

CASE HISTORIES FROM EIGHT YEARS OF SUCCESSFUL TESTING AND REMEDIATION USING AEROBIC SOY BASED CO-METABOLISM FOR REMOVAL OF CHLORINATED HYDROCARBONS FROM GROUNDWATER

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ABSTRACT

During the period from 2000 through 2008, an aerobic co-metabolism technology has been successfully tested and employed at more than 10 field pilot test locations and full-scale remediation sites in several states. The technology has been successfully utilized for remediation of common halogenated hydrocarbons including trichloroethene, dichloroethene, tetrachloroethene, carbon tetrachloride, and chloroform, as well as several less common hydrocarbons and fluorocarbon compounds present in groundwater. Concentration reductions typically exceed 95% and have resulted in "no further action" (NFA) approval at several sites.

In situ co-metabolism was initially evaluated in 2000 at a Union Carbide Corporation (UCC) site in West Virginia, in an effort to simulate a toluene oxygenase enzyme co-metabolic process observed elsewhere on site at a mixed toluene and halogenated hydrocarbon plume. Various biodegradable vegetable-based mixtures were tested on the bench scale to evaluate delivery methods and dispersion/migration characteristics under simulated aquifer conditions. A soy methyl ester and a biodegradable surfactant blend has been tested and used extensively for full-scale field application.

Results from the applications have been documented in reports to U.S. EPA and State regulatory agencies, and indicate that the technology has reduced concentrations of chlorinated hydrocarbon and fluorocarbon compounds at the sites to levels meeting target cleanup criteria. Long-term data from the first two site-wide remediation projects indicate that site-wide average COC reductions greater than 96% were achieved within 6 to 8 months and re-sampling of site groundwater more than 2 years after the conclusion of active remediation indicated that only minimal rebound had occurred, with overall post rebound COC reductions exceeding 95% compared to pre-remediation concentrations. Comprehensive site information, including COC concentration data, indicator field parameters, and microbiological population counts from numerous sites where the technology has been successful applied over the past 6 years have been compiled, with representative examples provided below.

The process described within this paper combines several proven technologies, including air sparging, liquid/liquid extraction, and biological co-metabolism. Field application of the technique during the past 6 years at several pilot and full-scale remediation sites has resulted in rapid and dramatic decreases in groundwater COC concentrations with cleanup goals being achieved at several of the sites.

INTRODUCTION

During 1999 and 2000, a significant decrease in chlorinated hydrocarbons in groundwater occurred simultaneously with aerobic toluene biodegradation at a UCC remediation site in West Virginia. The remediation system consisted of conventional air sparging and vapor extraction (AS/VE) equipment designed to remediate toluene through the simultaneous use of volatilization and enhanced aerobic biodegradation. Biological activity was determined to be an important factor in the near total removal of the toluene, and was monitored qualitatively through microorganism population counts and carbon dioxide off gas emissions. The co-metabolic activity resulting from the generation of mono- and di-oxygenase enzymes during aerobic microbial degradation of toluene was thought to be the primary mechanism for the decrease in chlorinated hydrocarbons at the site.

Other areas of the same facility were known to contain relatively high concentrations of chlorinated hydrocarbons and fluorocarbons with no toluene or other non-halogenated hydrocarbons present at concentrations that would support aerobic co-metabolic processes. Conventional AS/VE systems were in operation in these areas for several years and had resulted in asymptotic reduction curves with total

COCs remaining at concentrations approaching 100 milligrams per liter (mg/l). As a result, the soy based co-metabolism process was developed and tested in an effort to simulate and enhance the successful aerobic co-metabolism observed at portions of the facility where the commingled toluene and halogenated plume had been remediated.

