

Accelerated Anaerobic Bioremediation of a PCE Source Area, Two Years Later at Site SS07, Dover AFB, DE

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ABSTRACT: A solvent source area (called SS07) consisting primarily of tetrachloroethene (PCE) was situated near Building 1306 at Dover Air Force Base (AFB), Delaware. High PCE concentrations (up to 32,000 micrograms per liter [$\mu\text{g/L}$]) in the shallow groundwater indicated a source area although no soil contamination was ever found. The selected remedy for the site was two-pronged, focusing 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. Groundwater monitoring data have demonstrated the effectiveness of the lactate/EVO combination at Site SS07. Analytical results showed that aquifer conditions rapidly became more reducing and favorable for anaerobic biodegradation within the first month after injection. Over the longer term, favorable aquifer conditions persisted and spread. One year after injection, PCE and trichloroethene (TCE) fell below their Federal drinking water maximum contaminant levels (MCLs) of 5 $\mu\text{g/L}$ for each contaminant in all site monitoring wells. Well into the second year of monitoring, organic carbon concentrations are still elevated and degradation continues. Increases in *cis*-1,2-dichloroethene (*cis*-1,2-DCE) and vinyl chloride (VC) concentrations are observed and ethene is found in most site wells providing evidence that complete anaerobic degradation is occurring. Rebound of PCE concentrations was a concern but no evidence of this has been seen.

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 PCE release site at Dover AFB (ORNL, 2006a,b). Although no solvent spill or leak was ever recorded, delineation data indicated that PCE most likely entered the soil off of one edge of the asphalt pavement surrounding Building 1306. (This building had been permitted for hazardous waste storage, but now serves as a 90-day accumulation point for limited quantities of drummed hazardous wastes.) The release is likely 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).

A relatively small area of elevated PCE and its first breakdown product TCE (total concentration greater than 500 $\mu\text{g/L}$) was delineated by direct-push groundwater sampling (Figure 1). This was the area in which AAB treatment was focused and occurred in March 2006. Intermediate monitoring results obtained during the nine months following injections were presented in a previous paper (Stenberg, 2007).

This paper describes the progress of remediation nearly two years after injection based on periodic groundwater monitoring data.

