

CO-SOLVENT-BASED SOURCE REMEDIATION APPROACHES

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ABSTRACT: Field pilot scale studies have demonstrated that co-solvent-enhanced *in situ* extraction can remove residual and free-phase nonaqueous phase liquid (NAPL), but may leave levels of contaminants in the ground water and subsurface formation higher than regulatory requirements for closure of a site. Various methods of improving delivery and recovery of co-solvent mixtures and of facilitating *in situ* mixing of these light remedial fluids with resident contaminants have been proposed and are being investigated. However, it is unlikely that these improvements alone will permit regulatory goals to be achieved via enhanced NAPL solubilization or mobilization. Recent laboratory and field tests have examined the feasibility and benefits of coupling co-solvent flushing with other remediation processes to achieve acceptable cleanup goals. For example, the potential for residual co-solvent to stimulate *in situ* biotreatment following partial dense nonaqueous phase liquid (DNAPL) source removal by alcohol-induced dissolution was evaluated at a former dry cleaner site in Jacksonville, Florida. Contaminant and geochemical monitoring at the site suggests that biotransformation of the tetrachloroethylene (PCE) was enhanced and significant levels of *cis*-dichloroethylene (*cis*-DCE) were produced in areas exposed to residual co-solvent.

INTRODUCTION

Chlorinated solvents were used and released to the environment in massive amounts during the 1950's, 60's, and 70's. These contaminants have migrated through the subsurface and impacted ground water at over 1000 DoD sites. Their widespread use and the physical/chemical properties of these compounds have resulted in the chloroethenes being the most commonly detected class of organic contaminants in ground water. Parent chloroethenes (PCE and TCE) can become human health hazards after being processed in the human liver or via reductive dehalogenation in the environment. This has generated a high degree of interest in efficient and cost effective technologies which can be used to remediate soils and ground waters contaminated with PCE and TCE.

The objective of this research was to demonstrate the feasibility of a treatment train approach to remediate a DNAPL contaminated aquifer. Experience has shown that conventional *pump and treat* systems are inadequate for cleaning up aquifers contaminated with DNAPL, and the highly toxic nature of these environments suppresses bioremediation. Recent advances in our understanding of the impact of organic co-solvents on NAPL behavior in porous media suggest that co-solvent-enhanced *in situ* extraction can remove residual and free-phase DNAPL. While laboratory and pilot-scale experiments have demonstrated the potential of this

method for mass removal, residual amounts of solvents and contaminants are expected to remain at levels which could preclude meeting regulatory requirements. However, with the bulk of the DNAPL extracted, *in situ* biotreatment becomes a viable "polishing" procedure. *In situ* biotreatment may transform the remaining contaminants to non-hazardous compounds at a rate in excess of the rate of dissolution or displacement and at lower costs.

The efficacy of *in situ* bioremediation of solvents is usually limited by transport considerations, i.e., supplying electron donor at the appropriate levels and in conjunction with exposure to the chlorinated solvent. In this case the concurrent exposure to electron donor (co-solvent) and electron acceptor (chlorinated solvent) is facilitated by the delivery and extraction process as well as the co-solvency effect. The synergism between these abiotic and biotic processes could minimize problems associated with the individual approaches. The development of the Solvent Extraction Residual Biotreatment (SERB) technology could attenuate or eliminate the risks posed to human health and the environment by these highly contaminated sites.

MATERIALS AND METHODS

The SERB pilot demonstration was conducted at the former Sages dry cleaner site in Jacksonville, Florida where an area of PCE contamination was identified. Pre-treatment characterization of the site indicated near saturated concentrations of PCE in ground water samples collected near the source zone. Low or non-detectable levels of normal biodehalogenation daughter products were found. The zone of contamination was from 26 to 31 ft. (7.9 to 9.5 m) below ground surface and this area was targeted for remediation.

Figure 1 shows the site and location of the wells used for the SERB demonstration. The contour lines on the map represent the pre-co-solvent flush area of PCE contamination. Three injection wells (IW) and six recovery wells (RW) were placed in the source zone in July of 1998 and used for the co-solvent extraction experiment. Previously installed monitoring wells (MW) were utilized for monitoring ground water concentrations during the field experiment. Additional ground water monitoring was done with a series of 1 inch PVC wells (C), which were installed along a transect in the general direction of groundwater flow in Sept., 1998, after the co-solvent extraction test.

