Document No. 1219

An Assessment of

Zero Valence Iron

Permeable Reactive Barrier Projects

In California

Prepared by:

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April 22, 2008

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Executive Summary

The development of permeable reactive barriers (PRBs) to treat chlorinated solvents in ground water emerged in the mid -1990's. Granular zero valent iron (ZVI) has been the most common material emplaced in PRBs, which have been installed primarily to treat chlorinated solvents such as trichloroethylene. To assess the current status of this technology's deployment in California, PRB installations completed at California hazardous waste sites were identified and evaluated.

A review of the available databases, the literature, and a survey of site mitigation project managers within Cal/EPA identified 15 PRB installations in California. Most used ZVI as the reactive treatment medium. Of these 15 projects, 10 were found suitable for analysis and reviewed in detail to identify successful practices and outcomes, as well as lessons learned that could be shared with a broader audience.

In most projects evaluated, the PRB treated influent contaminated water to below maximum contaminant levels (MCLs) by the time it reached monitoring wells located in the middle of the PRB itself. However, when compared to upgradient conditions, very little improvement in downgradient water quality was observed in most of the 10 case studies. This was the result even in several instances where the PRB had been in place for many years of operation.

These results are consistent with observations made for other PRBs discussed in the literature, and are attributable to the complex behavior of chemical contaminants in aquifers. It should also be noted that long term improvements both up and downgradient of the PRB were observed at some of the sites, presumably due to natural attenuation or other factors.

While some PRBs may have been installed with the hope that contaminated ground water plumes could be remediated relatively quickly, this has not been the case. Based on the results from the 10 projects evaluated in this report, it should not be expected that a PRB made of ZVI will provide near-term improvement of water quality very far below the installation. The same levels observed downgradient of a PRB before its installation can persist for extended periods-often decades-despite the presence of a PRB.

1 Introduction

Before the advent of zero valent iron permeable reactive barrier (ZVI PRB) technology, most sites utilized an expensive system of pumps, air strippers, and carbon absorption systems to extract and treat groundwater contaminated with chlorinated solvents. These systems were capital intensive and required significant expenditures for operation and maintenance.

When ZVI's ability to dehalogenate chlorinated solvents in contaminated groundwater was discovered, some remediation professionals hoped that they had found a "silver bullet" alternative. If a ZVI PRB could be placed across a contaminated groundwater plume, the contamination source would eventually be treated as it passed through the barrier with groundwater flow. The resulting clean groundwater front exiting the PRB would dilute the downgradient contaminant plume, which then would be reduced to acceptable levels relatively quickly via natural attenuation processes.

"One of the "unrealistic expectations" we have encountered is the presumption that the existing plume downgradient of a PRB will dissipate in a short time frame. Most PRBs are installed within a plume. The detection of VOCs downgradient of the PRB (for an extended period) has caused considerable consternation among regulators and designers."

Comment on Draft "White Paper" entitled "A Review of Permeable Reactive Barrier Performance" – 316010, John Vogan, EnviroMetal Technologies, Inc. (ETI),31 May 2000.

The initial purpose of this study was to investigate remediation projects in California using various permeable reactive barrier technologies. An extensive search of records on the internet and at several government agencies identified 15 potential PRB project sites, 11 of which used ZVI to remediate chlorinated solvent contamination in groundwater. The study was then limited to focus on an evaluation of PRBs that used zero valent iron. One of the 11 PRBs had only recently been installed and was not considered in this study for lack of available data.

This report provides an in depth review of the remediation performance for each of 10 ZVI PRB projects implemented in California. Hopefully this document can be a guide to present lessons learned from past projects and set realistic expectations in future projects.

1.1 Dehalogenation of Chlorinated Compounds by Zero Valent Iron

In the early 90's it was realized that chlorinated solvents passing over granular (zero valent) iron in-situ would dehalogenate to non-chlorinated compounds which were less toxic and less persistent in the environment. Extensive experience with laboratory and field testing has proven the technology to be effective at dechlorinating a large number of chlorinated compounds. As a result, there have been over 600 publications on the

chemistry of contaminant reduction with zero-valent iron. The Center for Groundwater Research at the Oregon Graduate Institute (OGI) School of Science and Engineering maintains a searchable database of these publications that can be accessed at http://cgr.ese.ogi.edu/iron/. This database contains information on reaction pathways for a variety of chlorinated ethenes, methanes, and ethanes.

The most common contaminants treated with ZVI include:

Trichloroethylene (TCE)
Carbon Tetrachloride (CT)
Dichloroethylene cis and trans (DCE)
Tetrachloroethene (PERC)
Vinyl Chloride (VC)

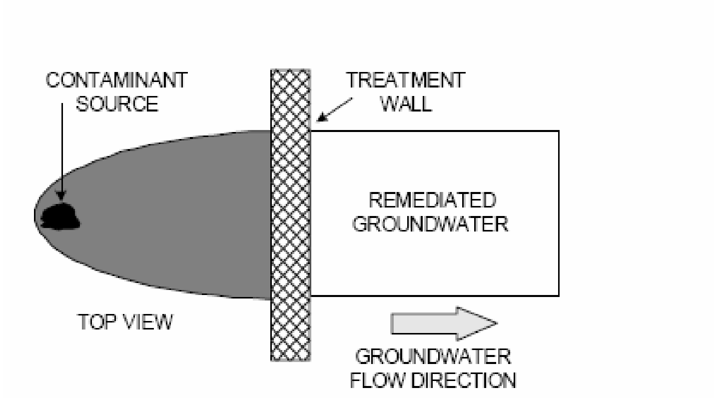
Many other chlorinated compounds are also reduced by ZVI. Appendix C is a list of compounds that have been confirmed to be amenable to treatment by zero valent iron.

1.2 The Basic Zero Valent Iron Permeable Reactive Barrier

ZVI PRBs are placed in the ground to intercept a groundwater plume contaminated with chlorinated solvents. The solvents are dehalogenated as they passed through the barrier underground. The methods of placing the iron into the ground vary, and range from basic trench and fill techniques, to injecting a gel and iron slurry into the ground, to propagating fractures through the ground with a gel iron mixture.

The actual configuration of the barrier also varies from a simple wall design to a gated barrier design, where impermeable wing walls extend from the reactive cell to guide contaminated groundwater flow through the ZVI. The movement of groundwater through a ZVI PRB is depicted in schematic form in Figure 1.

Figure 1 Reactive Barrier Schematic



Taken from:

Treatment Walls, GWERTAC, Technology Evaluation Report TE-96-01, October, 1996.

Remediation professionals hoped that ZVI PRB technology would passively clean up solvent contaminated groundwater and require only routine monitoring to check on system performance.

"It is currently believed that these systems, once installed, will have extremely low, if any, maintenance costs for at least five to ten years. There should be no operational costs other than routine compliance and performance monitoring."

Executive Summary, *Permeable Reactive Barrier Technologies for Contaminant Remediation*, USEPA-RDTF, EPA/600/R-98/125, September 1998

It was hoped that the expense of the pump and treat systems might be eliminated at many of the remediation sites contaminated with chlorinated solvents. These features made ZVI PRBs attractive options relative to other potential remedies.

The process of determining whether a site is suitable for a PRB project and its optimal design is beyond the scope of this report. PRB design and optimization, however, is more than adequately covered in the available literature (See Appendix D References.) This report instead provides a detailed look at the design and performance of 10 specific ZVI PRB projects in California.

1.3 Projects in California

In April, 2006 the Office of Pollution Prevention and Technology Development (OPPTD) began the process of identifying PRB projects in California. First, a thorough search of the Internet was performed. Next, various remediation project managers at the Department of Toxic Substances Control and the Regional Water Quality Control Boards were contacted and asked to identify any PRB projects under their oversight. Staff in OPPTD eventually identified 15 projects which initially appeared to be permeable barrier projects.

As the majority of the projects involved using ZVI as the treatment medium, the scope of the study was narrowed to look at only ZVI PRB projects. This eliminated 4 of the projects from further consideration. The final list of 10 projects selected for final design and performance review are presented in Table 1.

Table 1 ZVI Permeable Reactive Barrier Projects Reviewed

	Site Name and Address	Project Scale	Installation Date	Material Construction Method	Wall Thickness Depth Length	Contaminants
1	Mohawk Laboratories Sunnyvale, Ca	Full Scale	Installed in 2003	continuous sand/zvi mix guar gum used to maintain trench	2 ft-4 ft. thick surface- 33 ft. bgs. 700 ft. length	Dichloroethene Trichloroethylene Perchloroethylene
2	Intersil Sunnyvale, Ca	Full Scale	Installed in 1995	100% granular zvi Trench and fill	4 ft. thick 6-20 ft. bgs. 40 ft. length	Dichloroethene Trichloroethylene Vinyl Chloride Freon 113
3	DuPont Oakley, Ca	Pilot Scale Full Scale	Pilot Scale 2001 Full Scale 2005	azimuth controlled hydraulic fracturing injection of ZVI/gel mixture	3-6" thick 35 ft. - 117 ft. bgs. 485 ft. length	Carbon Tetrachloride Trichloromethane CFC-11
4	Alameda NAS Alameda, Ca	Pilot Scale	Installed 1996	zvi funnel and gate excavation	10 ft. thick surface- 23 ft. bgs 15 ft. long	Dichloroethene Trichloroethylene Vinyl Chloride
5	Moffett Field Mountainview, Ca	Pilot Scale	Installed 1996	zvi funnel and gate trench and fill	6 ft. thick surface- 25 ft. bgs	Dichloroethene Trichloroethylene Perchloroethylene
6	BP Hitco Gardena, Ca	Pilot Scale	Installed 2003	azimuth controlled hydraulic fracturing	3-4.5" thick 18 ft. -100 ft. bgs. 100 ft. long	Trichloroethylene Perchloroethylene
7	Sierra Army Depot Herlong, Ca	Pilot Scale	Installed 2003	azimuth controlled hydraulic fracturing injection of ZVI/gel mixture	4.5" wide 90 ft. -115 ft. bgs. 75 ft. long	Trichloroethylene
8	Sierra Army Depot Herlong Ca,	Pilot Scale	Installed 2001	ARS Patented Ferox injection	70 ft. wide 90 ft. - 110 ft. bgs. 160 ft. long	Trichloroethylene
9	Travis AFB Fairfield, Ca 94535	Pilot Scale	Installed 1999	jet grout guar gum polymer zvi	5 ft. wide 15 ft. - 50 ft. bgs. 91 ft. long	Dichloroethene Trichloroethylene Vinyl Chloride
10	Fairchild Sunnyvale, Ca	Pilot Scale	Installed 1995	zvi excavation and fill continuous wall	10 ft. thick 30 ft. long 25 ft. deep	TCE other VOC's

The five projects eliminated from further review are described in Table 2. One project, Aerojet, is a more recent ZVI PRB project and was not reviewed because performance data were not available at the time of this report.

