

In-Situ Chemical Oxidation and Enhanced Anaerobic Biodegradation of a PCE Plume

David G. Dixon, PG (dgdixon@treadwellrollo.com) and Dustyne Sutherland.
(Treadwell & Rollo, Inc., San Francisco, California, USA)

ABSTRACT: A chemical oxidation, enhanced anaerobic biodegradation, and monitoring program was conducted by Treadwell & Rollo, Inc (Treadwell & Rollo) to address a tetrachloroethene (PCE) plume in a two zone shallow aquifer below an active commercial building. The program succeeded at reducing PCE in groundwater with an average baseline concentration of 45,000 micrograms per liter ($\mu\text{g/L}$) to below reporting limits within a year. The PCE degradation process resulted in a rise in vinyl chloride concentrations in groundwater from below laboratory reporting limits to as high as 4,500 $\mu\text{g/L}$, presenting new concerns regarding groundwater and indoor air quality. The Site is located in Santa Clara, California and had releases of halogenated volatile organic compounds (HVOCs), primarily PCE, from a subsurface sump. Prior to beginning cleanup, PCE concentrations in groundwater below the building averaged approximately 45,000 $\mu\text{g/L}$ in the shallow zone (7 to 12 feet below ground surface) and 13,000 $\mu\text{g/L}$ in the deeper zone (19 to 25 feet below ground surface). Shallow zone concentrations were too high to effectively bioremediate the PCE in a reasonable and cost-effective timeframe, so a method to rapidly decrease PCE concentrations to closer to 10,000 $\mu\text{g/L}$ prior to bioremediation was needed. In 2006, Treadwell & Rollo implemented an in-situ remediation program to reduce the overall mass of HVOCs below the water table using an oxidizing compound (RegenOx[®]) followed by anaerobic bioremediation using a hydrogen release compound (HRC[®]) to further reduce the HVOCs. This was the first site where these two compounds had been used together. Three years of groundwater monitoring data have documented the degradation of PCE and the corresponding rises and falls in daughter products. Injecting 9,000 gallons of RegenOx into fine-grained soil was challenging, and the experiences of this project helped the manufacturer develop new application guidelines. The success of this project helps demonstrate the viability of conducting enhanced anaerobic bioremediation immediately after an aggressive oxidation treatment, and show that indigenous microbial flora can survive an aggressive oxidation process and rapidly re-colonize.

INTRODUCTION

The goal of this project was to cleanup 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. Treadwell & Rollo conducted the characterization and cleanup activities on behalf of the property owner who had voluntarily investigated their site and reported the results to regulatory agencies. The lead regulatory agency that has issued a cleanup order for the Site is the Bay Area Regional Water Quality Control Board (RWQCB), which is part of the California Environmental Protection Agency (RWQCB 2003).

The facility was built in a commercial area in Santa Clara, California, and was used for manufacturing precision metal parts for the semiconductor industry (Site). The site building is a single-story structure constructed in 1984 with a former metal shavings storage area at the north western side of the building (Figure 1). The ground surface lies at an approximate elevation of 8 feet above mean sea level and slopes slightly away from the rear of the building towards the northern property line.

Soil and groundwater sampling and analysis conducted in 2001 indicated that halogenated volatile organic compounds (HVOCs) 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 reportedly 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 micrograms per liter ($\mu\text{g/L}$) in the shallow zone (in source area Monitoring Well MWTR07A) and 13,000 $\mu\text{g/L}$ in the deeper zone (source area Monitoring Well MWTR08B). The concentrations of HVOCs in the deeper zone were generally 30 to 40% lower than in the shallow zone and more limited in lateral extent. PCE concentrations detected in soil at the sump location during its removal were as high as 3,900 milligrams per kilogram (mg/kg).

