg/L)	<2	50 to 500
Total iron (mg/L)	<1	elevated
Sulfate (mg/L)	10 to 15	<2
Cis-1,2-DCE (µg/L)	0 to 1	Not applicable
VC (µg/L)	0 to 1	Not applicable
Methane (µg/L)	0 to 10	Elevated
Ethene (µg/L)	0	Not applicable

*Air Force Center For Environmental Excellence (AFCEE), 2004

There is some evidence that natural attenuation occurs in deeper zones of the source area as well as in portions of the downgradient plume. However, the degradation rate did not appear adequate to prevent off-site migration of contaminants at concentrations above U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs).

REMEDY DESIGN AND IMPLEMENTATION

A pump test was conducted in February 2006 to evaluate the feasibility of using different carbon substrate injection methods. The results of this test indicated that the formation did not have the permeability necessary for delivery of the injectate using permanent injection wells. Thus, a direct-push rig and pump truck were used to inject the substrate into a closely spaced network of temporary direct-push boreholes. The direct-push injection locations are shown in Figure 2.

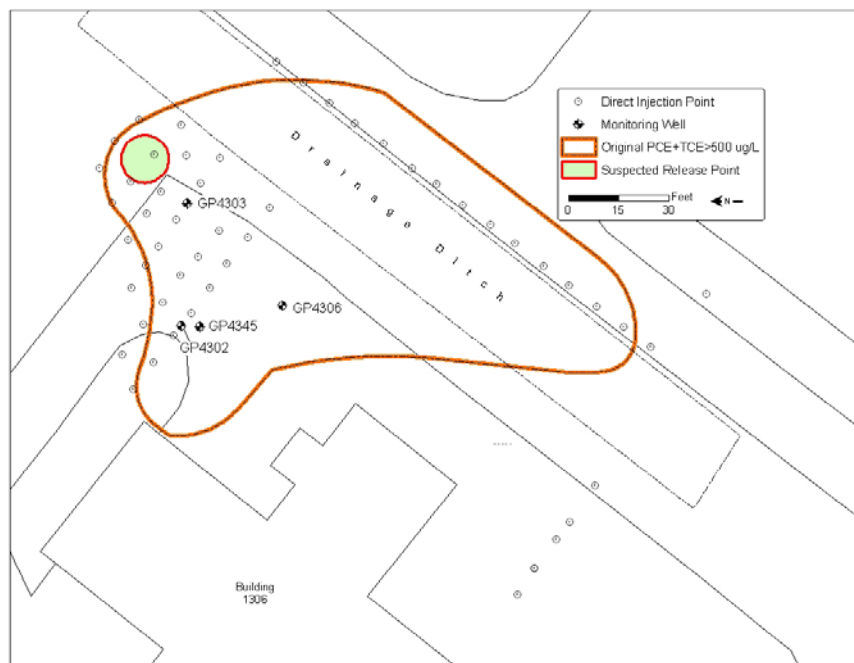


FIGURE 2. Injection treatment locations.

The injection points were chosen based on: the location of the suspected release point; the area identified for treatment by the 500 $\mu\text{g/L}$ PCE and TCE contour; underground utilities at the site; and a drainage ditch that runs through the site (Figure 2). The majority of injection points (32 of 53) were positioned on a grid with approximate 10-ft (3-m) spacing in the area where the highest solvent concentrations were detected in the shallow groundwater. In this portion of the treatment area, substrate was injected at intervals between 5 and 25 ft (1.5 to 7.5 m) bgs. A portion of the injection solution was injected above the water table in an attempt to flush out any residual contamination located in the unsaturated zone.

The remaining 21 injection points were positioned approximately 10 ft (3 m) apart along two perpendicular transects downgradient of the primary source area. At these locations, injections occurred between 10 and 30 ft (3 to 9 m) bgs. These points were positioned to ensure that groundwater did not leave the source area without passing through an AAB treatment zone.

