



SUMMARY

A bioremediation pilot study using the emulsified carbon substrate ABC-Olé was conducted from July 2013 through October 2014 near Blackstone, Virginia. Contaminants of concern at the site include several chlorinated alkenes. The pilot study was completed to determine the effectiveness of enhanced anaerobic bioremediation to treat groundwater *in situ* and to provide site-specific data for a full scale design.

SITE BACKGROUND

The site is a former landfill located in the Piedmont physiographic province of South Central Virginia. Contaminants associated with historical waste disposal at the landfill include the chlorinated alkenes of tetrachloroethene (PCE) and trichloroethene (TCE). Groundwater at the site occurs within a single, unconfined aquifer system consisting of saprolite overlying fractured bedrock.

When the pilot study was initiated, PCE concentrations in groundwater at the test wells ranged from 53.6 to 79.3 ppb, and TCE concentrations ranged from 21.2 to 33.5 ppb. Total chlorinated alkene concentrations, inclusive of parent and daughter compounds, were less than 130 ppb. Natural sulfate concentrations varied from 17.6 to 24.3 ppm in groundwater.

PILOT STUDY METHODS

The pilot study was conducted using single well “push-pull” methods at the injection well (IW-1) combined with groundwater monitoring at four performance monitoring wells (PW-1, PW-2, PW-3 and PW-4). The performance monitoring wells were located at distances of 5 feet or 10 feet hydraulically down gradient and/or slightly side gradient from the injection well. Two ABC-Olé injection events were performed at IW-1 eight months apart. The first injection event in August 2013 used 500 pounds of ABC-Olé mixed with groundwater purged from IW-1 to create 130 gallons of injectate liquid. Carbon substrate concentrations and volumes were increased to 1,500 pounds of ABC-Olé in 225 gallons of injectate fluid for a second injection event in April 2014.

Pre-injection and post-injection groundwater sampling was performed at IW-1 and the four down gradient monitoring wells to assess the impact of the ABC-Olé on the subsurface microbial community, changes in groundwater geochemistry, and biodegradation of chlorinated alkenes. A baseline groundwater sampling event was performed in July 2013, one month prior to the first injection. This was followed by two performance sampling events in November 2013 and February 2014. Two additional groundwater sampling events were performed in July 2014 and October 2014 after the second ABC-Olé injection event (April 2014).

Push-pull tests performed with each injection event at IW-1 consisted of two stages. In the first stage (the “push” step), the ABC-Olé liquid substrate was injected into test well IW-1. The injectate fluid was allowed three months to migrate away from the injection well. After each injection event, the “pull” stage was initiated whereby groundwater was extracted periodically from IW-1 for analyses of chlorinated alkenes, biogeochemical parameters and microbial populations. Groundwater affected by ABC-Olé injection was also monitored at the four down gradient wells.

Dissolved gases (i.e., methane, ethene and ethane), chlorinated alkenes and chloride were analyzed during each groundwater sampling event to provide direct evidence of reductive dechlorination. Volatile fatty acids (VFAs) and total organic carbon were analyzed to provide information on the distribution, required dosing rates and dosing frequencies of the carbon substrate for the full-scale remedial design. Geochemical parameters and/or terminal electron acceptors including dissolved iron, sulfate, nitrate, pH and oxidation-reduction potential were analyzed during each groundwater sampling event to monitor the progress of reducing conditions. Phospholipid fatty acid (PLFA) analysis and analyses for Dehalococcoides spp. (DHC) dechlorinating bacteria were also performed.

RESULTS

Groundwater showed varying responses in chlorinated alkene concentrations, biogeochemical parameters, and microbial populations during the 15-month pilot study. Well IW-1 and the two monitoring wells located directly downgradient of the injection well (PW-2, PW-4) had the largest reductions of parent chlorinated alkenes. Reductions of PCE concentrations occurred at all five wells and ranged from 95.6% to 15.7% at the end of the pilot study. PCE reductions were not attributable to dilution based on several lines of evidence, including ratios of PCE to cis-1,2-dichloroethene (cDCE) that were maintained in the wells, increases in chloride and ethene, and stable background concentrations of chlorinated alkenes during the study.