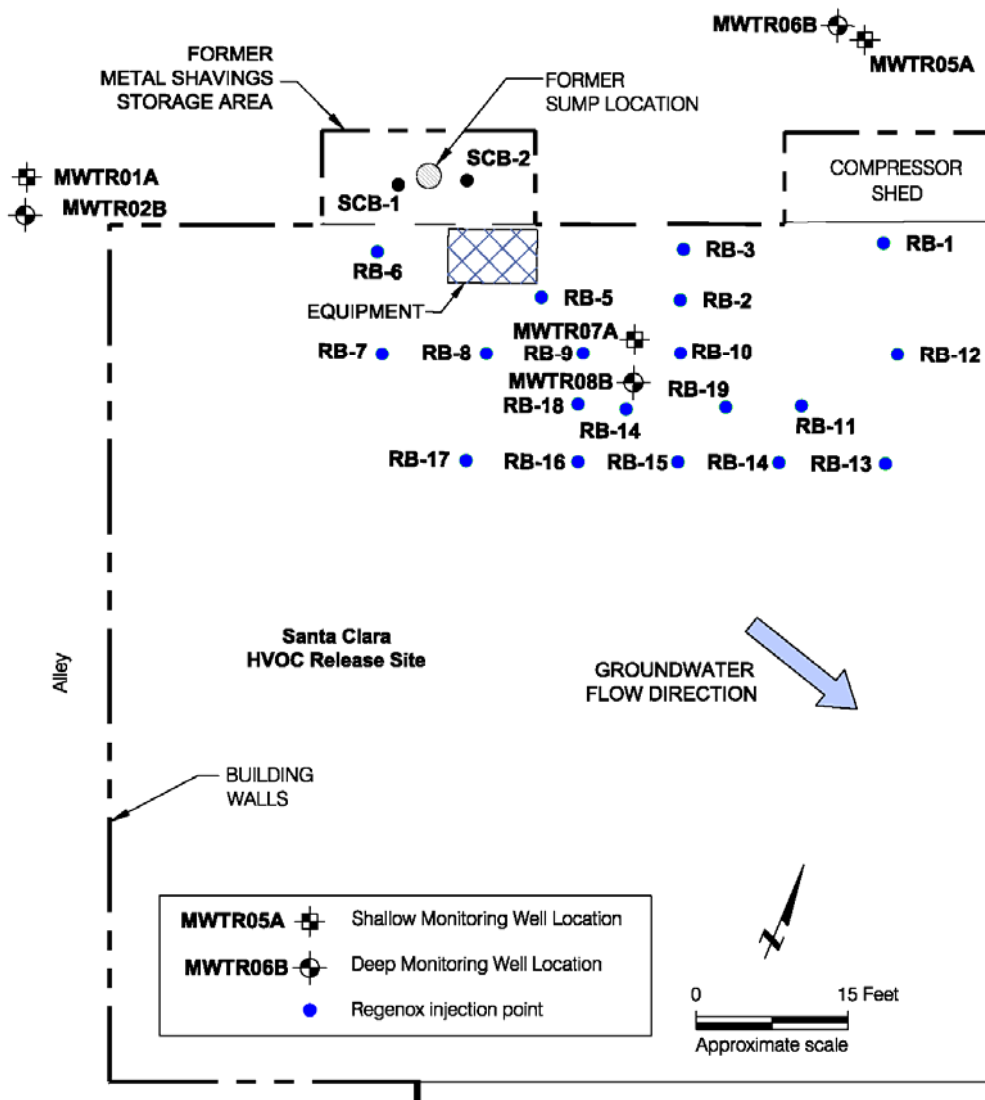


Figure 1 - Site plan and Regenox injection points.

SITE CONDITIONS

The Site is located in the flatland area of the San Francisco Bay and is underlain by interbedded clay and clayey sand units. Dark brown to black and stiff clay extends from the surface to 1 to 4-feet below ground surface (bgs). This clay is underlain by tan to gray mottled dense clayey sand to stiff sandy clay layers to approximately 20 feet bgs. The lower sand unit, between 20 and 23 feet bgs, consists of 1 to 3 feet of saturated sand and silty sand and is underlain by dark brown stiff clay.

Two saturated zones (defined as shallow and deep zones) are present at the Site at approximately 7.5 to 12 feet bgs and 20 to 23 feet 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 gradients of approximately 0.002 feet per foot.

T&R conducted several characterization and remedial feasibility investigations at the Site between 2001, when the release was discovered, and 2006, when the Remedial Action Work Plan (RAW) was prepared. The investigations included sampling soil, groundwater and indoor air, and installing groundwater monitoring wells. In 2004, the sump and contaminated soil were removed, and a hydrogen release compound (HRC[®]) was placed into the excavation (which extended to below the shallow groundwater zone) to assist with biodegradation of the HVOCs. This provided a temporary 40% reduction in HVOCs in groundwater, which showed the potential benefit of a site-wide enhanced biodegradation program. The rebound in HVOC concentrations also indicated that residual HVOC concentrations were too high for the bacteria to efficiently continue reductive dechlorination.

