ANAEROBIC IN SITU BIOREMEDIATION OF CHLORINATED SOLVENTS AT AN INDUSTRIAL SITE*

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ABSTRACT: After installation of an in situ bioremediation treatment system, groundwater monitoring has shown substantial reductions in soil and groundwater contamination of perchloroethene (PCE) at a large industrial facility. The entire site covers over 32 acres (13 hectares) and the manufacturing plant building is greater than one-quarter mile (402 m) in length. Large areas around the building were contaminated with high concentrations of PCE (over 100,000 μg/L at some locations).

A microcosm study was performed using soil and groundwater samples from the site. The study showed that adding electron donor solutions effectively stimulated the indigenous bacteria to biodegrade PCE and its daughter products, trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride (VC) during a nine month to one-year period.

A remediation system was designed and installed to effectively deliver an electron donor solution to targeted areas at the site. BioLuxing was chosen as an effective system for this purpose. BioLuxing consists of constructing stacked and spaced fractures (BioLuxes) below ground surface by injecting special porous ceramic pellets (Isolite®) saturated with the special electron donor solution formulation. At some locations the solution was added to the pancake-shaped BioLuxes after installation. The BioLuxes installed were approximately 0.5 inch (1.27 cm) thick, relatively circular, horizontal and about 50 to 60 feet (15.2 to 18.3 m) in diameter. The BioLuxes are substantially more permeable than the natural soil conditions and thereby create preferential pathways for the migration of fluids, groundwater, non-aqueous phase liquids (NAPL) and the reagents. The impacted fluids pass through the in situ Isolite reservoirs that have been colonized by indigenous microbes and energized by the electron donor solution. The microbes promote the complete dechlorination of PCE and its daughter products to ethene and ethane.

Routine monitoring has shown at approximately one-third of the monitoring locations, that PCE and TCE have apparently been biotransformed to MCL's within a period of nine (9) months after installation of the treatment system. At the location with the highest concentration of PCE (104,000 μg/L) the PCE concentration was reduced by 82 percent to 19,100 μg/L and the TCE concentration was reduced by 68 percent from 31,500 to 10,000 μg/L. Transient accumulations of VC were observed and DCE was detectable. These preliminary remediation results suggest high concentrations of chlorinated solvents can be eliminated or significantly reduced relatively quickly by using a BioLuxing delivery system to stimulate indigenous bacteria with a properly designed formulation of electron donors. Laboratory process development results have been successfully transferred to the field-scale remediation. The cost of the BioLuxing system at this site was approximately one-half the cost of an alternative system previously planned for the site. The process used at this site may be duplicated at similar

sites contaminated with chlorinated solvents or other recalcitrant contaminants. If the appropriate indigenous bacteria are not present at the site, such bacteria can be cultured in the laboratory and delivered to the BioLuxes during the installation process or after installation.

SITE DESCRIPTION & SETTING

Groundwater monitoring has shown substantial soil and groundwater contamination of PCE at a large industrial facility. The entire site covers over 32 acres (13 hectares) and the manufacturing plant building is greater than one-quarter mile (402 m) in length. Large areas around the building have been found to be contaminated with high concentrations of PCE (over 100,000 µg/L at some locations). NAPL PCE has been observed in some areas. The depth to groundwater varies across the site from 1 to 10 feet (0.3 to 3.1 m) below ground surface (bgs). Contamination exists in the surficial unconsolidated sediments composed of clayey sands overlying clays ranging in depth between 8 and 22 feet (2.4 to 6.7 m) with a hydraulic conductivity of 3×10^{-5} centimeters/second (cm/sec) and in the underlying formation composed of sandy, phosphatic, calcareous clay with a hydraulic conductivity of 3×10^{-6} cm/sec. The underlying formation is approximately 66 feet (20.1 m) thick. Groundwater is moving slowly to the north toward a marshy area at the property boundary. The possible off-site contamination of the marshy area has been a concern of the State Department of Environmental Quality (DEQ).