BENCH TESTING AND CO-METABOLITE SELECTION

Several non-toxic co-metabolites were tested on a bench scale to identify a product that maximized specific criteria, including dispersion characteristics within the aquifer, liquid/liquid extraction capabilities, ease of application, cost, non-toxicity, and commercial availability. Following approximately 1 year of progressive bench scale testing, a blend of soy methyl ester and food grade surfactant was selected as the co-metabolite that best met these criteria. Various potential co-metabolite mixtures were tested on a bench scale to evaluate delivery methods and dispersion/migration characteristics. Tests were initially conducted to compare emulsion-forming characteristics of various vegetable oil and surfactant mixtures. Oil emulsions and neat oil products were then evaluated in static sand-packed jar and column tests. Finally, bench testing was conducted using 6-inch (15 cm) diameter by 40-inch (100 cm), long, clear PVC columns containing various material types ranging from fine poorly sorted sand to coarse well-sorted sand. Various co-metabolite products were injected at the bottom of the column and observations were made regarding dispersion and migration through the sand- and water-filled test columns. Tests were performed under static and sparged column conditions and a Sudan IV biological stain (Red oil dye) was utilized to aid in visual comparison of potential co-metabolite compounds. Observations of each test were made after injection of the co-metabolite and were used to evaluate methods for optimizing dispersal and upward migration within the columns.

Based on the desired co-metabolite characteristics, as well as the observations made during bench testing, a specific blend of soy methyl ester and food-grade surfactant was selected for further evaluation. The co-metabolite, a methyl ester of a fatty acid, includes a hydroxyl functional group attached to a medium-length fatty acid. This arrangement is a non-toxic alternative to phenol and toluene (aromatic ring compounds with hydroxyl functional group), two well documented co-metabolites which support production of oxygenase enzymes through microbial metabolic processes. Following product selection, additional bench tests were performed to optimize product delivery and dispersion within material types characteristic of those encountered at the first project site.

INTEGRATION OF REMEDIAL PROCESSES

The technique incorporates multiple concurrent processes designed to concentrate COCs from the impacted portion of the aquifer into the soy oil matrix through the co-solvent properties of the methyl ester surfactant mixture. These co-solvent properties are also considered useful for de-sorbing and subsequently degrading COCs from the aquifer matrix, minimizing future rebound after active remediation is terminated. Vertical migration toward the water table occurs as a result of the low specific gravity of the co-metabolite and is enhanced by the upward movement of sparge air through the aquifer. The combined co-solvent effect and the gradual migration of the emulsion toward the biologically active upper portion of the aquifer are thought to play an important role in the rapid COC removal response observed at the test sites completed to date. Aerobic conditions are maintained by continuous air sparging, thereby supporting biodegradation of the methyl ester and consequent microbial generation of oxygenase enzymes. These enzymes rapidly oxidize several types of halogenated hydrocarbon molecules.

FIELD PROCESS DESCRIPTION

Field application of the conceptual approach was first initiated during May 2002. The general methodology established during early testing, and refined during subsequent tests and full-scale applications, involves injection of an emulsion consisting of the methyl ester/surfactant and water to a depth below the level of contamination within the aquifer. Following injection, the mixture is dispersed in the vicinity of the injection wells through a pulsed air process termed "forced air dispersal." Following dispersal of the co-metabolite, aerobic conditions are maintained throughout the period of active remediation. Current applications include injection to depths below the base of contamination, targeted injection to treat vadose zone COC smearing, and application to treat unsaturated zone material through the use of infiltration wells and galleries.

LIMITATIONS FOR TECHNOLOGY APPLICATION

The aerobic co-metabolism technology has been applied by the authors at sites characterized by widely varying historical uses and hydrogeologic conditions. Target COCs have varied significantly in species and concentration at these sites. In general, significant reduction in COC concentrations has been achieved for all halogenated hydrocarbons regardless of the initial concentrations prior to technology application. Limiting factors are primarily associated with the feasibility of initiating and maintaining oxidizing conditions throughout the remediation area. Establishment and maintenance of aerobic conditions has been most effectively achieved through the use of continuous air sparging. Therefore, the hydrogeologic limitations are essentially the same as those associated with a typical air sparging project. To date, the technique has not been applied in fine-grain materials, such as uniform silt and clay, and has not been applied under confined or karst conditions, although design for confined and possibly karst sites is likely achievable. An apparent limitation was observed at one site where a pH greater than 11 is believed to have precluded adequate microbial activity to support the biological processes necessary for enzyme generation and concurrent co-metabolic degradation. An additional limitation was apparently observed at a site characterized by the presence of chlorinated hydrocarbons, chloroethers, and amides. At this site, the chlorinated hydrocarbons were degraded to levels below MCLs, while the amides and chloroethers were essentially unaffected by the co-metabolism process. However, no limitation has been observed to date for commonly encountered halogenated hydrocarbon compounds.

