

IN SITU BIOREMEDIATION OF CHLORINATED SOLVENTS IN OVERBURDEN AND BEDROCK USING BIOAUGMENTATION

P. Stephen Finn (sfinn@golder.com) and Allen Kane (Golder Associates Inc., Cherry Hill, NJ, USA)

John Vidumsky (E.I. DuPont de Nemours and Company, Wilmington, DE, USA)

David W. Major (GeoSyntec Consultants, Guelph, Ontario, Canada)

Nicholas Bauer (Saltire Industrial, Inc., Reston, Virginia, USA)

ABSTRACT: The Caldwell Trucking Superfund Site is located in Essex County, NJ, and covers approximately 15 acres. Groundwater contamination involves chlorinated ethenes and ethanes, impacting both glacial deposits and fractured bedrock, extending approximately 4,000 ft (1200 m) downgradient of the site. TCE concentrations in the source area were as high as 700,000 µg/L (about 60% of TCE solubility). Natural biodegradation is present over much of the site; however some areas, particularly near the source, appeared to be substrate limited. Following microcosm studies which demonstrated that complete degradation of the contaminants could be achieved a comprehensive groundwater remedy was proposed that included bioremediation of the source area. A field pilot test of in-situ enhanced bioremediation in the source area was initiated in 2001. The layout included six nutrient injection wells, screened in glacial deposits and fractured bedrock, and seven monitoring wells. Injection wells were bioaugmented with a culture of naturally occurring microorganisms (KB-1 Culture including *dehalococcoides ethenogenes*) in March 2001. In over 20 months of operation, the system was optimized by adjustment of the amendment composition and the injection frequency. Gene probe techniques were used to verify initial and continued survival and propagation of the *dehalococcoides ethenogenes* organisms.

INTRODUCTION

The Caldwell Trucking Company Superfund Site Trust (Trust) is currently undertaking the remediation of the Caldwell Trucking Company Site (Site) located in Fairfield Township, Essex County, New Jersey. Beginning in the early 1950s, the site was used for disposal of septic waste, from residential and industrial sources, in unlined lagoons. Previous remedial actions have included vadose zone treatment utilizing soil vapor extraction and solidification/stabilization. A significant groundwater source area remains associated with a former lagoon area, and a dissolved phase plume of chlorinated solvents extends 4,000 feet (1200 m) downgradient. After undertaking laboratory microcosm studies that showed complete degradation of TCE, the Trust proposed to perform a field Pilot Test of Accelerated Biological Treatment with bioaugmentation in the source zone. Accelerated Biological Treatment is being considered as part of an alternative to the groundwater remedy proposed in 1993, which comprised pumping and treating of groundwater.

FIELD PILOT STUDY

Pilot Study Area Layout. The Pilot Test configuration included three nested pairs of injection wells (each consisting of a deep overburden, B-zone, well and an upper bedrock, C-zone well) and three nested pairs of monitoring wells 25 to 40 feet (7.6 to 12.2 m) downgradient screened in the corresponding units. An existing nearby sidegradient well (C-15) is also monitored as a control well.

Hydraulic Testing. Hydraulic conductivity values were estimated for each well by conducting rising head slug tests in all the wells. Using the Hvorslev and Bouwer and Rice methods, geometric mean values for hydraulic conductivity of the overburden and upper bedrock were calculated as 1×10^{-3} centimeters per second (cm/sec) and 2.4×10^{-5} cm/sec, respectively.

Tracer Testing. In order to assess groundwater velocity and connectivity between wells in the pilot test zone, potassium bromide tracer tests were conducted. In summary, the bromide testing demonstrated that wells throughout the pilot test zone are hydraulically connected and groundwater flow velocities range between 1.4 and 2.5 ft/day (0.43 and 0.76 m/day) in the deep overburden (B-Zone) and 1.8 and 3.0 ft/day (0.55 and 0.91 m/day) in the upper bedrock (C-Zone).

Baseline Sampling. Baseline sampling of the pilot test wells showed high concentrations and dominance of TCE and tetrachloroethene (PCE) in the C-zone wells, along with the virtual absence of cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC), indicating that biodegradation was negligible in the C-zone in the pilot test area. In the B-zone, some conversion to cis-DCE had occurred but production of vinyl chloride was very limited.

