Compatible Technologies to Improve In-Situ Remediation of Chlorinated Solvents: A Case Study

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ABSTRACT: A chlorinated solvent plume (perchloroethylene or PCE) was discovered in the shallow ground water as a result of historical operating practices surrounding a Houston area dry cleaning facility. Permeable shallow soil at the site allowed rapid vertical migration at the source and lateral migration in the shallow ground water. This migration resulted in an off-site migration of the plume beneath an apartment complex causing concern for potential vapor intrusion hazards; as well as, a decrease in property value. A ground-water extraction and treatment system was installed to address the dissolved phase concentrations. The system reduced the total volatile organic compound (VOC) concentration in the source area from 115,400 to 36,500 µg/l. However, over time, operating maintenance and cost escalations were exceeding the ongoing remedial benefit. The system was shut down after nine years of operation. A review of available remedial technologies that could be implemented within the physical constraints of the site was conducted. In-situ enhanced aerobic bioremediation was selected to address the remaining ground-water concentrations because of the permeability of the formation, the relatively aerobic conditions, and the benefit of reducing the risk of VC accumulation.

INTRODUCTION

Innovative in-situ technologies have gained considerable favor recently as it has become apparent that pump-and-treat technologies alone require considerable time and money and may not decrease contaminant concentrations to the desired goals. Recent developments and applications with *in situ* technologies have demonstrated that different types of chemical and biological agents can act as oxidizers or dechlorinators and considerably reduce ground-water treatment to time frames that are generally measured in months rather than years. Through these processes, the contaminants are converted to innocuous compounds typically found in nature, and consequently, long-term operation and maintenance costs associated with the pump-and-treat technologies are eliminated. The most effective type of treatment is selected based upon the nature and location of the contamination, the size of the contaminated area, the type of soil present, and the hydrogeology of the area.

Bioremediation by enhanced microbial cometabolism is an ever emerging technology for the in-situ treatment of chlorinated solvents (PCE and its related breakdown products) in ground water. This paper describes the process of aerobic cometabolism using a commercially available, proprietary blend of microbes called CL-Out®. CL-Out® is a consortium of *pseudomonas* bacteria that have been isolated from sites with contaminated soils where the naturally occurring microbes had adapted and developed the ability to cometabolize the contaminants under an aerobic condition. Typically, PCE and TCE biodegrade under anaerobic conditions which creates an accumulation of 1,2-DCE and potentially VC. Since the latter two degrade more readily under aerobic conditions, developing or isolating a bacterial strain that degrades under aerobic conditions would prevent the accumulation of these constituents. The bacteria contained in CL-Out® are facultative in nature and will augment the naturally existing bacterial population to increase the rate of bioremediation.

DESCRIPTION OF THE BIOREMEDIATION PROCESS

Pseudomonas bacteria are well known for their ability to metabolize a wide range of organic compounds. The specific microbes were selected for their ability to degrade chlorinated solvents in an aerobic atmosphere in the presence of a dextrose stimulant. The laboratory selection process of the CL-Out® focuses on the creation of a consortium that can be reliably produced in commercial quantities without losing their genetic traits that enable cometabolism under aerobic conditions. The product was also verified to be pathogen-free and contaminant-free.

The aerobic cometabolism of halogenated aliphatic compounds has been demonstrated using microbes stimulated by numerous carbon sources including methane, phenol, toluene, and other regulated organic compounds. CL-Out® cometabolism, however, is stimulated by the addition of simple dextrose, which may be added without concerns associated with the addition of regulated or toxic compounds.

The cometabolic process is a fortuitous effect of the microbial metabolism of a primary substrate, in this case, dextrose. The CL-Out® cometabolism reduces PCE and TCE to cis-1,2-DCE. The degradation of cis-1,2-DCE continues by the mono-oxygenase enzyme that bridges the double carbon bond in cis-1,2-DCE to form an epoxide. The epoxide breaks the double carbon bond. The resulting (unstable) molecule is readily degraded to CO_2, and water. The advantage of this breakdown pathway is the elimination of VC as a potential degradation product. While some VC may be generated by other native organisms during the degradation processes, it is typically short lived given the aerobic conditions of the treatment zone.