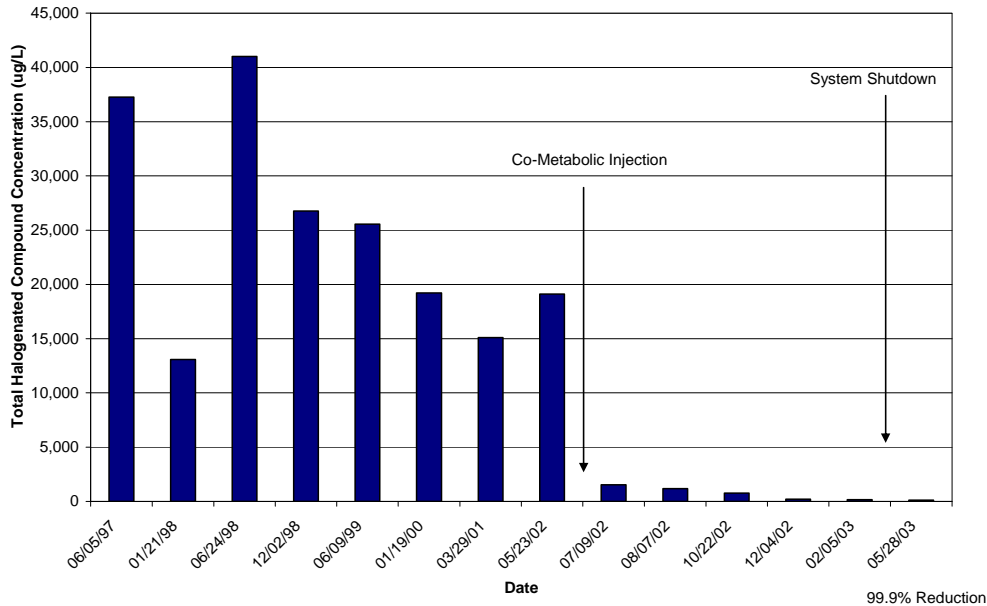
CHARACTERISTICS OF SITES WELL SUITED TO AEROBIC CO-METABOLISM

The technique is particularly well suited for sites characterized by high concentrations of halogenated hydrocarbons present in groundwater, particularly when these COCs are targeted within an area of relatively limited aerial extent, such as COC source areas, dry cleaners, or other "hot spots." Sites where air sparge systems have been employed and COC reduction trends have reached asymptotic levels above remedial goals are excellent candidates for application of the aerobic co-metabolism process. Degradation of recalcitrant COCs may be significantly enhanced at these sites with minimal additional cost or system modification.

CHRONOLOGY AND SUMMARY OF KEY FINDINGS AND RESULTS FOR PILOT AND FULL-SCALE TESTS PERFORMED BETWEEN 2002 AND 2008

Field Pilot Test - May 2002 The first pilot scale field application was initiated at a UCC site in Charleston, West Virginia. COCs at the site included carbon tetrachloride, trichlorofluoromethane, chloroform, tetrachloroethene, and dichlorodifluoromethane. The test consisted of the injection and dispersal of a co-metabolite and water emulsion into each of two injection wells. Both wells had been operated as air sparge points for several years, prior to the injection of the co-metabolite. Five years of pre-test COC concentration data were available for a well near the center of the test area. This well was re-sampled prior to co-metabolite injection and at five subsequent monitoring dates during the 8 months following injection. By the end of the 8-month period, the two primary COCs (carbon tetrachloride and trichlorofluoromethane) had each been reduced by greater than 99% from pre-injection concentrations, and all five of the halogenated compounds detected at the site had been reduced by an average of 96%. These data are graphically presented on Figure 1. When comparing pre- and post- co-metabolite injection data it should be noted that all system operation and monitoring activities remained identical throughout the period from 1997 through the end of the test period, with the exception that the co-metabolite was injected during May 2002, strongly suggesting that the post co-metabolite COC reductions were largely or entirely the result of the co-metabolism process.

