

Remediation of 1,1,1-Trichloroethane via Sequential Thermally Enhanced Hydrolysis and In Situ Chemical Oxidation

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ABSTRACT: Multiple areas of 1,1,1-trichloroethane (TCA) contamination were encountered during investigations at a former aerospace manufacturing plant. In one area, leaks from a former degreaser pit resulted in TCA concentrations exceeding 1% of its aqueous solubility (13,300 micrograms per liter [$\mu\text{g/L}$]). Dense nonaqueous-phase liquid (DNAPL) also was present in the source zone. The objective of the remedial effort was to reduce contaminant concentrations in the source zone to below the 1% TCA solubility value. After extensive laboratory treatability testing, the selected remedy for the site included heating of the saturated zone in the source area to enhance TCA removal via hydrolysis, followed by the injection of sodium persulfate to oxidize remaining dissolved-phase TCA and hydrolysis byproducts. Remedial investigations were conducted to develop the remedial design basis for the project necessary to achieve the site's remedial objectives. A greater understanding of the hydrolysis reaction rates and by-product formation; oxidation rates at varying temperatures; and remedial time frame estimates also were explored.

INTRODUCTION

The site was a vacant industrial building formerly used to manufacture aerospace components. Multiple environmental units (EUs) were present beneath the facility that required remediation. Below the slab, the geology consists of fill material and sands to a depth of approximately 15 feet, where a clayey silt confining unit was encountered. Groundwater is encountered at approximately 10 feet and has relatively low velocity. In one particular area, TCA was present at concentrations above saturation and solubility limits. The remedial objective (as agreed to by state regulating agency) was to reduce volatile organic compound (VOC) concentrations to less than 1% of the aqueous solubility of TCA (13,300 $\mu\text{g/L}$). The impacted volume was fairly small, consisting of only 5 feet of saturated thickness and less than 1,000 square feet requiring remediation.

Bench-Scale Laboratory Testing. Bench-scale laboratory testing was conducted to evaluate the use of in situ chemical oxidation (ISCO) to remediate TCA. Specifically, the bench-scale testing was designed to identify the most effective activator, activator strength, and oxidant strength for the selected oxidant, sodium persulfate. The first round of bench testing attempted alkaline activation at two different concentrations of sodium persulfate (5 and 10 grams per liter [g/L]). Sodium hydroxide was used to raise the pH to approximately 11.0. As shown in Figure 1, alkaline activation proved ineffective, only marginally reducing TCA concentrations as compared to the control sample.