Ethanol was selected as the co-solvent for the *in situ* co-solvent extraction test. The alcohol flushing pilot test began on August 9, 1998, and ended on August 15, 1998. Post-test hydraulic containment began on August 15, 1998 and was discontinued on August 25, 1998, after the ethanol concentration in the treatment system influent dropped below the 10,000 mg/L termination criterion. Pre- and post-treatment partitioning tracer tests were also conducted during this time for estimation of the mass of PCE contaminant removed with the co-solvent extraction. After pumping ceased, ground water samples were collected periodically for chemical analysis. Analytes included PCE, TCE, *cis*-DCE, ethanol, methane, ethane, ethene, chloride, sulfate, and acetic acid. Approximately one year after the co-

solvent extraction test, ground water samples in the source area were analyzed for dissolved hydrogen.

Sage's Dry Cleaner Site Well Location and PCE Contamination

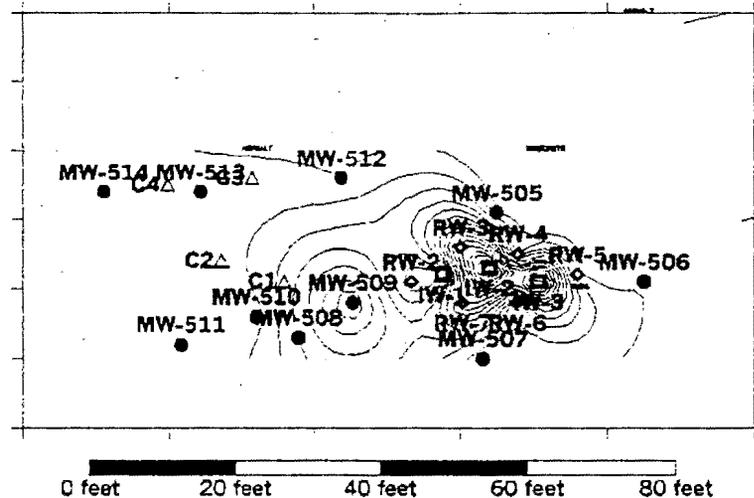


FIGURE 1. Location of ground water monitoring wells and injection/recovery wells. Pre-co-solvent extraction test contour plot of PCE contamination. PCE concentration range is 0 to 80 mg/L.

RESULTS AND DISCUSSION

Enhanced dissolution and solubilization of PCE was demonstrated as a result of the ethanol co-solvent extraction test. Analytical data from RW-7 showed that the peak PCE concentration was 80 to 90 times higher than the initial PCE concentration. In other recovery wells, the ratio of peak PCE concentration to initial PCE concentration was on the order of 30 to 40. The partitioning tracer data indicated that approximately 30.4 L of PCE was removed during the co-solvent extraction test. This is approximately 70% of the PCE mass estimated with the pre-treatment partitioning tracer test. Actual PCE concentrations monitored in the recovery well effluent indicated that approximately 41.5 L was recovered. Although there is error associated with each method of estimating PCE mass recovery, both methods showed that a significant mass of PCE was recovered with the co-solvent extraction test.

PCE concentrations in the ground water decreased immediately following the co-solvent extraction and then rebounded, as expected, to near initial concentrations. An area of PCE contamination was also detected down-gradient of the co-solvent flush when the C-wells were installed post co-solvent flush (Sept. 10-15, 1998). Monitoring wells near this location had significant concentrations of PCE in the ground water prior to the co-solvent extraction and C-well installation, but this area

was not targeted with the co-solvent flood. This area of contamination may be remediated by an additional co-solvent flush in the future.

Post co-solvent extraction monitoring of the ground water indicates that degradation of the PCE contaminant is beginning to occur. Data was averaged from three of the recovery wells (RW-2, RW-3, and RW-7) where the co-solvent extraction test was conducted. This data shows the change in water chemistry over the monitoring period, where Day 1 (first data point) is pre-co-solvent extraction and Day 55 (second data point) is 1 month post-co-solvent extraction (Figures 2 and 3). Figure 2 shows the chlorinated hydrocarbon and ethanol data and Figure 3 shows the inorganic data and acetic acid and methane data.