Because TCE is a parent contaminant at the site and is also a dechlorination daughter product of PCE, its concentrations fluctuated and showed higher variability at each well during the pilot study. TCE reductions ranging from 94.5% to 51% were observed at IW-1, PW-2 and PW-4, while minor increases in TCE occurred at the two side-gradient wells PW-1 and PW-3. Concentrations of other dechlorination daughter compounds (cDCE and vinyl chloride) also varied during the pilot test.



Sulfate was reduced and both dissolved iron and VFAs increased at the five test wells. Methane, which was naturally-occurring in groundwater beneath the landfill, also increased at four of the wells.

IW-1: The largest reductions in PCE and TCE (>94%) occurred at injection well IW-1 shown in Figure 1. PCE and TCE concentrations decreased from pre-injection levels of 53.6 µg/L and 21.2 µg/L, respectively, to 2.35 µg/L (PCE) and 1.16 µg/L (TCE) during the push-pull tests conducted at this well. Concentrations of PCE and TCE were relatively unchanged from the baseline concentrations for six months after the first ABC-Olé injection, but decreased significantly following the second injection.

Decreases in PCE and TCE concentrations were accompanied by the corresponding generation of ethane at IW-1 toward the end of the pilot study. Chloride concentrations also increased up to 3.7-fold at the end of the test compared to the baseline levels. DHC microbes were below 4.00E-01 cells per milliliter (cells/mL) in the baseline sampling event, increased to 1.36E+01 cells/mL six months after the first ABC-Olé injection, and then declined to baseline levels at the end of the pilot study. This indicates that DHC growth was temporarily stimulated by introduction of the organic substrate.

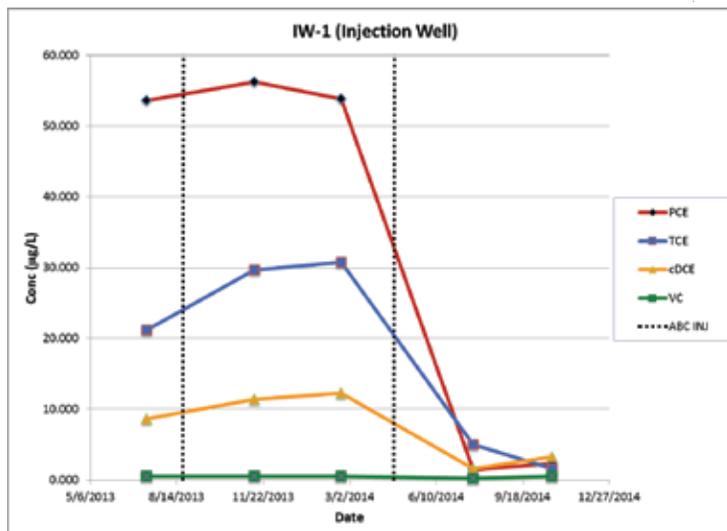


Figure 1: IW-1

PW-2: As shown in Figure 2, well PW-2 also showed evidence of chlorinated alkenes biodegradation in groundwater following the ABC-Olé injections. PCE concentrations decreased 74%, from pre-injection levels of 77.2 µg/L to 19.7 µg/L at the end of the pilot study. TCE also decreased 51% during this time period, from 33.5 µg/L (baseline) to 16.5 µg/L at the pilot test conclusion.

Although cDCE concentrations at PW-2 remained relatively unchanged during most of the pilot test, they increased by 100% compared to baseline levels toward the end of the pilot study. The pre-injection ratios of PCE to cDCE changed significantly at PW-2 during the pilot study, from 5.3 during the baseline sampling event to a ratio of 0.7 at the end of the test. Vinyl chloride and ethane were also produced at various times during the test. Chloride increased two-fold compared to the baseline levels, providing further evidence that the parent chlorinated alkenes were dehalogenated.