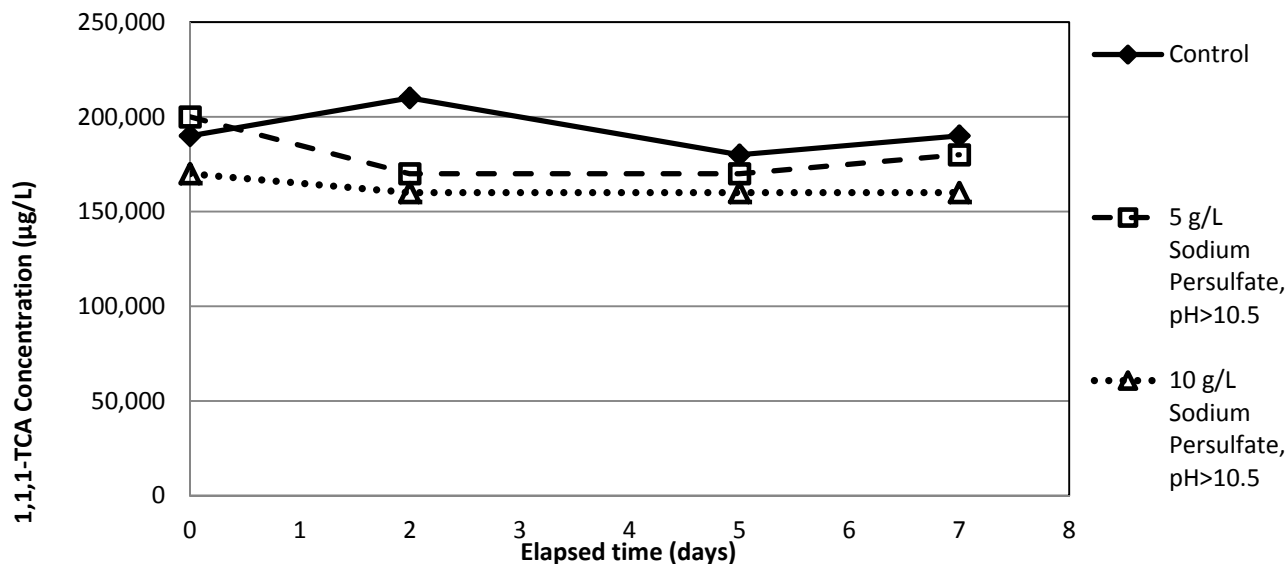


FIGURE 1. Phase I bench-scale results for alkaline activated sodium persulfate.

A second phase of laboratory testing was conducted to compare multiple activation methods, including heat (45°C), chelated iron (using citric acid with ferrous sulfate and ferric citrate), and hydrogen peroxide at an oxidant strength of 40 g/L, a higher oxidant concentration than was tested in first phase. Results are shown in Figure 2.

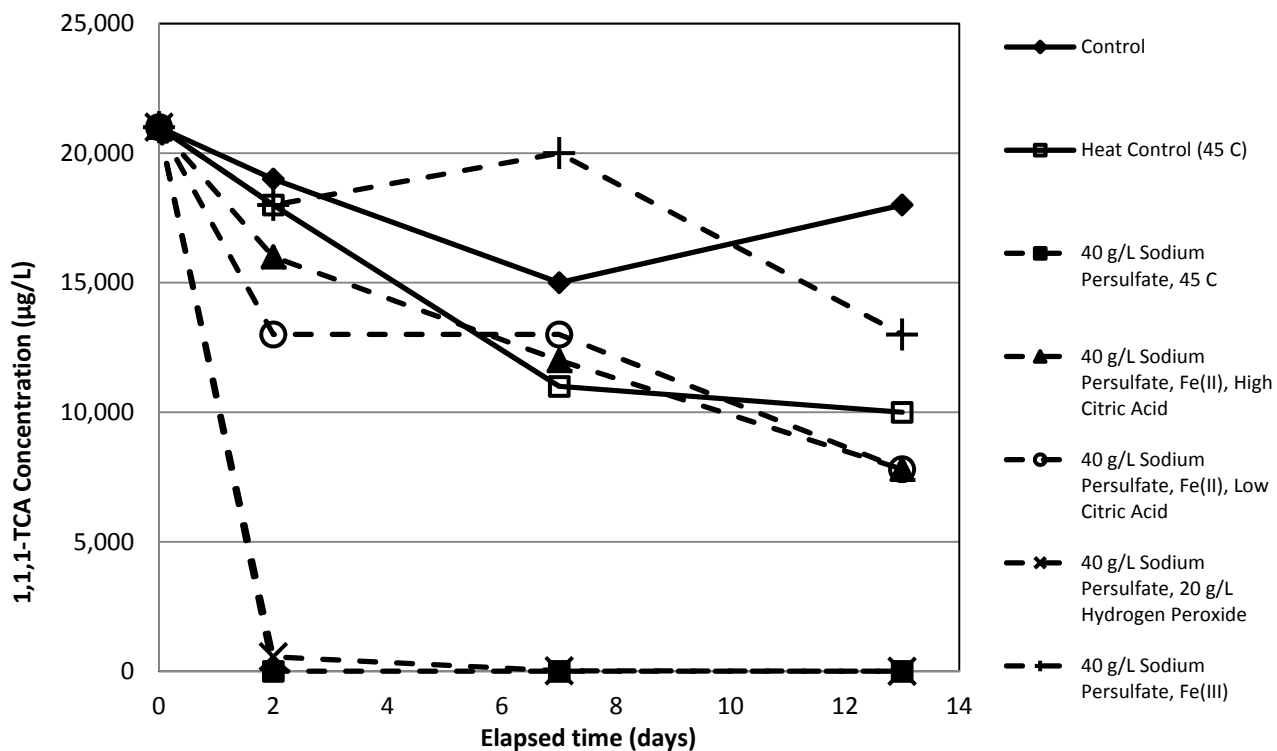
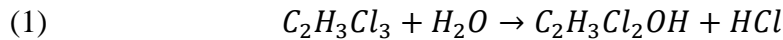