Nutrient Addition and Bioaugmentation. Nutrient injections were initiated in February 2001 using approximately 100 gallons (380 L) of nutrient solution for each B-zone well and approximately 50 gallons for each C-zone well. Nutrient solutions were prepared under anaerobic conditions using site groundwater and each injection was followed by a “wash” consisting of 50 gallons of groundwater without added nutrients. The nutrient concentrations and injection frequency have been varied throughout the pilot test as shown in the table:

Period	Injection Frequency	Molar Ratio (4500 mg/L total)
February 2001 – April 2001	Monthly	1 Methanol: 1 lactate: 1 acetate
May 2001 – January 2002	Weekly	1 Methanol: 1 lactate: 1 acetate
February 2002 – Date	5 x per week	1 Methanol: 2 lactate

All upgradient injection wells were inoculated in March 2001 with 10 to 15 liters of the KB-1 consortia of microorganisms while downgradient well C-22 was inoculated on May 30, 2001 to address the higher concentrations of constituents present in this well.

DHE Trends. PCR-based tests for DHE (PCR assay) allow the detection and relative quantification of the dechlorinating microorganism *Dehalococcoides ethenogenes* (DHE) in soil and groundwater samples. Standard control tests are undertaken together with each set of assays for quality assurance purposes. The results of the DHE testing generally show widespread presence and high "intensity" (a measure of the relative abundance) of the dechlorinating microorganism, DHE. In particular, (1) DHE is present and has been sustained in *all* of the injection wells and *all* of the monitoring wells; and, (2) The signal strength is high in 9 of the 12 wells and comparable between injection and monitoring wells, indicating that a treatment zone is established in both the B and C aquifer zones between the injection and monitoring wells.

Degradation of Chlorinated Ethenes. The pilot test data for the chlorinated ethenes are presented for a representative B and C zone monitoring well pair in Figures 1 and 2. The Figures show concentration-time graphs for each of the constituents in order of the anticipated degradation chain (PCE → TCE → cisDCE → VC). Results from the control well, which has not been treated, are shown in Figure 3 for comparison purposes.

The following presents a summary of the significant results as presented on the Figures:

- Very substantial declines in PCE and TCE concentrations have been achieved in all of the injection and monitoring wells. The average reductions in both PCE and TCE are 93% and 94% across the treatment zone, respectively. As TCE is produced from the degradation of PCE, this is a net reduction and the actual reduction in TCE exceeds 94%. These reductions have occurred equally in the injection wells and monitoring wells indicating that a continuous treatment zone is present across the pilot test area;
- The reductions in PCE and TCE in the injection wells and the monitoring wells have been accompanied by production of cis-DCE, VC and ethene. Within two months of bioaugmentation, cis-DCE increased in the B-zone wells, and was produced at elevated levels in the C-zone wells. Presently, indications are that cis-DCE may have started to decrease. It is expected that degradation of cis-DCE and VC will accelerate in the future consistent with behavior observed at other sites (Ellis et al, 2000; Major et al, 2001). VC and ethene have been produced since early in the test, however, production was initially inconsistent. Nutrient injection frequency was increased from monthly at the start of the test to weekly and finally to daily to supply a more uniform dosage of nutrients to the *Dehalococcoides* microbes, allowing them to maintain activity, and more recent production of ethene has been consistent, nearly all trends are steeply upward, and all wells are at or near historic highs for both VC and ethene;
- Monitoring well C-15, the side-gradient control well, provides a clear contrast for untreated conditions in the source area. The data show no reductions in PCE and TCE, and there is little or no production of cis-DCE, VC and ethene.