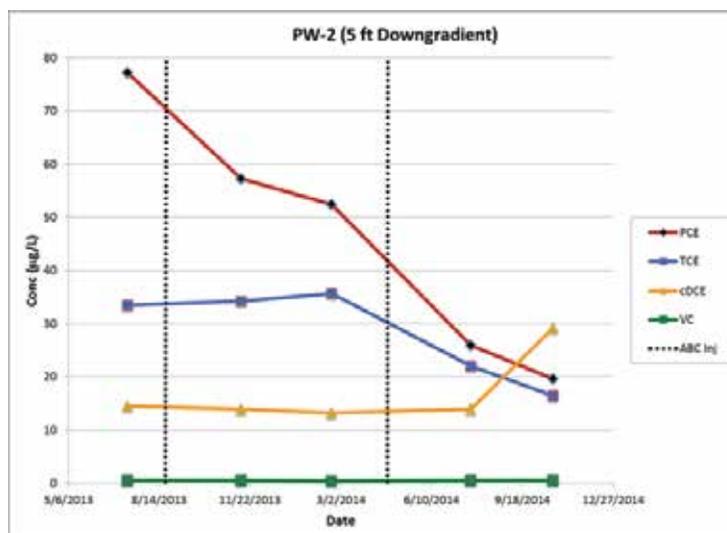


Figure 2: PW-2



MICROBIAL RESPONSES

PW-4: Monitoring well PW-4, located 10 feet hydraulically downgradient of the injection well, also showed evidence of PCE and TCE dechlorination in groundwater following the injections. PCE concentrations initially declined 77% within three months following the first injection, remained near these levels throughout the pilot test, and were reduced by 80% after 14 months. TCE concentrations showed a similar trend, in which there was a substantial initial reduction (68%) after three months followed by maintenance of reduced levels for the remainder of the pilot study.

Groundwater at PW-4 showed the largest percentage increase in cDCE compared to the other monitoring wells. Following the initial ABC-Olé injection, the cDCE concentrations declined up to 72% during the first six months of monitoring. The six-month period following the second ABC-Olé injection produced a 290% increase in cDCE compared to the initial baseline concentrations. Vinyl chloride and ethene were not detected at PW-4 during any sampling events, and chloride remained unchanged. However, sulfate was reduced by 69% and dissolved iron increased more than one order of magnitude at this well.

Microbial analyses indicated that DHC bacteria were not detected at PW-4 during the baseline sampling event or the first two post-injection sampling events. DHC populations increased from non-detectable ($<4.00E-01$ cells/mL) to $7.20E+01$ cells/mL following the second injection event.

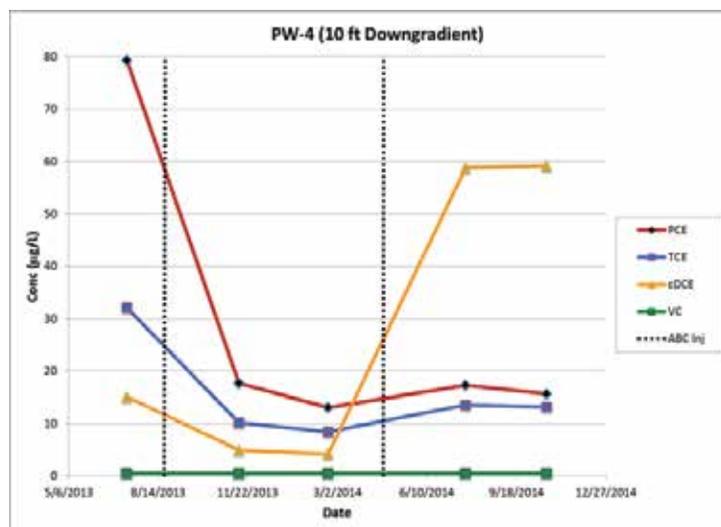


Figure 3: PW-4

MICROBIAL RESPONSES

Chemical and geochemical data, combined with the results for DHC, provide strong evidence of complete biological reductive dechlorination of PCE to ethene at wells IW-1 and PW-2. DHC bacteria populations generally increased in ABC-Olé substrate-enhanced groundwater, although the magnitude of the increases showed spatial and temporal variability. In addition, with the exception of well PW-3, groundwater analyzed for PLFA generally showed an increase in total microbial biomass by one to two orders of magnitude.

CONCLUSION

The pilot study was conducted using single well “push-pull” methods at injection well I combined with groundwater monitoring at four performance monitoring wells. Results showed 95.6% PCE, 95.5% TCE, 91.5% sulfate with increases in DHC microbes and chloride.