Table 2 Projects Considered but not Reviewed

	Project Name	Reason Project was not Included in Review
1	Hunters Point Navy Shipyard San Francisco, Ca 94124	In-situ ZVI injection study; Study involved Injection wells, not a permeable reactive barrier wall.
2	Louisiana Pacific 32600 Holquist Lane Fort Bragg, Ca 95437	A wall using carbon canisters to absorb contaminants
3	Aerojet Sacramento	Installation after the cutoff date of October 2006. Too early to see any results as the installation was in November 2006.
4	Vandenberg AFB ORC MTBE	This is a biological treatment reactive barrier, not an Iron barrier which this report focuses on. This barrier is constructed with pea gravel matrix with Oxygen Release Compound (ORC) injected into the ground in to stimulate a biological treatment.
5	French Camp Grain Elevator LLC 9504 South Harlan Rd French Camp	This project involves injection of ZVI into the aquifer in a source zone area, not a permeable reactive barrier wall.

2 PRB Design Comparison Calculations

The calculations used to develop a simple mathematical model for the breakdown of chlorinated solvents (parent products only) in the presence of ZVI are presented in Appendix A. The main equation developed to determine the required barrier thickness for the breakdown of contaminants using ZVI is:

$$\frac{W}{A} = F\frac{un}{k_1}\ln\left(\frac{P_0}{P}\right) \quad (1)$$

Where,
W = mass of iron in the wall, g
A = frontal area of the wall, cm^2
F = safety factor (4)
μ = groundwater flowrate, cm/day
n = soil porosity (0.30)
k_1 = temperature compensated rate constant, cm^3/g day.
P_0 = initial contaminant concentration, ppb
P = final contaminant concentration, ppb
L = barrier thickness, cm
ρ_{iron} = bulk density of iron = 2.2 g/cm^3

Using relationship (2) below:

$$\frac{W}{A\ \rho_{iron}} = L \quad (2)$$

Equation (1) can be simplified by rearranging terms and replacing terms with constants to yield the following equation:

$$L = \frac{0.54}{k_1}\ u\ Ln(P_0/\ P) \quad (3)$$

With equation (3) and the rate constants from column studies listed in Table 3 below, the equations to determine an adequate design wall thickness for degrading carbon tetrachloride, and trichloroethylene, and cis 1,2-DCE were developed as shown in Table 4.

Table 3 Chlorinated Compound Half Lives in ZVI

Contaminant	Half Life (hrs) in ZVI	Half Life Relative to cis 1,2-DCE	Estimated Rate Constant
Carbon Tetrachloride	0.2 hours	0.065	k_1=31.0 cm^3/g day
Perchloroethylene	0.3 hours	0.097	k_1=20.7 cm^3/g day
Trichloroethylene	0.6 hours	0.19	k_1=10.3 cm^3/g day
Cis 1, 2-DCE	3.1 hours	1.00	k_1=2.0 cm^3/g day
Vinyl Chloride	4.7 hours	1.52	k_1=1.31 cm^3/g day

Table 4 ZVI Wall Thickness Design Equations for Chlorinated Compounds

Modified Appendix A PRB design equations	Chlorinated Hydrocarbon
L = 0.27 u Ln(Po/P)	for **cis 1,2-DCE**
L = 0.017 u Ln(Po/P)	for **Carbon Tetrachloride (CT)**
L = 0.052 u Ln(Po/P)	for **Trichloroethylene (TCE)**

These equations in Table 4 were used to assess the design (iron wall thickness) of each of the PRB projects in this report. TCE and Carbon Tetrachloride are contaminants commonly treated with ZVI PRBs. Cis-1,2-DCE is a breakdown product of TCE and can be the critical contaminant to design for since it is more difficult (slower) to treat via ZVI.

These calculations are for comparison purposes and should not be used in the design of PRBs. For actual PRB design, mathematical models accounting for the kinetics of intermediate product generation and degradation should be used, along with column test data from the specific iron to be used and samples of the actual contaminated ground water.

2.1 PRB Comparison Calculation Summary

Table 5 lists each site along with the maximum groundwater concentration of the main contaminant at the site, maximum expected groundwater flowrate at the site, the treatment target concentration, and details of the thickness of the PRBs at each site. With the exception of Mohawk, the treatment targets for each site have been assumed to be the California MCLs for the given contaminants. The wall thickness required is calculated using the equations in Table 4 along with the design parameters listed for each site in Table 5 below. The calculated wall thickness required includes a safety factor of four.

Table 5 Design Parameters and Wall Thickness

Facility	Main Contaminant	Max Concentration P_0	Groundwater Flowrate	Cleanup Target P	Wall thickness required	Wall thickness actually used
Travis	TCE	8,000 ppb	0.27 ft./day	5 ppb	0.10 ft.	0.65 ft.
BP Hitco	TCE	100,000 ppb	0.15 ft./day	5 ppb	0.08 ft.	0.375 ft.
Mohawk	Cis 1,2-DCE	4600 ppb	5.6 ft/day	440 ppb	3.6 ft.	4.0 ft.
Sierra Army Depot-ARS	TCE	2500 ppb	0.5 ft./day	5 ppb	0.16 ft.	0.083 ft.
Sierra Army Depot-GeoSierra	TCE	2500 ppb	0.5 ft./day	5 ppb	0.16 ft.	0.375 ft.
Alameda	TCE	100,000 ppb	0.1 ft./day	5 ppb	0.05 ft.	5.0 ft.
Moffett	TCE	3000 ppb	1.5 ft./day	5 ppb	0.50 ft.	6.0 ft.
Fairchild/Applied Materials	Cis 1,2-DCE	2000 ppb	0.5 ft./day	6 ppb	0.78 ft.	4.5 ft.
DuPont Oakley	CT	50,000 ppb	0.3 ft./day	0.5 ppb	0.06 ft.	0.5 ft.
Intersil	TCE / *cis 1,2-DCE*	210 ppb *1415 ppb*	1.2 ft./day	5 ppb *6 ppb*	0.23 ft. *1.77 ft*	4.0 ft.

The column to the far right in Table 5 is the effective (100% iron) iron wall thickness actually used for the PRB project at the site. The actual thickness column has been color coded using the key below in Table 6.

Table 6 Design Factor Color Code Key

Design Safety Factor	Color key
Greater than 10	
Greater than 2 but less than 10	
Greater than 1 but less than 2	
Less than 1	

In every case except Sierra Army Depot – ARS Technologies, the PRB was designed with more than enough iron to theoretically reach the treatment target.

3 Site Performance Reviews

Each of the 10 projects identified as suitable for analysis is discussed below. Not every project was amenable to a detailed and quantitative analysis. However, sufficient data was available on each project to at least allow a qualitative assessment of performance.

3.1 Evaluation of the Alameda NAS PRB Project

Site History

The U.S. Naval Air Station, Alameda operated from 1938 until its closure in 1997. During the Base Realignment and Closure Process, an area of contamination was identified from old historical aerial photos showing liquid waste pits on the west side of the island. Investigations uncovered several chlorinated solvents along with benzene, toluene, ethyl benzene, and xylenes (BTEX) in the groundwater and soil beneath the site. The total groundwater concentration of the chlorinated solvents (trichloroethylene, cis-1, 2-dichloroethylene, and vinyl chloride) exceeded 100,000 ppb. Toluene was found at levels of up to 10,000 ppb.

Site Hydrology

A significant portion of the island was built up from dredging activities which placed sandy fill material onto the existing bay silts and clays. This resulted in a shallow sandy aquifer 22-24 feet thick overlying a relatively impermeable silt/clay layer 15 to 20 feet thick. Depth to groundwater in the area ranges from 4 to 7 feet below ground surface. The groundwater flow is from east to west at approximately 0.05 feet/day.

PRB Pilot Project

In 1996, the Navy participated in a pilot scale permeable reactive barrier project. The Navy's PRB was a gate design consisting of a zone of zero valence iron followed by a biosparge zone.

The area for the gate was excavated down to the bay silt/clay layer (22 ft. bgs) and a 2 ft. thick concrete pad was poured to prevent the barrier assembly from settling. The 14 ½ feet thick barrier was installed in the following sequence: 18 inches of sand mixed with 5% iron, 5 ft. of 100% granular iron, a 3 ft. pea gravel transition zone, a 3 foot biosparge zone, and finally a 2 ft. pea gravel zone.

The iron and biosparge zones extended from 7 to 20 ft. bgs. Ten (10) ft. long funnel walls were installed on either side of the barrier as shown in figure 2 and 3 below.