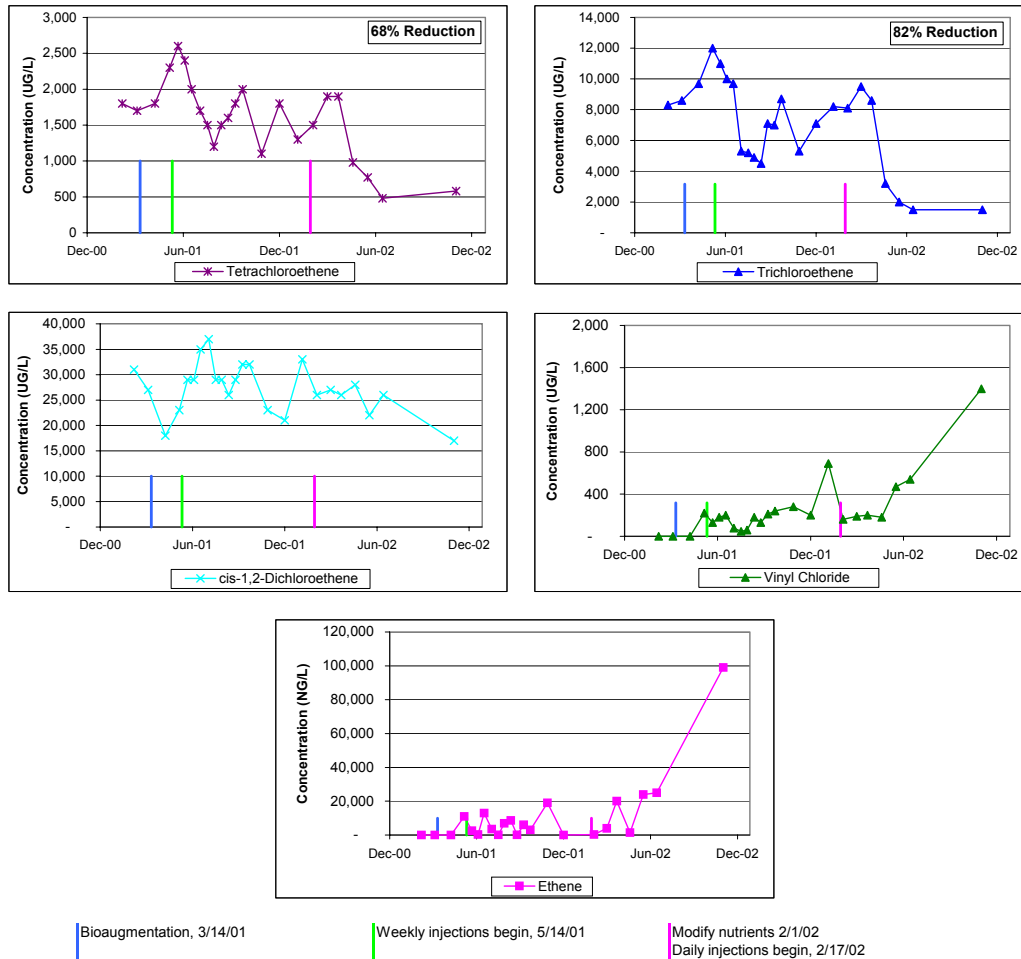


FIGURE 1. Degradation sequence of chlorinated ethenes in pilot B-zone well.

Well C-22 Performance. Downgradient well C-22 contained baseline concentrations an order of magnitude higher than other wells for several chlorinated VOCs, and so direct nutrient addition and bioaugmentation was initiated in this well on May 30, 2001 as part of the pilot study program. The results obtained include the following:

- PCE has been reduced by 99.0% from 27,000 ug/L to 260 ug/L;
- TCE, once as high as 680,000 ug/L has been reduced by 99.8% to 1,700 ug/L;
- cis-DCE concentration increased from non-detect up to 36,000 ug/L and has now declined to 27,000 ug/L; and,
- Production of VC and ethene is sustained with VC at 2,000 ug/L and ethene at 30-40 ug/L. Concentrations of VC are expected to decline in the future.

These improvements are attributable to biodegradation as evidenced by the production of daughter products and confirmed by the PCR assay results, which indicate that healthy levels of DHE are being maintained in this well.