REMEDIATION APPROACH

Previous technologies have been applied at this site. These technologies have included groundwater pump and treat with air stripping, vacuum extraction, total fluids recovery, and horizontal recovery wells. The amount of contaminant removed by these processes was negligible after spending hundreds of thousands of dollars. Furthermore, the DEQ had originally approved the installation of an iron filing funnel and gate system to serve as a barrier to off-site migration of PCE and other chlorinated solvents. The barrier was to be operated for 50 to 100 years since no steps were originally planned to reduce the source level contamination around the building. In 2000, recommendations were made for the installation of a BioLux system that would provide both a biologically reactive barrier to off-site migration of PCE and daughter products and treatment of source contamination. The BioLux system was expected to demonstrate that natural bioremediation processes were taking place, and that the anaerobic biodegradation of PCE could be greatly accelerated with the treatment system. The net effect would be an overall reduction in the time required for site remediation. Furthermore, the BioLux system could be installed and operated at a fraction of the cost of the funnel and gate system. A pilot test was proposed to gather information for the BioLux system design. The pilot test and well installations were approved by the DEQ.

BIOLUXING SYSTEM

The purpose of the patented BioLuxing system is to enhance natural bioremediation by establishing a luxurious underground environment for naturally occurring microbes that will degrade the contaminant of concern. This can be done through biostimulation, bioaugmentation, or a combination of both. An ideal in situ environment is achieved by constructing injection wells and then creating horizontal pancake-shaped permeable treatment lenses by hydraulic fracturing and simultaneously injecting a treatment slurry including special porous ceramic pellets. These pellets serve as the proppant to keep the fractures propped open to maintain a permeable reactive treatment system. The pellets also serve as a matrix for the microbes, and as a carrier for nutrients and amendments for the microbes. For this project, Isolite® was used as the porous ceramic pellets. Isolite is a porous fired ceramic media with a pore size of 1 to 2 microns and a permeability of 0.3 cm/sec.

The conductivity contrast between the BioLuxes and the natural sediments create preferential pathways for the migration patterns of the contaminated groundwater. As the impacted groundwater passes through the preferential flow network of the BioLuxes, the chlorinated solvents are transformed and detoxified. The reactive treatment system can be recharged from the surface through the capped injection wells by introducing additional nutrients, specific microbes or other amendments to maintain an optimal system for contaminant treatment. Normally two (2) to ten (10) BioLuxes are stacked above each other in 1.5 to 4 foot (0.46 to 1.2 m) intervals, depending on soil conditions and the depth of the contamination amid the fluctuation of the groundwater levels. Each stack of BioLuxes is called a BioNet.

LABORATORY MICROCOSM EVALUATION

A microcosm study was conducted using soil and groundwater samples from the site to determine the effectiveness of adding electron donor solutions to stimulate the indigenous bacteria to biodegrade PCE and its daughter products TCE, DCE, and VC. The performance criterion for the microcosm tests was to determine the treatment amendments that most effectively stimulated complete dehalogenation of PCE to ethene with the highest rates of biotransformation. The amendments tested included lactate, benzoate/yeast extract/lactate in combination with a mixture of trace metals (BY) and a mixture of solid and water soluble humates. BY results are shown in FIGURE 1.

