

The Role of Solid Amendments in Promoting the Accelerated Anaerobic Bioremediation of Groundwater Containing High Concentrations of cis-1,2-Dichloroethene

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ABSTRACT: *In-situ* anaerobic bioremediation is an elegant method for decontaminating groundwater containing halogenated hydrocarbons and other toxic contaminants. Successful bioremediation is predicated on establishing and maintaining groundwater that is deoxygenated, electrochemically reducing and pH neutral. Solid remediation amendments, including zero valent metals and carbonate buffers, provide an opportunity to establish and maintain the fertile environment that supports effective anaerobic bioremediation. Zero valent metals are strong reductants that can rapidly render the affected groundwater deoxygenated and electrochemically reducing. Similarly, calcium carbonate is a slow-acting base that has long-term buffering capabilities to help maintain pH neutral conditions. This approach was successfully employed at a large industrial facility in the Southwestern U.S. where prior remediation efforts had resulted in a slowly degrading cis-1,2-dichloroethene plume with concentrations as high as 250 mg/L. This remediation program involved adding sub-micrometer zero valent metal, calcium carbonate and emulsified vegetable oil (EVO) to 60 injection wells within a 120 meters long by 30 meters wide treatment area. The product's small particle size allowed for a uniform distribution of the solid remediation amendments within the treatment area at injection pressures ranging from 200-600 kPa. Shortly after applying the remediation amendments, an acid-resistant microbial consortium containing dehalococoides etheneogenes was added to 15 of the injection wells. Within seven months of product application, c-1,2-DCE concentrations had decreased by over 99% in the most contaminated monitoring well with a similar response in down gradient monitoring wells. Vinyl chloride concentrations peaked about six months after product application and have since degraded mostly to ethene, indicating that a biotic pathway was the primary degradation mechanism.

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1 SITE BACKGROUND

A ruptured degreaser introduced trichloroethylene (TCE) into groundwater at an industrial facility in Stephenville, TX. Groundwater in monitoring wells near the source zone (30m by 15m) had TCE concentrations near 500 mg/L, suggesting that un-dissolved contaminant was present. Aqueous phase TCE and c-1,2-DCE had migrated 150 m down gradient with little vinyl chloride (VC) or ethene. Site lithology consisted of 1 m of coarse fill over silty sand. Typically, groundwater was about 2 m below ground surface.

2 2008 REMEDIATION PROGRAM

In Fall 2008 and Spring 2009, 4900 kg of Z-Loy™ nanocrystalline zero valent iron (NZVI, OnMaterials) and 42,600 kg of NewmanZone™ (RNAS, Brooklyn Center, MN) were mixed with 151,400 liters of deoxygenated water and injected through a network of sixty 3m deep, 5cm diameter PVC wells. Z-Loy™ contains zero valent metals (iron and aluminum) deposited onto the surface of sub-micrometer carrier particles; this application used 12 m²/g aluminum oxide as the carrier. NewmanZone™ is a sub-micrometer oil-in-water emulsion providing both fast-release and slow-release electron donors.

The 2008 remediation program resulted in the nearly complete elimination of TCE, including in two source zone wells that originally had TCE concentrations consistent with the presence of DNAPL. TCE degradation was accompanied by an substantial increase in c-1,2-DCE, suggesting that biotic degradation was the primary mechanism [1]. Smaller amounts of 1,1-dichloroethene (1,1-DCE) and ethane, not typical biodegradation products, suggested that some abiotic degradation had occurred. The incomplete dechlorination was probably the result of pH that was too low for native bacteria and the absence of critical bacteria species needed for complete dechlorination.

3 2011 REMEDIATION PROGRAM

3.1 Material Selection

A follow up remediation program was performed in February and March 2011. Materials were selected to maximize the probability of achieving rapid, sustained, and complete anaerobic bioremediation.

The Z-Loy™ used for the 2008 remediation program was modified to provide additional pH neutralization; 2500 kg of Z-Loy™ and 143,100 kg of NewmanZone™ were injected. In addition to the small amount of sodium bicarbonate present in the NewmanZone™, 4500 kg NeutralZone™ (RNAS), a calcium carbonate buffer, were used in 2011. Twenty-two kg of phosphorous and nitrogen in a water soluble commercial lawn

fertilizer and 2 g of vitamin B12 were added to the groundwater. Finally, a commercial anaerobic culture was added after other materials were injected (Bioremediation Consulting Inc., Watertown, MA). The product contains acid-tolerant microbes that extend the effective pH range of the degrading microbes to as low as pH 5.7 [3].

3.2 Product Application

A total of 74,000 liters of mixed suspension was injected through the same wells used in 2008 at 70-200 kPa and typical injection rates of 4-20 lpm. Each well was chased with a minimum of 200 liters of deoxygenated, reducing water. The groundwater was allowed to equilibrate over the weekend then 50 liters of the acid-tolerant BCI culture was delivered to 15 of the injection wells using nitrogen as a cover gas followed by a minimum of 400 l of deoxygenated chase water per well.

3.3 Program Results

A few days after applying the microbes, water was extracted from the monitoring wells and tested. For five monitoring wells in the treatment area, the data indicate that compared to conditions of December, 2010 (pH of 6.1 and ORP of -96 mV), the injected material created conditions ideal for the anaerobic bioremediation of chlorinated ethenes within about five months (August, 2011; pH 6.7 and ORP -224 mV) and maintained those conditions for at least one year (pH 6.6 and ORP -104 mV).

TCE was not found in monitoring wells by the end of the first treatment program (Table 1). A small TCE spike was observed in two wells immediately after the second injection, but quickly disappeared and TCE concentrations have remained at non-detect in all monitoring wells except one on the property fringe that in March 2013 that had 0.3 mg/L TCE, below the critical commercial groundwater PCL (PCL) of 0.5 mg/L.

