DESTRUCTION OF DNAPL THROUGH A GREEN TECHNOLOGY – TCE SOURCE AREA BIOREMEDIATION

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ABSTRACT: A single-injection of a proprietary electron donor additive remediated a trichloroethene (TCE) dense non-aqueous phase liquid (DNAPL) source, reducing TCE concentrations by 99.99 percent in less than 9 years. The remedial program achieved the enhanced reductive dechlorination (ERD) of chlorinated volatile organic compounds (cVOCs) within an overburden groundwater source area at a site located in central New Hampshire, USA. The baseline TCE concentration was 97,400 micrograms per liter (µg/L) in September 2001 and decreased to less than 10 µg/L by May 2010.

This green technology destroyed the DNAPL and has shown great promise at other cVOC-impacted sites for both full-scale and Proof-of-Concept remedial programs. The Proof-of-Concept test, which is discussed at the end of the paper, is an economical means to evaluate feasibility and advance a site toward cost-effective full-scale remediation.

INTRODUCTION

Background - Contamination was first discovered at a manufacturing facility in New Hampshire (Site) in 1992 during the closure of a fuel oil underground storage tank (UST). The UST was closed in-place and post-closure samples indicated elevated concentrations of chlorinated volatile organic compounds (cVOCs). The source of the cVOC contamination was manufacturing wastewater containing primarily trichloroethene (TCE) that was discharged directly to an onsite dry well prior to 1990 with possibly secondary contributions from a nearby former aboveground TCE tank. Rainfall runoff from a roof drain discharging to a dry well sometime after 1993 enhanced TCE mobility in Site groundwater (Figure 1).
The cVOCs detected in overburden groundwater include the reactants (parents) TCE and tetrachloroethene (PCE), as well as the degradation byproducts (daughters) 1,1-dichloroethene (1,1-DCE), cis/trans-1,2-dichloroethenes (1,2-DCEs), and vinyl chloride (VC). The primary contaminant of concern was TCE detected at concentrations up to 97,400 μg/L.

**Figure 1. Site and Injection Location Plan.**

**Hydrogeology** - Site geology includes lacustrine varved silts and clays that formed two distinct hydraulically conductive zones consisting of fine sand with silt and clay, bounded above and below by non-conductive clay at the Site. The upper hydraulically conductive zone is located approximately 18 to 26 feet (5.5 to 7.9 meters) below ground surface (bgs) and the lower hydraulically conductive zone is located at approximately 30 to 34 feet (9.1 to 10.4 meters) bgs. Groundwater flow direction is generally toward the south, but varies seasonally for each unit.

**Groundwater Quality Data** - Monitoring wells were installed in both hydraulically conductive overburden zones (upper unit zone wells MW-101S, MW-102S, MW-103S, and MW-104S; lower unit zone wells MW-101D, MW-102D, MW-103D, and MW-104D) to delineate the TCE plume (Figure 1). Groundwater samples detected cVOCs in both conductive zones, with the greatest concentrations detected in the deeper portion of the source area (well MW-104D). The baseline TCE concentration in MW-104D was 97,400 micrograms per liter (μg/L) (approximately 9 percent solubility) that was consistent with the presence of a dense non-aqueous phase liquid (DNAPL). The parent compounds TCE and PCE (10 μg/L) were detected at well MW-104D, along with the dechlorination byproducts: cis-1,2-DCE (300 μg/L), 1,1-
DCE (41 μg/L) and VC (34 μg/L). The molar ratio of the parent compounds to total cVOCs in September 2001 was approximately 99.6 percent, indicating minimal degradation of cVOC source mass.

TCE concentrations at the property boundary well MW-102D, approximately 160 feet (50 meters) downgradient from MW-104D, ranged up to 40 μg/L, which exceeded the action level (5 μg/L). The significantly lower TCE concentrations at MW-102D and no detectable daughter products indicated that natural attenuation was occurring along the TCE flow path, but likely via an abiotic mechanism such as hydrodynamic dispersion as opposed to a biotic mechanism. However, the presence of residual source mass at well MW-104D would serve as an ongoing source for cVOC groundwater contamination for perhaps decades. Therefore, the objective of the remediation program was to decrease TCE concentrations in the source area to less than 1,000 μg/L, such that the Site could segue to monitored natural attenuation (MNA) for managing the dissolved-phase plume.