Several HVOCs were identified in soil and groundwater, with the predominant one being PCE. The PCE concentrations in groundwater were highest near the former sump location and the plume extended below the building in a southeasterly direction. Shallow zone concentrations were too high to effectively bioremediate the PCE in a reasonable and cost-effective timeframe, therefore a method to rapidly decrease PCE concentrations closer to 10,000 µg/L was needed.

The RAW presented an analysis of remedial alternatives, and selected in-situ remediation using RegenOx[®], a chemical oxidation compound followed by enhanced anaerobic bioremediation using HRC, a hydrogen release compound, to reduce PCE to concentrations to an acceptable level for commercial uses. The oxidizer completes its reaction within a few weeks and the hydrogen release compound is believed to release hydrogen for at least 24 months. The in-situ remediation program was designed to reduce the overall mass of HVOCs by 30 to 50 percent using the oxidizer, and then to change the oxidizing environment to a reducing environment with the hydrogen donor compound and anaerobic



Photo 1 Injections Inside the Facility

biodegradation, to further reduce the HVOCs. The oxidizer was to be injected into the areas of the plume with the highest HVOC concentrations, generally greater than 10,000 µg/L total HVOCs, and the hydrogen release compound was to be injected over a much wider area. It should be noted that RegenOx was a relatively new product at the time of the injection activities, and this was the first site where these two products had been used together.