In the treatment area, concentrations of c-1,2-DCE averaged about 113 mg/L in March, 2010, steadily decreased after treatment and have remained at or near zero for more than one year (Table 1). Since July 2012, all twenty monitoring wells in the facility have had c-1,2-DCE concentrations below the critical commercial groundwater PCL limit.

In March 2010 vinyl chloride averaged 0.3 mg/L and increased to a peak of 4.4 mg/L in Oct 2011 (Table 2). The increase coincides with the establishment of a reducing and pH neutral environment by August 2011. As of March 2013, eighteen of twenty monitoring wells at the facility have concentrations below the PCL of 0.2 mg/L. Methane concentrations have remained high (9.1-38.1 mg/l) throughout the remediation program indicating that a methanogenic environment had been established.

Table 1: c-1,2-DCE concentrations (mg/L) in five monitoring wells

	Mar 2010	Mar 2011	Aug 2011	Oct 2011	Mar 2012	Jul 2012	Nov 2012	Mar 2013
MW-1	485	167	86	0.1	0.3	0.0	0.0	0.0
MW-9	33.1	56.6	16.6	11.7	0.0	0.0	0.0	0.0
MW-10	32.9	5.7	0.0	0.0	0.0	0.0	0.0	0.0
MW-12	6.7	17.3	2.2	0.1	0.0	0.0	0.0	0.0
MW-13	8.0	4.4	0.0	0.0	0.0	0.0	0.0	0.0
Average	113	50.2	21.0	2.4	0.1	0.0	0.0	0.0

Table 2: VC concentrations (mg/L) in five monitoring wells

	Mar 2010	Mar 2011	Aug 2011	Oct 2011	Mar 2012	Jul 2012	Nov 2012	Mar 2013
MW-1	1.0	0.4	4.6	15.7	6.5	0.7	0.0	0.0
MW-9	0.2	0.4	6.8	5.6	0.4	2.2	0.3	0.4
MW-10	0.3	0.2	0.1	0.0	0.0	0.0	0.0	0.0
MW-12	0.2	0.1	0.2	0.5	0.5	0.5	0.5	0.4
MW-13	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0
Average	0.3	0.3	2.3	4.4	1.5	0.7	0.2	0.2

The sequential biodegradation of TCE to ethene in source zone MW-1 is illustrated in Figure 1. TCE was converted mostly to c-1,2-DCE after the 2008 remediation program. After the 2011 remediation program, residual c-1,2-DCE was converted to the terminal ethene product through a VC intermediary that was observed in smaller quantities.

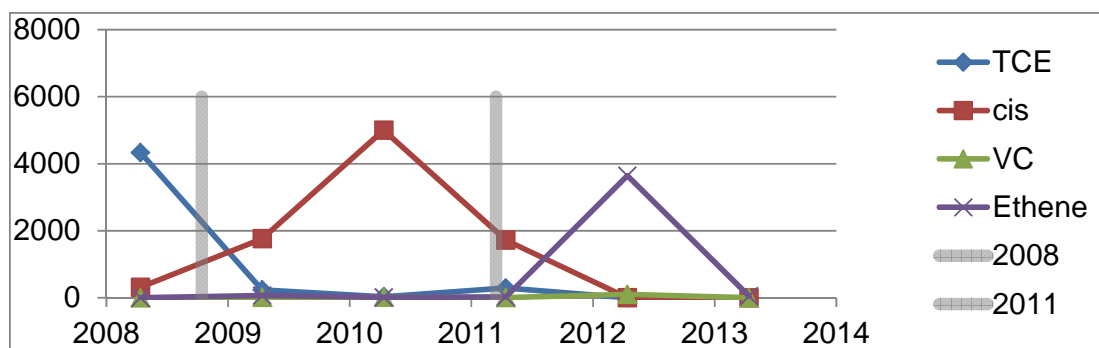


Figure 1: Concentrations of chlorinated ethenes in source zone MW-1, 2008-2013. Vertical lines indicate remediation injections.

4 CONCLUSIONS

In early 2011, a mixture of particulate and water soluble remediation amendments were applied to groundwater that had been rendered mildly acidic (pH = ~6) and mildly reducing (ORP ~ -100 mV) by a prior remediation program. Shortly thereafter, a mixed anaerobic culture containing Dhc capable of operating at a lower pH was added to 15 of the 60 injection wells. Five months later, the zero valent metal and calcium carbonate pH buffer had produced groundwater in the treatment area with an average pH of 6.7 and an average ORP of -224 mV. This environment was favorable for anaerobic bioremediation. c-1,2-DCE was completely eliminated within a year, and in 2013 remains at non-detect levels in all twenty on-site monitoring wells. VC concentrations peaked seven months later in October 2011 and ethene concentrations peaked about a year later in March 2012.

Two years later in 2013, groundwater has again trended acidic with an average pH of 6.2 and an average ORP of -106 mV. This suggests that the effective lifetime of the NZVI and calcium carbonate amendments was at or near its end while the longer acting EVO remediation amendment continued to degrade into fatty acids. However, most of the chlorinated contaminants, originally present at concentrations as high as 500 mg/L, had been completely eliminated during the timeframe when appropriate bioremediation conditions were present. Of twenty on-site monitoring wells, eighteen had no contaminants above the commercial groundwater PCL. Exceptions were two monitoring wells in the treatment area that each had 0.4 mg/L residual VC (PCL = 0.2 mg/L). These two wells had 13.6 and 0.9 mg/L ethene suggesting that bioremediation was still active at a pH of about 6.0; this is possibly attributable to the extended pH range provided by the acid-tolerant used in the remediation program.

4 REFERENCES

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