Figure 2 Plan View of Alameda Funnel and Gate PRB System

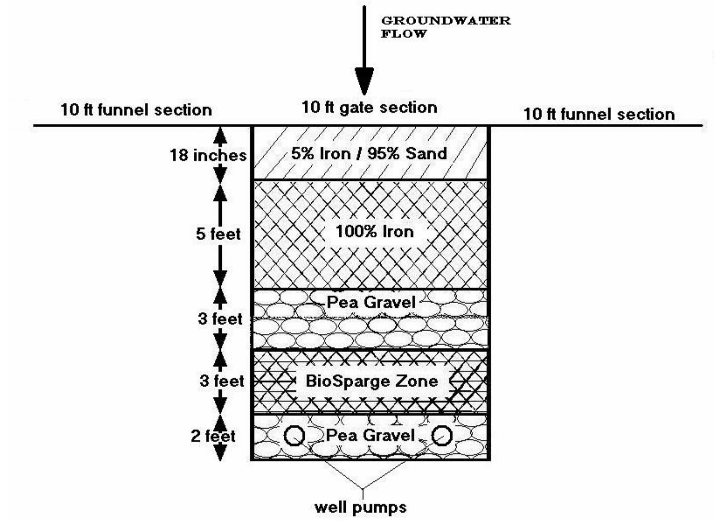


Figure 3 Alameda PRB Cross Section View

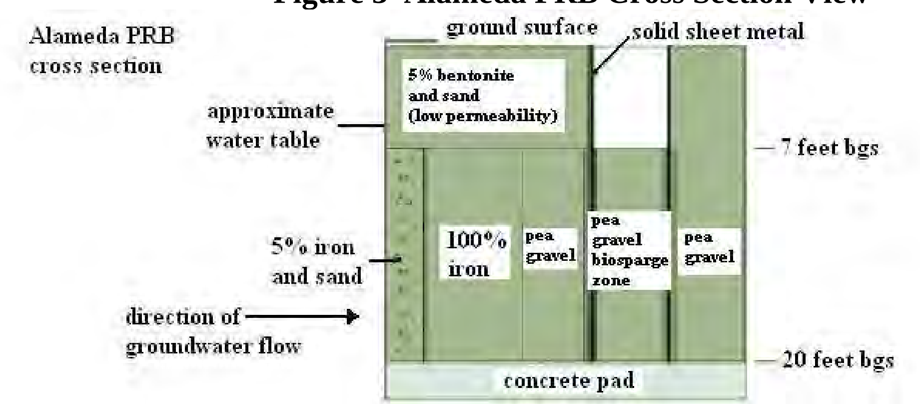


Figure 2 and 3 Taken from: *Permeable Reactive Walls,* RITS 98 PRB 1 NFESC

Operation

For the first 70 days, the well pumps were used to establish a groundwater flow rate of 0.35 feet per day. At this rate, breakthrough was detected at downgradient monitoring points. The well pumps were then adjusted to a near natural conditions flowrate of 0.1 feet per day. The system was operated at this flowrate for one year. Finally, the barrier was allowed to operate under natural conditions without the well pumps.

Results

This was a very short term project that was monitored for only a year (May 1997 through May 1998) at the near natural ground water flow conditions of 0.1 ft. /day. Only summary results were available from the following report:

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Technology Innovation Office Permeable Reactive Barriers Interim Summary Report: Permeable Reactive Barriers Using a Funnel and Gate Configuration May 2002 http://costperformance.org/pdf/PRBSummaryFG0617.pdf

The summary results are as follows:

a) Degradation of greater than 90% of the chlorinated organics was observed across the barrier at high influent concentrations (>100,000 ppb total VOCs)

b) At lower influent VOC concentrations, almost complete degradation (>99%) was observed.

c) High sparging rates in the biosparge zone caused volatilization of contaminants from the water column. An estimated 66% of the VC and 30% of the cis 1,2-DCE was volatilized in the sparge zone".

References

Battelle for NFESC (1998), *Permeable Reactive Wall Slide Presentation*, Retrieved, July 7, 2006, from https://portal.navfac.navy.mil/pls/portal/url/ITEM /23CCAB8395DD28ACE0440003BA8967D9 -

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Technology Innovation Office (May 2002), *Permeable Reactive Barriers Interim Summary Report: Permeable Reactive Barriers Using a Funnel and Gate Configuration,* Retrieved, May 15, 2006 from: http://costperformance.org/pdf/PRBSummaryFG0617.pdf

Radisav D. Vidic, PhD for GWRTAC (November 2001), *Permeable Reactive Barriers: Case Study Review*, Retrieved, April 28, 2006 from: http:// www.prbnet.qub.ac.uk/prb_net /new_site/Reports/gwrtac1.pdf

Permeable Reactive Walls, RITS 98 PRB 1 NFESC Chuck Reeter or Jed Costanza, Battelle Arun Gavaskar, Neeraj Gupta, or Bruce Sass, RITS 98 PRB Agenda -- Topics on Permeable Reactive Walls.

3.2 Evaluation of the BP-Hitco Permeable Reactive Barrier Project

Site History

This PRB project is located on a facility in an industrial area of Gardena. Over the years, the facility has changed ownership many times. It was owned by Zenith Plastics (1947-1956), 3M (1956-1961), H. I. Thompson Company (HITCO) (1961-1969), Armco Steel (1969-1985) and several other companies through 1997. From 1997 to present, the site has been operated by HITCO Carbon Composites.

HITCO currently manufactures high tech composite structural assemblies and high temperature materials at the facility. The company products include aircraft and automotive brake components, jet engine flaps and seals, solid rocket motor nozzles, and heat shields. Current and past production at the plant used a variety of solvents, paints, resins, and adhesives in the manufacturing process.

Site/Contaminant Hydrology

The Bellflower Aquiclude underlies the facility. It consists of a heterogeneous mixture of fine-grained sediments that extends to 130 feet bgs. The formation is characterized by low permeability interbedded clay, silt, and sand sequences forming discontinuous lateral beds. At 30, 50, and 70 ft bgs there are 5 foot thick silty sand layers that are saturated with water and have the characteristics of a confined aquifer. These three layers are considered to be hydraulically connected.

In 1995, extensive groundwater and soil investigations were performed in the area and a plume of chlorinated hydrocarbon contamination was found to extend offsite to the southeast. The primary contaminants in the plume were trichloroethylene (TCE), and perchloroethylene (PCE). Due to the low groundwater gradient of 0.0008 ft in the area, the plume has not migrated very far offsite or increased much over the last 11 years.

PRB Design/Goal

This pilot project was designed to show that an iron based PRB could effectively treat the highest TCE levels encountered at the site. Specific remediation goals were never established for this project.

In August 2003, GeoSierra installed the pilot PRB at the site using their patented hydrofracturing process. The installed wall was 100 feet long and extended from 18 to 100 feet bgs. About 250 tons of granular iron was used to construct the 4.5 inches thick PRB. A 675 foot extension of the PRB was also planned, depending on success of the pilot phase.

Using the EPA Scoping Calculations equation modified for TCE with a groundwater flowrate of 0.15 ft/day and an initial TCE concentration of 100,000 ppb and a cleanup goal of 5 ppb, the computations call for a design thickness of 1 inch of iron. The 4.5 inches actually used for the PRB should be able to adequately remediate the TCE contamination to MCL level.

PRB Performance Measurements

Locations of monitor wells installed to evaluate PRB performance are show in Figure 4. Well screen intervals or other constructions details on these monitoring wells could not be found. The different sample depths reported for each monitoring well are given in Table 7.

