

Enhanced Bioremediation of Tetrachloroethene in Central Indiana Glacial Till

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ABSTRACT: The goal of this project is remediation of soil and groundwater impacted by tetrachloroethene (PCE) that infiltrated the vadose and uppermost saturated zone below an active dry cleaning facility in central Indiana. PCE was released and transported to depths less than five meters via the primary porosity of thin sand and silt stringers and via secondary porosity of fractures in lodgment till. Impact to shallow groundwater ranged to 24 milligrams per liter (mg/L). Impact above one mg/L extended over an approximate area of 150 square meters. Significant remediation progress was achieved via the concurrent application of complementary abiotic (micro-scale zero-valent iron [ZVI]) and biotic (electron donor-enhanced) reductive dehalogenation remediation technologies. After substantiating the presence of PCE-degrading bacteria in groundwater, a patent-pending, remediation compound-injection technology was applied to the site in May 2002 and in September 2003. Primary remediation compounds included ZVI and Hydrogen Release Compound (HRC™). Favorable conditions were engendered throughout the area of application, with reduction of PCE through trichloroethene (TCE) to cis-1,2-dichloroethene (cis-1,2-DCE) in several wells after three months, and significant reduction of cis-1,2-DCE to vinyl chloride (VC) after nine months. The project is progressing well, and recent monitoring indicates that VC is degrading in several areas.

INTRODUCTION

In 1998, the site, a dry cleaning facility in central Indiana, was entered into the Indiana Voluntary Remediation Program (VRP) after the discovery of PCE impact to soil and groundwater. Under the VRP, innovative remediation technologies are generally well received, and sufficient flexibility is provided to pilot test promising technologies. In-situ chemical oxidation (ISCO) was attempted by others on a pilot scale in 1998 using low-pressure-injected hydrogen peroxide, however this effort proved unsuccessful in reducing PCE impact in the saturated zone. Groundwater-monitoring results indicated that the implementation of ISCO may have caused an *increase* in PCE at several monitoring locations and a slight reduction in PCE metabolites (chlorinated volatile organic compounds [CVOCs] produced by the anaerobic biodegradation of PCE) in all but a few outlying monitoring locations. The consensus regarding these unremarkable results is that the combination of the ephemeral "life" of hydrogen peroxide and relatively impermeable glacial till precluded the contact time and distribution necessary for the chemical oxidation of PCE. Further, induced aerobic conditions may have hampered naturally occurring anaerobic metabolic activity associated with the reductive dehalogenation of PCE.

In 2000, the site and remedial approach were evaluated by the authors. Considerations for evaluation of potentially applicable technologies at the site included its commercial setting, geologic setting (fractured low permeability till with thin silt and sand stringers), relatively high concentration of PCE (58 mg/L), area and depth of impact (approximately 150 square meters through 5 meters depth), depth to uppermost groundwater (approximately 3 to 5 feet below ground surface [bgs]), potential to influence and maintain low oxidation-reduction (redox) potential in groundwater, and evidence of anaerobic bacteria that degrade PCE. Based on these considerations, a two-step approach was recommended: 1) aggressively reduce source area concentrations of PCE through direct-contact chemical reactions, and 2) reduce residual concentrations of CVOCs through the enhancement of naturally occurring biodegradation processes. Thus, a combination of short-term abiotic and longer-term microbially-enhanced technologies were selected for a pilot-scale, and follow-up full-scale, application.

REMEDICATION METHODS

Direct-Push Perforated Rod Placement. Recent experience at a similar project site in southern Indiana indicated that, if remediation compounds could be delivered to the more permeable silt/sand lenses and fractures in the subsurface, relatively stable and depressed redox conditions favored by anaerobic bacteria could be engendered and reasonably maintained over a relatively large area where the hydraulic gradient and hydraulic conductivity are relatively low. Based on this information, a direct-push unit was used to drive a perforated rod to depths ranging from 10 to 12 feet bgs to be in close proximity to one of the more permeable silty or fine sandy layers that were identified during characterization of the site. These more permeable layers are those believed to be the preferential pathways through which CVOCs were transported and accumulated.

