

D&H Manufacturing

In Situ Chemical Oxidation—Biostimulation

Site Name: D&H Manufacturing

Site Location: 2301 Calle de Luna, Santa Clara, CA 95054

Technology Used:

- In Situ Chemical Oxidation (ISCO)—RegenOx[®]
- Biostimulation—Hydrogen Releasing Compound (HRC[®])

Regulatory Program: San Francisco Bay Regional Water Quality Control Board

Remediation Scale: Full

Project Duration: October to December 2006. Quarterly groundwater monitoring since March 2006.

Site Information: The D&H facility was built in a commercial area in Santa Clara, California, and was used for manufacturing precision metal parts for the semiconductor industry. The site building is a single-story structure constructed in 1984 with a former metal shavings storage area at the northwestern side of the building.

Contaminants: Soil and groundwater sampling and analysis conducted in 2001 indicated that volatile organic compounds (VOCs) associated with the use of chlorinated cleaning solvents, were present in soil and groundwater at a sump located in the former metal shavings storage enclosure at the rear of the building. The sump was installed in 1987 to collect residual fluids draining from metal shavings storage bins stored in the enclosure. A tetrachloroethene (PCE) plume was identified in two zones of the shallow aquifer with an average baseline concentration of 45,000 µg/L in the shallow zone and 13,000 µg/L in the deeper zone. Other VOCs at the site included trichloroethene (TCE); 1,1,1-trichloroethane (1,1,1-TCA); 1,1 dichloroethene (1,1-DCE); *cis*-1,2- dichloroethene (*cis*-1,2-DCE); and vinyl chloride.

The concentrations of VOCs in the deeper zone were generally 30% to 40% lower than in the shallow zone and more limited in lateral extent. The plume extended below the building in a sou-

theasterly direction. PCE concentrations in groundwater were highest near the former sump location. PCE concentrations detected in soil at the sump location during its removal were found up to 3,900 milligrams per kilogram (mg/kg).

Hydrogeology: The site is located in the flatland area of the San Francisco Bay and is underlain by interbedded clay and clayey sand units. Stiff clay extends from the surface to 1 to 4 ft below ground surface (bgs). This clay is underlain by dense clayey sand to stiff sandy clay layers that extend to approximately 20 ft bgs. The lower sand unit, between 20 and 23 ft bgs, consists of 1-3 ft of saturated sand and silty sand and is underlain by dark brown stiff clay.

Two saturated zones—the shallow and deep zones—are present at the site at approximately 7.5 to 12 ft bgs and 20 to 23 ft bgs, respectively. The vertical gradient between the two zones, if present, is very low. The local groundwater beneath the site is flowing to the east-southeast in both zones with low hydraulic gradients of approximately 0.002 feet per foot.

Project Goal(s): The primary goals of this project were to clean up the chlorinated solvents that had leaked from a subsurface sump and impacted groundwater, and to comply with a regulatory agency cleanup order for the site. Maximum Contaminant Levels (MCLs) were set for groundwater cleanup goals.

Cleanup Approach: ISCO and subsequent enhanced anaerobic bioremediation were chosen to reduce PCE to desired concentrations at the site. ISCO was chosen as the first step because shallow zone PCE concentrations were too high to effectively bioremediate the area in a reasonable and cost-effective time frame. RegenOx[®] was chosen as the ISCO compound to reduce PCE concentrations closer to 10,000 µg/L. HRC[®] was chosen for its ability to slowly release lactic acid (as an electron donor) into the groundwater. Fermentation of the lactic acid generates hydro-

gen for microbial use in reductive dechlorination of the chlorinated hydrocarbons.