Figure 4 BP Hitco Monitoring Well Layout

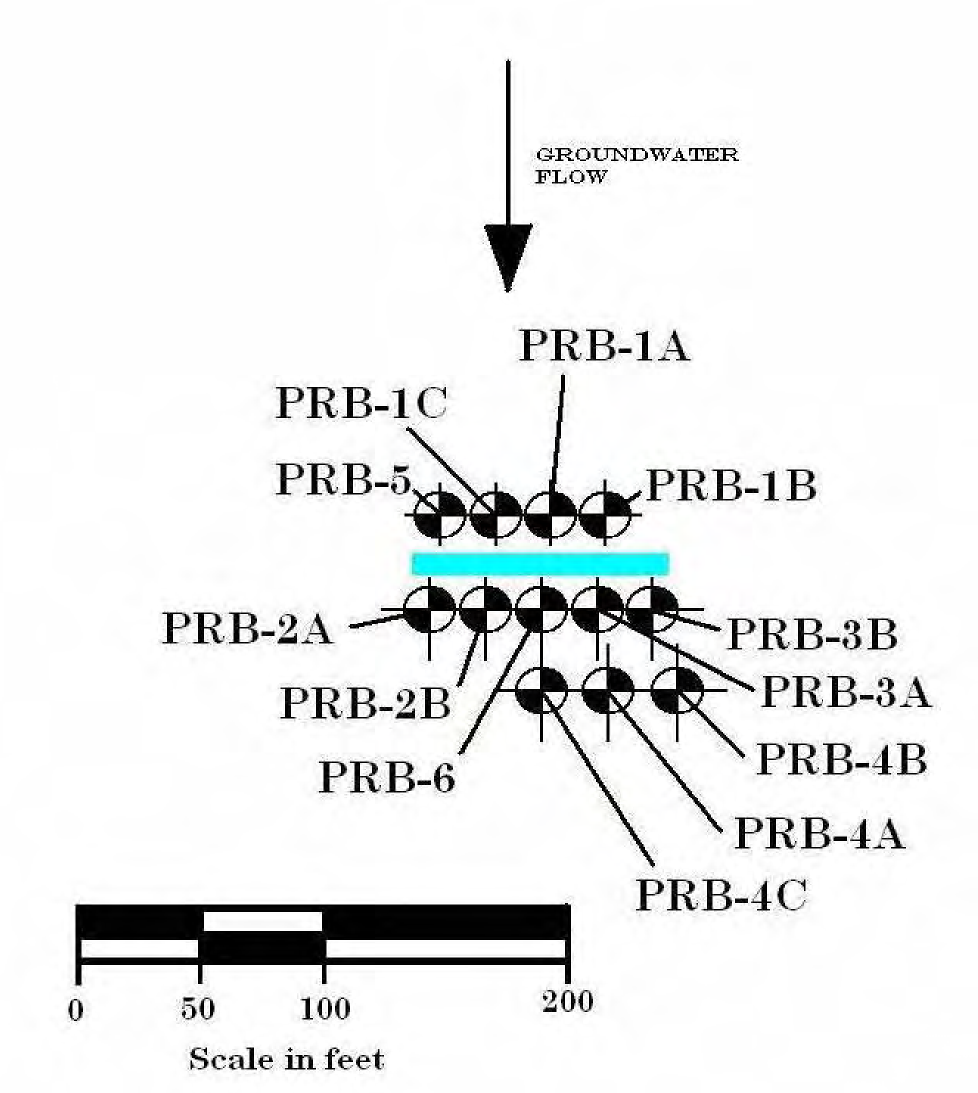


Table 7 BP Hitco Monitoring Well Details

Well	Location	Sample Depths (ft. bgs)
1A	Upgradient	30
2A	downgradient	30
3A	downgradient	30
4A	downgradient	30
1B	Upgradient	50
2B	downgradient	50
3B	downgradient	50
4B	downgradient	50
1C	upgradient	100
4C	downgradient	100
5	upgradient	70
6	downgradient	70

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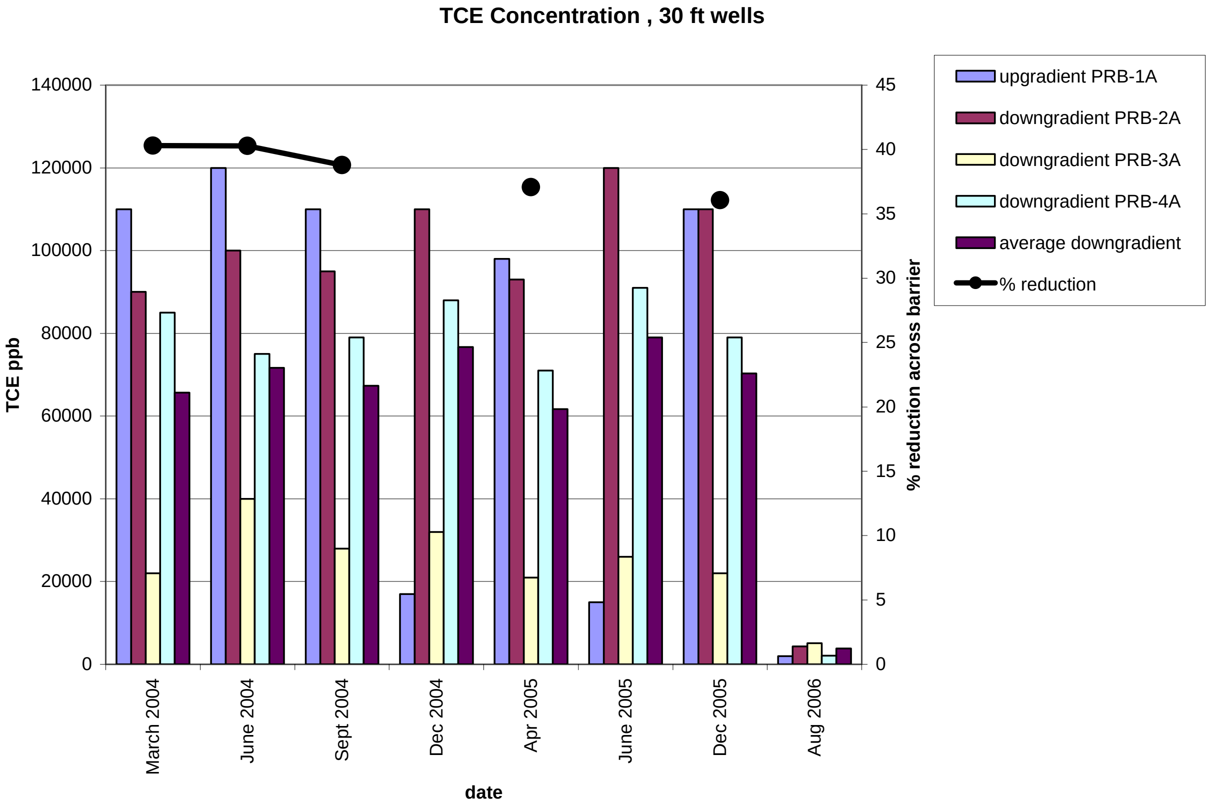
PRB Performance Analysis

Figure 5 and 6 below show the TCE and PCE concentrations across the PRB at the 30 foot level. In figure 5, the TCE concentration reduction across the barrier averages about 40% for the first three quarters of 2004. In December of 2004, however, the upgradient TCE concentration drops from over 100,000 ppb to less than 20,000 ppb with virtually no change in the downgradient concentrations. The upgradient TCE levels then alternate between high levels around 100,000 to lower levels around 20,000 every quarter with little change in downgradient levels until August 2006. In August 2006, all of the TCE levels dropped to record low levels below 5000 ppb.

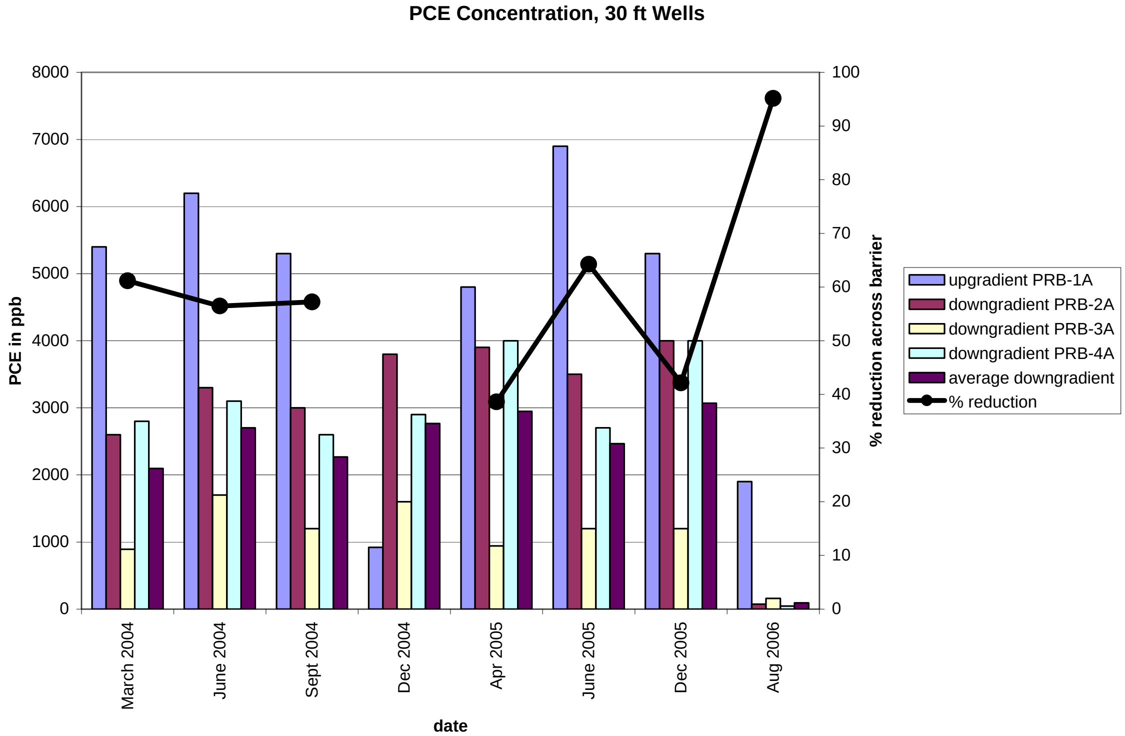
The results at the 30 foot level have been highly inconsistent. With exception of the latest sampling event results, August 2006, the greatest percent reductions in TCE and PCE was less than 65% and 45%, respectively. For several sampling events, downgradient concentrations for PCE or TCE were higher than upgradient concentrations. Then for the most recent sampling event data, all downgradient PCE and TCE concentrations and the upgradient TCE concentration inexplicably dropped an order of magnitude. As upgradient PCE concentrations didn't change, there appeared to be a >95% reduction for PCE.

Figure 5 BP Hitco TCE Concentration, 30 ft. Wells



The PCE levels at 30 feet show a similar trend of ambiguous results across the barrier.

Figure 6 BP Hitco PCE Concentration, 30 ft. Wells



Figures 7 and 8 below show the 50 ft. level history of the TCE and PCE concentrations across the PRB. The downgradient wells, 3B and 4B, have TCE and PCE levels much higher than the upgradient well. The testing results at this level do not show the consistent concentration reductions that would be expected with a viable PRB in place.

The results at the 50 foot level do not show any reduction in contaminant levels across the PRB with the exception of well 2B and in fact show increases over most of the quarters.