During injection activities, surfacing of substrate was a reoccurring problem. A number of utility conduits are present at the site, which served as preferential flow paths for the substrate. Injection solution surfaced through the asphalt-pavement as well as the drainage ditch during injections at some locations. The volume of solution injected was reduced to minimize surfacing at these locations.

A combination of organic carbon substrates (EVO and sodium lactate) and nutrients (dibasic ammonium phosphate [DAP]) were injected into the subsurface to stimulate the biodegradation of chlorinated solvents. EVO and sodium lactate were added to potable water in equal parts by volume and at rates that resulted in a concentration of approximately 17,500 mg/L TOC in the injection solution. DAP was added to the mixture at an approximate carbon to nitrogen to phosphorous ratio of 100:5:5.5. The

potable water was obtained from a fire hydrant and was first processed through activated carbon to remove residual chlorine.

The substrate was mixed at a relatively high TOC concentration because the site was aerobic prior to the AAB injection. Sodium lactate was used to provide readily available carbon to create anaerobic conditions in the aquifer in a short period of time. EVO was used as a slow release carbon source to maintain anaerobic conditions for an extended period of time, minimizing the need for re-injection. DAP was included with the substrates to provide metabolic nutrients.

Approximately 102,000 gallons (386,000 liters) of injection solution were injected in 11 days in March 2006.

DATA SUMMARY AND DISCUSSION

After injections were completed, the groundwater in the treatment zone was sampled frequently to assess substrate distribution and monitor the aquifer conditions. Three months after the injection, a quarterly sampling program began to monitor solvents and dissolved gas concentrations, in addition to geochemical parameters. A network of 11 wells, ten located within or just downgradient of the treatment area and one background well, was used for this purpose. Four of these wells, selected based on location and data quality, are used to illustrate the major trends observed (Figure 2). Wells GP4302, GP4303, and GP4345 are located within or very close to the primary injection grid. GP4306 is located approximately 15 ft (4.5 m) downgradient of this area.

TOC concentration trends for the selected wells are shown in Figure 3. All monitoring wells have significantly elevated TOC concentrations for most rounds of monitoring. The average TOC detections for the selected wells across all sampling rounds following injection range from 90 to 2,040 mg/L. GP4303 is closest to an injection point and thus shows a high initial concentration that quickly falls. Most wells, such as GP4345, exhibit a slight downward trend, but have remained significantly elevated since injection occurred.