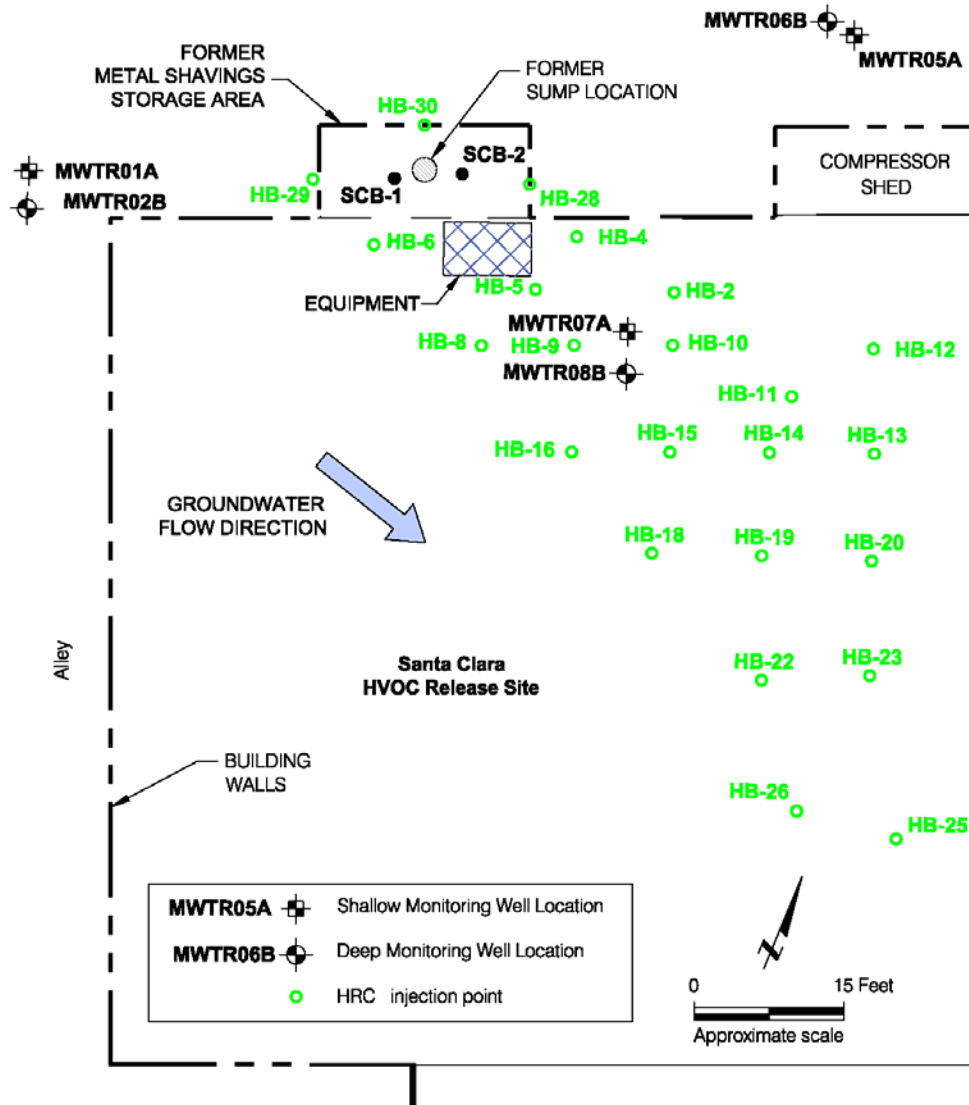


Figure 2 - HRC injection points.

IN-SITU REMEDIATION IMPLEMENTATION

From 14 to 16 October 2006, the initial injection of 3,200 gallons of RegenOx was performed at nine locations by Vironex, Inc. using direct push technology (Figure 1, Photo 1). The oxidizer application procedures recommended by Regenesis, the product manufacturer, were used. RegenOx is a two part product; Part A is a sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$), sodium carbonate (Na_2CO_3) based powdered oxidizer and Part B is a sodium silicate and ferrous sulfate based liquid activator.

These two parts were mixed to create an 8% RegenOx solution prior to injection between 10 and 22 feet bgs. The initial injection was done with average pressures of approximately 90 pounds per square inch (psi) but with initial pressures exceeding 300 psi to attempt to hydrofracture and penetrate the fine-grained soils, and increase the radius of influence. This application method increased the radius of influence more than anticipated, at one location causing preferential pathway migration and surfacing in the paved parking lot approximately 75 feet from the injection point inside the building. Product surfacing was observed in seven of the initial 9 injection points. Based on this field experience, and consultations with Regenesys personnel who visited the site, the following changes were made for the subsequent RegenOx injections to reduce the incidence of preferential pathway migration and surfacing:

- Increasing the number of proposed injection points and decreasing the injection volume per point;
- Reducing the initial injection pressures;
- Reducing the RegenOx solution to 5%; and,
- Injecting more volume in the deeper sections of the injection points.

During the second injection event between 23 and 27 October 2006 approximately 5,733 gallons of RegenOx were injected at 10 boring locations at depths ranging between 10 and 22 feet bgs (Figure 2). 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. From 11 to 13 December 2006, approximately 3,030 lbs of HRC (280 gallons) was injected in the subsurface at 23 boring locations between 5 and 22 feet bgs (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.

RESULTS AND DISCUSSION

Treadwell & Rollo has conducted eleven quarterly monitoring events at the Site since the injections (RAW implementation), and sampled groundwater for HVOCs and natural attenuation parameters. Groundwater monitoring conducted approximately 30 days after the oxidizer was injected indicated that HVOC concentrations dropped by up to 50%. Redox conditions in both the source area monitoring wells changed from a highly oxidizing state immediately after the oxidizer injections to a highly reducing state within a few months of the HRC injections. Within 12 months PCE concentrations in the areas with the highest groundwater impacts were reduced to slightly above or below laboratory detection limits.

In the two source area monitoring wells, MWTR07A and MWTR08B, PCE concentrations have reduced by 99% and 98% respectively. These wells had the highest concentrations of HVOCs at the Site and are generally representative of changes observed in other site wells with HVOC impacts. Degradation of the HVOCs occurred approximately twice as fast in the shallow zone as in the deeper zone. Table 1 summarizes the groundwater monitoring results for HVOCs for wells MWTR07A and MWTR08B from three quarters before the RAW implementation in October 2006, through November 2009. The previous four years of groundwater data are not summarized, but generally showed a trend of very slowly decreasing HVOC concentrations due to natural attenuation.