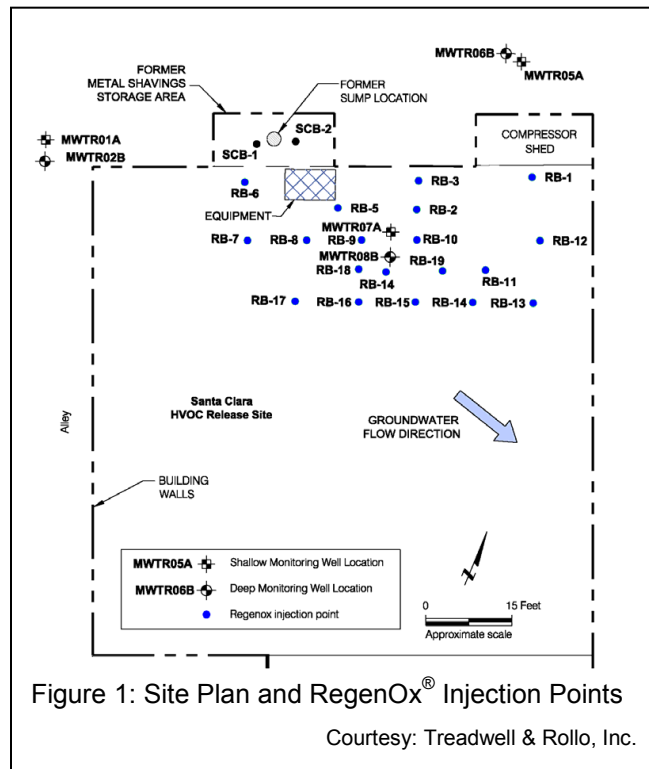
RegenOx[®] is a two-part product: part A is sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$), a sodium carbonate-based powdered oxidizer; part B is a sodium silicate (Na_2SiO_3) and ferrous sulfate-based liquid activator. The oxidizer completes its reaction within a few weeks and the hydrogen release compound is assumed to release hydrogen for at least 24 months.

The in situ remediation program was designed to reduce the overall mass of VOCs by 30-50% using the oxidizer, and then to change the oxidizing environment to a reducing environment with the hydrogen donor compound and stimulate anaerobic biodegradation to further reduce the VOCs. The oxidizer was targeted to be injected into the areas of the plume with the highest VOC concentrations, generally greater than 10,000 $\mu\text{g/L}$ total VOCs. The hydrogen release compound was targeted to be injected over a much wider area.

In situ chemical oxidation was implemented in two phases. During the first injection phase on October 14-16, 2006, the sodium percarbonate, and sodium silicate- and ferrous sulfate-based components of RegenOx[®] were mixed to create an 8% solution. About 3,200 gallons of RegenOx[®] were then injected at nine locations using direct push technology (see Figure 1). RegenOx[®] was injected between 10 and 22 ft bgs, with average pressures of approximately 90 pounds per square inch (psi), though initial pressures exceeded 300 psi to hydro-fracture and penetrate fine-grained soils and increase the radius of influence.

This application method increased the radius of influence to a greater extent than anticipated. Product surfacing was observed in seven of the initial nine injection points. At one location, the product migrated along the preferential pathway and surfaced in a paved parking lot located approximately 75 ft from the injection point. Based on this outcome, the following changes were made for the subsequent RegenOx[®] injection to reduce the incidence of preferential pathway migration and surfacing:

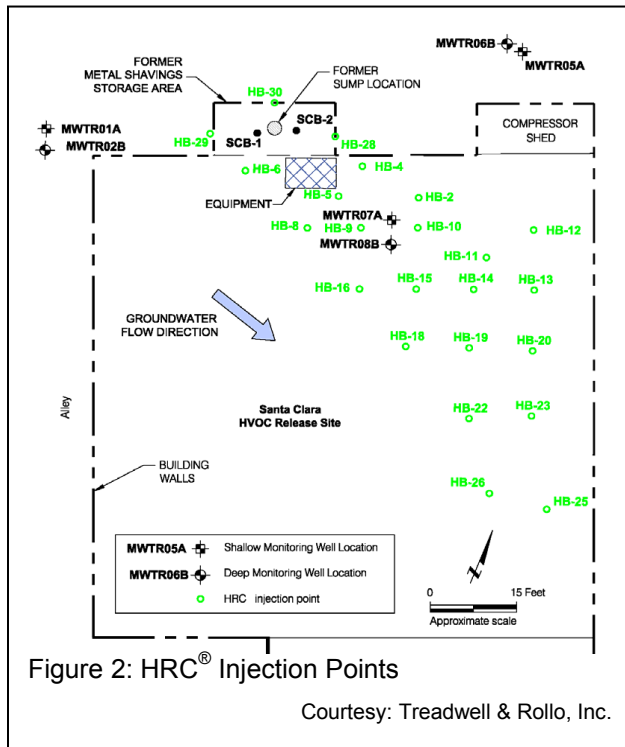
- The number of proposed injection points were increased and the injection volume per point was decreased.
- Initial injection pressures were reduced
- RegenOx[®] solution concentration was reduced to 5%.
- More product volume was injected in the deeper sections of the injection points.