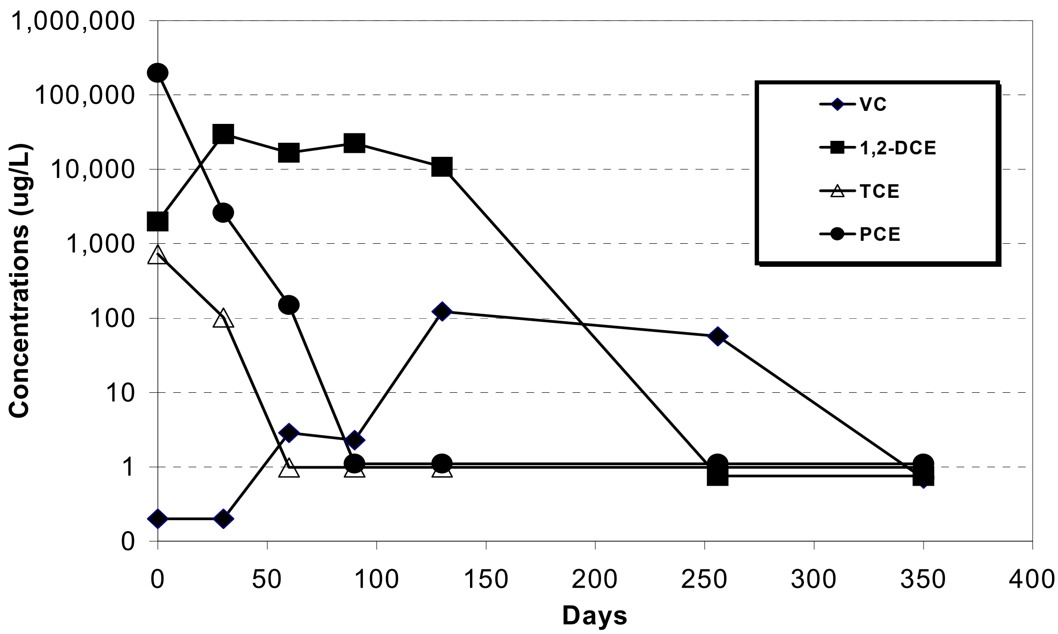

FIGURE 1. Results of Microcosm Test Using Benzoate, Yeast Extract and Lactate

The bench scale microcosm tests have demonstrated conclusively that the indigenous microbial community in the source area is capable of rapid transformation and in situ treatment of chlorinated impacts. It was concluded that the BY plus trace metals treatment amendment is an effective mixture for stimulating the complete dechlorination of PCE and its daughter products to ethene and ethane. While there is a transient accumulation of daughter products, TCE, DCE and VC, indications are that they are subsequently transformed as witnessed by the elevated ethene production levels seen in all microcosms.

REMEDIATION DESIGN

A groundwater modeling evaluation was performed to determine a reasonable spacing of the BioLuxes and BioNets in order to effectively capture most of the groundwater moving through the relatively less permeable soils. The USGS Modular Three-Dimensional Ground Water Flow Model (MODFLOW), in conjunction with the solute transport code MT3D and the PATH3D particle tracking module, was used to evaluate the capture effectiveness of the geometry of an individual BioNet. A three-dimensional MODFLOW model and flow vector module were used to evaluate the spatial influence of a BioNet on the ground water flow field. The model simulations indicated that a BioNet made of one-half inch (1.3 cm) thick BioLuxes, having a diameter of 40 feet (12.2 m) and a between BioLux spacing of three (3) feet (0.9 m), would effectively capture 90% of the ground water moving through the area. The simulations also indicated that a single BioNet would have a capture zone of 60 feet (18.3 m) in the upper formation and 70 feet (21.3 m) in the underlying formation. By using PCE degradation rates previously established at a similar site, the simulations predicted an approximate 65 percent reduction in PCE concentration in the upper formation and a 90 percent reduction in PCE concentrations in the underlying formation.

The model simulation results were used to design a remediation system for contaminated areas identified at the site. Ten BioNets were installed side-by-side as a permeable reactive treatment barrier along the northeast edge of the property, upgradient of the marshy area (receptor). The other twelve (12) BioNets were strategically placed in the source areas around the facility. By remediating the source areas, the amount of contamination eventually reaching the protective barrier will be greatly reduced or even eliminated.

REMEDIATION INSTALLATION

A pilot test was performed in December 2000 to verify that usable hydraulic fractures (BioLuxes) could be installed at the site. Four BioLuxes were installed between 10 and 23 feet (30.5 to 7 m) bgs. The ground surface uplift monitoring during installation showed that all of the BioLuxes were relatively circular, horizontal and about 50 feet (15.2 m) in diameter.