Table 1 - Groundwater Monitoring Results for Selected HVOCs

Date Collected	TCE	PCE	1,1,1-TCA	1,1-DCE	cis-1,2-DCE	Vinyl Chloride
Units in micrograms per liter (µg/L)						
Monitoring Well MWTR07A						
11/23/09	< 0.5	0.8	< 0.5	< 0.5	1.8	85
08/06/09	1.0	2.0	< 1	< 1	< 1	190
04/16/09	1.8	4.5	< 1	< 1	1.4	170
01/06/09	50	39	< 25	< 25	510	4,300
09/30/08	9/8.6	120/83	< 2.5/< 0.5	3.9/4.0	53/59	970/790
06/27/08	1.1	4.8	0.5	< 0.5	3.3	240
04/01/08	< 25	< 25	< 25	< 25	25	4,500
12/20/07	180	< 83	< 83	210	11,000	1,700
10/04/07	85	< 71	< 71	83	11,000	1,200
05/31/07	80	78	< 71	80	14,000	< 71
02/07/07	740	12,000	99	130	3,000	69
12/11/06	Hydrogen Donor Compound Injected					
11/28/06	230	11,000	78	240	460	< 63
10/23/06	Second Round of Oxidizing Compound Injected					
10/14/06	Oxidizing Compound Injected					
08/30/06	1,200	23,000	310	600	3,900	800
06/14/06 ¹	1,300/1,200	32,000/29,000	330/310	560/520	2,500/2,400	600/530
3/30/2006 ¹	710/350	30,000/31,000	780/370	990/430	1,300/620	300/<200
Monitoring Well MWTR08B						
11/23/09	30	5.6	< 3.6	< 3.6	85	510
08/06/09	48	< 5	< 5	< 5	160	860
04/16/09	27	< 8.3	< 8.3	< 8.3	80	1,300
01/06/09	17	< 8.3	< 4.2	< 4.2	15	1,100
09/30/08	120	330	< 17	23	960	2,000
6/27/2008 ¹	45/46	< 17/< 20	< 17/< 20	31/26	2,000/1,900	3,000/3,200
4/1/2008 ¹	98/100	33/39	< 17/< 17	32/29	1,600/1,800	3,000/3,100
12/20/07 ¹	55/53	61/74	< 20/23	32/36	2,800/2,900	1,600/1,800
10/4/07 ¹	100/110	85/110	33/36	26/32	3,400/3,400	850/850
5/31/07 ¹	1,700/1,700	3,800/3,600	130/130	63/65	2,300/2,300	< 17/15
2/7/07 ¹	1,100/1,300	5,100/4,400	200/220	51/59	1,900/2,100	< 36/< 31
12/11/06	Hydrogen Donor Compound Injected					
11/28/06	370	13,000	280	91	730	< 31
10/23/06	Second Round of Oxidizing Compound Injected					
10/14/06	Oxidizing Compound Injected					
08/30/06	610	13,000	330	220	2,000	130
06/14/06	910	19,000	320	290	2,400	210
03/30/06	600	20,000	460	300	1,100	< 83