During the second injection phase on October 23-27, 2006, approximately 5,733 gallons of 5% RegenOx[®] were injected at 10 boring locations at depths ranging between 10 and 22 ft bgs. During this phase of the work minor surfacing close to the injection points was only observed at two of the locations.

One month after the second oxidation treatment, the hydrogen release compound was injected into the subsurface to stimulate bioremediation. From 11 to 13 December, 2006, approximately 3,030 pounds of HRC[®] (280 gallons) was injected in the subsurface at 23 boring locations between 5 and 22 ft bgs (see Figure 2). The volume of the hydrogen release compound that was

injected was much lower than the oxidizer volume, and significant surfacing issues did not occur.



Project Results: The chemical oxidation and enhanced anaerobic biodegradation program has successfully reduced VOC concentrations and exceeded the initial reduction projections. Groundwater monitoring conducted approximately 30 days after the final ISCO injection indicated that VOC concentrations dropped by up to 50%. Within 12 months of HRC[®] injection, PCE in the areas with the highest groundwater concentrations was reduced to slightly above or below laboratory detection limits. Concentrations of 1,1,1-TCA had declined as well, from over 350 µg/L to below 83 µg/L in the source area monitoring wells. By November 2009, PCE concentrations had declined by 98% to 99% in the two source area monitoring wells where VOC concentrations were highest (See Table 1). Degradation of VOCs occurred approximately twice as fast in the shallow zone as in the deeper zone.

Reductions in PCE concentrations were accompanied by spikes in the concentrations of *cis*-1,2-DCE, along with subsequent, corresponding in-

creases in vinyl chloride concentrations. Vinyl chloride concentrations peaked approximately 18 months after remedy implementation, at 4,500 µg/L in the shallow groundwater zone and at 3,000 µg/L in the deep groundwater zone. To determine whether a sufficient population of *Dehalococcoides* was present at the site or if additional steps such as bioaugmentation or changing subsurface conditions would be necessary, a genetic census of bacteria was conducted. DNA analysis reports indicated that a sufficient *Dehalococcoides* population was present. Natural attenuation parameters indicated that conditions continued to be favorable for biologic degradation. Subsequent natural attenuation monitoring has shown elevated concentrations of Fe²⁺, manganese, and anaerobic gases including methane, carbon dioxide and ethane – which are indicative of biological anaerobic degradation. About 24 months after remedy implementation, clear vinyl chloride degradation trends have been observed in both the shallow and deep groundwater zones during subsequent monitoring events.

| Date Collected | PCE | TCE | Vinyl Chloride |
|---------------------------|---|-------------|----------------|
| 11/23/2009 | 30 | 5.6 | 510 |
| 04/16/2009 | 27 | < 8.3 | 1,300 |
| 04/01/20081 | 98/100 | 33/39 | 3,000/3,100 |
| 02/07/20071 | 100/1,300 | 5,100/4,400 | < 36/< 31 |
| 12/11/2006 | Hydrogen Donor Compound Injected | | |
| 11/28/2006 | 370 | 13,000 | < 31 |
| 10/23/2006 | Second Round of Oxidizing Compound Injected | | |
| 10/14/2006 | Oxidizing Compound Injected | | |
| 03/30/2006 | 600 | 20,000 | < 83 |
| 1 - Duplicate sample pair | | | |

In November 2010, the concentrations of PCE and TCE remained below laboratory reporting limits of 0.5 µg/L in one of the source area wells; vinyl chloride concentrations in the well have also continued to decrease (See Figure 3). In the second source area well, PCE and TCE concentrations were 24 µg/L and 20 µg/L, respectively (See Figure 4). VOC levels in the second source area well and in four additional wells that were sampled generally remained within the range of historical detections.