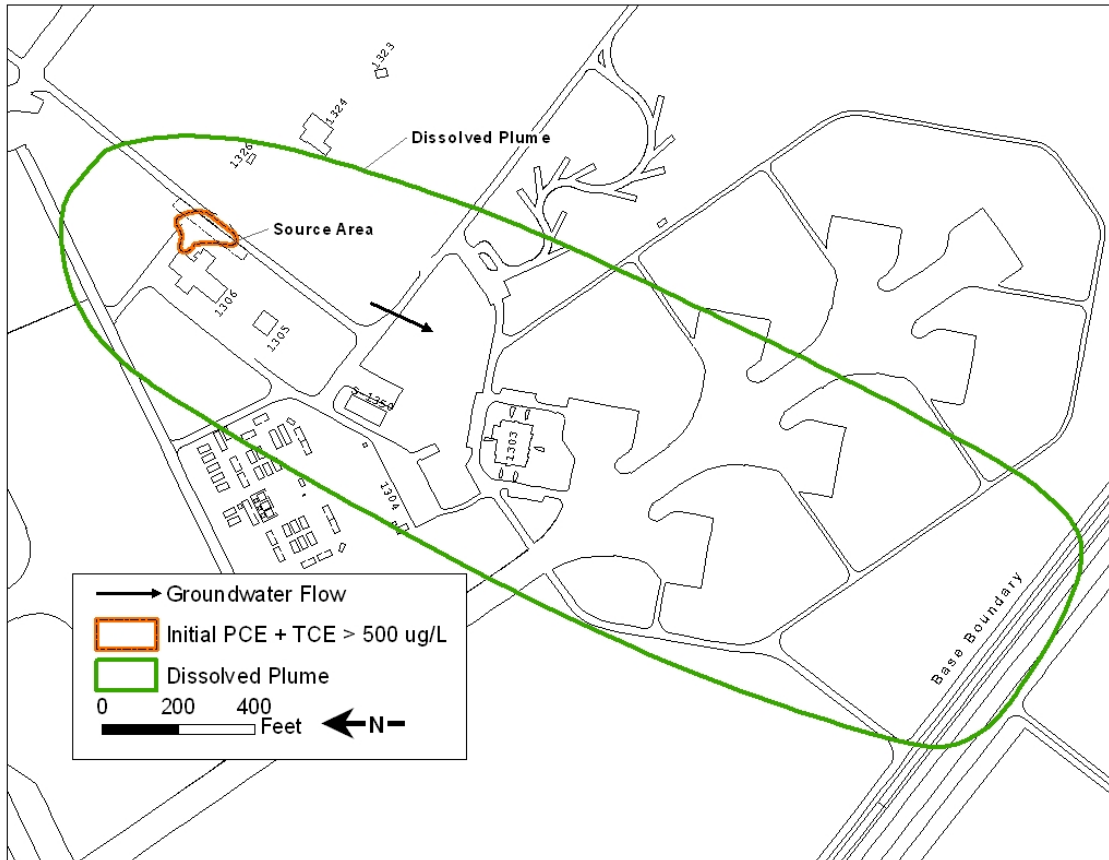


FIGURE 1. SS07 source area and plume map.

SITE SETTING AND INITIAL CONDITIONS

The shallow lithology at the site consists of unconsolidated Pleistocene deposits of the Columbia Formation. Silts and clays dominate to about 10 ft below ground surface (bgs) (3 m) and become 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 is an aquitard to the downward migration of contaminants.

The water table is encountered approximately 10 to 16 ft (3 to 5 m) bgs, but varies with precipitation. The horizontal gradient in the Columbia Aquifer is relatively flat at the site and was calculated to be about 0.0006 ft/ft. Groundwater flow is generally to the southwest towards the Base boundary (Figure 1).

Shallow groundwater analyses identified elevated (>500 $\mu\text{g/L}$) combined PCE and TCE concentrations in an irregularly shaped area (Figure 1). 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 extent of the 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 some evidence of degradation (minor amounts of cis-1,2-DCE) is observed in the downgradient portion of the plume.

In early 2006 and prior to treatment, four wells inside the treatment zone were sampled to assess initial aquifer conditions. 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** |
|---|---------------------|----------------------------|
| Dissolved oxygen (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 |
| PCE + TCE (µg/L) | up to 34,200 | Not applicable |
| 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 |

*Data originally presented in previous paper (Stenberg, 2007).

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

Although there is some evidence that natural attenuation occurs in portions of the plume, degradation rates did not appear adequate to prevent off-site migration of contaminants at concentrations above Federal drinking water MCLs. Therefore, active remediation was conducted.

SOURCE AREA TREATMENT

Shallow groundwater in the source area was treated using a combination of organic carbon substrates (EVO and sodium lactate) and nutrients (dibasic ammonium phosphate [DAP]). EVO and sodium lactate were added to potable water in equal parts by volume that resulted in a concentration of approximately 17,500 mg/L TOC. DAP was added to the mixture at an approximate carbon to nitrogen to phosphorous ratio of 100:5:5.5.

The solution was injected using a direct push rig into a closely spaced network of 53 points shown in Figure 2. Most points were positioned on a grid with an approximate 10-ft (3-m) spacing in the area where the highest solvent concentrations were detected in the shallow groundwater. Here, substrate was injected at intervals between 5 and 25 ft (1.5 to 7.5 m) bgs. Substrate solution was also intentionally injected above the water table to flush residual contamination that may have remained in the unsaturated zone. Additional injection points were positioned approximately 10 ft (3 m) apart along two perpendicular transects downgradient of the primary source area. Injections here were a little deeper, between 10 and 30 ft (3 to 9 m) bgs, and with a lower TOC concentration substrate. These points were positioned to ensure that groundwater did not leave the source area without passing through an AAB treatment zone. Approximately 102,000 gallons (386,000 liters) of the substrate solution were injected in 11 days in March 2006.