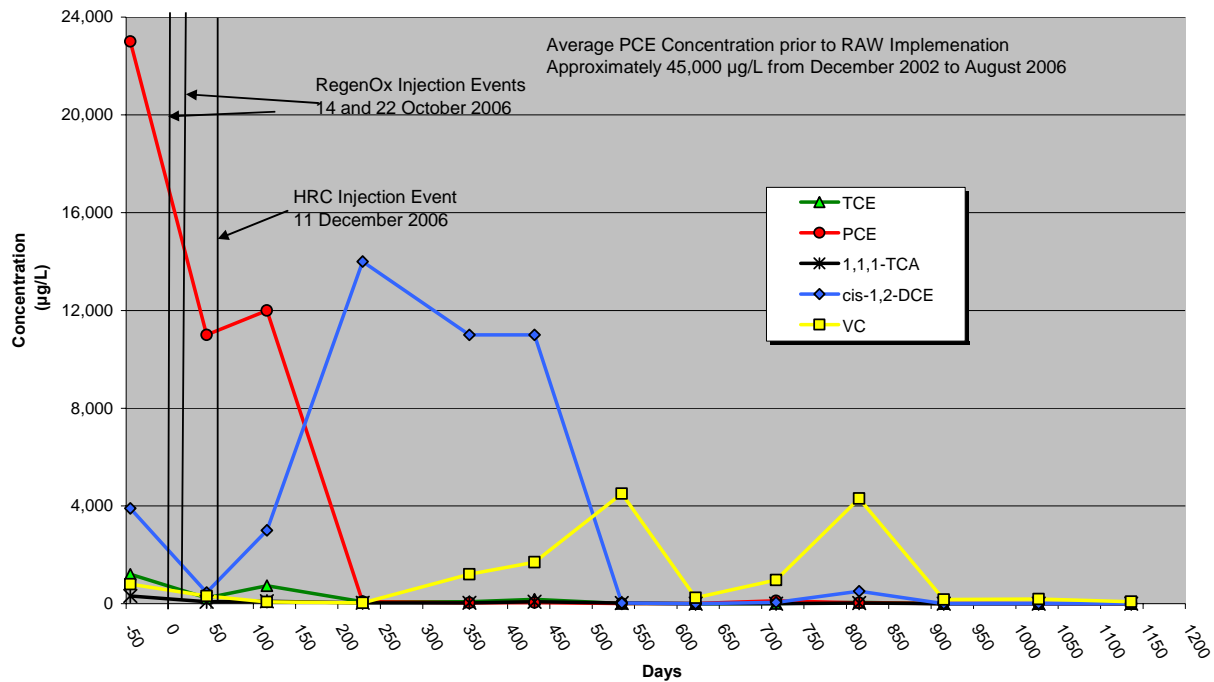
Table Notes

DCE – Dichloroethene
TCA – Trichlorethane
PCE – Tetrachloroethene

TCE - Trichloroethene
¹ - Duplicate sample pair

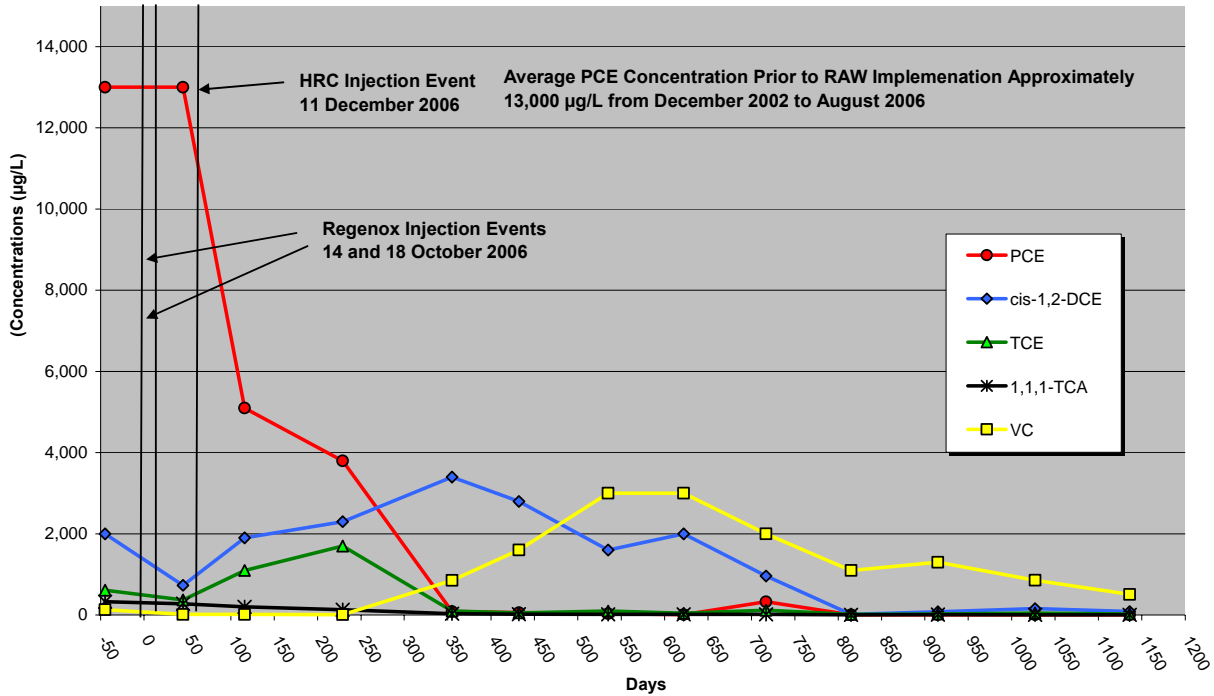
As expected during reductive dechlorination, reductions in PCE concentrations were accompanied by spikes in the concentrations of cis-1,2-DCE, along with subsequent, corresponding increases in vinyl chloride concentrations. Natural attenuation monitoring has shown elevated concentrations of Fe²⁺, manganese and the anaerobic gases including methane, carbon dioxide and ethane, which indicate that biological anaerobic degradation is continuing to occur three years after the RAW implementation. Figures 3 and 4 are graphs of the HVOC data presented in Table 1 and show the degradation trends progressing from PCE to cis-1,2-DCE to vinyl chloride, and the subsequent drop in vinyl chloride concentrations.