Figure 7 BP Hitco TCE Concentrations, 50 ft. Wells

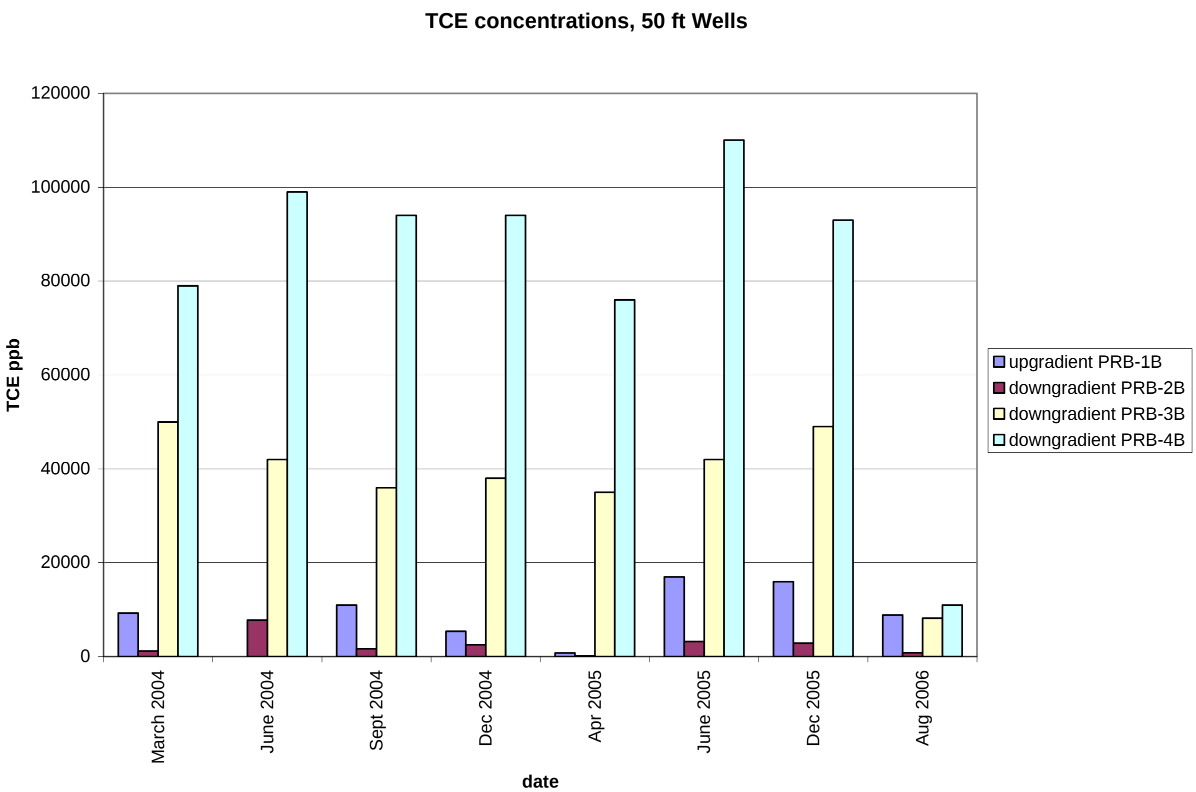
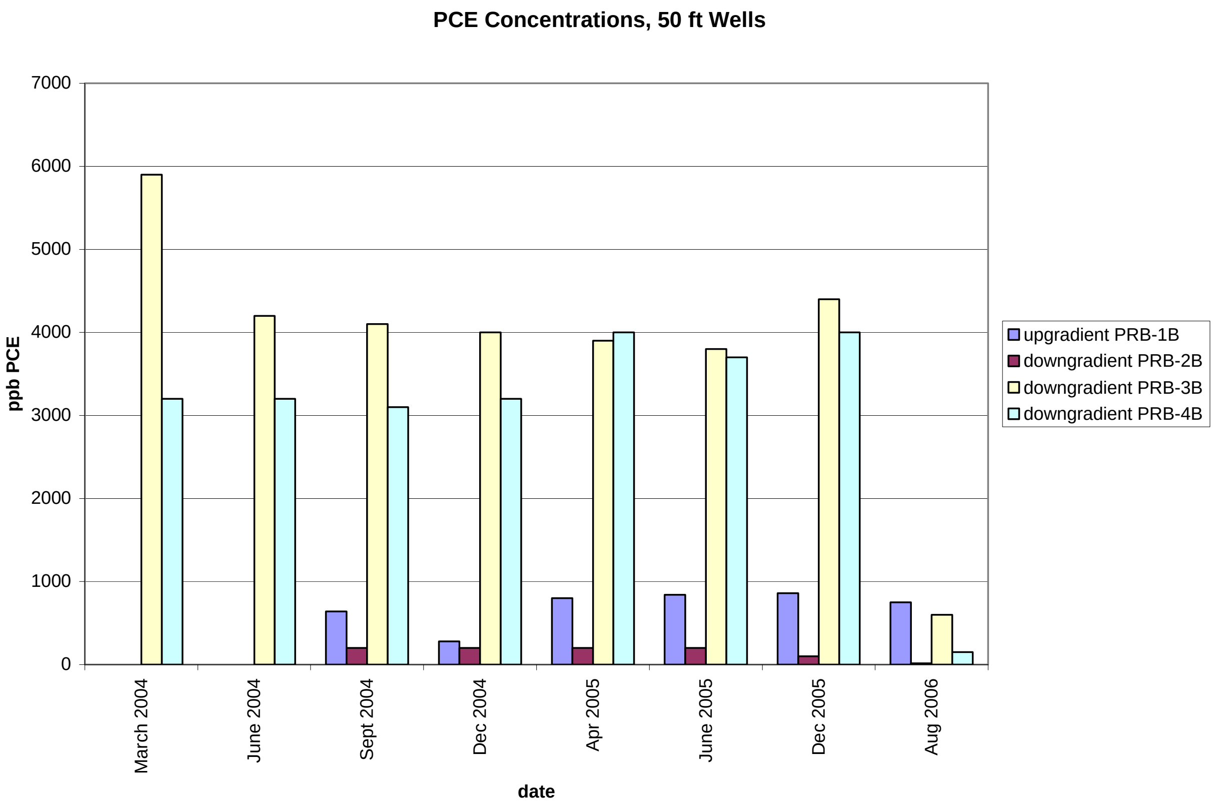


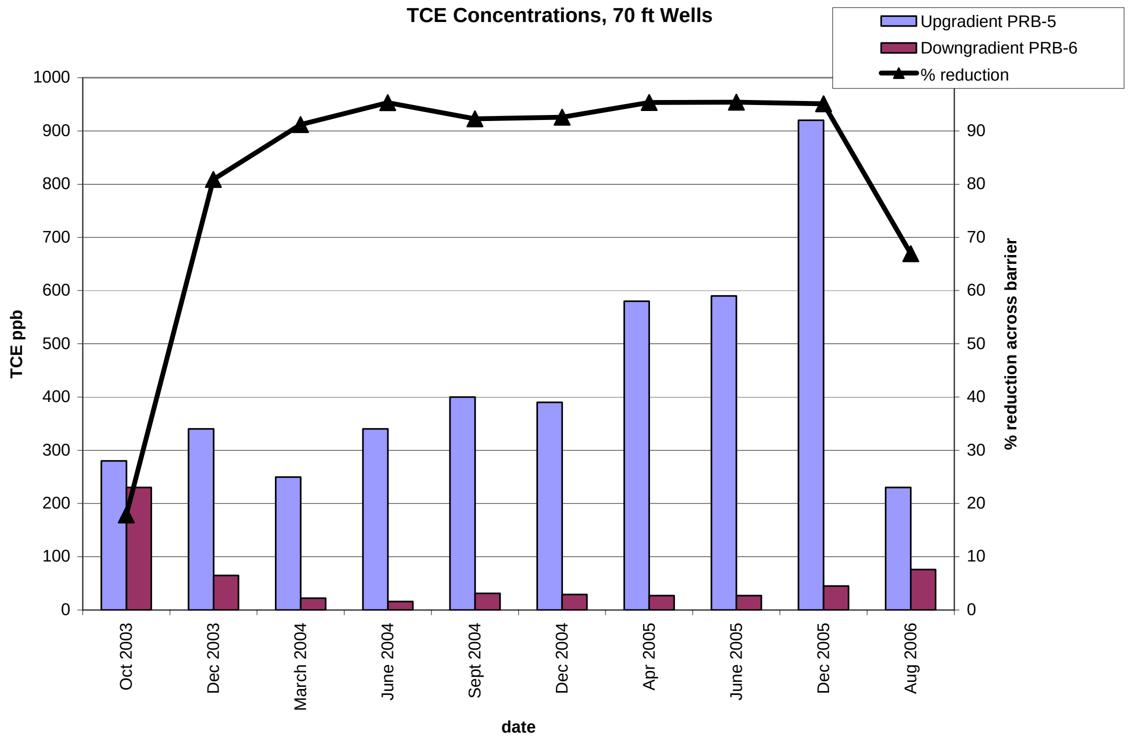
Figure 8   BP Hitco PCE Concentrations, 50 ft. Wells



The 70 ft. wells showed non-detectable levels of PCE, but did detect significant levels of TCE. A graph of the 70 foot level TCE concentrations upgradient and downgradient of the PRB is shown below in Figure 9. The percent reduction in TCE concentration across the barrier appears favorable at over 90% for most of the period. However, the overall upgradient TCE concentration is very low compared to the TCE concentrations at 30 feet and 50 feet.

The deep wells, 1C and 4C, showed virtually non detectable levels of TCE and PCE from 2003 to present.

Figure 9 BP Hitco TCE Concentrations, 70 ft. Wells



Summary and Conclusions

For the most contaminated zone at the 30 ft. depth, high concentrations of TCE (~10,000 ppb) and PCE (~5000 ppb) were reduced about 40% and 60%, respectively. Overall, these results do not support the expansion of the project.

At the 50 ft. depth, all monitor wells with the exception of well 2B indicated a concentration increase across the PRB. Further investigation with additional monitoring wells would be needed to understand why well 2B consistently indicates low levels of TCE and PCE. This may be due to subsurface heterogeneities and resulting horizontal variations in groundwater contamination flow patterns passing through the barrier. Tracer studies between up and downgradient monitoring wells might help explain why is occurring. Baseline data at MW locations prior to construction of a barrier would serve to answer such anomalies.