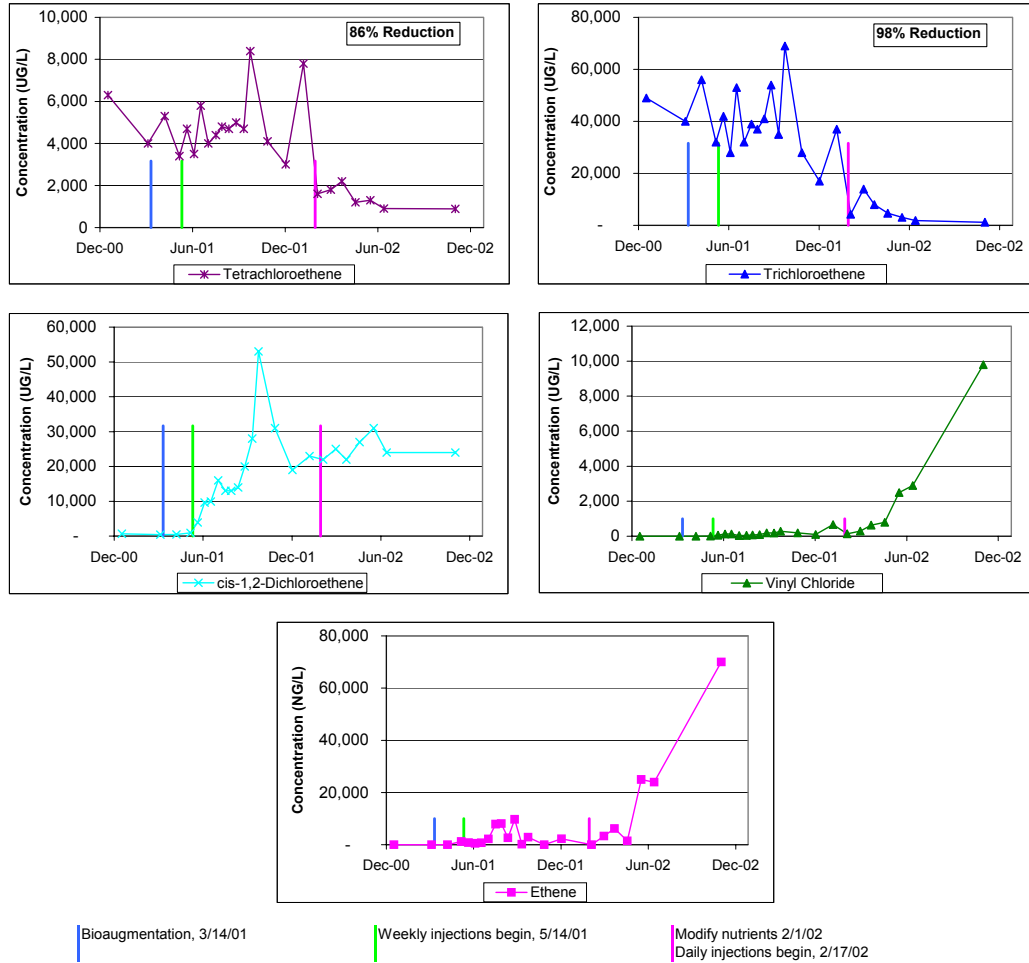


FIGURE 2. Degradation sequence of chlorinated ethenes in pilot C-zone well.

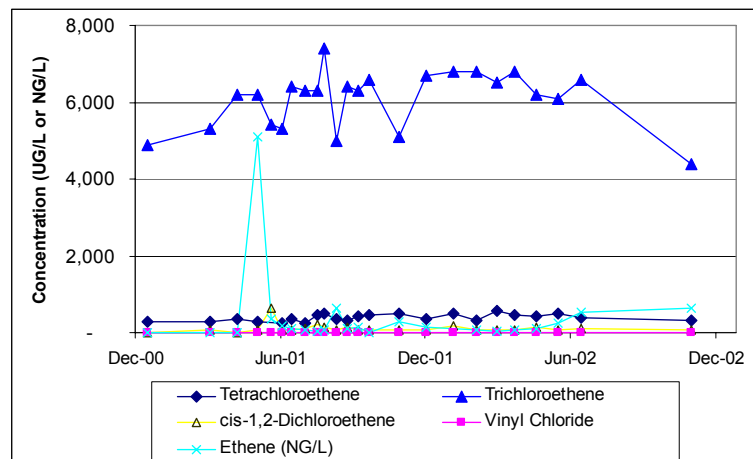


FIGURE 3. Degradation sequence of chlorinated ethenes in control well.

Degradation of Chlorinated Ethanes. 1,1,1-TCA can degrade in the environment by both abiotic and biotic mechanisms. The abiotic mechanism (specifically hydrolysis)

results in production of acetic acid (80%) and 1,1 dichloroethene (20%), and published half-lives are on the order of 1 year (Montgomery, 2000; Schwarzenbach et al, 1993; Howard et al, 1991). 1,1-dichloroethene (1,1-DCE) degrades biotically to vinyl chloride, which may be oxidized or further degrade to ethene, depending upon the conditions. The biotic degradation pathway produces 1,1-dichloroethane (1,1-DCA), which breaks down biotically to chloroethane and subsequently ethane. Both the biotic and abiotic pathways can occur simultaneously.

Significant conclusions from the Caldwell pilot test data are summarized below:

- An initial upward trend in concentration was observed and is concluded to be the result of mole fractionation, i.e., TCA solubility from residual source material increases with the removal of TCE from the source resulting in increasing concentrations of TCA in the dissolved phase. This trend was expected to be temporary and is now reversing with concentrations of TCA having been reduced in all wells from historic high concentrations by an average reduction of 51%.
- The abiotic pathway of degradation (1,1-DCE) has been shown to be consistently active in all wells.
- The biotic pathway of degradation (via 1,1-DCA), previously not evident in many wells (notably in the C-zone) has been stimulated by the bioaugmentation and nutrient additions with all wells showing significant levels (600 ug/L to 2,100 ug/L).
- Complete biotic degradation of TCA, represented by ethane, has been observed in all wells throughout the test zone, and recent data shows consistent presence at significant levels.
- The control well, C-15, has shown little evidence of biotic degradation of TCA. Abiotic degradation, via 1,1-DCE, is present.