Figure 1
Field Scale Pilot Results
Total Halogenated Compounds
Source Area Well I-2



Full-Scale Site-Wide Application - October 2002 Based on the results of the May 2002 pilot test described above, the technology was applied for the first time on a full-scale site-wide basis. The first full-scale test consisted of the injection of the co-metabolite at six additional locations. These locations, combined with the two injection wells included in the May 2002 pilot test, treated the entire site area targeted by the original AS/VE remediation system installed and operated at the site since 1997. Similar to observations made during the first test, dramatic reductions in COC concentrations occurred throughout the site where the co-metabolite was injected into sparge wells, dispersed, and an aerobic environment was maintained by continuous air sparging. During the 8-month duration of the project, the five primary halogenated COCs prevalent at the site were reduced in concentration an average of 98% and remedial goals for the site were met. Follow-up sampling 28 months after completion of the active remediation indicated that minimal rebound had occurred, with average site-wide COC concentrations remaining 93% below pre-start-up concentrations. Application of the pilot and full-scale treatment technology was performed under the approval of the U.S. EPA and West Virginia DEP.

Figure 2
First Full Scale Remediation Trends
Sitewide Average Concentration

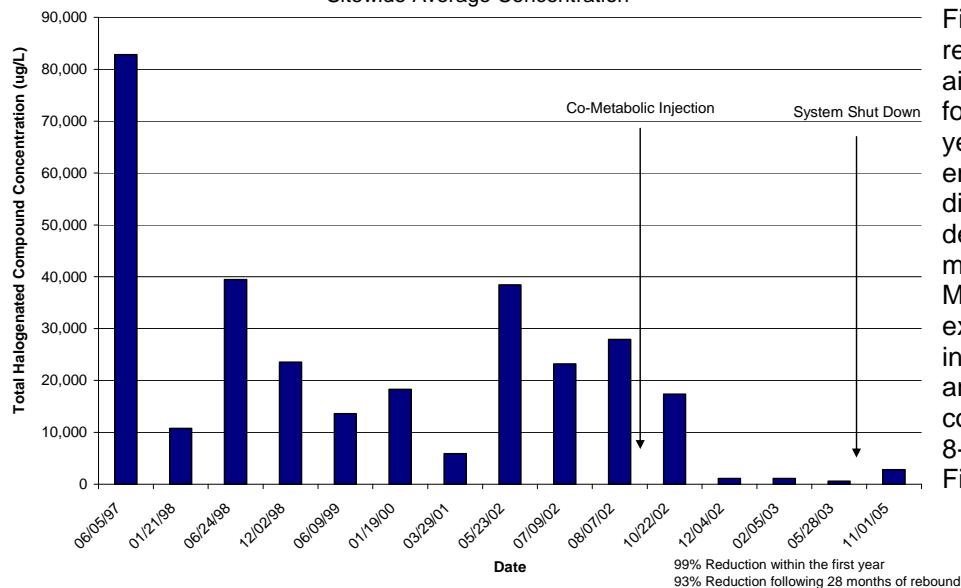


Figure 2 presents the results of over 7 years of air sparging at the site followed by less than 1 year of air sparging enhanced by the injection, dispersion, and aerobic degradation of the co-metabolite (August 2002 to May 2003). With the exception of co-metabolite injection, all site operation and sampling remained consistent throughout the 8-year period shown on Figure 2.

Figures 3 and 4 provide heterotrophic plate count and dissolved oxygen concentration data for the site during the remediation period. The sharp spike in microbe populations and the low dissolved oxygen concentration (high biological oxygen demand), combined with the simultaneous decrease in COC concentrations strongly support the conclusion that co-metabolism was the primary mechanism for COC reduction.