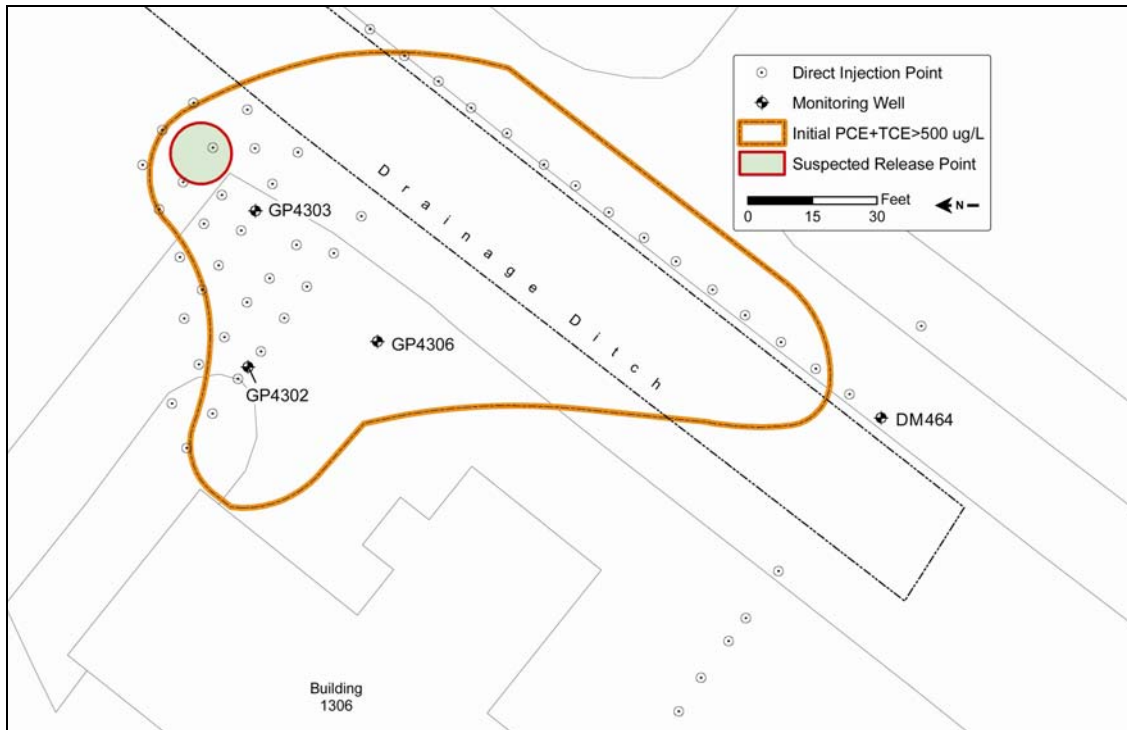


FIGURE 2. Injection treatment locations.

DATA SUMMARY AND DISCUSSION

A network of 11 monitoring wells is used to assess substrate distribution and aquifer conditions. Groundwater samples are analyzed for solvents, dissolved gases, and other geochemical parameters (currently on a semi-annual schedule). Four of the monitoring wells were selected based on location and data quality to illustrate the major trends in contaminant degradation and aquifer properties (Figure 2). Wells GP4302 and GP4303 are located within the primary injection grid. GP4306 is located approximately 15 ft (4.5 m) downgradient of this area. DM464 is situated near the south end of the treatment area just downgradient of the 500 $\mu\text{g/L}$ total PCE and TCE concentration contour.

TOC concentration trends for the selected wells are shown in Figure 3. All monitoring wells had significantly elevated TOC concentrations for most rounds of monitoring. TOC concentrations vary 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. GP4303 is closest to an injection point and thus shows high initial TOC concentrations that steadily decline over time. During the most recent sampling round (January 2008), TOC is about 30 mg/L in the two wells within the injection grid (GP4302 and GP4303) and is at background levels in the other two wells. Based on ORNL and URS experience at other Dover AFB sites, a TOC concentration between 15 and 30 mg/L is generally required to promote anaerobic biodegradation.

