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Understanding – and Treating- Chlorinated Ethanes and 1,1,1-Trichloroethane

In this edition of Peroxygen Talk, guest authors Michael Marley and Dr. Brant Smith of XDD discuss a problematic class of contaminants, chlorinated ethanes, and in particular 1,1,1-TCA, and how to treat them. Mr. Marley is the co-founder and president of XDD and has over 29 years of experience in environmental and civil engineering. He has been at the forefront of developing design and application protocols for SVE, air sparging and ISCO technologies. Dr. Smith has over 12 years of specialization in water chemistry and hazardous waste remediation. He received his PhD in civil engineering from Washington State University under Prof. Rick Watts, and now directs XDD's treatability laboratory. XDD (www.xdd-llc.com) is an environmental engineering and consulting firm specializing in soil and groundwater remediation, site exit strategy development, remedial alternative analysis, regulatory negotiation, lab and field pilot testing, and full-scale implantation. Mr. Marley and Dr. Smith can be reached at marley@xdd-llc.com and smith@xdd-llc.com, respectively.

Chlorinated ethenes and chlorinated ethanes: what a difference a vowel can make. The treatment of chlorinated ethenes, such as trichloroethylene (TCE) or perchloroethylene (PCE), has become somewhat commonplace as such contaminants are known to be reactive with a wide variety of in-situ treatment technologies including in-situ chemical oxidation (ISCO), in-situ chemical reduction and anaerobic bioremediation. However, the treatment of chlorinated ethanes has proven to not be as easy.

A key difference in treatment hinges on how the carbon molecules are bonded. The carbon atoms in chlorinated ethenes are connected with a double bond while the carbon atoms in chlorinated ethanes are connected with a single bond. Both single and double bonds include a sigma bond, but the double bonded chlorinated ethenes contain a second bond – the pi bond – which is more accessible to transformation than the sigma bond.

Chlorinated ethanes have been used primarily as organic solvents in the role of cleaners and degreasers but they are also used as industrial intermediates, aerosols and even as anesthetics. Common with any cleaning solvent, chlorinated ethanes are usually found in the presence of the chemicals they were used to clean or co-solvents that were added to enhance specific properties. Compounds typically found with chlorinated ethanes include 1,4-dioxane, TCE, PCE, PCBs and various hydrocarbons similar to kerosene and diesel fuel.

1,1,1-Trichloroethane (TCA) is a common chlorinated ethane. It was introduced in the 1950's as a replacement for industrial cleaning solvents such as carbon tetrachloride, but it has also been used in paints, adhesives, and in aerosols. While the production of TCA for domestic use has been banned in the United States since 2002, TCA is now found at approximately 50 percent of all National Priorities List (NPL) sites identified by the EPA.

Current research indicates that TCA can adversely affect the liver, circulatory and nervous systems. (There is no evidence to suggest that TCA is a carcinogen.) However, the primary impact of TCA may be to the environment. TCA can persist in the atmosphere for years and its atmospheric breakdown products can contribute to the depletion of the ozone layer.

The following characteristics can be used to better understand the potential fate, transport and treatment options for TCA in the subsurface environment:

- Water solubility (657 mg/L) is lower than TCE (1,312 mg/L) and several other chloroethanes (5,060 mg/L for 1,1-dichloroethane). Thus, if a significant amount of mass is present at a site, it is likely in a non-aqueous phase (either as a NAPL or on soil) which can be more difficult to treat.

- TCA is denser than water (specific gravity of 1.34) meaning that if present in pure liquid phase it will sink to the bottom of aquifers (i.e., dense non-aqueous phase liquid or DNAPL);
- TCA has a partitioning coefficient of log K_{ow} of 2.33 (same as TCE) indicating that it would prefer to partition onto organic matter rather than stay in water, making it more difficult to treat; and,
- The potential for biodegradation varies depending upon the conditions, but the data seem to suggest a very low likelihood of reactivity under aerobic conditions and slow rates of reaction under highly reductive/anaerobic conditions. Further, when TCA is biotically reduced, it breaks down into products such as 1,1-dichloroethane and chloroethane. Natural abiotic reduction (e.g., reactions with reduced metals in the environment) can also form additional products including 1,1-dichloroethene and vinyl chloride.

When these characteristics are considered, TCA is a potential DNAPL that faces significant remedial challenges, and if left untreated, it could form additional compounds that have the potential to be more problematic.

XDD, a New Hampshire-based environmental consulting firm specializing in remediation, has recently had great success in treating 1,1,1-trichloroethane (TCA) with a pair of ISCO technologies. Catalyzed hydrogen peroxide (CHP or Fenton's reagent) and alkaline activated persulfate (AP) have been applied in full-scale applications at separate sites by XDD after first evaluating the technologies and tailoring the chemistry to suit site specific concerns in a bench scale evaluations. The treatment with ISCO has been successful enough that the site treated with two applications of AP and significant portions of the site treated with a single application of CHP have both met their remedial goals.

At a site with TCA DNAPL, the results have shown greater than 80 percent reduction in average TCA groundwater concentration after a single application of CHP. The reduction of TCA in the DNAPL and soil phases has been enough (up to 99 percent reduction) that much of the areas targeted in these applications are now below the remedial goals. Results from application of AP at another TCA site have shown TCA reductions of up to 99.9 percent, with the final TCA concentrations mostly in the low $\mu\text{g/L}$ range, which readily achieves the remedial goals for the site.

CHP and AP are ISCO technologies with different characteristics that will allow XDD the opportunity to consider and select which technology is most appropriate for any particular site. For example, the greater typical subsurface persistence and lower evolution of gas and heat will favor the application of AP at sites with contamination under buildings. However, where there is more oxidizing potential in a pound for pound comparison, the application of hydrogen peroxide maybe be favored at DNAPL sites.