Figure 3
Heterotrophic Plate Count

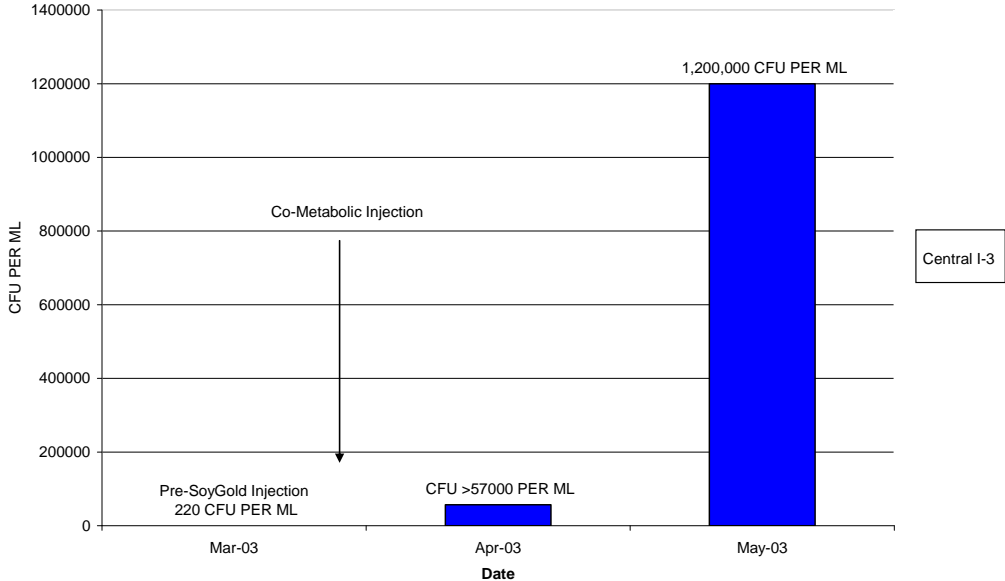
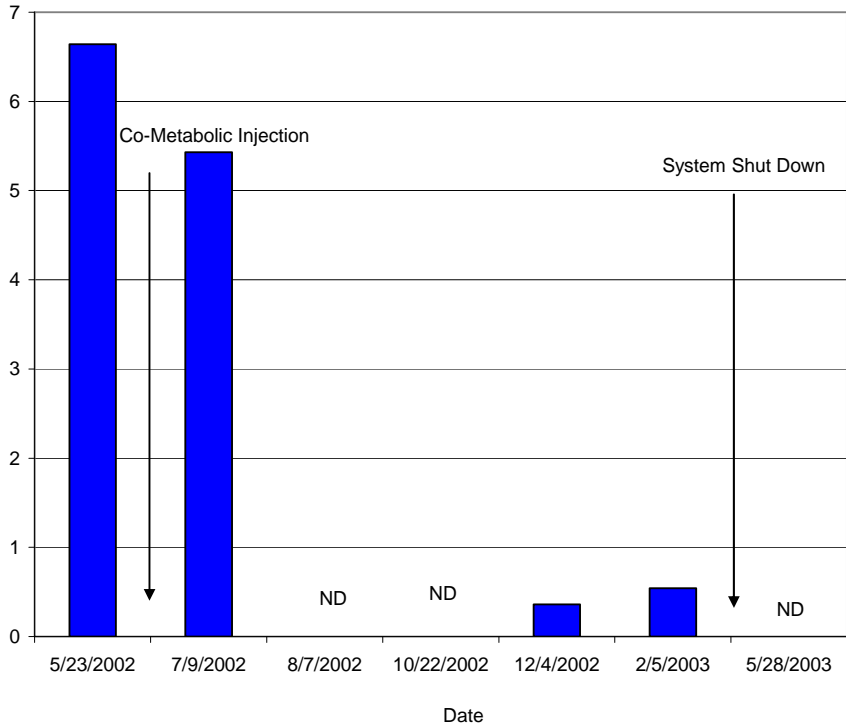
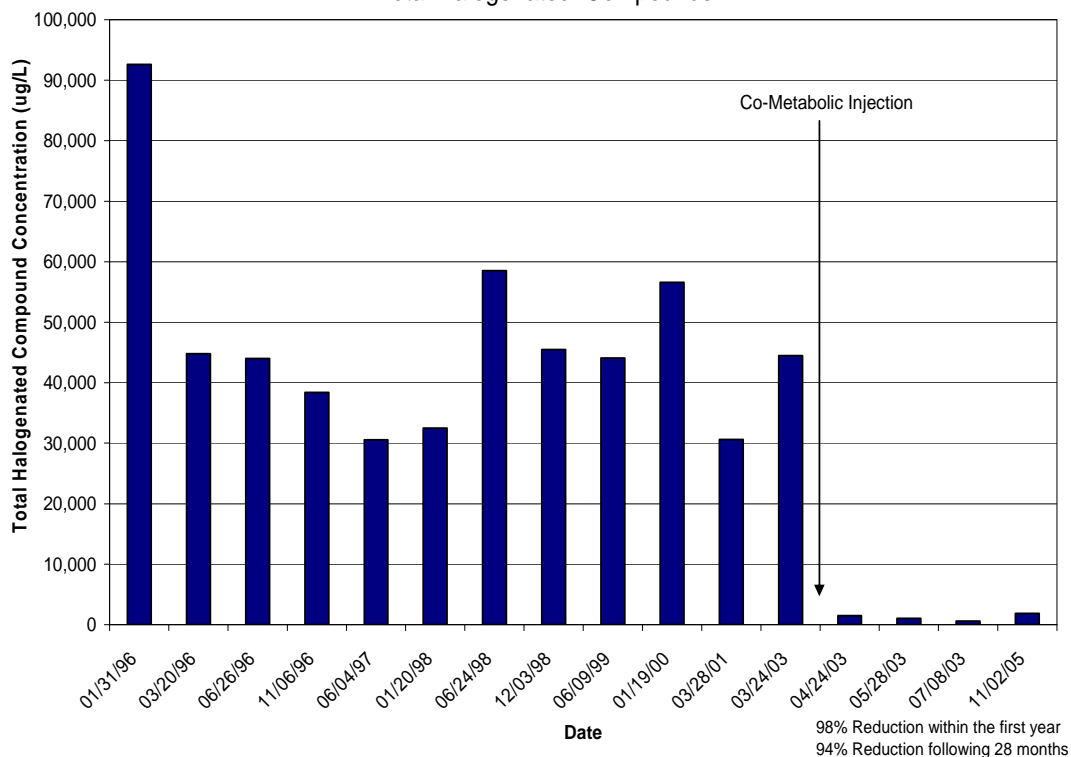


