IN SITU ANAEROBIC REDUCTIVE DECHLORINATION AT A FORMER AS/SVE SITE

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ABSTRACT: After several years of operating an AS/SVE system at a former industrial site (Site) and achieving a reduction of over 85% of the VOCs in groundwater, the remedial approach was converted to an anaerobic system, conducive to the reductive dechlorination of the residual contaminants. The acceleration of in-situ bioremediation via anaerobic reductive dechlorination (ARD) by the injection of an electron donor/carbon source (substrate) into the subsurface, is intended to be the final technology sequence step for the in-situ treatment of chlorinated solvents (PCE, TCE) in groundwater at the Site. Following a successful ARD pilot test onsite, the full-scale application was accomplished utilizing the existing air sparge and soil vapor extraction system in conjunction with direct-push injection points to facilitate the distribution of the electron donor substrate into the subsurface. After eighteen months of operation, the mobilization of contaminants, the creation of biodegradation end products (ethene and ethane) along with the increased reduction of the constituents of concern, has demonstrated that a former AS/SVE remedial approach can be modified to promote the anaerobic reduction of the residual chlorinated VOCs in the subsurface.

INTRODUCTION

Based on remedial requirements and applicable remedial technologies in 1993-1994, the air sparge/soil vapor extraction (AS/SVE) remedial technology (including dewatering technology) was initiated at an industrial site to address VOCs in the core area of shallow groundwater and VOCs in soil. This remedial strategy was subsequently expanded as access to adjacent properties was granted. The expansion was intended to enhance the remediation process by maintaining an aggressive approach and adapt to increased on and off site assessement data. After several years of operation and removal of an estimated 515 pounds of VOCs (as of October 1997), the long term monitoring data for operation of the AS/SVE system showed a diminishing return capacity (less significant reductions) in the system's progress. In response to the diminishing return other remedial action alternatives such as dual phase extraction (DPE), reactive permeable barrier walls (zero valence iron), Fenton's reagent, and other technologies were evaluated to enhance and compliment the remediation strategy. Due to the complimentary aspect of the DPE technology to the AS/SVE system and the potential for future integration of anaerobic reductive dechlorination approach a DPE pilot test was conducted. Based on positive DPE pilot test results, a DPE remedial system was installed to compliment the AS/SVE system operations and to address recalcitrant remediation areas while expanding remedial actions to previously untreated areas identified by additional investigation activities.

The combined operation of AS/SVE and DPE systems continued to remove pounds of contaminants (estimated at 647 cumulative pounds as of January 2001), but groundwater monitoring showed only moderate VOC concentration decreases and fluctuating VOC concentrations in recalcitrant areas (location dependent). In an effort to continue remedial progress at an accelerated rate, an in situ anaerobic reductive dechlorination pilot study was conducted from April through November 2001. Based on the findings of the pilot study, a full-scale in situ anaerobic reductive dechlorination bioremediation program was implemented throughout the Study Area in March 2002. As of December 2003, implementation of the full-scale bioremediation program for the Site has shown that VOC concentrations in the groundwater are actively being reduced at an accelerated rate. Additionally, VOC concentrations in surface water (attributed to the discharge of shallow groundwater to a storm water utility line) have decreased to below MCLs and are typically at non-detectable levels.

SITE DESCRIPTION

The surficial soils are represented by recent alluvium (cobbles, gravel, sand, silt, and clay) from local streams and artificial fill. This surface formation is underlain or grades into gravel deposits consisting of rounded cobbles with variable amounts of sand, silt, and clay. The gravel deposits are underlain by three separate formations that consist of fine to coarse-grained sand interbedded with lenticular silt and clay. The undifferentiated formations are unevenly underlain by bedrock. The bedrock formation is described as a medium to coarse-grained light gray muscovite-biotite granite with quartz plagioclase, microcline, lesser muscovite and biotite, and occasionally garnet.

The geological strata observed during shallow and deep well installations across the Site consisted of cobbles, gravel, sand, silt, and clay underlying the ground surface. The recent alluvium/horizontal fill horizon was found at all well locations and ranges from ground surface to a depth of 17 feet below grade (bg). This soil horizon is underlain or grades into the gravel deposits consisting of rounded cobbles with variable amounts of sand, silt, and clay at variable depths dependent upon well location. The formations underlying the gravel deposits consisted of fine to coarse grained sand interbedded with lenticular silt and clay at variable depths ranging from 5 to 24 feet bg. This formation is non-conformly underlain by weathered bedrock (saprolite). The bedrock/overburden surface dips from southwest to northeast with some noted undulations in the bedrock surface due to possible historical erosion effects.