HYDROGEOLOGICAL CONDITIONS

The ability of the bacteria to degrade the contaminants of concern in field applications depends primarily on the site-specific geologic and geochemical conditions. The success and cost effectiveness of in-situ bioremediation requires two general conditions. First, the impacted soil or ground-water environment must be favorable for the viability of the microbes. Second, the subsurface permeability must be sufficient to allow for the distribution of microbes throughout the contaminated zone.

Favorable environmental conditions for CL-Out® bioremediation require the presence of sufficient dissolved oxygen to sustain metabolic activity of the microbes. Although the microbes may be viable at lower dissolved oxygen levels (less than 1.0 mg/L), higher dissolved oxygen concentrations will support larger populations that are necessary to rapidly reduce the contaminant mass. The natural dissolved oxygen level in ground water may be supplemented by air sparging or adding a synthetic oxygen-release compound. Inorganic nutrients, such as nitrogen and phosphorus, and micronutrients are also required to sustain metabolic activity.

The bioremediation process may be self-limiting when microbes consume the available nutrients or dissolved oxygen or by reducing the ground-water pH to levels that cannot support microbial activity. System monitoring is important to track the consumption of nutrients or changes in subsurface conditions so that appropriate measures can be taken to maintain the bacteria viability. The addition of excess dextrose can be utilized by competing bacteria and consume the available oxygen without beneficial cometabolism.

The distribution of bioremediation amendments in the subsurface relies on diffusion and advective flow within the ground water. Thus, the subsurface permeability affects the distribution of the CL-Out® microbes, which can affect the effectiveness of CL-Out® bioremediation and ultimately the cost and time required for site remediation. With a favorable permeability, fewer injection points are required to achieve optimum distribution of the CL-Out® solution, primary substrate and nutrients across the contaminated area. Effective distribution of CL-Out® through the contaminated zone will increase the cleanup rate and reduce the risk of rebound from mobilized contamination from untreated zones.

CASE STUDY – DRY CLEANER IN HOUSTON, TEXAS

As a result of historical operations at a Houston area dry cleaning facility, shallow soil and ground water were impacted with dry cleaning solvents. The constituents of concern were PCE and its breakdown products [TCE; 1,2-DCE (cis- and trans-) and VC]. Shallow soils beneath the property are relatively permeable which allowed for rapid vertical migration at the source area. The ground-water flow beneath the property is relatively slow which resulted in upgradient, off-site migration of the plume. The off-site plume had migrated beneath an apartment complex causing concern for potential vapor intrusion hazards; as well as, property value considerations.

Hydrogeology. The uppermost ground water below the property is associated with the Chicot aquifer which generally consists of discontinuous layers of sand and clay. The first saturated unit was encountered at a depth of approximately 15-feet below grade. It is classified as sand to silty-sand zone terminating at approximately 20-feet below grade. The ground-water unit appears to be under confined conditions based on site geology and ground-water elevation measurements.

The natural direction of ground-water flow at the property was measured towards the south at a gradient of approximately 0.002 feet/foot. Based on ground-water extraction data collected during the operation of the ground-water remediation system, sustainable well yield was determined to be sufficient to produce usable quantities (greater than 150 gallons per day) to meet the Texas Commission on Environmental Quality (TCEQ) definition for a potential drinking water source.

Nature and Extent of Contamination. Between 1996 and 2000, several phases of site investigations were conducted to delineate the chlorinated solvent ground-water plume. Upon completion of the investigations, 14 monitoring wells had been installed with ten (10) of the wells located off-site within the adjacent apartment complex to the north. The investigations identified the source area along the northern edge of the dry cleaner along the common boundary with the apartment complex. The well nearest the source was located off-site. Ground-water monitoring and sampling reported PCE concentrations near the source area in excess of 26,000 µg/L. The applicable TCEQ regulatory cleanup standard for PCE is 5 µg/L. Once delineation was completed, the ground-water plume was determined to be approximately 200 feet in length. The ground-water plume prior to conducting any response action activities is shown in Figure 1 below.