Degradation of PCE in the area of the co-solvent extraction test is indicated by the averaged recovery well data shown in Figure 2. PCE concentrations decreased immediately following the co-solvent extraction, but then rebounded to initial concentrations. TCE concentrations remained low throughout the monitoring period. Production of *cis*-DCE began approximately 4 months post-co-solvent extraction and is an indication of reductive dechlorination of PCE. Ethanol concentrations remained relatively high during the monitoring period and served as an electron donor source.

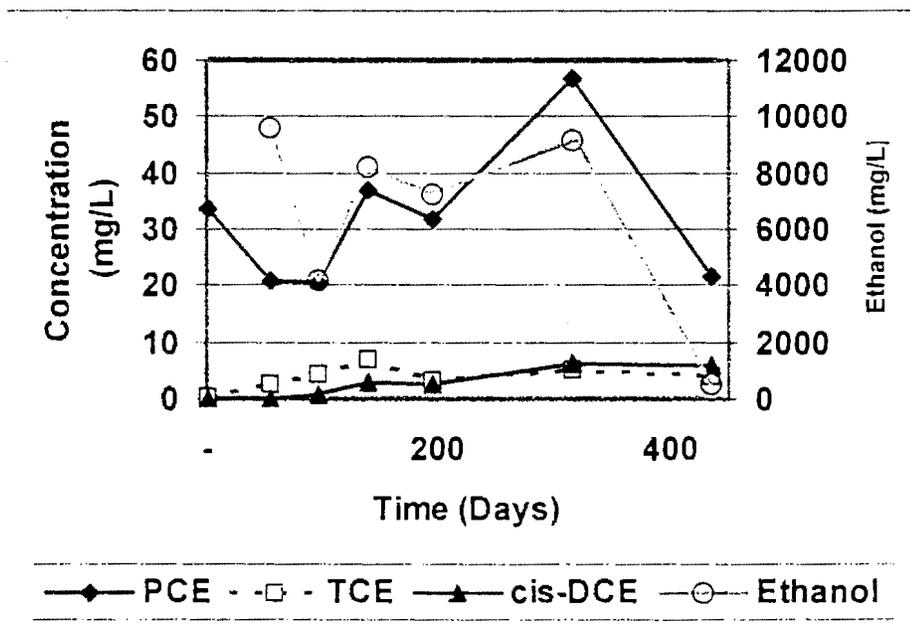


FIGURE 2. Average chlorinated hydrocarbon and ethanol concentrations in RW-2, RW-3, and RW-7 over the monitoring period.

The indication that the reductive dechlorination process is beginning is also supported by additional ground water data collected from the recovery wells (Figure 3). Chloride concentrations initially increased after the co-solvent extraction and then tailed off to near initial concentrations over time. Sulfate was utilized quite

rapidly and after approximately 2.5 months sulfate concentrations decreased to approximately 5 mg/L. Acetic acid was produced immediately following the co-solvent extraction test and remained at a relatively high level over the course of the monitoring. Approximately 2.5 months after the co-solvent extraction test methane production was detected.

