

Enhanced in situ bioremediation of chlorinated solvents

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Abstract

Anaerobic enhancement of in *Situ* bioremediation of a shallow, confined, silty sand aquifer has resulted in a substantial biodegradation of a dissolved tetrachloroethene (PCE) plume at an abandoned metal finishing facility located within residential area in northern New Jersey. The injection of a proprietary time-release hydrogen compound rapidly converted ambient aquifer aerobic conditions to anaerobic. This enhancement effectively induced and facilitated the successive reductive dechlorination of PCE and daughter products. Field results confirmed this anaerobic biodegradation enhancement within the overburden aquifer resulted in substantial degradation of PCE and its daughter products in the underlying sandstone bedrock aquifer.

The pre-injection dissolved PCE levels of 5 to 8 mg/l at the source declined by 90 to 96% within 2 months of injection. Degradation rates of 96% to 100% were obtained for TCE and t-DCE, whereas the degradation rates of c-DCE were slower and smaller at 30 to 70%. The potential presence of residual product and larger adsorbed solvent mass in the source area resulted in seemingly smaller but faster PCE and TCE overall degradation rates in comparison to downgradient areas. The c-DCE mass degradation during the same period was apparently greater and faster near the source than in the downgradient area.

Of interesting significance was the rapid degradation of VC, which was scarcely detected during the monitoring period. Carbon dioxide and methane levels increased by more than 10 fold indicative of VC degradation under both aerobic and anaerobic conditions. Local changes in the REDOX state and in oxygen levels coincided with preferential reduction of competing species (*e.g.*, sulfate), and apparently facilitated the degradation of VC.

Introduction

The 1½-acre project site is located in a northern New Jersey and is surrounded by residential dwellings. The site operated since 1947 for nearly 30 years as a metal plating and finishing facility [1]. The underlying overburden aquifer consists of 10 feet (3.3 m) of silty sand below a clay layer and is under confined conditions as illustrated in figure 1.

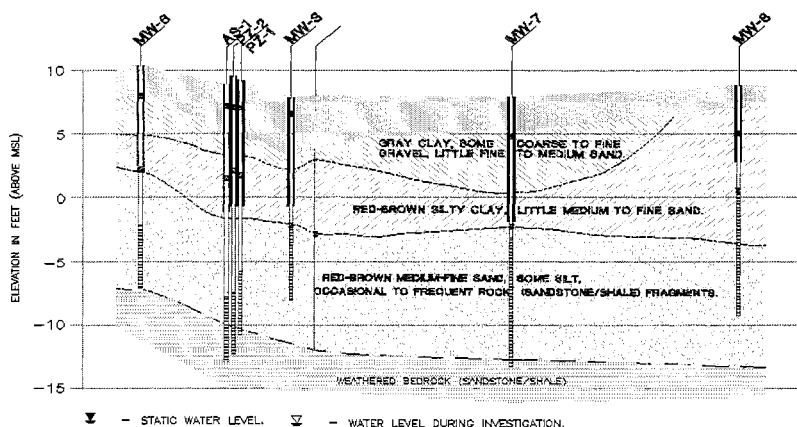


Figure 1: Geologic cross section

The overburden is underlain by bedrock that consists of a Triassic age sandstone, siltstone and shale [1]. A layer of residual soil made up of silt, clay and weathered bedrock fragments separates the overburden from the bedrock. Groundwater within the bedrock is also confined.

The depth to groundwater within both the overburden and bedrock wells varied between 0.2 feet and 4 feet (0.1 to 1.3 m) below existing grade levels. The piezometric levels of groundwater within the shallow bedrock zone appear to be generally higher and more seasonally stable than those in the overburden aquifer indicative of a downward groundwater flow potential. Laterally, the groundwater flows in a northerly to easterly direction. The average hydraulic conductivity within the overburden aquifer was estimated [1] to be on the order of 1-3 ft/day (4×10^{-4} to 1×10^{-3} cm/sec). Accordingly, for an average lateral hydraulic gradient of 0.01 at the site, the lateral groundwater velocity varies between approximately 0.02 to 0.2 feet/day (0.006 to 0.06 m/d).

Nature and extent of the contamination

Available data [1] indicated past on-site operations had impacted the soil and groundwater under the site. These impacts primarily consisted of chlorinated

volatile organic compounds (VOCs) including tetrachloroethene (PCE) and its breakdown daughter products. Subsequent groundwater investigations [1] revealed the presence of groundwater dissolved PCE plume at levels above applicable groundwater quality criteria. The plume had originated in the southeastern portion of the site, in the vicinity of a former dry well, and migrated along the general groundwater flow direction in a northerly-easterly direction as shown in figure 2. The chlorinated solvent plume had migrated more than 600 feet (200 m) under the nearby downgradient properties.