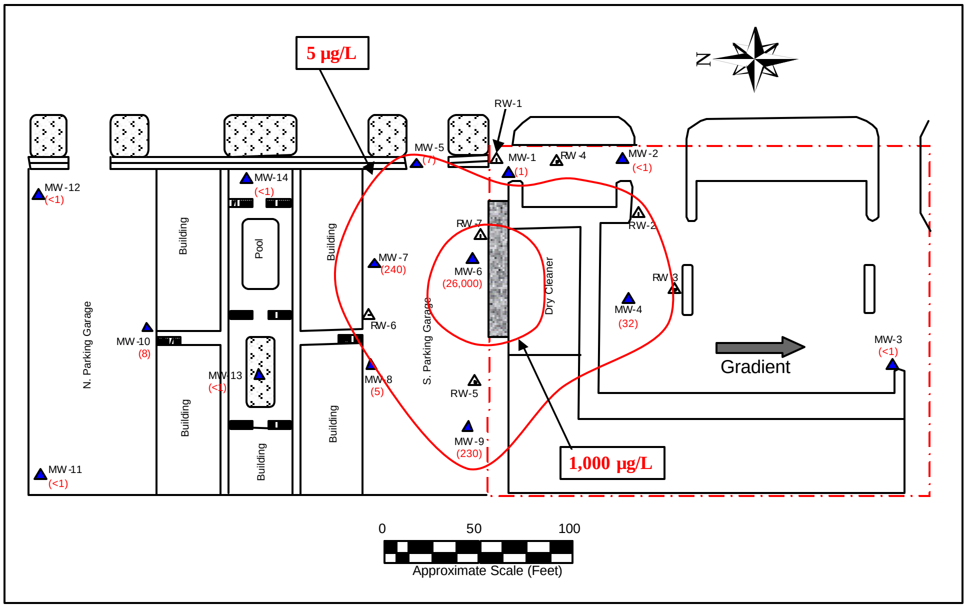

FIGURE 1. Site map showing June 1999 PCE concentrations.

TREATMENT STRATEGY AND OBJECTIVES

The objective of the ground-water response action was to remediate both the on-site and off-site portions of the plume to the documented health-based, residential cleanup standards. Initially, a source removal action was initiated within the narrow alleyway along the northern edge of the dry cleaner. The source removal included removing accessible impacted soil and installing a concrete cap to eliminate leaching from remaining impacted soil.

Ground-water Extraction and Treatment. Immediately following the source removal and the construction of a source-area cap and cover system, a ground-water extraction and treatment system was installed. The system initially recovered ground water from four recovery wells for a period of two years (September 1996 through December 1998). The system was shut down to monitor progress and allow natural conditions to equilibrate. After several years of ground-water monitoring, the remediation system was reconfigured to include only three additional recovery wells located off-site within the apartment complex. The system was restarted in November 2000 and operated until December 2004. During the nine years of operation, approximately 1.2 million gallons of ground water were treated. In January 2005, concentrations in the affected wells had decreased to near the target goals and operating maintenance and cost escalations were exceeding the ongoing remedial benefit.

In-Situ Aerobic Bioremediation. Although, the ground-water extraction and treatment was successful, it did not achieve the desired remediation goals on the off-site property. Therefore, a review of response action alternatives was conducted. Considering the decreased dissolved phase concentrations, the presence of adequate dissolved oxygen levels, and the reduced risk of VC accumulation, in-situ bioremediation was selected since introduced bacteria could easily colonize in pore spaces of the soil and provide longer treatment residence times. CL-Out® from CL-Solutions, LLC was selected for the bioremediation.