Trends in the geochemical data, chlorinated solvents, and dissolved gases are presented for the same four monitoring wells in Figure 4. For each well, the solvents and dissolved gases over time are plotted in graphs. The geochemical parameters are tabulated.

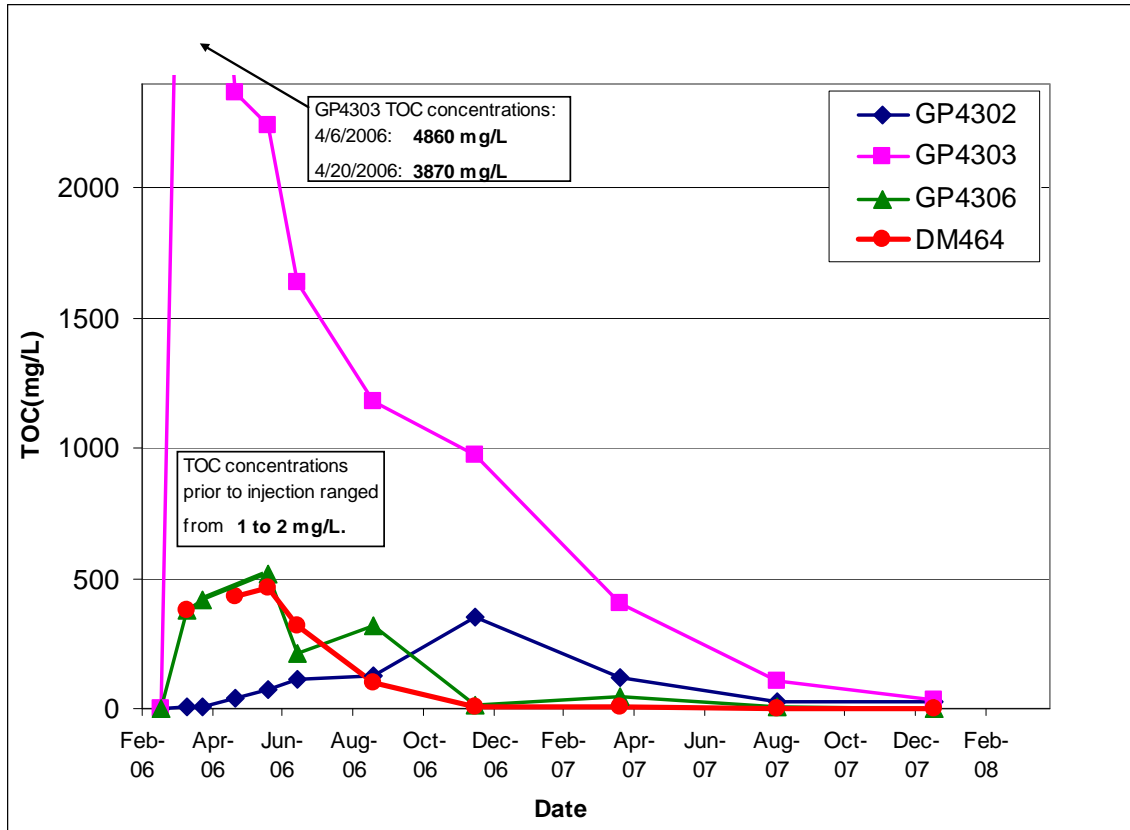


FIGURE 3. TOC over time in selected wells.

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 concentrations, demonstrate that anaerobic conditions favorable for reductive dechlorination were well established within six to nine months after injection. Anaerobic conditions have been maintained for nearly two years after injection.