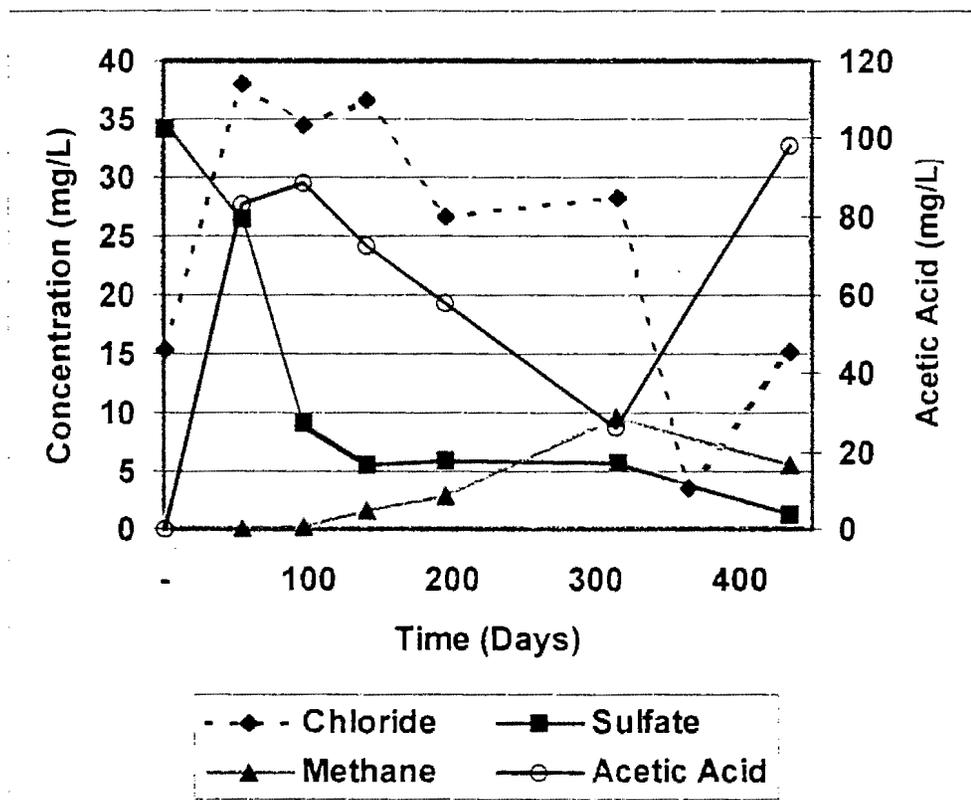


FIGURE 3. Average concentrations in RW-2, RW-3, and RW-7 over the monitoring period.

Data from MW-509, which is immediately down-gradient of the treatment zone, also indicates that reductive dechlorination is occurring (Figure 4). PCE concentrations decreased following the co-solvent extraction test and did not rebound as in the treatment zone. Ethanol concentrations increased following the co-solvent extraction test and then decreased after approximately 10 months post-extraction. Even at the lower concentrations, ethanol supplied excess electron donor to the system. TCE concentrations remained relatively constant throughout the monitoring period. After approximately 4 months post-co-solvent extraction, *cis*-DCE production began and concentrations remained low.

Additional data from MW-509 (Figure 5) followed a similar trend as the recovery wells. There was an initial increase in chloride concentrations that tailed off with time. Sulfate was utilized immediately and remained at a low level over the monitoring period. As sulfate concentrations decreased, acetic acid production

began and remained relatively high. Methane production began approximately 6 months after the co-solvent extraction test.

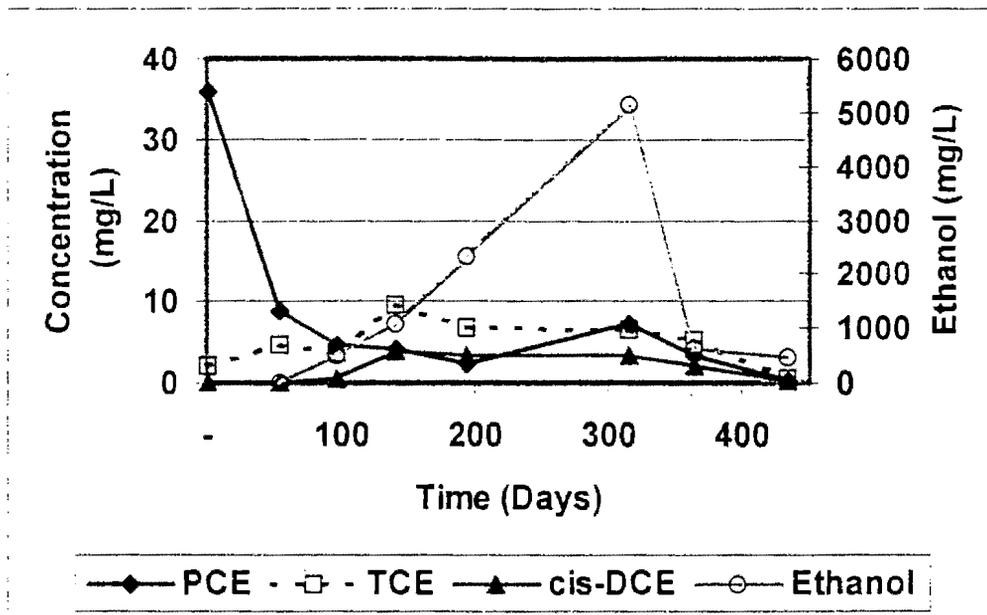


FIGURE 4. Chlorinated hydrocarbon and ethanol concentrations in MW-509 over the monitoring period.