An additional eighty-four (84) BioLuxes were created at the site using hydraulic fracturing techniques. These BioLuxes were filled with Isolite and located to form twenty-two (22) BioNets around contaminant source and boundary areas. Each BioNet consisted of from three (3) to as many as eight (8) BioLuxes at depths ranging from 6 to 33 feet (1.8 to 10 m) bgs depending upon soil and contamination conditions.

Eighty-three (38) fractures were created with design volumes of solids. Uplift measurements indicated BioLux diameters ranged from 30 to 75 feet (9.1 to 22.9 m) with a median diameter of 47 feet (14.3 m). The remaining five vented before two-thirds or less of the design volume had been injected. Their estimated diameters are commensurately smaller but are efficient for injecting and distributing nutrient solutions in the subsurface.

The project was completed on time, within budget, and with essentially no impact on the client's business operations.

The nutrient formulation, identified above, which was based on results of the bench scale microcosm tests, was added to the Isolite prior to creation of the first twenty-eight (28) fractures. Nutrient solutions were subsequently injected into the remaining sixty (60) BioLuxes several days to several weeks after creation. Two nutrient "recharges" were completed in March and December, 2001.

RESULTS

Groundwater samples at the site are collected routinely. The last samples collected prior to installation of the BioNets were from 19 July 2000. Since the BioNets were installed, samples were collected on 16 January 2001 (3 months after installation) and on 25 July 2001 (9 months after installation). The results of these sampling events are shown in TABLE 1.

At six (6) monitoring wells (downgradient of BioNets BN-05, BN-10, BN-07, BN-17, BN-04, and BN-03) there has been a 100 percent reduction in both the PCE and TCE concentrations. Since installation, DCE concentrations were first analyzed in July, 2001, and were identified at nearly all monitoring wells at levels consistent with the biotransformation process. (See Table 1). Overall, the DCE concentration levels ranged from 30 to 107,000 μg/L. At these locations there has generally been an increase in the VC concentrations, further indicating that the normal reductive dehalogenation process is occurring. At three (3) monitoring wells (downgradient of BN-12, BN-11, and BN-06) there have been reductions in PCE concentrations ranging between 25 percent and 93 percent. At these same monitoring wells there has been reductions in TCE concentrations ranging between 45 and 100 percent. The VC concentrations at these locations may intermittently increase but then generally decrease. FIGURES 2 & 3 show the PCE, TCE, DCE, and VC concentration over time at two (2) monitoring locations (downgradient of BioNets BN-12 and BN-06)

At two (2) monitoring wells (downgradient of BN-10 and BN-01) there has been an increase in the concentrations of both PCE (from 2790 to 6410 μg/L at PW-1 and from 2290 to 246,000 μg/L at PW-2) and TCE (from 199 to 3170 μg/L and from 726 to 12100 μg/L, respectively) . The reasons for the increases at these locations are not definitely known. It is believed that the fracturing at these locations resulted in substantial conductivity contrast (3 to 4 orders of magnitude) between the NAPL bearing formation and the propagation. This may have caused a pooling of high concentrations and/or movement of free phase contaminant into these more porous reservoirs.