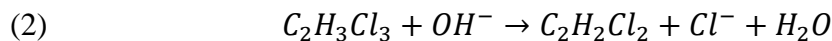
FIGURE 2. Phase II treatability results for various activators.

The second phase of bench-scale testing showed a nearly 50% reduction in TCA concentration by the heat control sample alone (due to hydrolysis) over the 13-day test period. Ferrous iron activated persulfate using high oxidant strength was moderately successful. Heat and hydrogen peroxide activation both resulted in a 100% reduction of TCA; however, in the hydrogen peroxide activated sample volatilization was shown to be the mechanism for the removal of TCA. As the treatability studies progressed, additional Site investigation confirmed that DNAPL was visibly present at the site over an area of approximately 337 square feet. Based on the confirmed presence of DNAPL, ISCO as a sole remedy was ruled out. However, the treatability study did indicate that reduction of TCA concentrations due to hydrolysis by heat offered success over the 13-day test and it was predicted that a sustained heat application at higher temperature would enhance the effectiveness as well as promote dissolution of DNAPL.

Hydrolysis. Hydrolysis is defined as a chemical reaction with water in which a dissolved compound is degraded by reaction with a hydrogen ion (H^+) or the hydroxyl ion (OH^-) (Washington, 1995). These reactions can be further defined as two separate pathways that can occur simultaneously: nucleophilic substitution (hydrolysis reaction) or elimination (dehydrohalogenation reaction). The hydrolysis reaction proceeds by the substitution of the halide atom with a hydroxyl anion. The resulting alcohol is generally more soluble and more susceptible to biodegradation. Equation 1 shows the hydrolysis reaction of TCA to produce 2-chloropropanol, which further degrades to acetic acid.



Dehydrohalogenation proceeds by the removal of the halogen from a carbon atom, with subsequent removal of a hydrogen from a neighboring carbon atom. As a result of the elimination of the halogen and hydrogen, a double bond is formed between the participating carbon atoms. For TCA, the dehydrohalogenation reaction produces 1,1-dichloroethene (1,1-DCE), as shown in Equation 2.



End products were summarized by Mabey and Mill (1978), and include a mixture of the newly formed alcohol and the chlorinated ethene for the examples given above. The dominant pathway of the hydrolysis and dehydrohalogenation reactions depends mostly on the pH of the groundwater. Scheutz et al. (2011) notes that hydrolysis and dehydrohalogenation reactions of TCA will yield approximately 80% acetic acid and 20% 1,1-DCE. Generally speaking, the lesser chlorinated reaction products are less toxic than the parent compounds, but may still require a polishing step.

Half lives for hydrolysis and dehydrohalogenation reactions can be determined using the Arrhenius equation in Equation 3:

$$(3) \quad K_{obs} = A \exp\left(-E_A/RT\right)$$

Where A is the pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the temperature (degrees Kelvin). Washington (1995) and Jeffers et al. (1989 and 1996) reported Arrhenius constants for common VOCs, resulting in a wide range of half lives. Considering various chlorinated VOCs, the half lives at typical groundwater conditions ($\sim 20^\circ\text{C}$) ranged from less than 1 year for 1,1,2,2-tetrachloroethane (1,1,2,2-TCA) and pentachloroethane (PCA) to greater than 1 million years for 1,2-dichloroethene (1,2-DCE), tetrachloroethene (PCE), 1,1-DCE, and trichloroethene (TCE) (Figure 3) confirming that the halogenated ethenes are recalcitrant with respect to hydrolysis reactions. The fastest reaction rate (shortest half life) achieved for TCE at 95°C ; for example, only attains $\sim 28,000$ days (76 years), indicating limited remedial effectiveness. In comparison, half lives for many of the chlorinated alkanes can be decreased to months or even days with just moderate heating (40°C to 80°C range).