Injection. A sequence of task-specific compounds, including ZVI and HRC[®], were injected through the perforated rod using a patent-pending, compressed nitrogen gas delivery system. The mass of injectants used in the pilot-scale application was based on a combination of a) the quantity of HRC[®] theoretically required to furnish a six to 12-month supply of organic substrate (as electron donor for reductive dehalogenation) to the targeted area, b) four pounds of ZVI per injection point (test quantity), c) previous experience, and d) field observations of surfacing of injected compounds (indicating that the assimilative capacity of the subsurface had been reached). Compounds were injected at 15 locations in May 2002 (pilot scale) and 19 locations in September 2003 (full scale), spaced on approximately 10-foot centers inside and outside the drycleaning facility

The stepwise injection process and intended effects are as follows:

1. **Compressed Nitrogen Gas.** Compressed nitrogen gas was used to anaerobically propel all injectants into the subsurface. Nitrogen gas was first injected into the subsurface at approximately 175 pounds per square inch until a significant pressure drop was observed at the injection pressure vessel. This process is referred to as pre-injection subsurface pathway development. The intent of this step was to open pathways in the subsurface for the injectants to follow. These pathways are similar in course to those more permeable pathways along which

- CVOCs are more likely to have migrated. Liquid and liquid-entrained injectants were then delivered with pressurized nitrogen gas to the pathways that were produced during the pathway development step.
2. Sodium Sulfite Solution. Sodium sulfite solution was used to scavenge oxygen from the subsurface to a) promote the anaerobic conditions and lower the redox potential to the range favorable to anaerobic microorganisms, and b) prevent dissolved oxygen from reacting with subsequently injected ZVI. Nutrients (nitrogen as organic ammonia and ortho-phosphate) were injected with the sodium sulfite solution to enhance the growth of the microbial population. Groundwater mounding was also promoted by completing a series of injections in localized areas over a relatively short period of time. Approximately 25 to 50 gallons of sodium sulfite solution were injected at each location prior to injecting the ZVI, depending largely on the ability of the subsurface to receive the solution.
 3. Micro-scale ZVI. Iron particles ranging from 1 – 3 microns in diameter were injected in a sodium sulfite solution to rapidly reduce relatively high concentrations of dissolved PCE to levels more suited to "polishing" by slower, enhanced natural degradation processes. The corrosion of ZVI by water also produces hydrogen that may be utilized by indigenous bacteria that metabolize PCE and its metabolites. Between four and 16 pounds of ZVI were injected at each location, depending on the concentration of CVOCs in nearby wells.
 4. HRC[®]. Between 20 and 60 pounds of HRC[®] were injected at each location as a food source (electron donor) for anaerobic microorganisms capable of degrading residual levels of PCE over a period of months.
 5. Vitamin B-12 and Yeast Extract. Several grams each of Pharmaceutical-grade Vitamin B-12 and commercial-grade yeast extract were co-injected with HRC[®] at each injection location because indications are that the metabolism of certain strains of bacteria, potentially including anaerobic dehalorespiring strains, are enhanced in the presence of B-12 and yeast extract (B-12 itself being produced by metabolic processes).

MONITORING METHODS AND BASELINE RESULTS

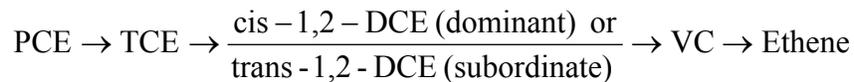
Methods. Baseline groundwater sampling of all monitoring locations was conducted in May 2002. The pH, temperature, conductivity, redox potential, and dissolved oxygen (DO) were measured with a YSI-6820 meter via a flow-through cell by low-flow sampling techniques specified in the IDEM Office Memorandum, dated December 1, 1999, "Micro-Purge Sampling of Monitoring Wells." Groundwater samples were collected for dissolved iron by EPA 6010, volatile organic carbon compounds by EPA 8260B, and chloride by EPA 9056.

Baseline Groundwater Sampling Results. Monitoring locations that were sampled inside the dry cleaning facility and adjacent business contained CVOCs ranging from 0.350 to 24 mg/L at the time the injection program was conducted. Monitoring locations that were sampled outside the building contained CVOCs ranging from non-detectable concentrations to 0.500 mg/L. Of the monitoring locations containing CVOCs, PCE

accounted for between 77 and 100 percent; trichloroethene (TCE) accounted for between zero and 4 percent; and cis-1,2-dichloroethene (cis-1,2-DCE) accounted for between zero and 19 percent of the concentration of CVOCs in each location. Vinyl chloride was present in only two monitoring locations (E-2 and E-8) at between 2 and 4 percent of the concentration of CVOCs in those locations. No CVOCs were detected in background monitoring locations MW-1 and MW-10 during the baseline groundwater-sampling event. Field instrument measurements taken during baseline groundwater sampling indicated that redox potential and DO were in the ranges favorable for reductive dehalogenation of CVOCs by indigenous bacteria.

RESULTS AND DISCUSSION

PCE and its daughter products were targeted by the injection program. A series of reduction reactions is needed to convert PCE to ethene; therefore, those reactions are the focus of the remediation and groundwater monitoring efforts. The reductive dehalogenation reaction sequence is as follows:



ZVI was used as the aggressive, short-term reductant to rapidly reduce the more chlorinated compounds (PCE and TCE). The presence of indigenous bacteria that degrade cis-1,2-DCE and VC was strongly suspected because of the presence and distribution of cis-1,2-DCE and VC; therefore bio-amendments as described herein were added to enhance the reduction of these compounds to ethene. The combination of injectants was fortuitous; evidence is mounting that an important kinetic relationship exists between dissolved iron and anaerobic bacteria. This unlooked for synergy is not the theme of this discussion, however it warrants further study.

