

# Anaerobic Bioremediation of Groundwater Containing High Concentrations of cis-1,2-Dichloroethene Using Solid Amendments

John Freim<sup>1</sup>, Clint Bickmore<sup>2</sup>, Richard Varnell<sup>3</sup>, Sam Fogel<sup>4</sup>, and William Newman<sup>5</sup>

## 1 SITE BACKGROUND

A ruptured degreaser introduced trichloroethylene (TCE) into groundwater at an industrial facility in Stephenville, TX. Groundwater 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. 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 sixty 3m deep PVC wells. Z-Loy™ contains zero valent metals (iron and aluminum) deposited onto the surface of sub-micrometer aluminum oxide particles. NewmanZone™ is a sub-micrometer oil-in-water emulsion providing both fast- and slow-release electron donors.

The 2008 program resulted in nearly complete elimination of TCE, including in two source zone wells suspected to have TCE present as 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 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 insure complete anaerobic bioremediation.

<sup>1</sup> John Freim, OnMaterials, 1291 Pacific Oaks Place, #121, Escondido, CA, 92029, USA, [john.freim@onmaterials.com](mailto:john.freim@onmaterials.com), 1-760-445-9934

<sup>2</sup> Clint Bickmore, OnMaterials, , [Clint.Bickmore@OnMaterials.com](mailto:Clint.Bickmore@OnMaterials.com), 1- 760-533-5932

<sup>3</sup> Richard Varnell, Cook-Joyce, 812 West Eleventh Street, Austin, TX, 78701, USA, [richard.varnell@cook-joyce.com](mailto:richard.varnell@cook-joyce.com), 1-512-474-9097,

<sup>4</sup> Sam Fogel, Bioremediation Consulting Inc., Watertown, Massachusetts, 02472, USA, [sfogel@bcilabs.com](mailto:sfogel@bcilabs.com), 1-617.923.0976

<sup>5</sup> William Newman, Remediation and Natural Attenuation Services, Inc., 6712 West River Road, Brooklyn Center, MN, 55430, USA, [bnewman@rnasinc.com](mailto:bnewman@rnasinc.com), 1-763-585-6191

The Z-Loy™ used for the 2008 remediation program was modified to provide additional pH neutralization; 2500 kg of Z-Loy™, 143,100 kg of NewmanZone™, and 4500 kg NeutralZone™ (RNAS), a calcium carbonate buffer, were used in 2011. Twenty-two kg of phosphorous and nitrogen 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 have an effective pH range 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 4-20 lpm. Each well was chased with of 200 liters of deoxygenated, reducing water. After equilibrating over a weekend 50 liters of the acid-tolerant BCI culture was delivered to 15 of the injection wells using nitrogen as a cover gas followed by 400 liters 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. A small TCE spike was observed in two wells immediately after the second injection, but quickly disappeared. TCE concentrations are at non-detect in all monitoring wells except one on the property fringe that in March 2013 had TCE below the 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 monitoring wells in the facility have had c-1,2-DCE concentrations below the 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, 18 of 20 monitoring wells have concentrations below the PCL of 0.2 mg/L. Methane concentrations (9.1-38.1 mg/l) indicate a methanogenic environment throughout the remediation program .

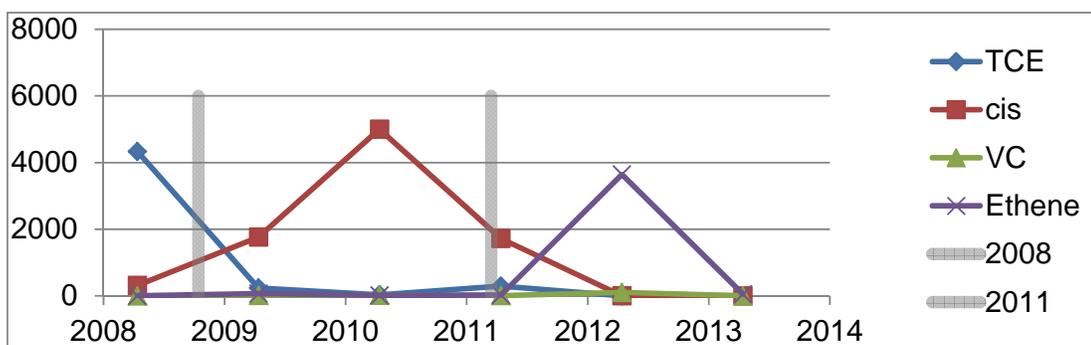
**Table 1: c-1,2-DCE concentrations (mg/L) in five monitoring wells**

	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, groundwater has again become acidic (pH of 6.2 and ORP of -106 mV). This suggests that the effective lifetimes of the NZVI and calcium carbonate were 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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