Table 1. Remediation Results

Location	Contaminant	Prior to Remediation (µg/L)	3 Months After Installation (µg/L)	9 Months After Installation (µg/L)	Change (µg/L)	Percent Removal
BN-05	PCE	6820	7	ND	6820	100
	TCE	550	50	ND	550	100
	DCE	*	*	46		
	VC	ND	144	54	NA	NA
BN-12	PCE	8780	3760	576	8204	93
	TCE	1610	2270	120	1490	93
	DCE	*	*	934		
	VC	ND	115	118	NA	NA
BN-10	PCE	102000	15	ND	102000	100
	TCE	51900	27	ND	51900	100
	DCE	*	*	474		
	VC	3260	221	541	2719	83
BN-07	PCE	20800	ND	ND	20800	100
	TCE	14300	ND	ND	14300	100
	DCE	*	*	75500		
	VC	1400	6540	18800	-17400	-1243
BN-17	PCE	13	ND	ND	13	100
	TCE	16	ND	ND	16	100
	DCE	*	*	1580		
	VC	75	140	107	-32	-42
BN-11	PCE	300	55	224	76	25
	TCE	164	16	91	73	44
	DCE	*	*	617		
	VC	40	7	37	3	8
BN-06	PCE	104000	19000	19100	84900	82
	TCE	31500	10700	10000	21500	68
	DCE	*	*	107000		
	VC	ND	3660	ND	NA	NA
BN-04	PCE	131	ND	ND	131	100
	TCE	133	ND	ND	133	100
	DCE	*	*	383		
	VC	ND	250	313	NA	NA
BN-03	PCE	20100	ND	ND	20100	100
	TCE	6300	ND	ND	6300	100
	DCE	*	*	30		
	VC	ND	697	99	NA	NA