**Remedial Alternatives** - After a review of potential remedial alternatives, typical options such as excavation, in-situ chemical oxidation and pump-and-treat were rejected due to costs and impact on Site operations. An enhanced reductive dechlorination (ERD) remedy was proposed to create an anaerobic treatment zone in the source area to enhance residual TCE source mass destruction. The ERD remediation program was proposed to stimulate native microflora to scavenge the terminal electron acceptors (TEAs) such as oxygen, nitrate, oxidized iron/manganese, and sulfate that can compete for electron donor and limit dechlorination. Also, the electron donor injections would provide an organic carbon source that microflora could ferment to ultimately yield the volatile fatty acids and molecular hydrogen that drive dechlorination. Although additional injections might be required at the Site in the future, the approach did not include a treatment system that could interfere with production activities at the Site. In addition, this green technology is performed *in-situ* without excavation and disposal, or long-term use of power-consuming and carbon dioxide-emitting motors.

To achieve this objective of the remedial program, injection of a proprietary, food-grade additive into the subsurface was proposed through direct-push technology (DPT) that would:

- Increase concentration gradients by degrading dissolved mass, thereby increasing the dissolution rate of the residual source mass;
- Enhance the desorption of the source mass by transforming the parents (TCE and PCE) to less-chlorinated daughters (DCE, VC, ethene), which have significantly lower sorption coefficients; and
- Serve as a co-solvent resulting in increased dissolution of residual source mass, thereby increasing its bioavailability.\(^1\)

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ELECTRON DONOR INJECTIONS
The bioremediation program was initiated in September 2001 to evaluate the effectiveness of an electron donor injection into the hydraulically conductive zones to stimulate ERD in overburden groundwater. The study included DPT injections of electron donor into both hydraulically conductive zones to establish an in-situ anaerobic treatment zone to remediate dissolved- and residual-phase TCE, and perform groundwater monitoring to evaluate ERD performance.

Electron donor borehole injections were performed using DPT. A total of 25 DPT injections were completed using a percussion-hammer method to advance probes, centered on the source area proximate to well MW-104D, in an injection point grid (Figure 1). Each borehole was completed to a depth between approximately 30 to 35 feet (9.1 to 10.7 meters) bgs. Based on the apparent connectivity of the hydraulically conductive zones, the injection spacing generally used an 8- by 8-foot grid within the immediate vicinity of well MW-104D. The electron donor additive was injected under pressure as drilling tools were removed. Approximately 2,600 pounds of the proprietary ERD additive was injected into the formation, averaging nearly 104 pounds of electron donor per borehole. The slurry was generally injected between 18 to 26 feet (5.5 to 7.9 meters) bgs and 30 to 35 feet (9.1 to 10.7 meters) bgs, and included angled borings to inject under the manufacturing building.

REMITATION PROGRAM RESULTS
The post-injection groundwater samples collected from well MW-104D, the source area monitoring well with the greatest historical concentrations, indicated that TCE concentrations decreased from a baseline concentration of 97,400 µg/L to 16,100 µg/L approximately 4 months following the injection program (>80 percent reduction). The dechlorination of dissolved-phase TCE likely created a concentration gradient and acted as a co-solvent, which increased the rate of TCE dissolution from the residual source mass into the groundwater, where it became increasingly more bioavailable for dechlorination. As presented in Figure 2, during the next 4 years the TCE concentrations in MW-104D fluctuated between 11,600 µg/L and 29,800 µg/L as residual DNAPL mass continued to dissolve in groundwater.

The TCE concentrations started significantly decreasing in May 2005 and decreased to less than 500 µg/L by September 2007 and to less than 10 µg/L in May 2010. This concentration was below the targeted remedial goal of 1,000 µg/L and represents a net decrease of approximately 99.99 percent. Significantly, there has been no rebound in TCE concentrations, which is consistent with the successful destruction of a residual DNAPL source mass.

