

## **Innovative Treatment of Chlorinated Solvents using In-Situ Reductive Dechlorination Synergistic Technologies**

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**ABSTRACT:** Green and sustainable remediation techniques were implemented to reduce the concentration of various chlorinated solvents from a site located in Bedminster, NJ that had soil and groundwater impacted by the use of drycleaning agents; tetrachloroethene (PCE) and trichloroethene (TCE).

Enhanced biological reductive dechlorination injections were performed, in conjuncture with micron-scale zero valent iron (ZVI), in order to treat the chlorinated volatile organic compounds (CVOCs). A combination of injection techniques and novel soluble organic hydrogen donors such as hydrolzed kelp, were utilized to treat the site. The remedial event was designed to reduce contamination concentrations in the targeted monitoring wells, as well as promote anaerobic conditions in the groundwater favorable to anaerobic bacteria that degrade CVOCs such as PCE and dichlorobenzene. The remedial design included the injection of a solution of nutrients, sodium sulfite, calcium propionate and soluble kelp, ZVI suspension, Vitamins B-2, B-12, EHC<sup>®</sup> and liquid hydrogen release compound (HRC).

The remedial design was implemented by Innovative Environmental Technologies, Inc. in January and February 2011. The concentrations of CVOCs showed significant decreases up to 99%, with PCE and TCE decreasing below the laboratory detection limit, and little to no daughter product formation.

### **INTRODUCTION**

Chlorinated solvents are one of the most frequently occurring types of contaminants in soil and groundwater at Superfund and other hazardous waste sites in the United States. They are organic compounds that contain chlorine atoms, and their properties make them ideal for many industrial-cleaning applications such as degreasing oils and fats. Common solvents include Tetrachloroethene (PCE) and Trichloroethene (TCE), used extensively in the dry-cleaning industry; 1,1,1 - Trichloroethane (TCA) and methylene chloride are commonly used as industrial degreasers.

Chlorinated solvents, when released into the subsurface will tend to sink through the saturated zone as they are denser than water. As a result small droplets (ganglia) get trapped in the soil 'pore-space' as a Non-Aqueous Phase Liquid (NAPL), which can act as a long-term source of dissolved phase contamination. These NAPL source zones can hamper any site remediation effort, as they are difficult to treat and detect.

Anaerobic reductive dechlorination is one treatment process that has been successfully used to remediate soil and groundwater contaminated with chlorinated solvents. The occurrence of different types and concentrations of electron donors such as native organic matter, and electron acceptors such as oxygen and chlorinated solvents, determines to a large degree the extent to which reductive dechlorination occurs during the natural attenuation of a site.

Reductive dechlorination only occurs in the absence of oxygen; and the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the

process. Remedial treatment technologies usually introduce an oxygen scavenger to the subsurface in order to ensure that this process would occur immediately.

Anaerobic conditions occur when anaerobic bacteria use the chlorinated contaminant as the electron donor and, in most instances, allow the microorganism to derive useful amounts of energy from the reaction. It has been shown that vinyl chloride (VC) can be oxidized to carbon dioxide, water, and chloride ion via Fe (III) reduction. Significant anaerobic mineralization of Dichloroethene (DCE), VC, and methylene chloride also has been reported in the literature.