Figure 4
Dissolved Oxygen Concentration



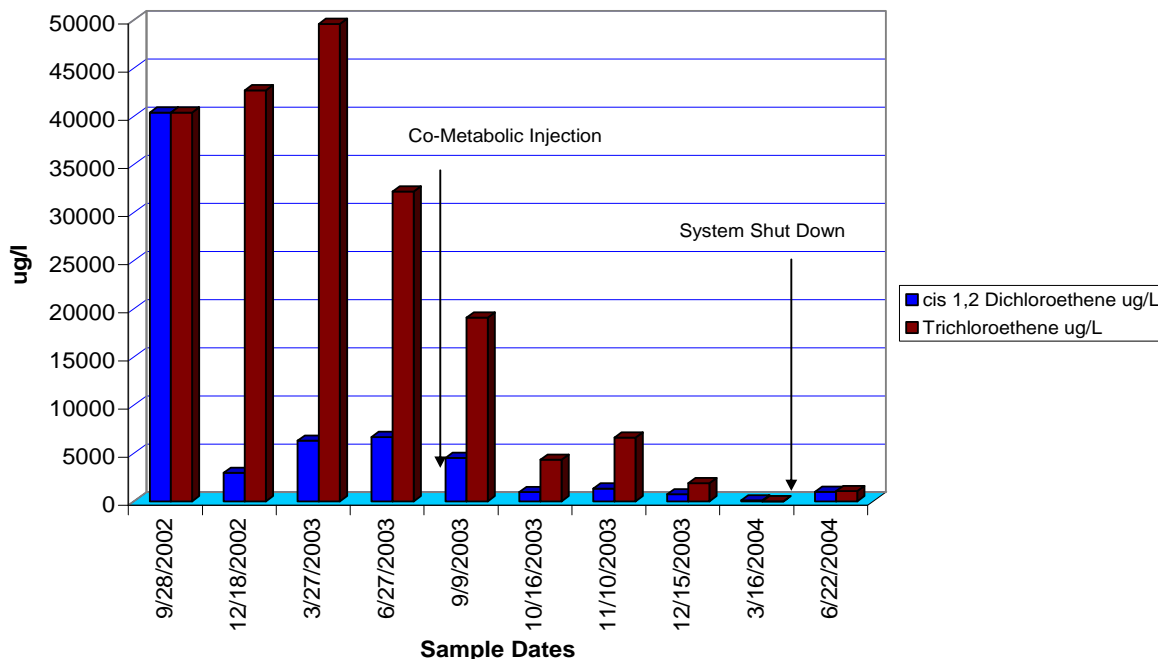
Full-Scale Site-Wide Application - March 2003 Based on the progress observed at the first full-scale application of the technology initiated during October 2002 and discussed above, a second full-scale application was conducted at a different site within the same industrial complex in Charleston, West Virginia. During the 5-month duration of the project, the five chlorinated hydrocarbon COCs prevalent at the site were reduced by an average of greater than 98%. Follow-up sampling 28 months after active remediation was terminated indicates that minimal rebound had occurred, with COC concentrations remaining 94% below pre-co-metabolic remediation concentrations. Analytical results for more than 7 years of active air sparge remediation followed by 5 months of co-metabolic remediation and 28 months of rebound are presented on Figure 5.