After the September 2001 injections, the cis-1,2-DCE concentrations in MW-104D increased dramatically from a baseline of 300 µg/L to 3,360 µg/L 4 months after the injection program to a peak of 154,000 µg/L approximately 5 years after the injection. The significant three orders of magnitude increase in cis-1,2-DCE concentrations is attributed to TCE dechlorination that yielded the daughter product cis-1,2-DCE.
Given that native microflora tend to preferentially dechlorinate more oxidized parent cVOCs (e.g., TCE) over less oxidized daughter products (e.g., cis-1,2-DCE) during growth-coupled dehalorespiration, the cis-1,2-DCE was being generated more rapidly by the dechlorination of the TCE than the dechlorination rate of cis-1,2-DCE to VC to eventually ethene.

The cis-1,2-DCE concentration data for well MW-104D are also presented on Figure 2 and was 960 µg/L in May 2010, which reflects a greater than 99 percent decrease from the peak concentration. As anticipated, the data indicate that the decrease in dissolved-phase cis-1,2-DCE concentrations did not occur until the dissolved-phase TCE approached non-detect, as this intermediate cVOC (cis-1,2-DCE) was dechlorinated to ultimately yield ethene.

Another daughter product of TCE is 1,1-DCE, which is less common than cis-1,2-DCE. The 1,1-DCE concentrations increased from 41 µg/L prior to injection of the ERD additive to 494 µg/L in November 2005 as the TCE concentrations started to decrease, and a year prior to the peak of the cis-1,2-DCE concentrations. The 1,1-DCE concentration continued to decrease and was less than 10 µg/L in May 2010.

VC, which is the byproduct of cis-1,2-DCE and 1,1-DCE dechlorination prior to ethene formation, was detected at a baseline concentration of 34 µg/L in well MW-104D prior to the September 2001 injection. The analytical results since then did not report detectable VC concentrations, except for a concentration of 50 µg/L in December 2004 and 180 µg/L in May 2010. VC was suspected to be present in the

Figure 2. Groundwater Concentrations (µg/L) in MW-104D.
groundwater at well MW-104D, however, the detection limit during the first 8 years was generally greater than 300 µg/L and may have masked actual concentrations.

The increase in \(\text{cis}-1,2\text{-DCE}\) and ethene concentrations during this period with only occasional detection of VC indicated that ERD was reducing TCE to \(\text{cis}-1,2\text{-DCE}\) with the majority of generated VC being rapidly reduced completely to ethene and/or carbon dioxide, which is highly favorable from a regulatory standpoint. It should be noted that short-term increases in VC have been observed at other ERD sites that have used this additive, but do decrease rapidly after the removal of cVOC source mass.

In May 2010, the groundwater concentrations in the former source area well MW-104D were all less than the reporting limit (generally less than 10 µg/L) except for \(\text{cis}-1,2\text{-DCE}\) (960 µg/L) and VC (180 µg/L). Total cVOC concentrations since the injection decreased almost 99 percent from 97,818 µg/L to 1,140 µg/L, with a continuing decreasing trend and no detectable TCE.

The injection program influenced monitoring well MW-104S, which is screened in the shallow impacted zone proximate to the source area. The TCE and \(\text{cis}-1,2\text{-DCE}\) concentrations prior to the injection in September 2001 were reported at 60 µg/L and 104 µg/L and increased to 129 µg/L and 257 µg/L by November 2002, respectively. The TCE concentrations fluctuated and have been non-detected since November 2005. The \(\text{cis}-1,2\text{-DCE}\) concentrations fluctuated with concentrations ranging as great as 1,500 µg/L in September 2007. COCs have not been detected in well MW-104S at concentrations greater than the analytical reporting limits (generally <2 µg/L) since May 2009.

The TCE concentrations at downgradient monitoring well MW-102D did increase as the TCE source was initially mobilized into the formation, which is attributed to additive injection. The TCE concentration increased from a baseline of 40 µg/L to a peak concentration of 828 µg/L in November 2005, then decreased to less than 2 µg/L in November 2008 and has remained minimal (≤ 16 µg/L) since then. The localized increase in \(\text{cis}-1,2\text{-DCE}\) concentrations at the source area (154,000 µg/L in MW-104D in November 2006) generally attenuated as groundwater flowed towards the property boundary. The \(\text{cis}-1,2\text{-DCE}\) concentrations at MW-102D essentially remained non-detect, except for a detection of 38 µg/L in September 2007 (about half the 70 µg/L action level), with concentrations remaining less than 2 µg/L since that time.