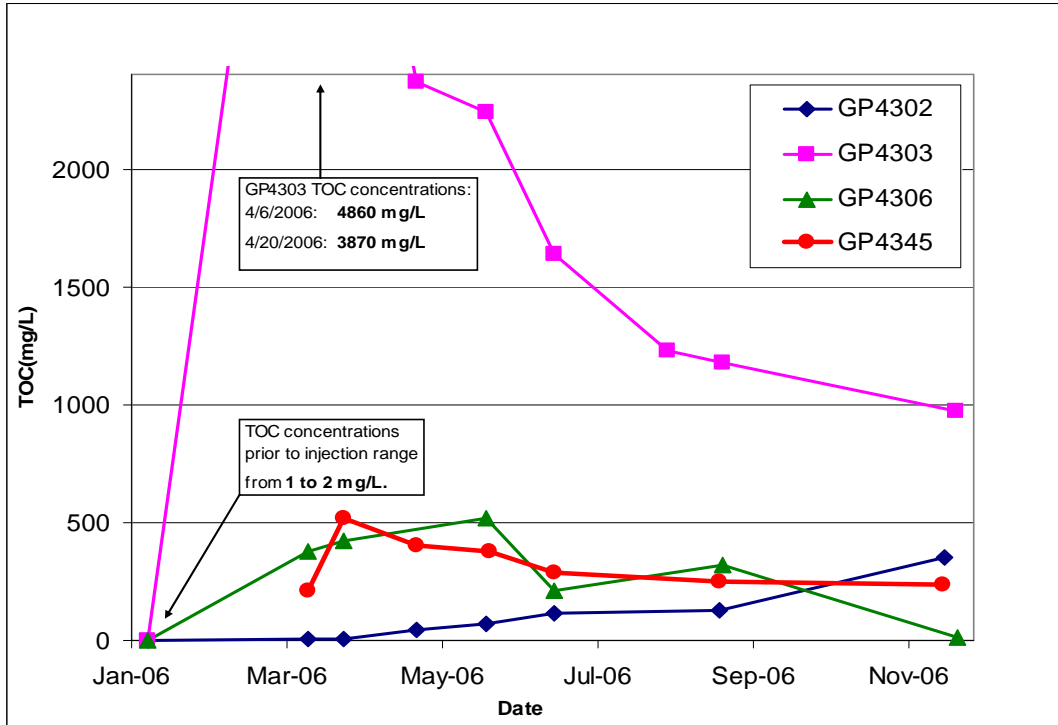


FIGURE 3. TOC over time in selected wells.

TOC concentrations vary greatly across the site, and do not exhibit any discernible spatial pattern or trend. The spatial distribution of TOC at the site is likely controlled by preferential flow paths and small-scale features within the formation. Based on ORNL and URS experience at other AAB sites at DAFB, a TOC concentration between 15 and 30 mg/L is generally required to promote anaerobic biodegradation. TOC concentrations in the four monitoring wells, and in most of the other wells at the site, are consistently within or above this range.

Solvents, dissolved gases, and geochemical data are presented for the same four monitoring wells in Figure 4. For each monitoring well, the solvents over time are plotted in graphs. Dissolved gases and geochemical parameters are tabulated. The most recent data available are highlighted in yellow.

Negative ORP readings indicate that the treatment area was converted from aerobic to anaerobic shortly after injection. This is confirmed by DO concentrations below 1 mg/L in most monitoring wells as early as two weeks after injection. Other electron acceptor trends, including increasing dissolved iron, non-detect sulfate concentrations, and increasing methane concentration, demonstrate that anaerobic conditions favorable for reductive dechlorination were established within six to nine months of injection.

On several occasions DO and ORP levels temporarily increased to values characteristic of aerobic conditions. These increases, which since reversed themselves, are probably related to rain fall and do not seem to be adversely affecting the overall anaerobic condition of the treatment zone.

PCE and TCE concentrations have fallen dramatically in most wells across the treatment zone. Many of the larger drops in concentrations occurred within three months of injection. In many wells, PCE and TCE were detected at concentrations near or below