Due to the variations in stratigraphy, permeability, and the geologic effects on the migration, adsorption, dispersion of the contaminants of concern, the remedial strategy was designed and augmented to adapt to the localized complexity of the subsurface.

METHODS AND MATERIALS

Implementation of the full-scale in situ bioremediation program was initiated in March 2002. The program consisted of the installation of 25 injection points via Geoprobe™ direct-push methodology on the Site to augment the existing AS and/or SVE injection points to be used for substrate injection. Four of the injection points were installed beneath the building adjacent to the area of the original VOC contamination.

The interior points were installed to investigate and address a suspected residual groundwater impacted zone beneath the foundation, which was believed to be affecting

the downgradient wells in the original pilot test area. Groundwater analysis from samples collected from the injection points beneath the building indicated a pre-injection (March 2002) total VOC concentration of 6,343 ppb with a TCE concentration of 5,619 ppb. This residual area under the north corner of the building foundation is being addressed by substrate injections in those points under the building, which will aid in solubilizing the contaminants making them more bioavailable for the anaerobic reduction process (Refer to Figure 1).

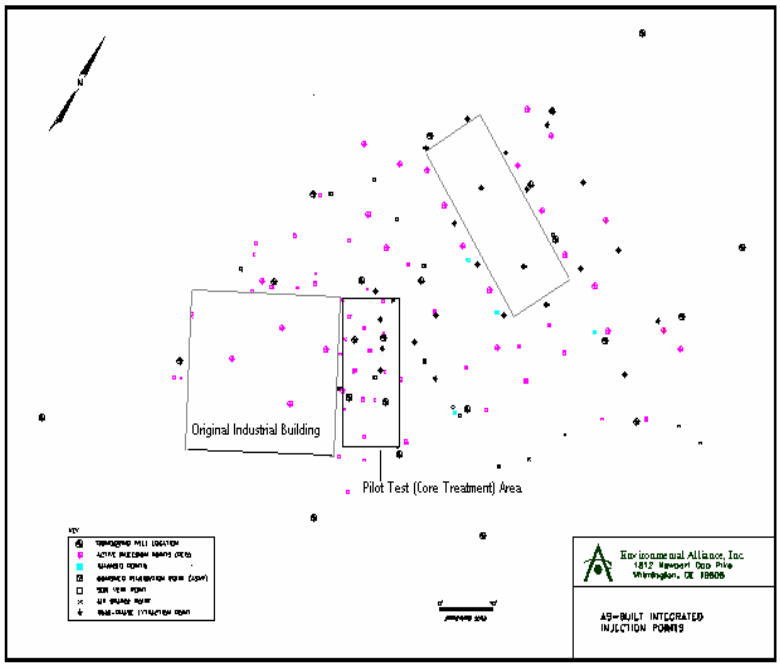

Figure 1 - Full-scale bioremediation substrate injection point location map

A total of approximately 1,000 pounds of calcium magnesium acetate (CMA) as a 5% solution was initially injected during the start-up (March to May 2002) of the site-wide bioremediation activities followed by approximately 1200 gallons of the insoluble vegetable oil substrate as a 5-10% emulsion from May 2002 to September 2003. This represents 25-30 times the required electron donor based on estimated average contaminant levels, available competing electron acceptors and total volume of water in the treatment area. Monthly groundwater monitoring of remediation parameters to evaluate progress of full-scale implementation of the bioremediation program was also conducted from May 2002 through January 2003 and then approximately quarterly from January to December 2003.

RESULTS AND DISCUSSION

Initial dissolved oxygen (DO) levels before initiation of bioremediation activities indicated an aggressively aerobic environment with an average of 5 mg/L site wide which was expected due to the level of air sparging previously conducted. DO levels across the Site decreased significantly since initiation of the in situ bioremediation program and

have been below 0.75 mg/L at most well locations within the treatment zone. ARD end products Ethene and Ethane have been detected at levels with the highest level being 7 ug/L in the core treatment area. Methane has also been detected at elevated levels in several wells throughout the Site since the inception of site wide bioremediation, indicating that methanogens are active in the subsurface. As low DO levels are maintained, the reduction of other competing electron acceptors (CEAs, i.e., ferric iron, nitrate and sulfate) continued as well as the anaerobic reduction of the remaining VOC's.