The desorption and destruction of residual TCE source mass near MW-104D, as demonstrated by the increased \(\text{cis}-1,2\text{-DCE}\) concentrations, is further supported by the increase in ethene concentrations. Ethene is a dechlorination product of chlorinated alkenes under anaerobic, chemically reducing conditions. Figure 2 indicates that the ethene concentrations increased approximately two orders of magnitude during the 4 years after the injection program, which supports the conclusion that the ERD resulted in the complete dechlorination of TCE to ethene at the Site. Figure 2 also shows that
the TCE remained stable initially for 4 years during source mass desorption, while the
\textit{cis}-1,2-DCE concentrations increased. As noted earlier, the dechlorination of TCE to
\textit{cis}-1,2-DCE was occurring at a greater rate than the dechlorination of \textit{cis}-1,2-DCE to
ethene, which explains why the concentrations of both \textit{cis}-1,2-DCE and ethene
increased during TCE mass desorption and dechlorination, until the TCE mass was
removed, allowing the \textit{cis}-1,2-DCE concentration to decrease.

Reductive dechlorination was also verified by the increase in chloride concentrations
in groundwater from well MW-104D from 27 milligrams per liter (mg/L) prior to the
injection program to a peak concentration of 120 mg/L in November 2006, which
coincides with the peak of the \textit{cis}-1,2-DCE concentration and 1 year after the apparent
removal of the DNAPL source area. As the mass of dissolved- and residual-phase
cVOCs decreased, the chloride concentrations in the source area have decreased and
have been less than the baseline concentration since November 2009. However, the
chloride concentrations in the downgradient well MW-102D increased from a
baseline of 27 mg/L to 120 mg/L by November 2006 and were 21 mg/L in May 2010.
The increase in downgradient chloride concentrations following the ERD injection
program likely reflect the migration of chloride ultimately yielded from cVOC
dechlorination during the first several years of the ERD program. As anticipated, the
downgradient chloride concentration has decreased due to reduced dechlorination
activity currently occurring in the former source area following removal of DNAPL
source mass.

\textbf{PROOF-OF-CONCEPT EVALUATION TEST}

\textbf{Background} - The primary purpose of A Proof-of-Concept test is to provide a ‘Go,
No-Go’ evaluation process under the actual groundwater geochemistry in which full-
site remediation is anticipated. Such studies provide stakeholders, Regulatory
Agencies, and Remedial Practitioners a level of assurance for success; creating
minimal overall impact to Site conditions. They are performed \textit{in-situ} using a
proprietary Passive Release Sock (PRS) technology and provide a representative but
conservative measure of the additive’s efficacy under actual Site conditions in a cost-
effective manner. PRSs are constructed of filter fabric material, sealed at each end to
contain the remedial additive and clean filter sand, which provides negative ballast to
sink them in the water column during deployment.

\textbf{Proof-of-Concept Test} - During an investigation at a manufacturing facility in New
Jersey, a vapor intrusion issue was detected in an office building. Air sampling
detected TCE and PCE in the indoor air at concentrations exceeding action levels.
The source of these cVOCs was attributed to cVOC groundwater impacts at other
portions of the site that may have migrated via the shallow utility pipe bedding that
runs under the building.

After installing a vapor intrusion abatement system, remedial options were evaluated
to address the long-term groundwater quality and vapor intrusion issues at the site,
which determined that remediating the cVOCs in the groundwater through ERD could
be the more cost-effective remedial alternative. PRSs filled with a proprietary ERD additive were deployed in an impacted monitoring well. Due to the limited area of influence of each PRS, groundwater monitoring and sampling were performed using non-purge techniques. Purging of the monitoring well could remove the majority of groundwater and microbial population affected by PRS deployment, adversely affecting rates of contaminant destruction and potentially skewing performance results to yield unrepresentative results.