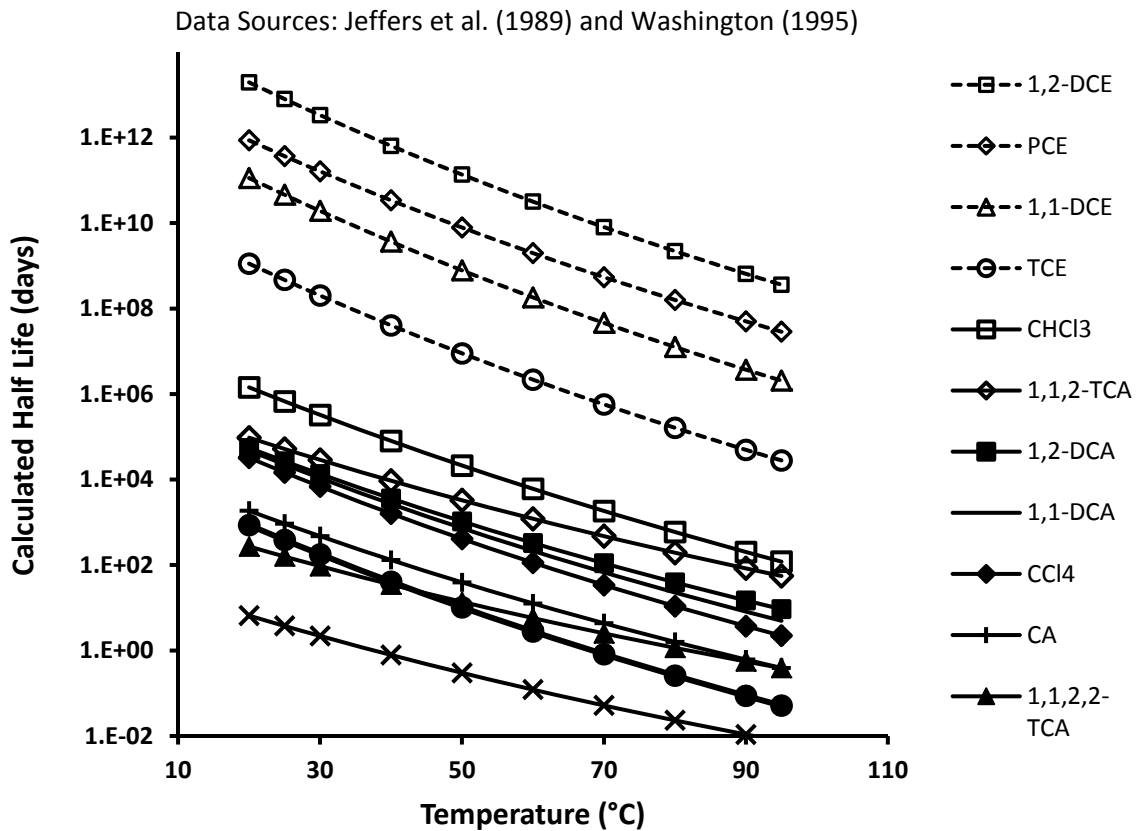


FIGURE 3. Rate constant versus temperature for various chlorinated ethanes and ethenes.

MATERIALS AND METHODS

Based on bench testing results and the visible presence of DNAPL, the selected remedial approach was thermally enhanced hydrolysis to treat source concentrations of TCA and promote the dissolution of DNAPL, followed by a heat activated sodium

persulfate injection to oxidize dissolved phase TCA and TCA hydrolysis byproducts such as 1,1-DCE and acetic acid.