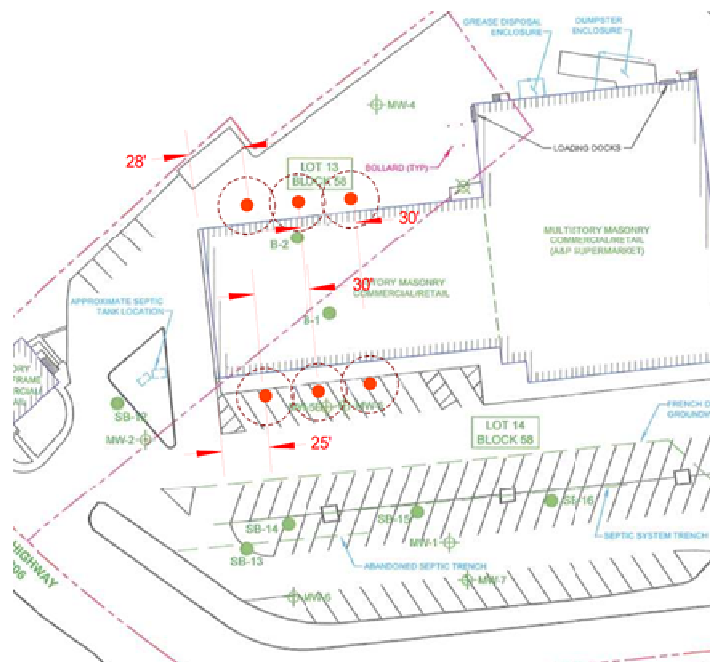
Halorespiration is a type of anaerobic respiration in which a chlorinated compound is used as a terminal electron acceptor. In this reductive dechlorination process, which enables the conservation of energy via electron transport phosphorylation, one or more chlorine atoms are removed and replaced by hydrogen. Halorespiration, also referred to as dehalorespiration, occurs when the organic compound acts as an electron acceptor (primary growth substrate) during reductive dechlorination. During dehalorespiration, the chlorinated organic compounds are used directly by microorganisms (termed dehalorespirators), such as an electron acceptor while dissolved hydrogen serves as an electron donor. It requires not only the presence of competent microorganisms, but also the appropriate quantity and quality of electron donors, which serve as the driving force for dehalorespiration. A variety of electron donors have been shown to sustain reductive dechlorination, however only recently, it has been recognized that dissolved hydrogen is the actual electron donor in dehalorespiration (Wang, 2000).

Dehalorespiration occurs as a two-step process which results in the interspecies hydrogen transfer by two distinct strains of bacteria. In the first step, bacteria ferment organic compounds to produce hydrogen. During primary or secondary fermentation, the organic compounds are transformed to compounds such as acetate, water, carbon dioxide, and dissolved hydrogen. Fermentation substrates are either biodegradable nonchlorinated contaminants, or naturally occurring organic carbon. In the second step, the nonfermenting microbial consortia utilize the hydrogen produced by fermentation for dehalorespiration. Although compounds produced during fermentation have been demonstrated to drive dehalorespiration, hydrogen appears to be the most important electron donor for this process.

Dehalorespiration is targeting the addition of sufficient substrate in order to establish and maintain anaerobic conditions, conducive to reductive dechlorination for a period of time, and sufficient to degrade all constituents of concern and their daughter products. Common substrates used include acetate, propionate, butyrate, benzoate, glucose, lactate, formate, methanol, toluene, molasses, cheese whey, corn steep liquor, corn oil, hydrogenated cottonseed oil beads, solid food shortening, beef tallow, melted corn oil margarine, coconut oil, soybean oil, and hydrogenated soybean. These compounds serve as the precursors to dissolved hydrogen generation via fermentation. Obligate proton reducers are required to ferment organic substrate present in the subsurface environment to waste products of acetate, formate, dissolved hydrogen, and carbon dioxide (Zehnder, 1988). After fermentation, dissolved hydrogen becomes available for subsequent use by other microorganisms, such as methanogens and dehalorespirators. This syntrophic relationship of hydrogen producers and consumers is known as interspecies hydrogen transfer. Dehalorespiration relies on the presence of fermentable organic substrates that produce dissolved hydrogen. In addition to the quality of an electron donor, the quantity needs to be addressed as well. Since the dissolved hydrogen produced from the fermentation of organic substrates can be used by a variety of microorganisms (e.g. methanogens and dehalorespirators), it is important to consider the competition for dissolved hydrogen when assessing the potential for dehalorespiration (Gossett and Zinder, 1997).

**Site Description and Treatment Areas.** The green and sustainable remediation technique that was implemented in order to reduce the concentration of various chlorinated solvents was tested in three different sites.

The site was the former Martha's Cleaners, located in Bedminster, New Jersey, which had soil and groundwater impacted by the use of drycleaning agents; PCE, 1,1-DCE, and chlorobenzene. The injection program was initiated on January 7th and 10th, 2011. Although the majority of the shallow injections could be accomplished under the normally operating equipment pressures, the deep injection wells presented challenges for the injection equipment at the operating pressures. Therefore the injection program was completed utilizing pneumatic fracturing equipment on February 24th and 25th. The treatment of groundwater located underneath the Former Martha's Cleaners site was addressed using three sets of permanent injections wells that were installed on the site prior to remedial activities. The injection event encompassed 2,115 square feet and treated vertical contamination from 20 to 35 feet below ground surface (bgs) and 50 to 60 feet bgs.