Between July 2005 and February 2006, three applications of CL-Out® were conducted across the remaining plume area. CL-Out® is a consortium of *pseudomonas* bacteria that are shipped in a freeze-dried state then re-constituted with clean tap water at the project site. Following a hydration period of 24 hours, food grade dextrose is added to "stimulate or activate" the bacteria. Once the bacteria have been "activated", the solution can be applied in-situ. During each treatment, the CL-Out® mixture was injected (under low pressure) into the contaminated ground-water zone through temporary injection points. Following each treatment, ground water was closely monitored to monitor concentration trends, water quality parameters and bacteriological counts.

The following table presents the ground-water concentrations following the completion of the extraction and treatment system and prior to implementing the CL-Out®.

TABLE 1. VOC concentrations ((μg/L) before biotreatment.

Well	PCE	TCE	cis-1,2-DCE	VC
MW-4	430	360	590	6.6
MW-6	4,100	2,500	34,000	<50
MW-7	45	61	610	18

Following the bioremediation period, total chlorinated VOC concentrations were reduced in the source area (MW-6) from 40,600 to 115 ug/L. Concentrations in the peripheral wells were similarly reduced from 1,386 to 9 ug/L (MW-4) and from 734 to <5 ug/L (MW-7). A review of the analytical results after the CL-Out® treatment (Table 2) shows that the total contaminant concentrations were reduced by greater than 98 percent across the contaminant plume.

TABLE 2. VOC concentrations ((μg/L) after biotreatment.

Well	PCE	TCE	cis-1,2-DCE	VC
MW-4	<5	<5	8.9	<5
MW-6	1.9	1.5	65	47
MW-7	<5	<5	<5	<5

The primary constituent (PCE) was reduced to levels below the target regulatory cleanup standards at each of the monitoring points. Figure 2 presents PCE iso-concentration contours measured in June 2006 following the final CL-Out® treatment period.

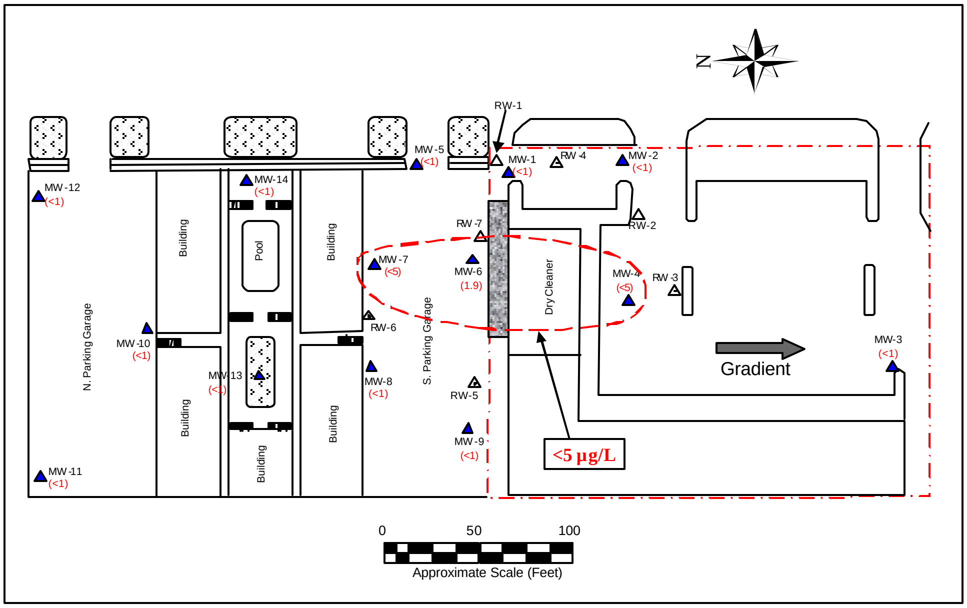

FIGURE 2. Site map showing June 2006 PCE concentrations.

The following charts illustrate the reduction in contamination. The charts present analytical results for the source area well (MW-6), an up-gradient well (MW-7) and a down-gradient well (MW-4). The charts show a reduction of greater than 99 percent in both PCE and total CVOC concentrations during the response action period. In each case, the accumulation of VC was minimal.