Monitor well locations do not appear optimally located. Ideally, wells sampling the same zone up and downgradient of the barrier should be along a transect parallel to the groundwater flow.

References

Parsons, *January 2005 GROUNDWATER MONITORING EVENT FORMER BP HITCO FACILITY 1600 WEST 135TH STREET GARDENA CALIFORNIA Regional Board File No. 95-101/SLIC Number 470* (March 25, 2005).

Parsons, *July 2006 GROUNDWATER MONITORING EVENT (Regional Board File No. 95-101/SLIC Number 0470) AND WASTE DISCHARGE REQUIREMENTS (Compliance No. CI-8596, Order No. R4-2002-0030, Series No. 026) FORMER BP HITCO FACILITY 1600 WEST 135TH STREET GARDENA CALIFORNIA* (September 22, 2006)

3.3 Evaluation of the DuPont Oakley PRB Project

Site History

In 1955, the DuPont Company purchased 552 acres of land north of Main Street in Oakley, California. The property extends to the San Joaquin River to the north and is bordered on the west by Bridgehead Ave. and on the east by Big Break Road.

In 1957 DuPont built a plant on 180 acres of the site which became known as the DuPont Antioch Works. The plant manufactured tetraethyl lead for use in gasoline, various Freon compounds used in refrigeration and cleaning, and titanium oxide used primarily as a white pigment. Over 600 employees worked at the plant at its peak in production.
With the introduction of catalytic converters on cars, the use of tetraethyl lead in gasoline started to be phased out. Many Freon compounds were phased out due to their adverse effects on the ozone layer. As a result, demand for the plants primary products was reduced. In 1998, the plant was officially closed.

Site Groundwater Contamination and Hydrology

Unconsolidated sand, silty sand, gravely sand, and gravel exist across the DuPont Oakley site in an interval ranging from 110 to 140 feet thick. Below this is the Montezuma Formation which consists of impermeable silty clay ranging from 200 to 300 feet thick. Two clay layers are present at approximately 10 to 20 feet deep and 40 to 65 feet deep. These clay layers divide the aquifer into three units, the Surficial Aquifer, the Upper Aquifer, and the Lower Aquifer. Thinner and less extensive clay and silt layers present in the Lower Aquifer have given rise to its further division into L1, L2, and L3 zones. Groundwater flow through the Aquifers is generally to the north at 0.30 to 0.60 feet per day. Below, Table 8 describes the various geologic layers at the Oakley site.

Table 8 DuPont Oakley Geologic Layers

Unit	Depth range (ft.. bgs)	Aquifer Type	Geological Description
Surficial Aquifer	0-15	Unconfined	Fine to medium grained dune sands
Surficial/upper confining unit	10-20	Aquitard	Silty clay
Upper Aquifer	20-50	Confined	Upward fining sands with minor gravel
Upper/Lower confining unit	50-55	Aquitard	Clay layers in silty matrix
Lower Aquifer	52-120	Confined	Upward fining sands and gravel
Montezuma Formation	120 - >200	aquiclude	Silty clay

In the 1980’s, DuPont sampled the groundwater at various locations at the site. Carbon Tetrachloride (0-50,000 ppb), 1, 1, 2 trichlorotrifloroethane (Freon 113) (0-200 ppb), trichlorofloromethane (Freon 11) (0-250 ppb) and 1, 2 dichloroethane (EDC) (0-350 ppb)

were found in the groundwater and soil at the plant site. The contaminants were characterized in 3 distinct plumes. The most significant plume, Plume #1, is considered to be the greatest threat to the environment with a peak carbon tetrachloride concentration of over 100,000 ppb in groundwater. Figure 10 below shows Plume 1 in relation to Plume 2 and Plume 3.

Figure 10 DuPont Oakley Groundwater Contamination Plumes

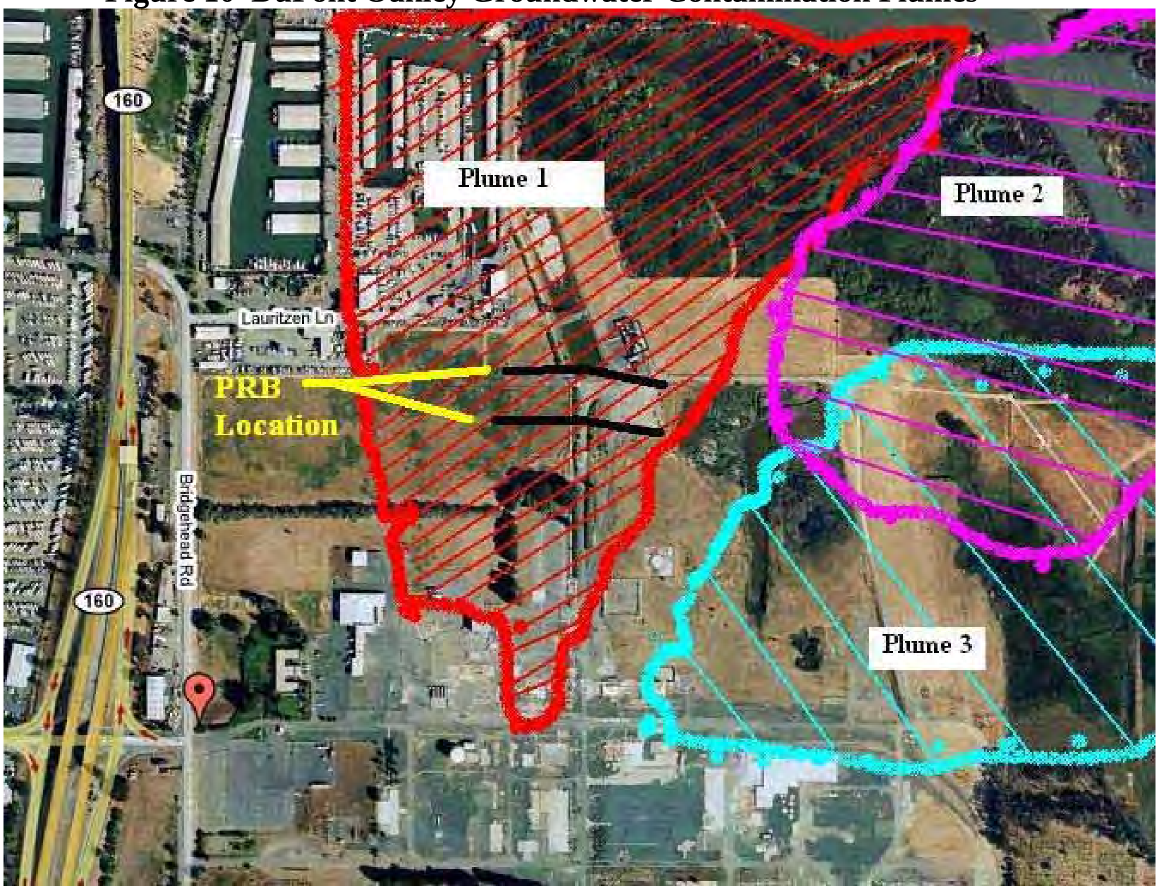


Figure 11 below shows the concentration of carbon tetrachloride in the upper aquifer section of Plume 1, along with the locations of the PRBs.

Figure 11 Upper Aquifer Carbon Tetrachloride Concentrations at DuPont Oakley

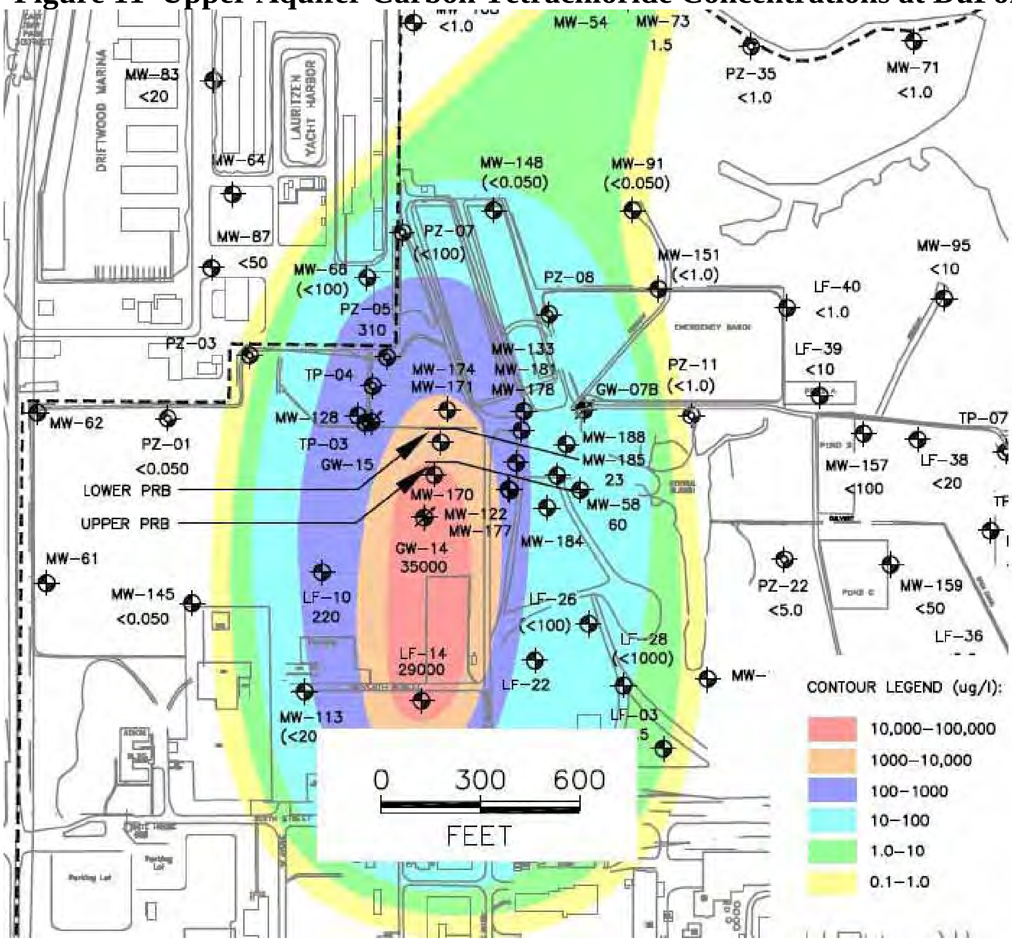


Figure 12 below shows the carbon tetrachloride concentration in the lower aquifer section of Plume 1, as well as the location of the PRBs installed at the site.