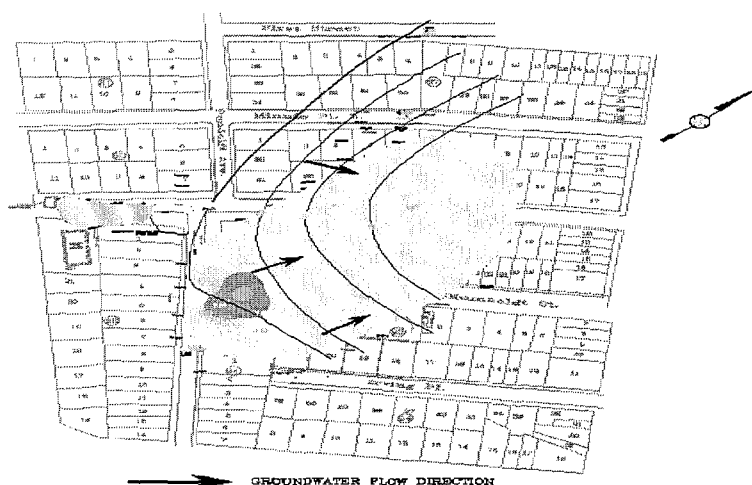


Figure 2: Site groundwater flow/plume map

The total mass of PCE and its breakdown daughter products was estimated [1] to be on the order of 17 to 20 lbs. It was further estimated that nearly 85% of the contaminant mass might be present on-site, and 15% distributed off-site.

Closure Criteria

The groundwater remedial targets are the applicable New Jersey Department of Environmental Protection (NJDEP) Groundwater Quality Criteria (GQC). Table 1 presents the closure criteria.

Table 1. NJDEP Closure Criteria

<u>Contaminant</u>	<u>Remedial Target (µg/l)</u>
Tetrachloroethene (PCE)	1
Trichloroethene (TCE)	1
Cis-1,2-dichloroethylene (cis-DCE)	70
Trans-1,2-dichloroethylene (trans-DCE)	100
Vinyl Chloride (VC)	5
Total Volatile Organics (TVOC)	500

Remedial Approach

Pursuant to the initial screening, in *Situ* chemical oxidation and in *Situ* bioremediation technologies were selected for further assessment and evaluation. These two technologies were primarily selected for further analysis due to site hydrogeologic conditions:

- The overburden aquifer is confined;
- The overburden aquifer is of limited thickness and extent;
- The plume has laterally migrated off-site and most of it is situated underneath residential homes and right of ways (i.e., streets, sidewalks)
- Relatively moderate to low hydraulic conductivity;
- The subsurface physico-chemical characteristics are amenable for degradation.

The assessment included:

- An oxidation bench-scale treatability study using hydrogen peroxide; and
- An anaerobic biodegradation bench-scale treatability study using a proprietary hydrogen release compound (HRC[®]).

A qualitative comparison was performed based on the above screening and compatibility of each alternative with the following assessment criteria:

- C-I. Remedial effectiveness and protection of human health & environment
- C-II. Efficiency (remedial duration);
- C-III. Technical feasibility and implementability;
- C-IV. Public response;
- C-V. Regulatory response; and
- C-VI. Estimated costs.

The comparative evaluation revealed that enhanced bioremediation using HRC, was the preferred remedial alternative.

Pilot study program

A field pilot test injection program was performed [1]. HRC solution was injected into 2-inch (5 cm) diameter boreholes throughout the saturated zone to the top of bedrock at depths of 15 to 20 feet (5 to 6 m) below surface grade. The boreholes were installed using a truck-mounted Geoprobe drill rig. The HRC was pumped through the unit and controlled by a flow restriction valve, intended to maintain a relatively constant pumping rate of approximately 6 gallons per linear foot.

Two injection areas were selected based on concentrations of VOCs and other chemical parameters including sulfate and pH levels. The first area represented the source area, whereas the second area represented downgradient conditions. Injection was completed in a grid pattern with a higher grid intensity and injection rate in the source test area. Different grid patterns from 7 to 10 feet (2.3 to 3.3 m) and injection rates of 4 to 6 lbs/foot were tested.