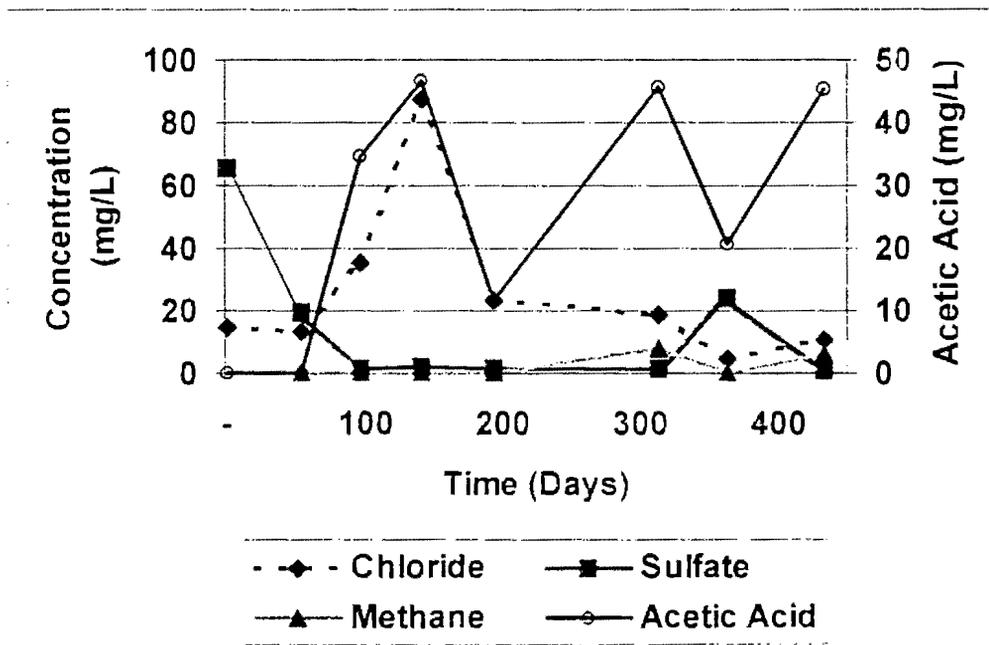


FIGURE 5. Average concentrations in MW-509 over the monitoring period.

The decrease in sulfate concentrations indicates that sulfate-reducing bacteria are active at the site. As the sulfate is reduced, more anaerobic conditions are created which can enhance the reductive dechlorination process. Methane production is another indication that the anaerobic microbial processes are enhanced and that methanogenesis is occurring. As the subsurface microorganisms adapt and become more active, reductive transformations are enhanced.

Under anaerobic conditions, ethanol can be biodegraded to acetate by incomplete oxidation or to carbon dioxide by complete oxidation. The production of acetic acid in our system indicates that the biodegradation of ethanol is beginning to occur. Hydrogen is a product of the oxidation of ethanol and is used in the dechlorination of PCE. Hydrogen analysis was conducted in the field on ground water from several wells. Production of hydrogen is higher in the area near the source area where the co-solvent extraction test was conducted (Figure 6).