Figure 12 Lower Aquifer Carbon Tetrachloride Concentrations at DuPont Oakley

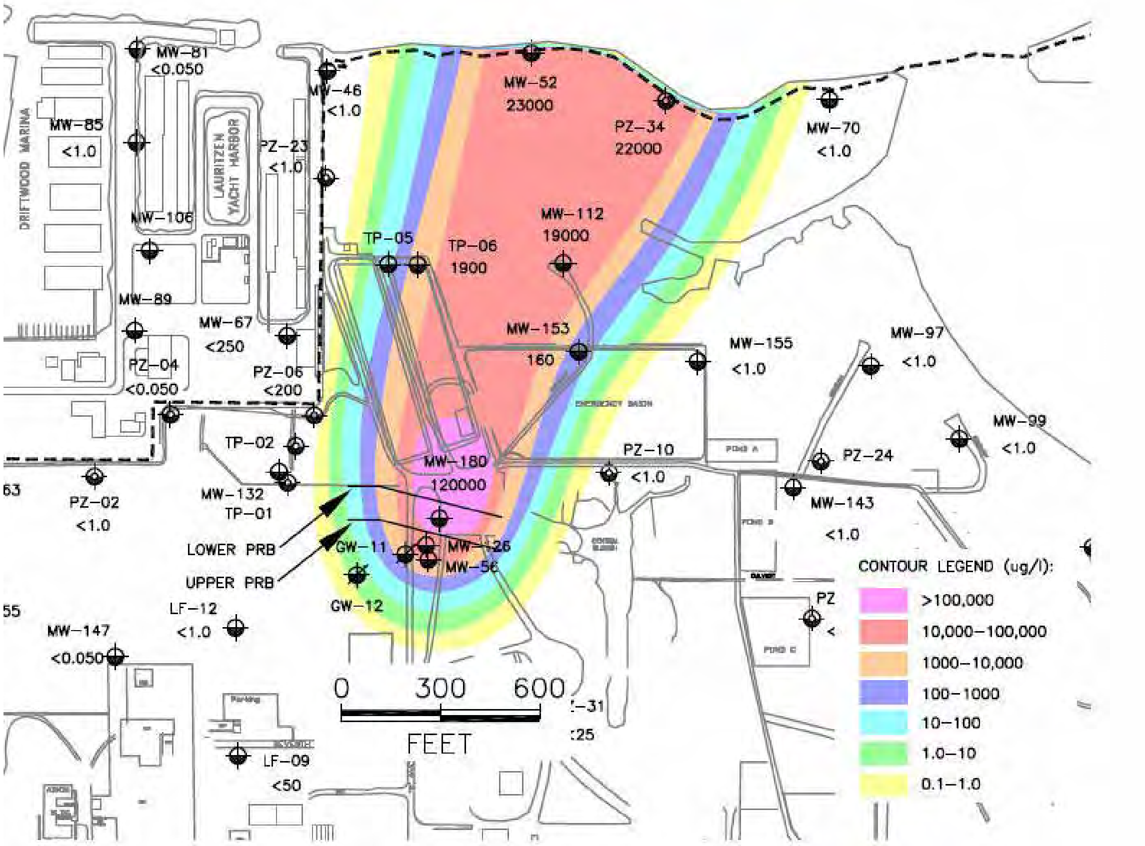


Figure 11 and Figure 12 were adapted from:
CORPORATE REMEDIATION GROUP An Alliance between DuPont and URS Diamond, *2006 ANNUAL GROUNDWATER MONITORING REPORT FOR DUPONT OAKLEY SITE*, February 28, 2007

Remediation Activities

In 1990, a groundwater treatment facility (GWTF) was installed to extract and treat groundwater at the site. In addition, over 130 monitoring wells were installed at the site. In its last year of operation, DuPont spent over $1,000,000 on the operation and maintenance of the GWTF. After 11 years of operation the GWTF was shut down because it had failed to stop migration of the contaminant plume (Plume #1) and had not significantly reduced the overall groundwater contaminant levels.

In the year 2000, a pilot zero valence iron PRB was installed. In 2005, two full scale PRB's were installed at the site based on the favorable performance of the pilot PRB.

Barrier Projects

In 2001 DuPont decided that an iron barrier might be the best way to stop the northward migration of the contaminant plume. Because the contamination plume extended to below 100 feet in depth conventional trenching techniques were not applicable at this site. DuPont contracted with GeoSierra to install the PRB using their patented hydrofracturing technology.

In March 2001, GeoSierra installed a nominal 6 inch thick by 110 foot wide zero valence iron barrier at the Oakley site as a pilot project using their hydrofracturing technology. The barrier extended across the depth of the Lower Aquifer from 40 to 117 feet below the ground surface. The PRB was installed as an Interim Measure intended to substantially reduce the source of continued plume migration to the river and to make a long term positive impact on water quality.

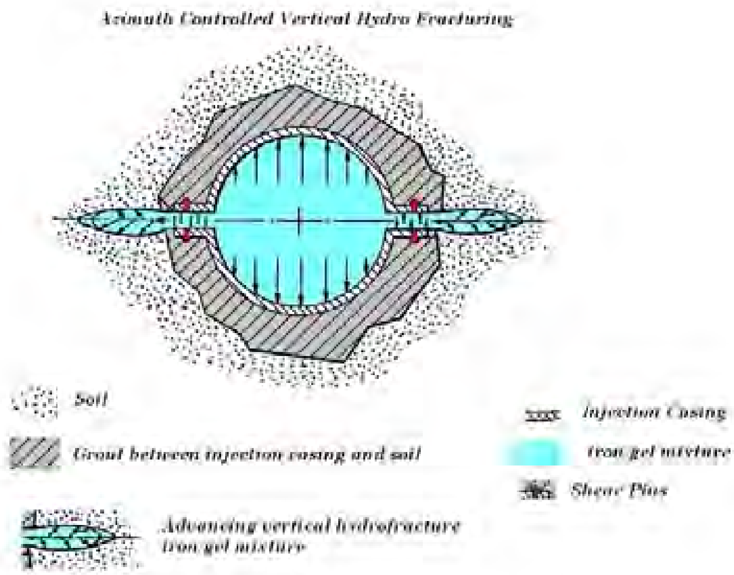
Azimuth Controlled Vertical Hydraulic Fracturing

GeoSierra's patented hydrofracturing technology injects a mixture of gel and iron into the ground to form a continuous permeable reactive barrier. First, the granular iron is mixed with the liquid gel. This mixture is next pumped to the fracture injection well head. A cross linking agent is added inline to thicken the gel and an enzyme is added to break down the gel after several hours. The gel/iron mixture is pumped into a specially designed fracture well casing where it is injected into the formation at a specified depth interval using packers to seal off sections above and below.

The fracture casing, which has been grouted in place, opens under the pressure of the gel/iron mixture and a fracture begins to propagate through the soil. Figure 13 below shows a top view (cross section) of gel/iron mixture being injected into the ground in the azimuth controlled vertical hydraulic fracturing process. The cross section is of the hydrofracture casing surrounded by grout. As the pressure of the gel/iron mixture in the casing increases, the casing splits the hardened grout and starts to separate. This initiates a fracture in the soil on each side of the casing.

Under controlled hydraulic pressure, the fractures on each side of the casing continue to propagate as vertical sheets for up to 8 feet from the fracture casing. Sheets from adjacent fracture well assemblies merge to form a continuous barrier of gel and iron. The enzyme added to the gel causes it to break down after several hours so that eventually there is no impediment to the groundwater flow though the barrier. GeoSierra monitors the entire process with sensors placed on each side of the forming barrier to ensure that the iron is getting placed as planned.

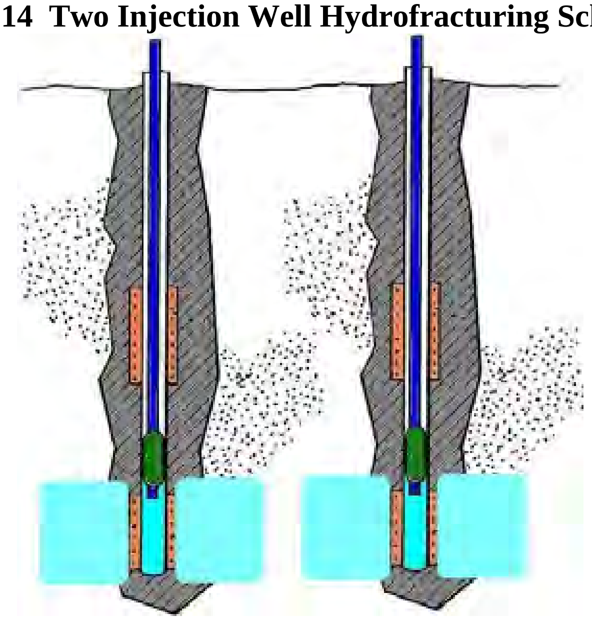
Figure 13 Azimuth Controlled Vertical Hydrofracturing



Adapted from: US Patent 6216783 Grant Hocking et al. April 17, 2001

Figure 14 depicts the continuation of the fracture process with the iron/gel fractures propagating away from two injection wells. The vertical panels of gel/iron from each well will merge and coalesce to form a continuous iron barrier.