HRC is a time-release polylactate ester that provides a lasting hydrogen source for anaerobic biodegradation of chlorinated solvents [2,3]. It facilitates and accelerates the anaerobic microbial activities and reductive dechlorination of these chlorinated solvents [2]. Native anaerobic microbes ferment the lactic acid provided by HRC, and in the process release hydrogen. Microbes utilize hydrogen to degrade chlorinated solvents (by successively removing and replacing chlorine by hydrogen) into non-toxic end products (*i.e.*, ethene, carbon dioxide, and water) as follows:



Table 2 summarizes the analytical results obtained during the pilot study for one of the test wells. A comparative assessment of pre-treatment and post-treatment analytical results indicated [1] that injection of HRC facilitated and augmented anaerobic biodegradation of PCE and its breakdown products.

Table 2. Groundwater laboratory results - HRC

Sample ID	MW-1						RW-2					
	Pre HRC Pilot Study			Post HRC Pilot Study			Pre Full-scale HRC			Post Full-scale HRC		
Sampling Date	9/1/1999	10/4/99	11/2/99	12/2/99	1/4/00	3/2/00	10/11/01	1/10/02	1/3/01	10/12/01	1/9/02	
Laboratory ID No.	1922331	1925755	1928354	1931533	1000188	1005198	11J0551-01	12A0439-05	254837	306866	326760	
Volatile Organic Compounds (mg/l)												
Tetrachloroethene	3.800	296	410	1,050	828	330	47	6.4	1,900	44	15	
Trichloroethylene	35.3	4,320	3,070	883	1,600	201	7.5	3.5	340	3.3	0.8	
cis-1,2-Dichloroethylene	7.5	6,180	7,960	1,520	1,430	1,390	62	21	150	7.2	9.6	
trans-1,2-Dichloroethylene	ND	106	85	ND	52.1	ND	19	17	ND	ND	ND	
Vinyl Chloride	ND	ND	ND	ND	ND	45.6	27	ND	ND	ND	ND	
TVOC	6,842.8	11,979.2	12,125.0	3,453.0	4,910.1	2,966.6	120.2	48.8	2,390	56.3	26.4	
Permanent Gases (mg/l)												
Ethane	ND	ND	ND	ND	ND	ND	0.3	0.021	NS	NS	NS	
Ethylene	ND	ND	ND	ND	ND	ND	0.021	ND	NS	NS	NS	
Carbon Dioxide	0.896	4.04	1.48	7.18	9.88	10.7	9.35	21	NS	NS	NS	
Methane	ND	ND	ND	0.0166	0.4210	1.7200	4.82	3.33	NS	NS	NS	
General Chemistry Parameters (mg/l)												
Dissolved Oxygen	0.3	0.7	0	1.14	0.7	8.36	2.3	NM	1.41	0.4	6.65	
pH	6.53	6.48	5.73	8.05	8.05	5.67	6.75	6.51	8.45	7.43	7.61	
Alkalinity as CaCO ₃	NA	172	207	570	NA	864	260	507	NS	NS	NS	
Sulfate	48	47	3	12	9.5	1	7.9	2.1	NS	NS	NS	
Total Organic Carbon	NA	8.7	133	1620	1470	1300	54.3	99.3	NS	NS	NS	
Oxygen Reduction Potential	304	-160	NM	NM	3	268	18	NM	-1306	141	-141	

Legend:
TVOC - Total Cumulative Concentrations of Volatile Organic Compounds
mg/l - milligram per liter
mg/l - micrograms per liter
330 - Concentration in excess of NADBP Groundwater Quality Criteria for Class IIA Aquifer (DQC)

Concentrations of all daughter by-products (*i.e.*, TCE, DCE, and VC) also significantly decreased following the initial increase due to production. The total mass loss of dissolved PCE, TCE, and DCE due to the pilot injection was estimated to be approximately 0.3 lbs. The total mass loss from both adsorbed and dissolved phases of PCE, TCE and DCE was estimated to be more than 2 lbs. The mass removed during the pilot test was estimated to correspond to about 10% of the initial contaminant mass within the entire plume.

Concentrations of dissolved carbon dioxide and methane, pH, alkalinity, metal (iron and manganese), TKN, and TOC increased and sulfate and nitrate concentrations decreased due to anaerobic/anoxic conditions. These observations along with the relatively stable to increasing levels of metabolic acids confirmed the sustainability of ongoing anaerobic biodegradation.

Full-scale remedial design and construction

Based on the pilot study, a full-scale bioremediation program of HRC injection was completed during August 2001 in order to achieve the site remediation goals. The bioremediation scheme optimized access to the majority of the overburden plume both on-site and off site (*i.e.*, roads, residential dwellings and streets). HRC was injected both in a grid pattern at the site and in a barrier pattern at off-site locations. Injection rates varied from approximately 3 to 5 gallons per linear foot with grid spacing of 7 to 10 feet. A total of 449 injection points were installed within the on and off-site grids and barriers. A number of overburden and adjacent bedrock wells were monitored closely following the full-scale injection.