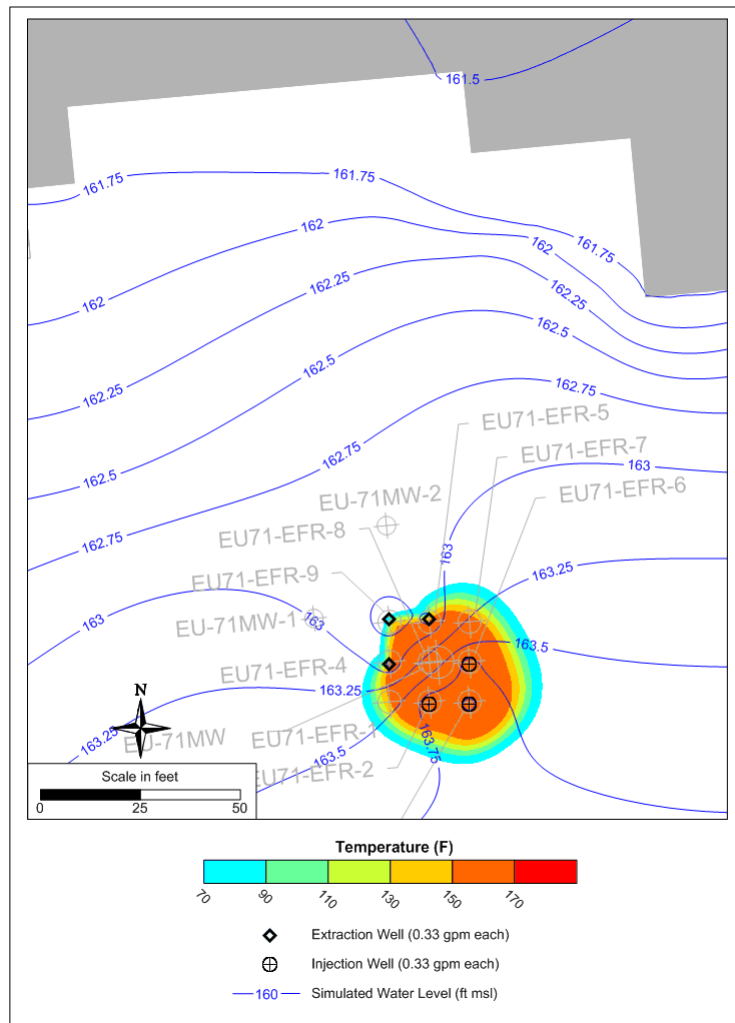


FIGURE 4. Simulated potentiometric surface and temperature distribution after 30 days of heating.

Prior to implementing hydrolysis at the Site, a groundwater flow and thermal transport model was developed using the SWIFT (Reeves 1985) groundwater simulator. In addition to hydraulic parameters used in the flow model, thermal parameters such as thermal conductivity (2.2×10^{-3} Joules second⁻¹ centimeters⁻¹ °K⁻¹) and average background temperature (17°C) were also defined. The resulting model simulated the aquifer conditions within the upper 1.7 meters of saturated aquifer thickness, as shown on Figure 4. The model was set up with three separate layers to simulate flow and thermal transport in the fine to medium-grained sand. The model confirmed that advective heating would be the dominant heat transport mechanism within the aquifer, but that conductive heat transport would also play an important role in expanding heat into the underlying lower

Hydrolysis Application. In situ heating was accomplished by circulating extracted groundwater through a tank-less hot water heater then reinjecting the heated water into the source area. The target temperature rise was 70°C in groundwater. At this temperature, TCA auto decomposes at a half life less than one day, according to the Arrhenius equation. The hydrolysis system was started on November 10, 2010 and was operated for 152 days. For the first 75 days of operation, the system maintained a groundwater recirculation flow rate of approximately 1.5 gallons per minute (gpm). After 75 days of operation, the groundwater recirculation rate was increased to approximately 3 gpm.