Degradation of Chlorinated Methanes. The chlorinated methanes, in particular chloroform (CF or trichloromethane) degrade biotically, primarily to methylene chloride (DCM). Significant conclusions from the Caldwell pilot test data are summarized below:

- Concentrations of CF were initially much lower than other constituents, with concentrations generally less than about 1,200 ug/L. An initial upward trend in concentration in some wells, possibly due to mole fractionation in a similar manner to the chlorinated ethanes, has been reversed, with all wells lower than their historic highs. Specifically, concentrations of CF have been reduced from historic high concentrations by 60 to 100%, with an average concentration reduction of 81%. The average concentration of all wells is reduced from 783 ug/L to 138 ug/L.
- The biotic pathway of degradation (via DCM), has been stimulated in all wells. Recently, DCM concentrations have been reducing with the average concentration of all wells now at 106 ug/L.
- Control well C-15 has shown little reduction in CF concentration, and no production of DCM, further confirming that bioaugmentation and nutrient addition are responsible for the observed concentration reductions in the pilot test zone.

Geochemical Conditions. Geochemical parameters have been monitored throughout the test and key conclusions are as follows:

- Dissolved oxygen levels have been maintained at near zero levels;
- Reducing conditions exist in the pilot test zone as evidenced by iron- and sulfate-reduction in all wells, throughout the duration of the test. Complete sulfate depletion has occurred in some wells and ferrous iron production is also substantial in all wells, with a maximum of over 6.0 mg/L. Control well C-15 has shown steady levels of sulfate of approximately 35 mg/L, and ferrous iron concentrations around zero, indicating no sulfate or iron reduction is occurring at this location.
- Levels of Biological Oxygen Demand (BOD) indicate the effectiveness of the distribution of nutrients throughout the pilot test zone. BOD levels have generally increased throughout the pilot test zone including both B and C zone monitoring wells, indicating nutrients have been distributed throughout the system.

All of the above geochemical trends are consistent with the sustained occurrence of biologically mediated reductive dechlorination.

Measured Field Half-Lives. Pilot study data have been interpreted with an analytical degradation model for estimating the half-lives of PCE and TCE. The spreadsheet-based model uses a formulation based on first-order decay kinetics, with the additional contribution of the decay of the parent compound included. The basic formulation is as follows:

$$C_{n,t} = [C_{n,t-1} + \varepsilon(C_{m,t-1} - C_{m,t})] \exp(-\lambda_n \Delta t) \quad (1)$$

where:
 C_n = concentration of compound n (daughter) ($\mu\text{g/L}$);
 C_m = concentration of compound m (parent) ($\mu\text{g/L}$);
 $t, t-1$ = current and previous time step (years);
 Δt = time step value (years);
 ε = (molecular weight of compound n)/(molecular weight of compound m); and,
 λ_n = decay constant of compound n (year^{-1}).

For PCE, the uppermost parent compound, equation (1) reduces to $C_{n,t} = C_{n,t-1} \exp(-\lambda_n \Delta t)$. The model solves equation (1) simultaneously for PCE and TCE. The resulting average half-lives are 25 days for PCE and 21 days for TCE. These values are approaching those measured in the laboratory microcosm studies and compare favorably to natural (unaccelerated) half-lives in the downgradient plume that are on the order of 500 days.

CONCLUSION

In summary, a continuous treatment zone has been established across the pilot test area that has achieved average reductions of PCE and TCE concentrations of 93-94% in a period of 20 months; continued concentration reductions are expected. Biological degradation of TCA and chloroform has also been stimulated. Sulfate and ferric iron reduction are significant and widespread. The results indicate that in-situ bioremediation

is a viable source treatment/control technology that is synergistic with monitored natural attenuation of a downgradient dissolved phase plume. The system is designed to drive rapid conversion of dissolved PCE and TCE to DCE, VC, and ethene, and thus to accelerate the dissolution of source material. The goal is not to achieve specific concentrations of parent and daughter compounds in the dissolved phase, but rather to accelerate the dissolution of source material, and so reduce the overall lifetime and impact of the source.

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