Results After One Week. Redox potential was reduced in most groundwater monitoring locations one week after completing the injection program. However, CVOCs concentrations did not vary significantly from baseline monitoring results.

Results After Three Months. Quarterly groundwater sampling conducted in August 2002 indicated a large shift in the distribution of CVOCs in most monitoring locations as follows:

- Monitoring locations E-2, E-8, I-1, I-3, and I-6 (wells that were regularly sampled) had concentrations of PCE ranging from 10 to 22 mg/L before conducting the injection program. After conducting the injection program, PCE concentrations in these wells dropped below laboratory quantifiable limits. Conversely, the concentration of cis-1,2-DCE in monitoring wells E-1, I-1, and I-3 increased to concentrations ranging from approximately 3 to 54 mg/L where cis-1,2-DCE was previously below laboratory quantifiable limits. Time-series charts for reductive dehalogenation occurring in monitoring locations E-2, E-8, E-3, and I-6 from May 2002 through March 2005 are presented in Figure 1.

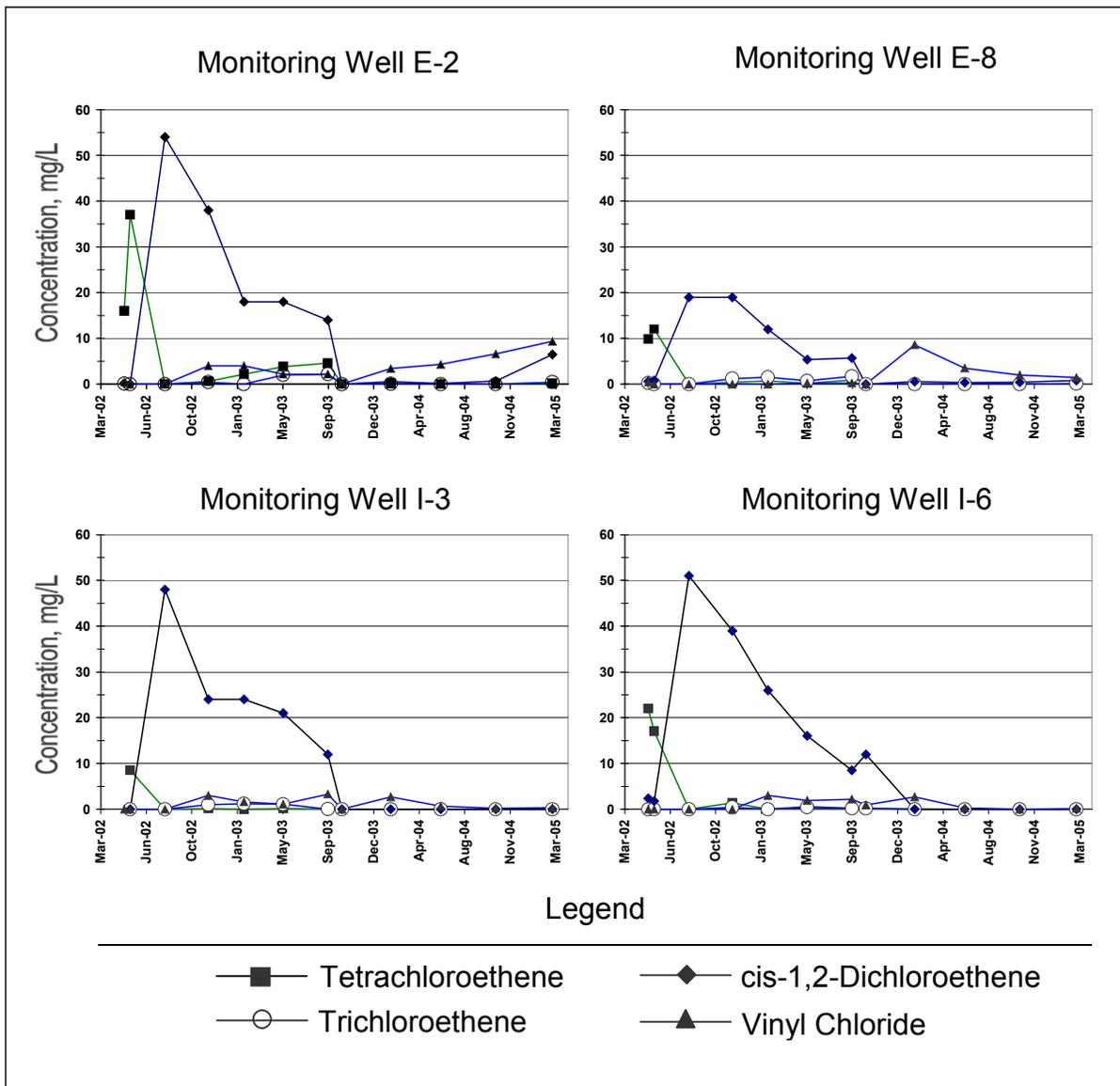


Figure 1. Reductive Dehalogenation of CVOCs in select wells.