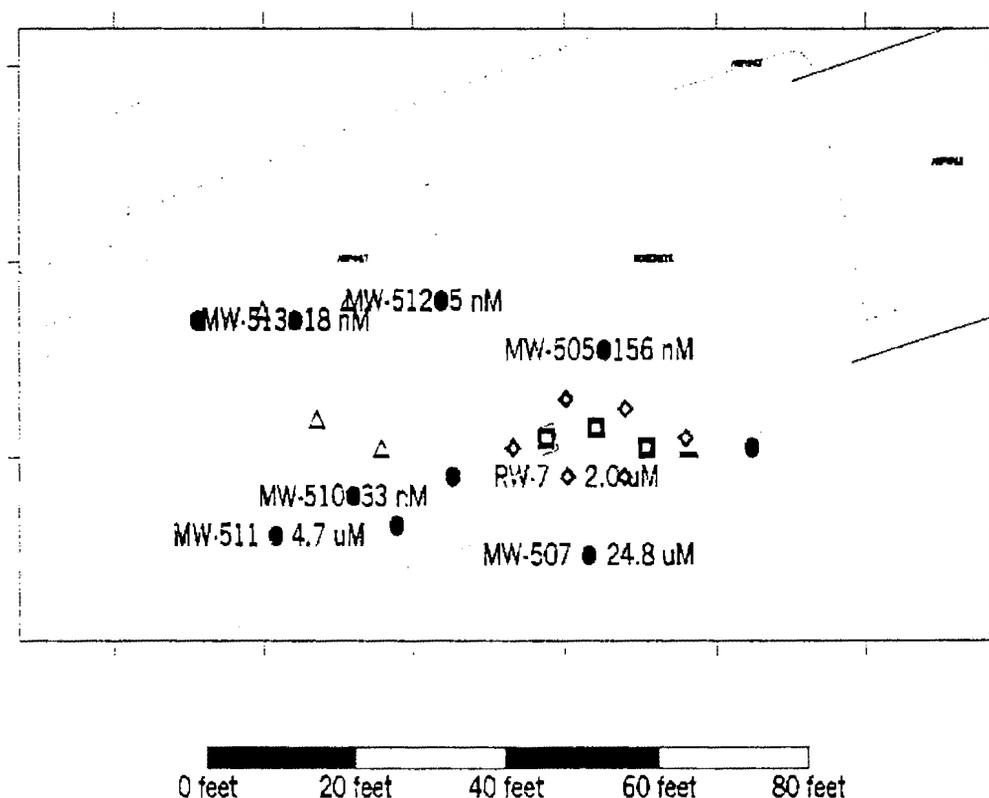


FIGURE 6. Hydrogen concentrations (nM and μ M) in ground water from selected wells approximately 11 months post-co-solvent extraction test.

Depending on the extent of the oxidation of ethanol, 1 to 2 moles are required to drive complete dechlorination of PCE. The average ground water concentration of ethanol in the treatment zone after the co-solvent extraction test was 8,000 mg/L. This corresponds to 560 Kg or 12,200 moles of available ethanol. If we assume 2 moles of ethanol are required per mole of PCE for complete

dechlorination, then there is 289 times the amount needed to remove the 21.1 moles of dissolved PCE in the source zone. An estimate of the total PCE in the source zone is 157.1 moles (126 moles residual PCE + 21.1 moles dissolved PCE). With the same assumption of 2 moles of ethanol per mole of PCE dechlorination, we calculate that there is 38.8 times the amount of ethanol needed for complete PCE dechlorination. While this estimate assumes no competing terminal oxidation processes, such as methanogenesis or sulfate reduction, an efficiency greater than 2% would still meet the theoretical demand.

The maximum and minimum observed rate of dechlorination based on *cis*-DCE production at the recovery wells are approximately 43.6 and 4.2 $\mu\text{g/liter/day}$, respectively. Extrapolation of these rates to a multi-step, concurrent, dechlorination process give a preliminary prediction that the dissolved phase PCE could be removed in 3 to 30 years, and that the total source zone PCE could be transformed in 24 to 240 years.

CONCLUSIONS

Co-solvent extraction was used successfully to remove a significant amount of the DNAPL contamination. The injection/extraction process aided in mixing the electron donor (ethanol) with the residual PCE so that biodegradation processes could occur. The system remains biologically active and the dechlorination products TCE, *cis*-DCE, ethene, and chloride are accumulating. High levels of acetate, methane, and hydrogen have also been detected in the treatment zone and indicate that dechlorination processes should continue. Calculated rates of dechlorination indicate that total source zone PCE transformation could take from 24 to 240 years. Monitoring of the system is continuing to better assess the reductive dechlorination process.

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DISCLAIMER

Although the research described in this article has been funded wholly or in part by the U.S. EPA, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency; no official endorsement may be inferred.

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