PCE and TCE concentrations fell dramatically in most wells across the treatment zone after injection. Many of the larger decreases in concentrations occurred within three months of injection. In three of the example wells, PCE and TCE were detected at concentrations below MCLs only six to nine months after injection. In DM464, MCLs were reached in about one year. Some of the initial dramatic decline could be 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 due to biodegradation. This is also confirmed by the lack of rebound in parent contaminants. In fact, by January 2008 PCE and TCE were below detection limits in three of the four wells and present at only trace concentrations in well GP4303. Breakdown products cis-1,2-DCE, VC, and ethene were rarely detected 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

GP4302

| INDICATORS | DO mg/L | Iron mg/L | ORP mV | Sulfate mg/L |
|------------|------------|--------------|-----------|-----------------|
| Feb-06 | 7.8 | 0.1 | 192.2 | 13.7 |
| Apr-06 | 0.4 | 1.5 | 52.6 | 15.2 |
| Apr-06 | 0.5 | 5 | 3.7 | 14.2 |
| May-06 | 0.5 | 25 | -115.7 | 5.59 |
| Jun-06 | 0.5 | | -65 | 2.49 |
| Jul-06 | 1.6 | 20 | 7 | 1.67 |
| Aug-06 | 1.0 | 36 | -58.7 | ND |
| Sep-06 | 2.0 | 50 | -39.1 | 1 |
| Dec-06 | 0.3 | 112 | -54.5 | ND |
| Apr-07 | 0.7 | 75 | -91.6 | ND |
| Jan-08 | 1.6 | 135 | -85 | ND |

ND - not detected

GP4303

| INDICATORS | DO mg/L | Iron mg/L | ORP mV | Sulfate mg/L |
|------------|------------|--------------|-----------|-----------------|
| Feb-06 | 7.2 | | 276 | 14.6 |
| Apr-06 | 0.6 | 4 | 150 | 51.4 |
| Apr-06 | 3.4 | 6 | 68.8 | 35.3 |
| May-06 | 1.0 | 5 | -47.3 | 20 |
| Jun-06 | 1.5 | | 40.9 | 10.6 |
| Jul-06 | 2.1 | 30 | 26.7 | 5.03 |
| Aug-06 | 0.5 | 80 | -0.8 | ND |
| Sep-06 | 1.8 | 60 | 268 | ND |
| Dec-06 | 0.6 | 90 | -42 | ND |
| Apr-07 | 1.4 | 75 | -87.2 | ND |
| Jan-08 | 2.3 | 10 | -23.2 | ND |

ND - not detected

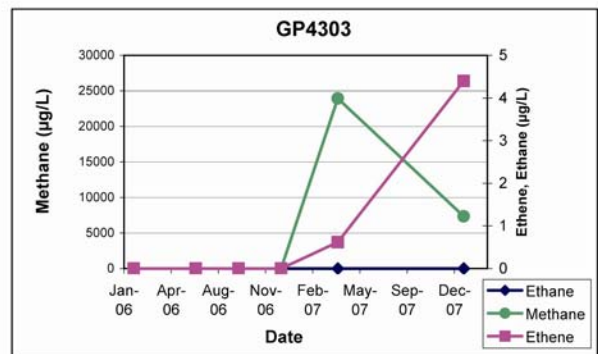
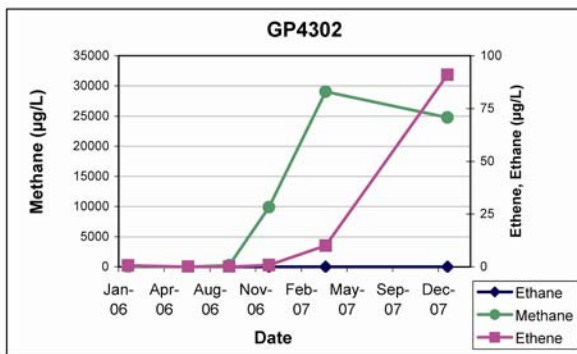
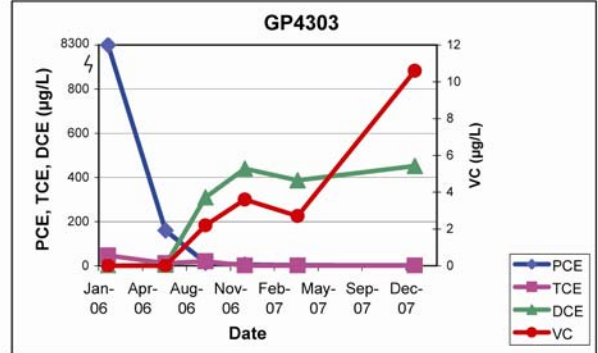
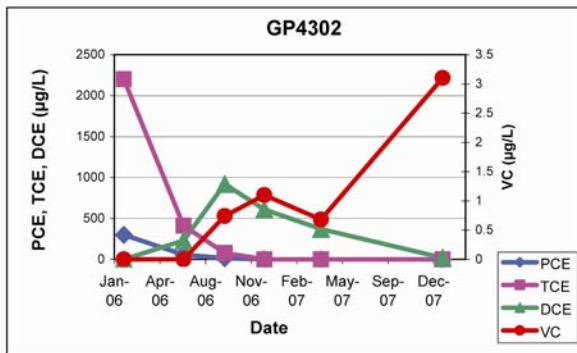