**Figure 1.** Site map and injection points in Bedminster, NJ.

## **MATERIALS AND METHODS**

Reductive dechlorination was the treatment process that was followed at the site. The injection mixture consisted of a solution of nutrients, sodium sulfite, calcium propionate and soluble kelp, zero-valent iron (ZVI) suspension, Vitamins B-2, B-12, EHC<sup>®</sup> and liquid hydrogen release compound (HRC<sup>®</sup>). The proposed remedial plan incorporates a variety of organic hydrogen donors; each of which has been selected and dosed based on the hydrogen release profile of the individual compounds. Slowly fermented substrates producing lower hydrogen (H<sub>2</sub>) levels are more effective and persistent "selective" stimulators of dechlorination than rapidly fermented substrates producing higher H<sub>2</sub> levels. Maintaining and extended a low hydrogen release profile as a result of a single injection event is the main target of this program. The mixed

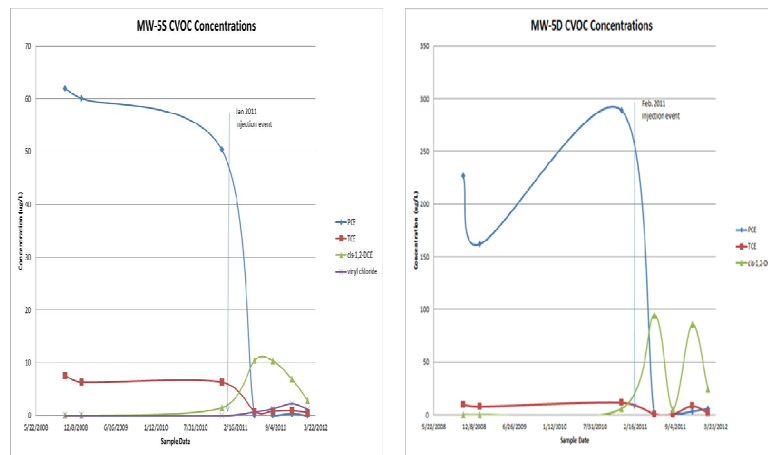
organic hydrogen donors promote this condition, utilizing various concentrations of the substrates based on loading and the individual injection areas.

## RESULTS AND DISCUSSION

The remedial event in Bedminster, NJ, was designed to reduce contamination concentrations in the targeted monitoring wells, MW-5S and MW-5D, as well as promote anaerobic conditions in the groundwater favorable to anaerobic bacteria that degrade CVOCs. The data received upon the completion of the injection event is presented below.

**MW-5S.** Monitoring well MW-5S is located in the front of the building treatment area. Based on the November 2011 sampling event results, MW-5S was strongly affected by the shallow injection event. The remedial event created a more reducing environment conducive for anaerobic bacteria and reduced CVOC concentrations by 82%. The concentrations of PCE and TCE, which were above the GWQS's (Groundwater Quality Standards) during the January 2009 pre-injection sampling event decreased by 99% and 90% respectively, while the concentration of cis-1,2-DCE remained below the GWQS.

**MW-5D.** Monitoring well MW-5D is also located in the front of the building treatment area. In MW-5D, the concentrations of PCE and TCE decreased by 98% and 85% respectively, while the total CVOC concentrations decreased by 58% compared to the pre-injection sampling event of January 2009. Figure 1 shows the changes in CVOC concentrations in both monitoring wells of site in Bedminster, NJ.



**Figure 1.** CVOC Concentrations in the two monitoring wells on Site 1.

## CONCLUSIONS

The technology presented above is a cost-effective and reliable technology to treat chlorinated hydrocarbon contaminants such as tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and vinyl chloride in groundwater.

The initial metabolism of chlorinated solvents in ground water involved a biochemical process described as sequential reductive dechlorination. The use of different types of electron donors successfully enhanced the effectiveness of reductive dechlorination, which occurs during the natural attenuation of a site. To facilitate, enhance and accelerate the natural processes, ZVI in conjunction positively affected and accelerated the microbial dechlorination processes. The use of the integrated coenzymes along with the presence of the organic hydrogen sources, the oxygen scavengers and the nutrients, assured that the biotic portion of the remedial program was efficient and rapid while successfully leading to the significant decrease in the concentrations of all chlorinated solvents in all three sites.

## **REFERENCES**

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