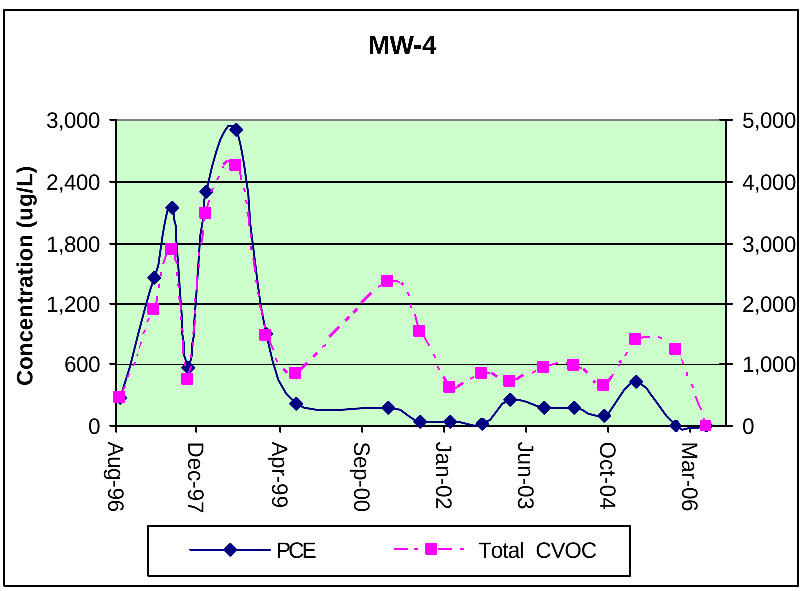

FIGURE 3. Chart showing PCE and total VOC concentrations over time for MW-4.

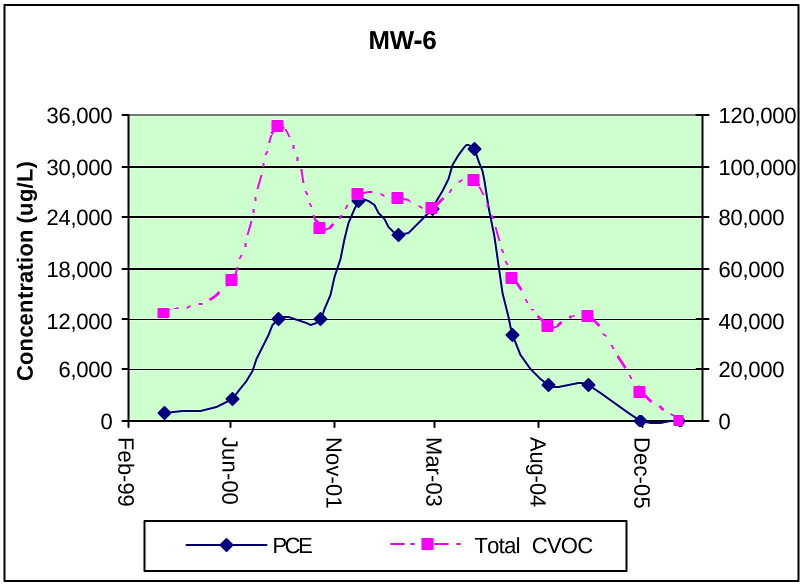

FIGURE 4. Chart showing PCE and total VOC concentrations over time for MW-6.