- Of the sampled wells containing CVOCs, PCE accounted for between zero and 100 percent; TCE accounted for between zero and 10 percent, and cis-1,2-DCE accounted for between zero and 100 percent of the concentration of CVOCs in each well. Vinyl chloride was detected only in monitoring well MW-4 and was approximately 28 percent of the total CVOC contribution at this location.

Field instrument measurements indicated the following

- Redox potential was significantly reduced in every monitored location, including MW-1, which is hydraulically upgradient of the injection area. Redox potential

was, on average, approximately -200 mV lower than before conducting the injection program.

- No significant change in pH was observed.

Subsequent laboratory testing (targeted polymerase chain reaction) indicated the strong presence of *D. ethenogenes* bacteria that are reportedly capable of anaerobically degrading CVOCs to ethene in the presence of an electron donor.

September 2003 Results. Groundwater monitoring results from September 2003 indicated that PCE continued to be degraded to cis-1,2-DCE and VC, both accumulating in the several mg/L range in several monitoring locations. TCE concentrations generally peaked before September 2003, and began to decrease rapidly thereafter.

The full-scale injection program was implemented in September 2003. The design for the full-scale program evolved from the field observations and from favorable analytical results of the pilot-scale injection program. The full-scale design included closer spacing of injection locations, slightly less sodium sulfite solution, and increased dosages of HRC[®] and ZVI where the effects of the pilot scale injection program were less pronounced.

Results to March 2005. Figure 2 (following page) is a map of the site and adjacent properties and depicts a plan view of the changing distribution of PCE, cis-1,2-DCE, and VC from May 2002 to March 2005. Over this 34-month period, a 90 percent reduction in total CVOCs was observed in groundwater samples collected from monitoring locations I-3, I-6, MW-6 and I-13. Over a 70 percent reduction in total CVOCs was observed in monitoring locations E-8 and I-8. Monitoring location E-2 indicated a 1.7 percent increase in total CVOCs, 39 percent of which was cis-1,2-DCE and 57 percent of which was VC. In general, PCE has been reduced to below 200 ug/L in all sampled locations; metabolites of PCE have been degraded through cis-1,2-DCE to VC; and VC concentrations increased and then decreased with each injection event, indicating the relative success of the enhanced biodegradation component of the injection program.

VC concentrations warrant additional evaluation with respect to supplemental applications of remediation compounds. VC continues to persist in several wells, however there is no evidence of VC in any perimeter wells, indicating that VC is being degraded to ethene within the project area. All monitoring wells outside the impacted area are strongly aerobic with redox in the +300mV range, therefore additional research may include the evaluation of an aerobic "front" at which VC is completely degraded to ethene. Additional monitoring will be conducted over the next two years to evaluate plume stability, VC reduction, and the potential for risk-based closure.

CONCLUSIONS

The goal of this project was met in that significant remediation progress was achieved via the concurrent application of complementary abiotic and biotic reductive dehalogenation technologies. Favorable conditions were engendered throughout the area of application, with the substantial reduction of PCE and its metabolites in approximately three years. The project is progressing well, and recent monitoring indicates that VC is continually degrading in several areas.

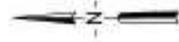


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FIGURE 2
CVOC DISTRIBUTION MAP
REDUCTIVE DEHALOGENATION
SEQUENCE

- LEGEND:**
- Injection Monitoring Location
 - Tetrachloroethene (PCE) Plume (>1.0 mg/L)
 - cis-1,2-Dichloroethene (DCE) Plume (>1.0 mg/L)
 - Vinyl Chloride (VC) Plume (>1.0 mg/L)
 - Dry Cleaning Machine

Injection Monitoring Location	Tetrachloroethene (PCE) Concentration (mg/L)	cis-1,2-Dichloroethene (DCE) Concentration (mg/L)	Vinyl Chloride (VC) Concentration (mg/L)
4.6	4.6	0.6	0.28
0.6	0.6	0.28	ND
0.28	0.28	ND	NS
ND	ND	NS	NS
NS	NS	NS	NS



ACKNOWLEDGEMENTS

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