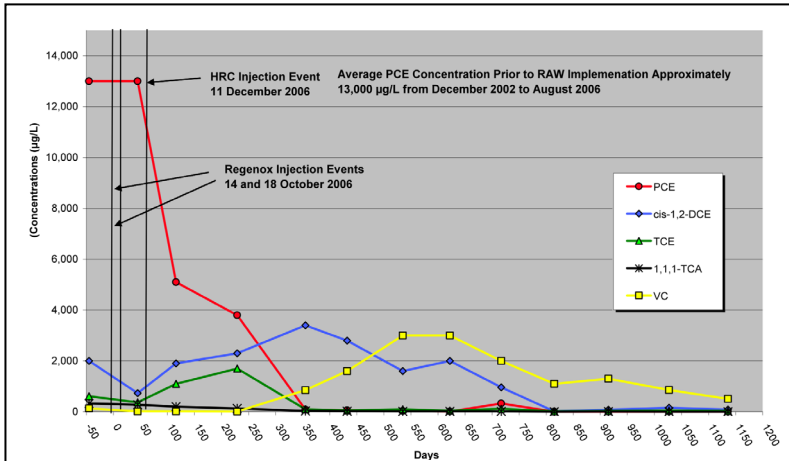


Figure 4: VOC Concentrations in Source Area Well MWTR08B

Courtesy: Treadwell & Rollo, Inc.

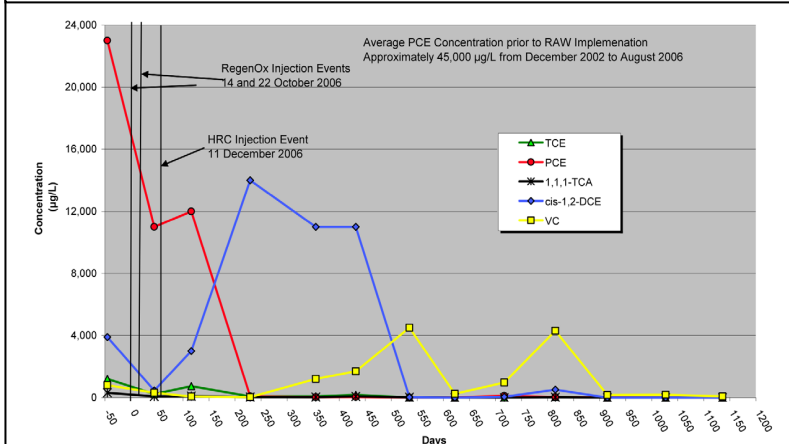


Figure 3: VOC Concentrations in Source Area Well MWTR07A

Courtesy: Treadwell & Rollo, Inc.

Since the completion of this project, the following changes to RegenOx[®] application have been suggested:

- Mixing Part A and Part B in situ rather than prior to injection. It is now recommended to inject the activator (Part B) first, followed by the oxidizer, Part A.

- Lowering RegenOx[®] solution concentrations to 3%
- Considering semi-permanent to permanent injection points to allow slower injections, and repeatable injection points.

The site continues to be monitored on a quarterly basis. Implementation of the remedy cost \$140,000, including \$40,000 for the oxidizing compound and hydrogen donor compound. Groundwater monitoring and reporting costs for 12 site monitoring wells cost approximately \$23,000 a year.

Sources:

Dixon, David and Dustyne Sutherland. 2010. In Situ Chemical Oxidation and Enhanced Anaerobic Biodegradation of a PCE Plume Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2010).

California State Water Resources Control Board. Geotracker. D+H Manufacturing http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=SL0608590095

Treadwell & Rollo, Inc. 2011. Fourth Quarter 2010 Groundwater Monitoring Report, 2301 Calle De Luna, Santa Clara, California.

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