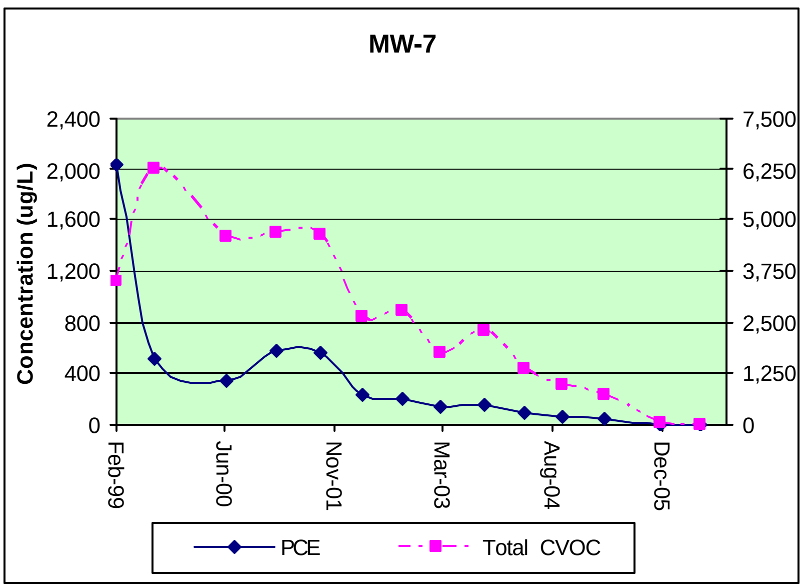

FIGURE 5. Chart showing PCE and total VOC concentrations over time for MW-7.

Currently, all of the off-site monitoring wells report PCE concentrations less than the target regulatory standard of 5 µg/L. During the response action period (extraction/treatment followed by bioremediation), the accumulation of daughter by products (cis-1,2-DCE and VC) has been minimal. The bioremediation under aerobic conditions minimized the generation of VC thereby reducing the toxicity of the contaminant plume.

Treatment Costs. The cost of the CL-Out® aerobic bioremediation at this site for the ground-water treatment has been less than $20,000 excluding monitoring and reporting to the regulatory agencies. In comparison, approximately $75,000 per year was spent operating the ground-water extraction and treatment system excluding capital expenditures.

CONCLUSIONS

Following a period of success reducing the chlorinated solvent plume and controlling plume migration with the ground-water extraction and treatment, increases in operating and maintenance expenses were exceeding the ongoing remedial benefit. Continued reduction in plume mass had begun to reach an asymptotic level. Enhanced microbial cometabolism (bioremediation) using CL-Out® was selected as a supplemental ground-water response action to address the residual constituent concentrations. Contaminant concentrations had been greatly reduced by the extraction and treatment; however, the reductions did not meet the target cleanup goals for the site. Based on the lower concentrations, the adequate dissolved oxygen levels, and the reduced risk of VC accumulation, in-situ aerobic bioremediation was selected. Following the approximate nine month treatment period, contaminant concentrations were reduced to levels at or below the cleanup goals throughout the plume.

Temporary injection points allowed an effective method of distributing the CL-Out® through the subsurface while minimizing disruptions to the property and residents. The distribution of the bacterial amendments in the subsurface relies on diffusion and advective flow within the ground water. Thus, the subsurface permeability affects the distribution of the CL-Out® microbes. This in turn affects the effectiveness of the CL-Out® bioremediation and ultimately the cost and time required for site remediation. Therefore, the subsurface permeability must be considered when designing the injection plan. As the formation permeability decreases, the number of injection sites will increase. An effective distribution of CL-Out® through the contaminated zone will increase the cleanup rate and reduce the risk of rebound from mobilized contamination from untreated zones.

Following the injections, ground-water quality parameters such as dissolved oxygen and pH were closely monitored. The most favorable environmental conditions for CL-Out® require the presence of dissolved oxygen to sustain metabolic activity of the microbes. The process may be self-limiting when microbes consume the available dissolved oxygen or reduce the pH to levels that cannot support microbial activity. If during the period of active bioremediation the dissolved oxygen levels being to decrease to near anaerobic concentrations (less than 1.0 mg/L), then amendments to the ground water may be necessary to maintain optimal microbial activity.

During the response action period (extraction/treatment followed by bioremediation), the accumulation of daughter by products (cis-1,2-DCE and VC) has been minimal. The bioremediation under aerobic conditions minimized the generation of VC thereby reducing the toxicity of the contaminant plume.

It has been demonstrated that single remedial technologies for dissolved phase chlorinated solvent plumes may not achieve the desired remedial goals. Each technology has pros and cons based on site specific parameters (concentrations, lithology, hydrogeology physical restraints, etc.). The use of multiple remediation technologies will typically increase the probability of meeting target regulatory goals in much shorter timeframes.