FIGURE 4. Solvent and indicator parameter trends (1 of 2).

GP4306

| INDICATORS | DO mg/L | Iron mg/L | ORP mV | Sulfate mg/L |
|------------|---------|-----------|--------|--------------|
| Feb-06 | 2.2 | 0.6 | 72.9 | 13.7 |
| Apr-06 | 0.3 | 10 | 16.1 | 47.2 |
| Apr-06 | 0.8 | 21 | -13.7 | 33.9 |
| Jun-06 | 1.0 | 20 | -57.7 | 1.23 |
| Jul-06 | 1.5 | 50 | -19.9 | 2.37 |
| Aug-06 | 1.7 | 90 | -15.9 | ND |
| Sep-06 | 1.0 | 60 | 204.5 | ND |
| Dec-06 | 0.4 | 45 | -76.7 | 1.4 |
| Apr-07 | 1.0 | 20 | -40.3 | ND |
| Jan-08 | 1.3 | 20 | -1.6 | ND |

ND - not detected

DM464

| INDICATORS | DO mg/L | Iron mg/L | ORP mV | Sulfate mg/L |
|------------|---------|-----------|--------|--------------|
| Apr-06 | 6.5 | 0.1 | 411.8 | 23.6 |
| May-06 | 0.5 | 5 | -127.4 | 19 |
| Jun-06 | 0.6 | 45 | -28.7 | 0.43 |
| Jul-06 | 1.2 | 66.5 | 6.7 | ND |
| Aug-06 | 0.3 | 75 | -26.7 | ND |
| Sep-06 | 0.9 | 50 | 4.8 | ND |
| Dec-06 | 0.3 | 20 | -98.6 | 1.62 |
| Apr-07 | 0.4 | 20 | -19.5 | ND |
| Aug-07 | 0.4 | 45 | -75.8 | ND |
| Jan-08 | 1.4 | 25 | 23.2 | ND |

ND - not detected

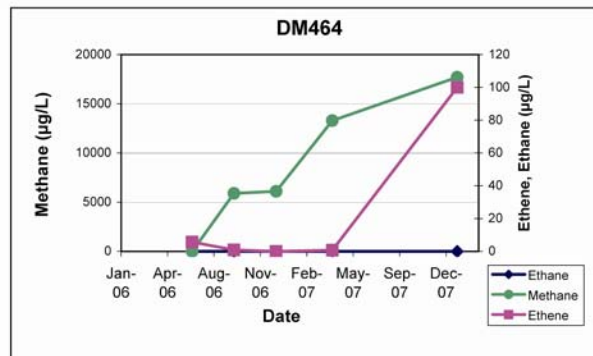
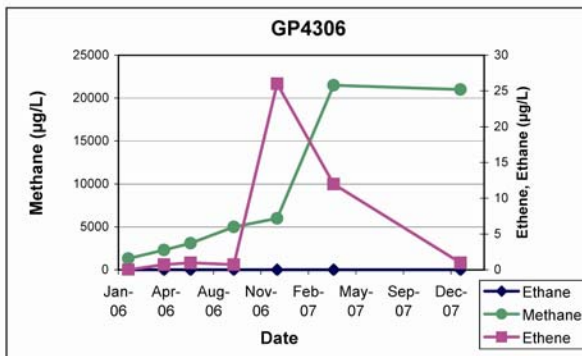
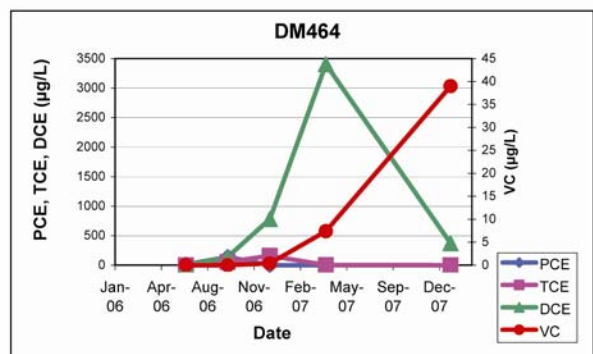
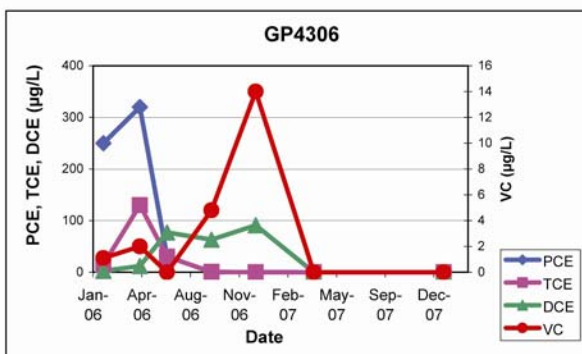