Figure 3
HVOC Concentrations in Monitoring Well MWTR07A



Approximately 18 months after the RAW implementation, vinyl chloride concentrations peaked at 4,500 µg/L in the shallow groundwater zone and 3,000 µg/L in the deep groundwater zone. This raised concern that the dehalococcoides strain of bacteria, predominantly responsible for the degradation of vinyl chloride, may not be present or have a sufficient population to degrade the vinyl chloride in a reasonable timeframe. A reasonable timeframe was loosely defined as showing a clear degradation trend within 6 to 9 months. Consequently, Treadwell & Rollo conducted a bacteria genetic census to determine if a sufficient population of dehalococcoides was present at the Site or if additional steps such as adding the bacteria (bio-augmentation) and/or changing subsurface conditions may be needed. The DNA analyses report indicated that a sufficient dehalococcoides population was present, and the natural attenuation parameters indicated that conditions continued to be favorable for biologic degradation. Based on this information, it was decided to wait on additional work. Within 6 months clear vinyl chloride degradation trends were observed in both the shallow and deep groundwater zones, and this trend is continuing.

Figure 4
HVOC Concentrations in MWTR08B



The chemical oxidation and enhanced anaerobic biodegradation program has successfully reduced HVOC concentrations and exceeded the initial reduction projections. Prior to implementing the RAW, it was believed that the Site would be closed to industrial/commercial criteria with deed restrictions, but the continuing trend in HVOC degradation indicates that the site may meet closure criteria for unrestricted Site uses. The results of this work indicate that the indigenous microbial flora can survive an aggressive oxidation program and rapidly re-colonize. The addition of the hydrogen donor compound within one month of the oxidizer compound was successful in providing nutrients for the native bacteria, and helped transform the oxidizing environment to a reducing environment that displayed clear HVOC degradation trends within 6 months of injecting the oxidizing compound.

COSTS

The cost to implement the RAW is summarized below:

Drilling and Injection Subcontractor	\$45,000
Injection Product and Delivery	
RegenOx	\$25,000
HRC	\$15,000
Consultant Oversight, Project Management and Reporting	\$55,000
Total RAW Implementation Costs	\$140,000

Groundwater monitoring and reporting costs for the 12 site monitoring wells are approximately \$23,000 a year. This is a relatively low monitoring cost because Treadwell &

Rollo sought out and received regulatory agency approval for reduced monitoring for wells with low to minimal impacts.

LESSONS LEARNED

The surfacing and preferential pathway migration issues that initially occurred at this project have helped the RegenOx manufacturer to develop the following new recommendations for RegenOx application:

- Part A and Part B should be mixed in-situ, and not prior to injection. It is now recommended to inject the activator (Part B) first, followed by the oxidizer, Part A.
- The recommended solution percent has been lowered to 3%.
- Much slower injections are recommended. Semi-permanent to permanent injection points should be considered as follow-up injection the oxidizer and hydrogen donor compounds can also use these points.

GENERAL CONCLUSIONS

- The results of this work show that indigenous microbial flora can survive an aggressive oxidation process and rapidly re-colonize.
- The results of this work demonstrate that a site with natural attenuation slowly occurring in an anaerobic environment can be rapidly transitioned to an oxidizing environment to chemically destroy HVOCs and back to a reducing one for enhanced biological reductive dechlorination of residual HVOCs.
- The chemical oxidation and enhanced anaerobic biodegradation program has successfully reduced HVOC concentrations to the extent that the Site may meet closure criteria for unrestricted uses. It was previously assumed that cleanup to commercial/industrial criteria with deed restrictions was the only economically feasible option at this Site. It should be noted that the estimated cost of merely negotiating and implementing deed restrictions for the Site were estimated to be approximately 30% of the RAW implementation.

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