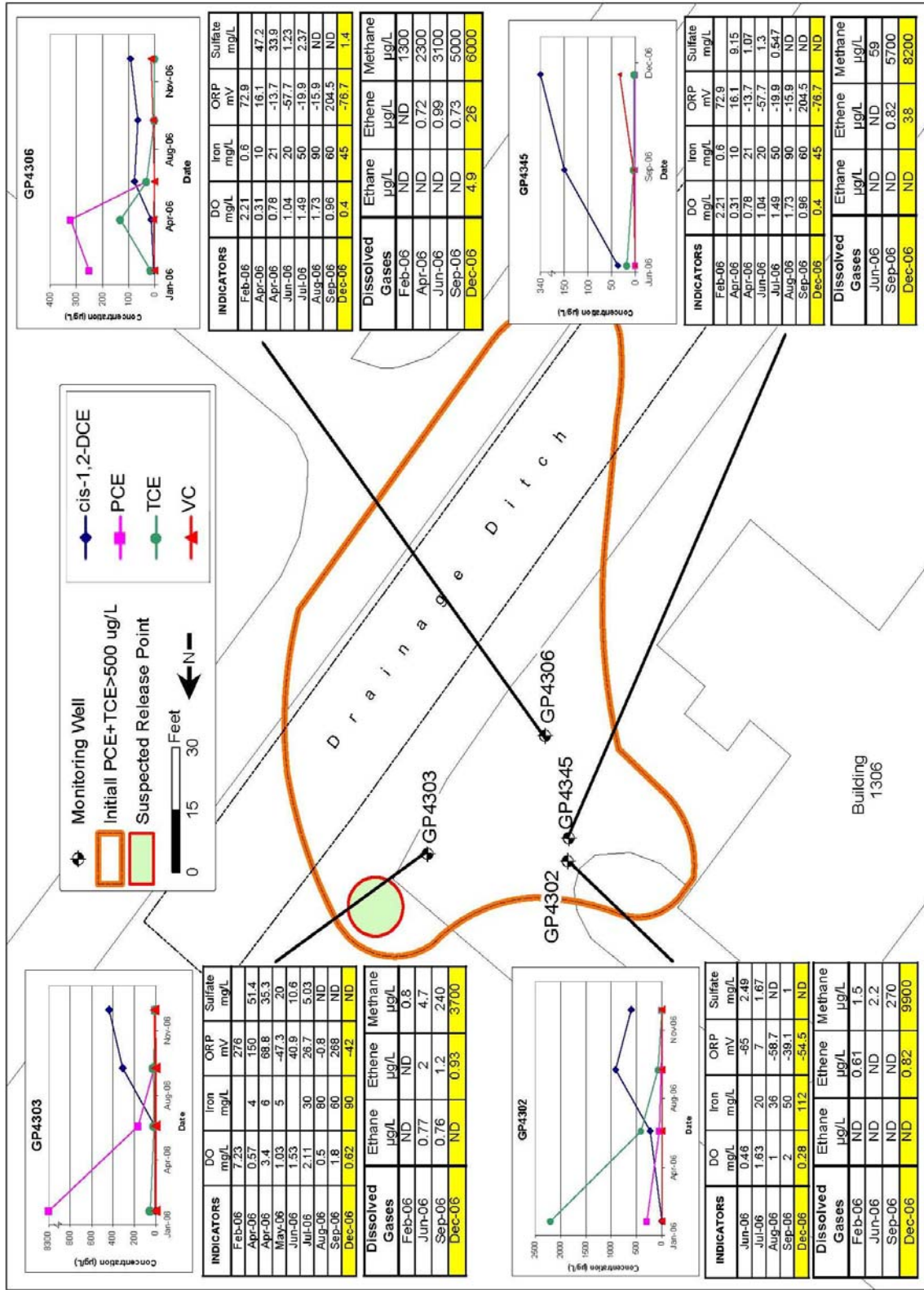


FIGURE 4. Solvent and indicator parameter trends.

MCLs only nine months after injection. Some of the initial dramatic decline is likely due to the partitioning of PCE and TCE into the vegetable oil. However, increasing concentration trends for the solvent daughter products and for dissolved gases indicate that sustained reductions in PCE and TCE are attributed to biodegradation. Cis-1,2-DCE, VC, and ethene were rarely found even at trace levels prior to injection. Three months after injection, cis-1,2-DCE was found in most wells and at concentrations as high as 920 µg/L. VC was detected in many wells nine months after injection and at concentrations up to 33 µg/L. Ethene, which is the end product of PCE and TCE degradation and indicates complete dechlorination, was also detected frequently; its highest concentration was 38 µg/L.

CONCLUSIONS

The following conclusions are made based on data collected during the first nine months following injection:

- Direct-push injection is an effective substrate delivery mechanism for sites with low hydraulic conductivity.
- Substrate distribution in a formation with low hydraulic conductivity, such as SS07, is strongly governed by preferential flow paths. A relatively uniform distribution of TOC will be difficult to achieve.
- The high TOC substrate mixture appears to be working well: (1) The lactate provided a readily usable carbon source which effectively converted the aerobic conditions to anaerobic within the treatment area within two months of the injection. (2) Although it is too early to determine the long-term effectiveness of the EVO as a slow release source of carbon, TOC concentrations remain more than adequate nine months after injection.
- PCE and TCE concentrations have dropped dramatically. Complete anaerobic dechlorination of PCE and TCE is occurring based on the appearance of daughter products. It is unclear how much of the initial decrease may be due to partitioning of the solvents into the EVO.
- Although SS07 was historically an aerobic system with little or no natural degradation occurring, bioaugmentation appears unnecessary.

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