FIGURE 4. Solvent and indicator parameter trends (2 of 2).

nine months after injection and at concentrations up to 39 µg/L. These two compounds have since started to decline except in GP4303 and in DM464 (VC only). Ethene, which is the end product of PCE and TCE degradation and indicates complete dechlorination, was also detected frequently; its highest concentration was found in DM464 at 100 µg/L in January 2008. Although only four wells were highlighted herein, MCLs have been achieved for both PCE and TCE in all 11 source area monitoring wells. Overall, cis-1,2-DCE and VC are still above MCLs (70 and 2 µg/L, respectively) in many of the wells with cis-1,2-DCE now on declining trends and VC still increasing in some wells.

CONCLUSIONS

The following conclusions are made based on data collected during the nearly two years of monitoring following injection:

- A single event of direct push injection of high concentration TOC substrate mixture has provided sufficient carbon to successfully stimulate AAB. The lactate provided a readily usable carbon source which effectively converted the aerobic conditions to anaerobic within two months of injection. After almost two years, the presence of TOC at concentrations above background indicates that the EVO provides a sustainable source of carbon in the aquifer over a longer time period.
- PCE and TCE concentrations are below their MCLs in all 11 source area monitoring wells. No rebound in concentration for either compound has been observed to date.
- Intermediate breakdown products cis-1,2-DCE and VC increased as PCE and TCE degraded and subsequently began decreasing in concentration in most wells. VC is still on an increasing trend in some wells. MCLs have not yet been achieved for these two compounds.
- Ethene, the final breakdown product, is ubiquitously present across the source area and indicates that complete dechlorination is occurring.

REFERENCES

- AFCEE, 2004. *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*, Air Force Center for Environmental Excellence, August 2004.
- ORNL, 2006a. *Interim Remedial Action Completion Report, Sites LF17, SS07, FT01, and LF18, South Management Unit, Dover Air Force Base, DE*, submitted by URS Group, Inc., Gaithersburg, MD, August 2006.
- ORNL, 2006b. *South Management Unit Remedial Action Work Plan [and Addendum] Dover Air Force Base, Delaware*, submitted by URS Group, Inc., Gaithersburg, MD, January 2006.
- Stenberg, L., A. Bloom, G. DeLong, R. Lyon, D. Fox, and A. Buell. 2007. "Accelerated Anaerobic Bioremediation of a Solvent Source Area Using Direct Injection, Dover AFB, DE." Paper K-21, in: A.R. Gavaskar and C.F. Silver (Symposium Chairs), *In Situ and On-Site Bioremediation-2007*. Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium. May 7-10, 2007, Baltimore, Maryland. Battelle Press ISBN 978-1-57477-161-9, Columbus, Ohio.

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