Results and discussions

Table 2 summarizes field and laboratory analytical results for one overburden well and an adjacent bedrock well. The concentrations trends of PCE and its daughter products in each of these wells are shown in figure 3 and 4. PCE concentrations declined significantly due to treatment in the all the source wells following the full injection. The decrease of PCE concentrations varied between approximately 99.9% at the source area and 45% at the downgradient area. Also, TCE, DCE and VC degraded significantly following injection. VC was only detected in wells near the source at low concentrations within about 5-6 months after injection and then rapidly depleted. Localized and temporary fluctuations of dissolved oxygen levels were observed likely due to changes in REDOX potential and concurrent biochemical reactions involving competing species including (*e.g.*, sulfate reduction). VC continued to degrade and fully deplete under both anaerobic/anoxic and aerobic conditions as both methane and carbon dioxide have been detected. Available literature [4] supports these VC degradation patterns.

The HRC enhancement of anaerobic conditions in the overburden aquifer was observed to induce substantial degradation of contaminants within the underlying shallow bedrock aquifer. The significant decline of PCE levels from 1,900 mg/l to 40 in the shallow bedrock well RW-2 shown in figure 4 supports that such in-situ enhancement of anaerobic biodegradation conditions would be effective in remediating the dissolved impacts within the bedrock aquifer.

Figure 3: VOCs results at overburden monitoring well MW-2

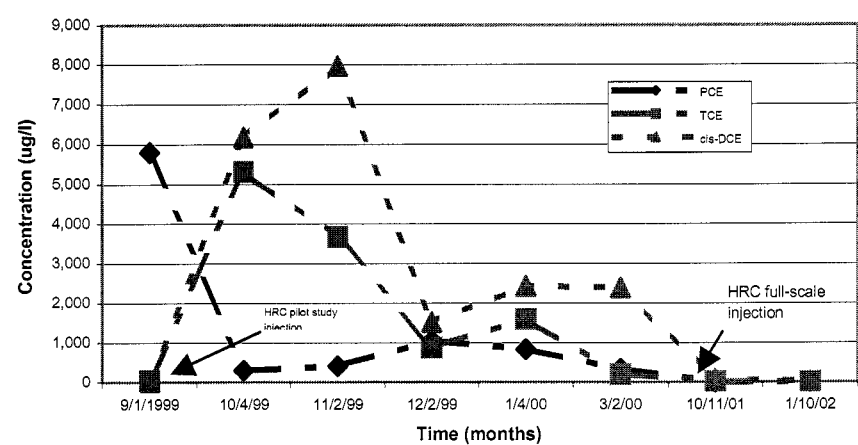
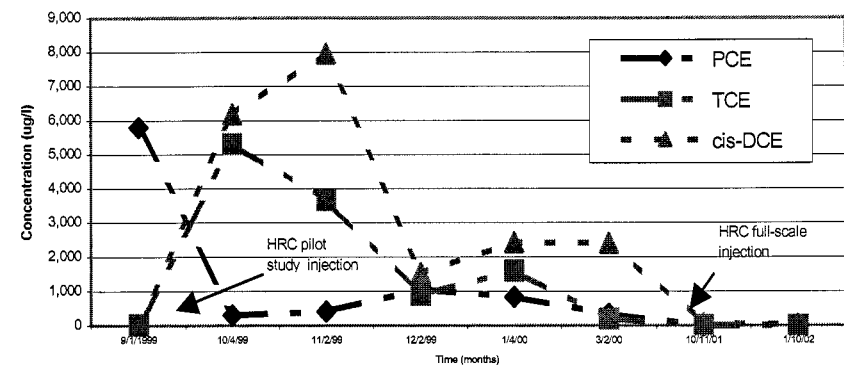


Figure 4: VOCs results at shallow bedrock well RW-2



Conclusion

This project demonstrates that enhanced bioremediation of chlorinated solvents aquifers is possible with minimal Site disturbance to the residential community.

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Levels of chlorinated solvents in the groundwater have been declining since the implementation of the enhanced bioremediation process. It is anticipated that a second full scale HRC application will be implemented to further the reductive dechlorination process and ultimately achieve effective site remediation within the shallow aquifer and regulatory closure of the case.

As part of an aggressive Brownfields Redevelopment, this abandoned Site, which stood as an eyesore to the residential community for years was mitigated to address imminent health risks associated with previous site operations and was successfully developed with a park.

The NJEDA HDSRF program provided funding for the site remedial investigations. Opinions presented herein do not necessarily reflect the views of the funding agency, and no official endorsement should be inferred.

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