Two 5-foot-long PRSs were deployed to span the 10-foot-long screen interval of the well. Groundwater samples were collected after 3, 6, and 12 weeks, with the spent PRSs replaced after week 6. Note that the additive was depleted from the PRSs when they were inspected during week 12, which resulted in the dramatic decrease of reductive dechlorination activity, as noted below.

**Proof-of-Concept Test Results** - The groundwater results from the test well are presented on Table 1. Based on the groundwater data collected during the Proof-of-Concept test, it was determined that the additive achieved successful destruction of dissolved-phase cVOCs at the site. The conclusions from review of the data include:

- The total organic carbon (TOC) increased significantly after the PRSs were deployed in the well, but returned to approximately baseline concentrations by week 12, reflecting complete utilization of the additive. Notably, the final TOC concentration was even less than baseline (13.3 vs. 8.9 mg/L) suggesting that the population density of the indigenous soil bacteria initially increased due to PRS deployment and consumed the available TOC from the additive, as well as naturally-occurring organic carbon from the formation.

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- The concentrations of PCE and TCE decreased by 96 and 98 percent respectively during the first 6 weeks of the test, and then nearly rebounded to
their baseline values after the additive was depleted and proximal untreated groundwater migrated into the screened interval of the monitoring well. The concentrations of DCE initially decreased after 3 weeks and then rebounded to approximately baseline concentrations by week 6. The rebound is suspected to be the result of a reduction of the driving force to dechlorinate the DCE (i.e., the organic carbon provided by the ERD additive was starting to become depleted).

- The concentrations of VC increased over 1,000 percent after 3 weeks as the DCE was dechlorinated to VC and the ethene concentrations increased over 40,000 percent in 3 weeks. Because ethene exists only as a gas at standard temperatures and pressures, its generation is attributed to VC dechlorination. The ethene concentrations decreased by one order of magnitude between weeks 3 and 6, which is suspected to be the result of the ERD additive starting to become depleted and the ERD process slowing down. Ethene concentrations returned to baseline concentrations by week 12 when the additive was completely depleted and dehalorespiration shut down.

- The generation of ethene and reduction in VC concentrations demonstrated that the site contains the genus of dechlorinating bacteria *dehalococcoides*, which is required to completely dechlorinate these cVOCs to ethene. This verification is a key reason to perform a Proof-of-Concept test.

- The molar ratio of parent (TCE + PCE) to total cVOCs decreased from a baseline of 30.9 percent to 1.3 percent during the first 6 weeks of PRS deployment and then rebounded to 29.7 percent when the ERD additive was depleted. The dramatic reduction in molar ratio during the first 6 weeks confirms the success of the Proof-of-Concept test. This success is further supported by the rebound to baseline conditions when the additive was depleted and untreated groundwater flowed back into the well.

Based on Proof-of-Concept test results, the client is moving towards a full-scale ERD remedy to address the cVOC-impacted groundwater and the resulting vapor intrusion issue. This technology will provide a sustainable and cost-effective remediation with a smaller carbon footprint than conventional remedial alternatives. In addition, it will be less disruptive to their operations while remediating beneath their manufacturing areas.

**SUMMARY**

As demonstrated by the single injection in New Hampshire, the proprietary ERD additive was able to destroy a TCE DNAPL source mass and decrease TCE concentrations from approximately 97,400 µg/L to less than 10 µg/L (99.99 percent reduction). Total cVOC concentrations were approximately 1,140 µg/L in May 2010, with a continuing decreasing temporal trend. MNA can now be implemented at this Site as the concentrations approach action levels and meet them at the property...
boundary. This green technology did not contribute to greenhouse gas emissions after the initial injection and was able to utilize off-spec material that would have been otherwise landfilled. The project provided a cost-effective solution to the DNAPL source, while not impacting Site operations after initial additive injection.

The Proof-of-Concept test discussed was able to demonstrate the effectiveness of the ERD additive (ERD\textsubscript{ENHANCED} from Plant Products Company Ltd.) in an economical manner and quickly provide the data needed to justify full-scale remediation. Both of these case studies demonstrate how this green-technology is effective at remediating cVOC-impacted groundwater systems and why ERD remediation is anticipated to become more prominent as a primary remediation technology.

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