ISCO Injection. At the end of the operational period of the hydrolysis system, the site was allowed to cool for approximately 30 days until the temperature was under 40°C before a single injection of sodium persulfate was conducted in the source area. The injection utilized the remaining heat for activation of the persulfate anion to form the

sulfate radical. At temperatures higher than 40 °C, oxidation kinetics can be so fast that the oxidant may be spent before achieving distribution. A total of 10,000 gallons of 60 g/L sodium persulfate solution (total of 5,014 pounds of sodium persulfate) was injected into 9 wells.

RESULTS AND DISCUSSION

During the operation of the hydrolysis system, groundwater injection temperatures ranged from 60°C to 71°C. Concentrations of TCA in groundwater were highly variable prior to startup of the hydrolysis system, typical of groundwater in contact with DNAPL. After 41 days of heating and recirculation of groundwater, production of 1,1-DCE was evident. An increase in both TCA and 1,1-DCE in downgradient monitoring wells at day 41 and 69 was an indication of insufficient capture by the extraction wells, which resulted in a system flow rate increase from 1.5 gpm to 3.0 gpm. Additionally, during the operation of the hydrolysis system, the pH of groundwater was observed to decline from an average of 6.9 to 4.5 indicating the production of acetic acid. After 100 days of operation, TCA was reduced below the remedial target of 13,300 µg/L in groundwater. The single injection of sodium persulfate 30 days after the completion of heating was successful in reducing the concentration of 1,1 DCE in the source area and downgradient. Performance trends shown in Figures 5 and 6 document the removal of TCA and subsequent production of 1,1-DCE during the operation of the hydrolysis system as well as the reduction of 1,1-DCE after the ISCO injection in the source area and downgradient, respectively.