PTW-1, which is within the original pilot test core treatment area (see Figure 2), is continuing to indicate the most significant reductions on the site. The laboratory analytical results are highlighted by the following data sets:

1. January 2002 – PCE of 186 ug/L, TCE of 5,261 ug/L, cis–1,2–DCE of 687 ug/L, and no VC
2. January 2003 -PCE of 54.8 ug/L, TCE of 1,384 ug/L, cis–1,2–DCE of 349 ug/L, and VC of 1.2 ug/L
3. December 2003 – PCE of 7 ug/L, TCE of 200 ug/L, cis–1,2–DCE of 100 ug/L, and no VC

This analytical data provides the most compelling evidence of the effectiveness of the ARD process over time, with a **96**% reduction of TCE from January 2002 to December 2003 and an **85**% reduction of cis-DCE, with no accumulation of VC. The data also indicates an **86**% reduction of TCE and a **71**% reduction of cis-DCE from January to December 2003 (Refer to Figure 3).

When all laboratory analytical data from January 2002 (prior to initiating full-scale ARD) for the core treatment area is averaged and compared with the averaged data collected in December 2003 at the same sampling locations, the following reductions over this two-year period are indicated:

- 79% reduction of PCE
- 80% reduction of TCE
- 61% reduction of cis-DCE
- VC detected at only one location at 6 ug/L

Evidence of the effectiveness of the full-scale application of the in situ ARD process is indicated by a comparison of the Site averaged data from just prior to initiation of the full-scale ARD process in January 2002 compared with the averaged data from December 2003 as follows:

1. January 2002 – PCE of 67.3, TCE of 1,662.5 and cis–1,2–DCE of 271.7 ug/L
2. December 2003 – PCE of 42.4, TCE of 928.4, and cis–1,2–DCE of 187.5 ug/L

This data represents a **37**% reduction of PCE, an **82**% reduction of TCE, and a **31**% decrease of cis-DCE with little to no overall accumulation of VC (Refer to Figure 4).

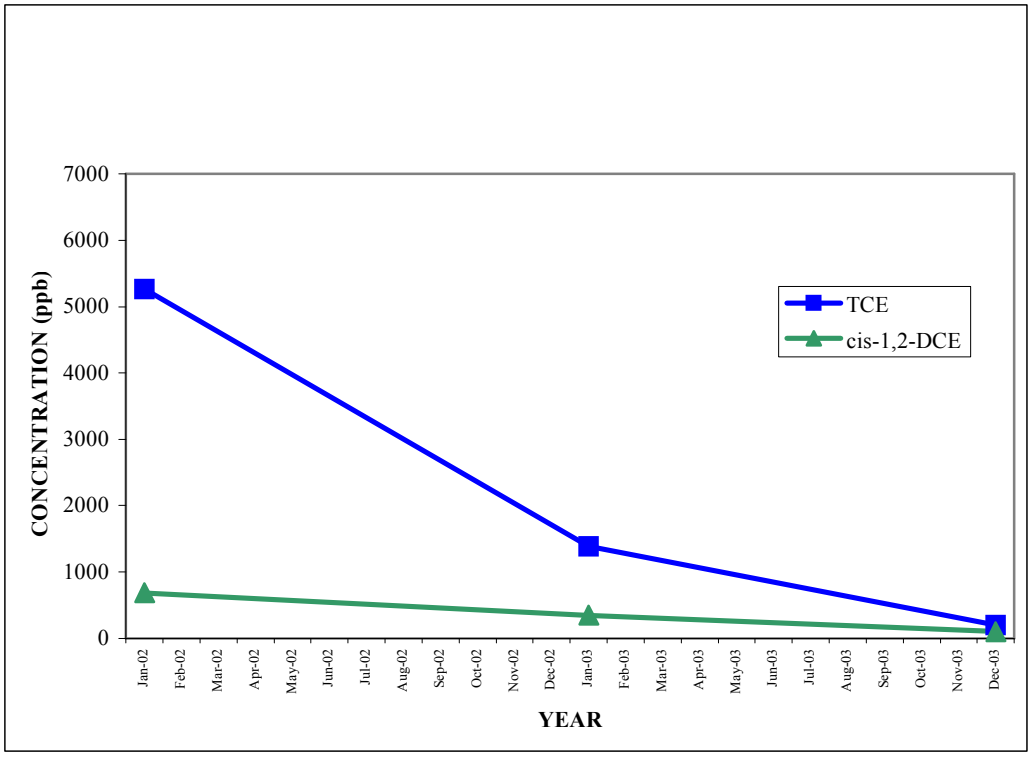

Figure 3 - PTW-1 TCE and cis-1, 2-DCE Concentration Jan 2002 (Prior To Full-Scale ARD) - Dec 2003