Figure 5
Second Full Scale Remediation
Sitewide Average Concentration
Total Halogenated Compounds



Kansas City Pilot Test - September 2003 A pilot test was initiated during 2003 at a UCC site in Kansas City, Kansas. The test consisted of two co-metabolite injection wells and four monitoring points located 10 to 20 feet from the injection wells. COC reduction in the injection wells was nearly 100% and reduction in the adjacent monitoring wells averaged more than 82% during the test period. Long-term COC trend data was available for one pre-existing monitoring well located within in the test area. Reduction of COCs (TCE and DCE) in this well was nearly 100% within 6 months after injection of the co-metabolite, as shown on Figure 6.

**FIGURE 6
KANSAS CITY PILOT TEST RESULTS
FOR TCE AND DCE**



West Virginia Superfund Site - September 2004 Two pilot tests were installed and operated at a Superfund site in Nitro, West Virginia during the third and fourth quarters of 2004. Data from the project indicated that reductions of cis- and trans-DCE, chloroethane, and dichloroethane were reduced by more than 90% in the test area during the 4-month pilot test duration. While chlorinated hydrocarbons were degraded to levels below MCLs at this site, other COCs including amides and chloroethers were essentially unaffected by the co-metabolism process. These compounds represented the first observed chemical limitations to the use of the technology.

Full-Scale Site Remediation in Kansas City, Kansas - December 2004 The UCC Kansas City pilot test discussed above was considered to be successful, and final design and installation activities were completed for a remediation project consisting of 17 injection locations throughout the 1-acre source area. Excluding a single recalcitrant well (subsequently addressed), site-wide TCE and cis-DCE concentrations were reduced by greater than 90% site wide during 18 months of operation. After 30 months, site-wide TCE and DCE concentrations had been reduced by an average of 98% and 93%, respectively. Application of the pilot and full-scale treatment systems are being completed under approval of the Kansas Department of Health and Environment.

2009 Activities

Several pilot and full-scale applications of the technology are currently in the design and planning stages and will be implemented during 2009, including sites in Texas, West Virginia, Virginia, and two locations in Kansas.

CONCLUSIONS

The aerobic co-metabolism technique employed during numerous pilot and full-scale remedial applications has proven to be highly effective for the remediation of halogenated hydrocarbons that are typically recalcitrant to aerobic degradation. These compounds also typically require extended time periods to degrade under anaerobic conditions and frequently partially degrade to daughter products that are equally toxic or more toxic than the original parent compound. The co-metabolism technique has been demonstrated to routinely reduce COC concentrations by well over 90%, typically in less than 1 year of active remediation. Completed sites have demonstrated that rebound is minimal after remediation, indicating that the technology is effective for both the aquifer matrix material and groundwater. The technology has been advanced from initial conceptual design through bench, pilot, and full-scale applications with consistent results, and the long-term effectiveness has been demonstrated through

follow-up sampling at pilot and full-scale remediation areas more than 2 years after shutdown of the remediation systems. The technique is highly applicable to sites characterized by the presence of halogenated hydrocarbons in groundwater and has been demonstrated to be cost-effective and reliable at sites where aquifer conditions support the application of standard air sparging techniques.