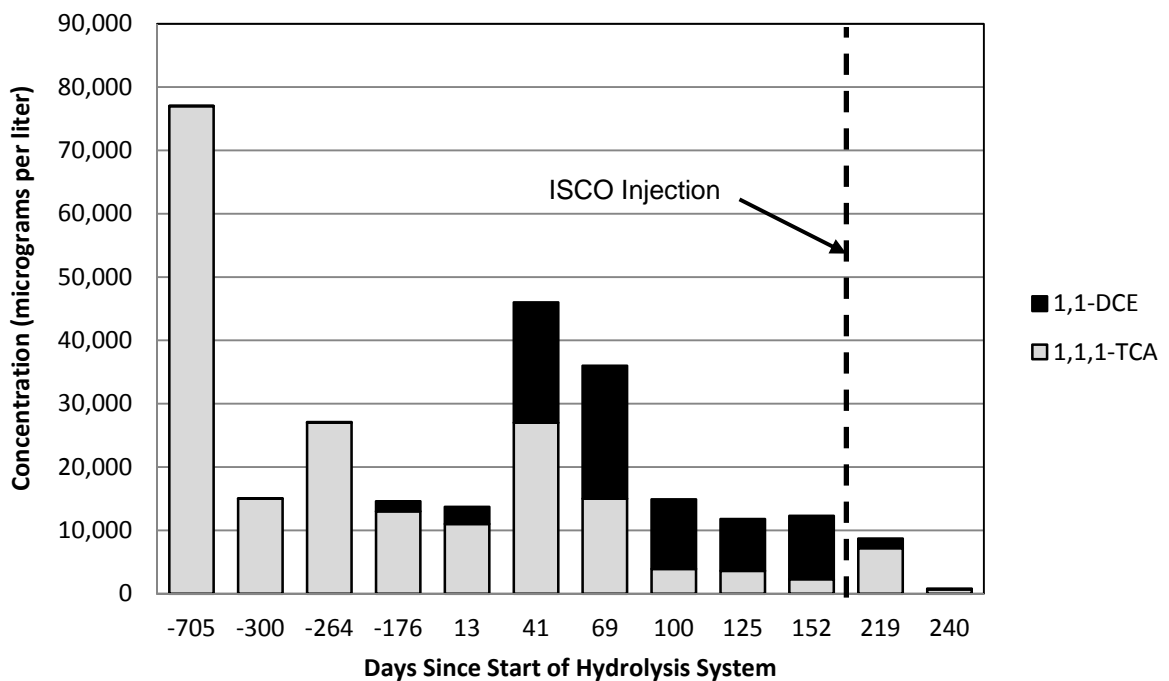


FIGURE 5. Performance trends in source area well.

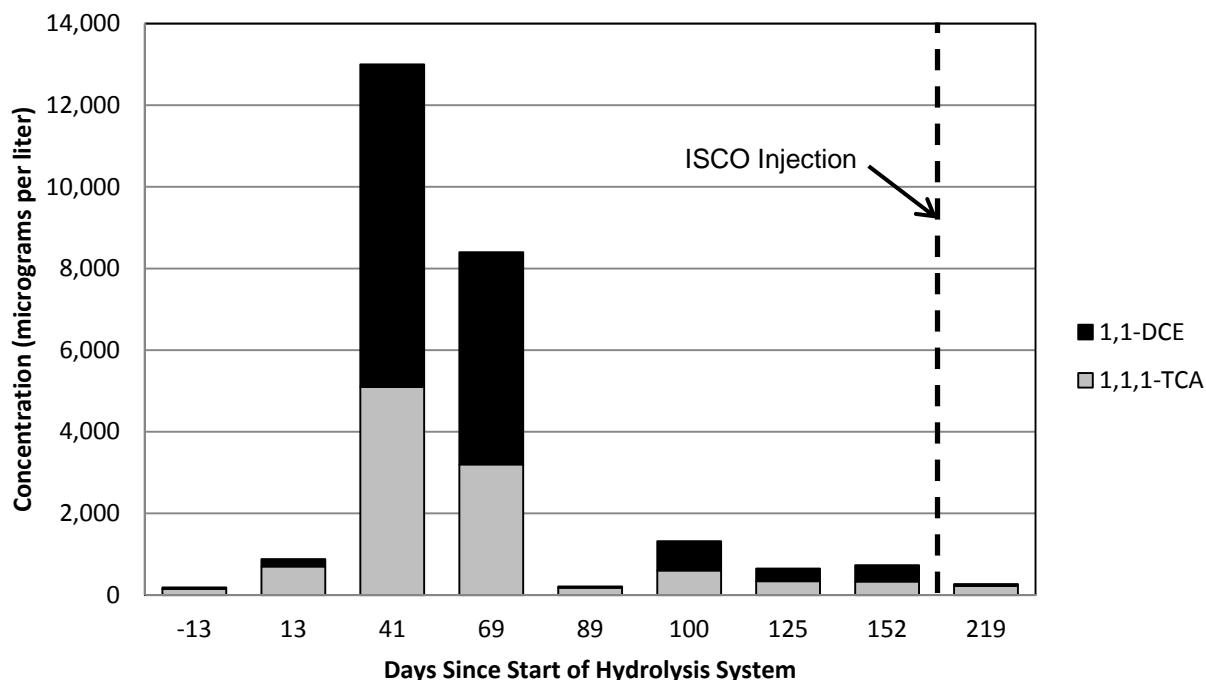


FIGURE 6. Performance trends in downgradient well.

CONCLUSIONS

For compounds such as chlorinated ethanes that are difficult targets for ISCO, hydrolysis may be an effective means for transforming these compounds to something that is easier to oxidize. This is even more important to consider the potential presence of DNAPL, which would typically rule out the use of ISCO as a cost-effective technology. The two technologies (in situ thermally enhanced hydrolysis and ISCO) are quite complementary, in this case study transforming a difficult oxidation target (TCA) and large amount of source mass to a more targetable compound (1,1-DCE) in the dissolved phase.

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