Notes: * = Not Analyzed, ND = Non Detect, NA = Not Applicable

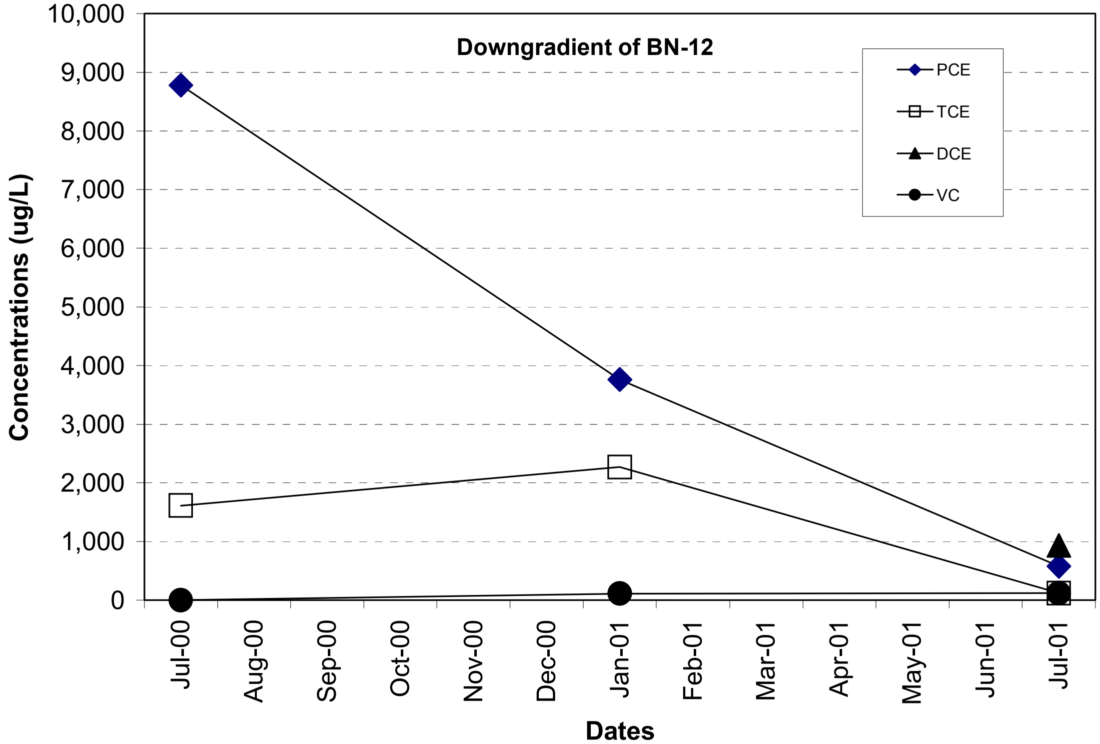

FIGURE 2. Contaminant Concentrations Downgradient of BN-12

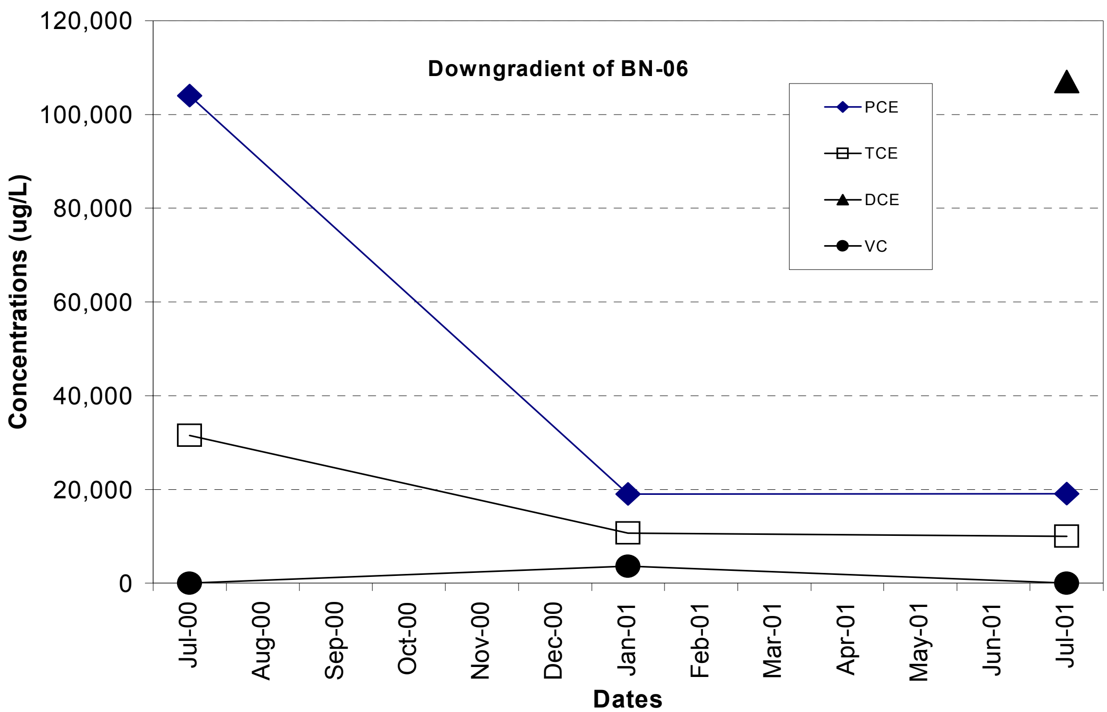

FIGURE 3. Contaminant Concentrations Downgradient of BN-06

CONCLUSIONS

Preliminary results from this PCE contaminated industrial site indicate that the in situ bioremediation system is working well and quickly. In thirteen (13) sampled locations where groundwater from monitoring wells exhibited PCE as high as 104,000 μg/L before the system installation, five (5) of the locations showed reductions to below MCL's; two (2) have declined by greater than 81 percent; and two (2) have declined by greater than 25 percent in a nine month (9) period. As an indicator to how well the bioremediation process is working at the site, seven (7) of these wells also showed significant (68 to 100 percent) reductions in the daughter product TCE. Some of the groundwater from the monitoring wells exhibited transient increases in VC levels, an anticipated result since the VC is generated as an intermediate product through anaerobic bioremediation. Remaining DCE and VC concentrations are expected to continue to decline as remediation progresses.

BioLuxing has proven to be an economically and technically effective remediation technology for the anaerobic bioremediation of chlorinated compounds, particularly in tight soil situations where other treatment system may be ineffective.

ACKNOWLEDGMENTS

The authors acknowledge the considerable contributions made on this project by Tom Harp of Terracon, who was the project manager for Terracon, and Dr. Fred Baker of Baker Associates who performed the modeling analysis to assist in the BioNet design.

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***Accepted for publication in the "Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 20-23, 2002, Paper Number 296," Battelle Press, Columbus, Ohio, 2002.**