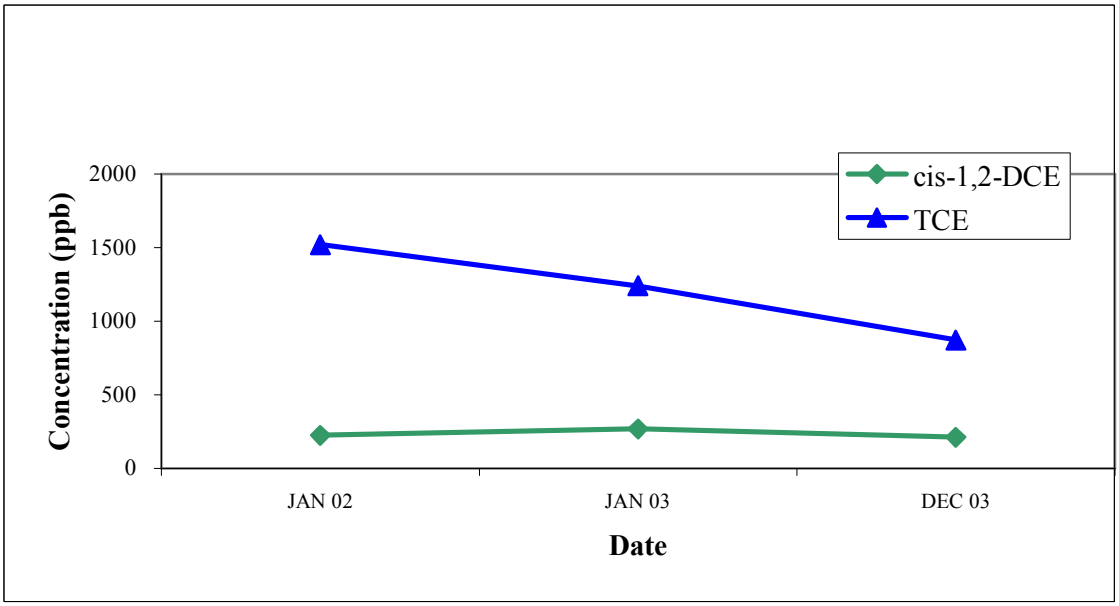

Figure 4 Site-Wide Average TCE and cis-1, 2-DCE Concentration Jan 2002 (Prior To Full Scale ARD) - Dec 2003

CONCLUSIONS

Site-wide, the laboratory analytical data for VOCs from the sampling event of December 2003 reinforces the field data collected during that sampling event, and indicates that the anaerobic reductive dechlorination (ARD) of TCE and daughter products is progressing as anticipated. Both data sets indicate that the core treatment area of the original pilot test that has been subjected to the ARD environment and process for the longest period of time (less than three years), is exhibiting the most conclusive VOC reductions.

The field and analytical data also indicates that some areas of the treatment zone, including the perimeter of the treatment zone and down gradient of the core treatment area, that have only been subjected to the full-scale ARD process since March 2002 (less than two years), may require additional injection points.

Also under evaluation is the modification of substrate injections to include a mix of soluble and insoluble substrates. The soluble substrates (either methanol or sodium lactate) travel farther in the subsurface and degrade very quickly, helping to reestablish the anaerobic environment necessary for the ARD process. The insoluble substrate (vegetable oil emulsion) is then left to function as a slow-release electron donor due to its longevity in the subsurface, facilitating the maintenance of the anaerobic conditions.

After twenty months of operation, the mobilization of contaminants, the detection of biodegradation end products (ethene and ethane) along with the reduction of competing electron acceptors has demonstrated that a former AS/SVE remedial approach can be modified to promote the anaerobic reduction of VOCs in the subsurface. The ARD process is presenting itself to be the polishing step in a remedial treatment train that has progressed with time. It is anticipated that with monitoring and maintenance of reducing conditions, the site will achieve acceptable risk based closure levels that are protective of human health and the environment within a more reasonable amount of time than would have been possible if only one remedial strategy had been applied to such.

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REFERENCES

Kent J. Boulicat, Robert Hinchee, et al. 2000 "Vegoil: A Novel Approach For Stimulating Reductive Dechlorination" The *Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds,* Monterey, California.

Michael D. Lee, Ron J. Buchanan Jr. and David E. Ellis 2000 "Laboratory Studies Using Edible Oils to Support Reductive Dechlorination" The *Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, California.

Interstate Technology and Regulatory Cooperation Work Group In Situ Bioremediation Work Team, 1999 *"Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices"*

Author-Anon at EPA Technology Innovation Office, GRA&I, Issue 23, 2000 "*Engineered Approaches to In situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications"*