Figure 14 Two Injection Well Hydrofracturing Schematic

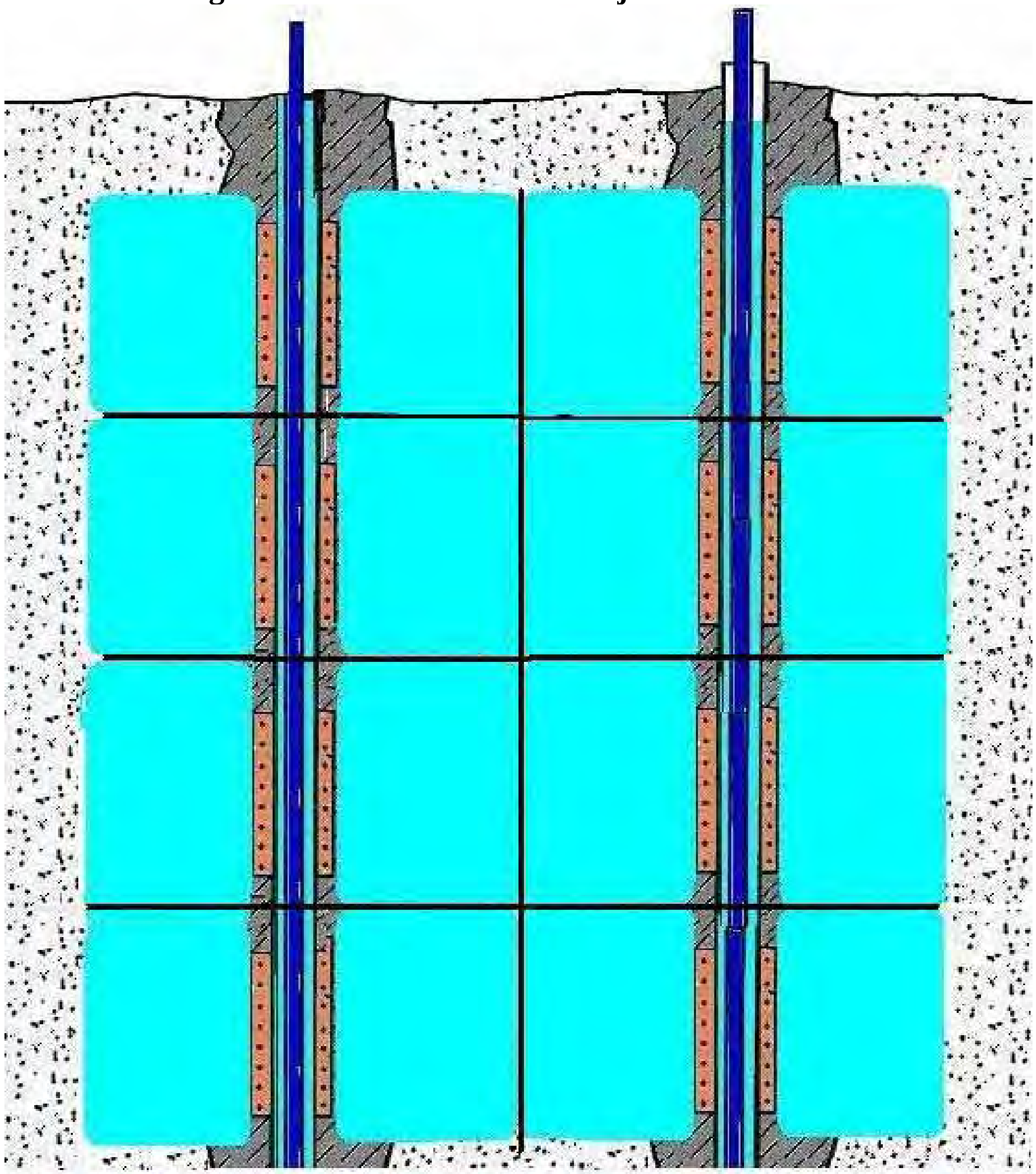


Adapted from: US Patent 6216783 Grant Hocking et al. April 17, 2001

Figure 15 below shows the completed panels of the PRB. With plugs placed above and below the desired fracture injection section, the iron/gel mixture is directed to the upper fracture casing of the well to initiate the fracture and propagation of the upper PRB panels. The upper panels will merge and coalesce with the adjacent vertical panels and also the lower panels to form a continuous barrier. There can be as many as 4 separate injections zones located up and down the injection well casing.

The lower PRB at DuPont Oakley was constructed using 4 injection levels at each injection well assembly as depicted below.

Figure 15 Two Well / 4 Level Injection Schematic



Adapted from: US Patent 6216783 Grant Hocking et al. April 17, 2001

DuPont Oakley PRB Project Description

Lower Aquifer

Phase I (pilot project phase) of the PRB project was installed in March of 2001. For this project, 7 fracture well casings were installed at 15 ft. apart. The panels were installed over a length of 110 feet and from a depth of 45 ft. to 117 ft. bgs. Multiple injections were made to yield an average wall thickness of 6" and an iron loading of 90 lbs of iron /sq ft. area.

Based on the favorable results from the Phase I pilot project, DuPont decided to continue the project by adding two full scale PRBs to the project in Phase II. In February 2005, preliminary construction activities were started for Phase II of the PRB project. The original pilot PRB was extended with fracture wells F8- F31 each spaced 15 feet apart. These wells had 4 fracture injection sections each to place iron/gel panels from ~ 40 ft. bgs to 110 ft. bgs. Panels from wells F8-F25 were injected to a thickness of 6 inches. The panels of wells F26-F28 were injected to 4.5 inch thickness. Finally, wells F29-F31 were injected to 3 inches thick. The injections were completed on July 11 2005.

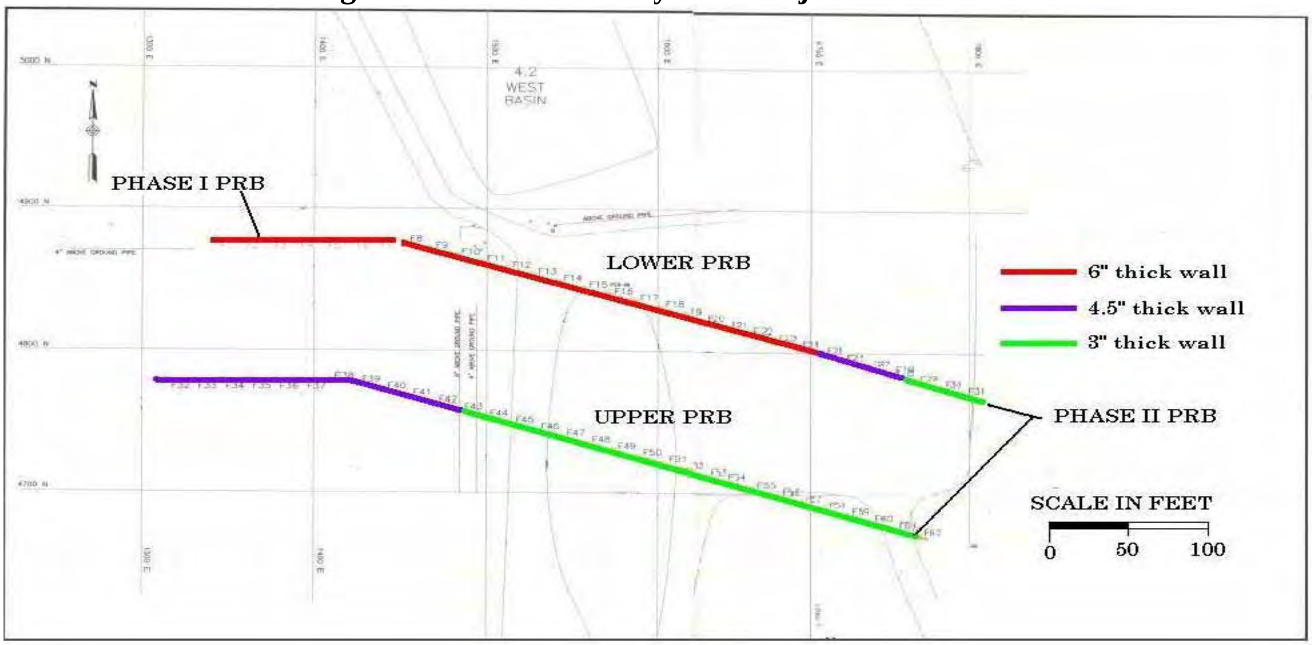
Upper Aquifer

Fracture injection wells F32-F62 were installed into the upper aquifer to inject panels from 30-45 feet bgs to 50-55 ft. bgs. The upper wall is 485 feet long and is 100 feet upgradient of the lower PRB. Fracture wells F32-F49 used one injection zone each. Wells F50-F62 used two injection zones each. Panels F32- F43 were injected to 4.5 inches thick and wells F44-F62 were injected to 3 inches thick.

The injection process was monitored by GeoSierra's resistivity imaging technology to insure the panels were being placed in the proper location and had the proper thickness. DuPont independently verified the placement and thickness of the panels using 30 degree inclined borings and electrical resistivity measurements at 10 locations across the two barriers. Two borings were redone at adjacent locations due to insufficient data to verify the thickness of the PRB. The data from the inclined borings and resistivity measurements showed that the PRB was installed to the correct thickness at the 10 locations along the PRB alignment

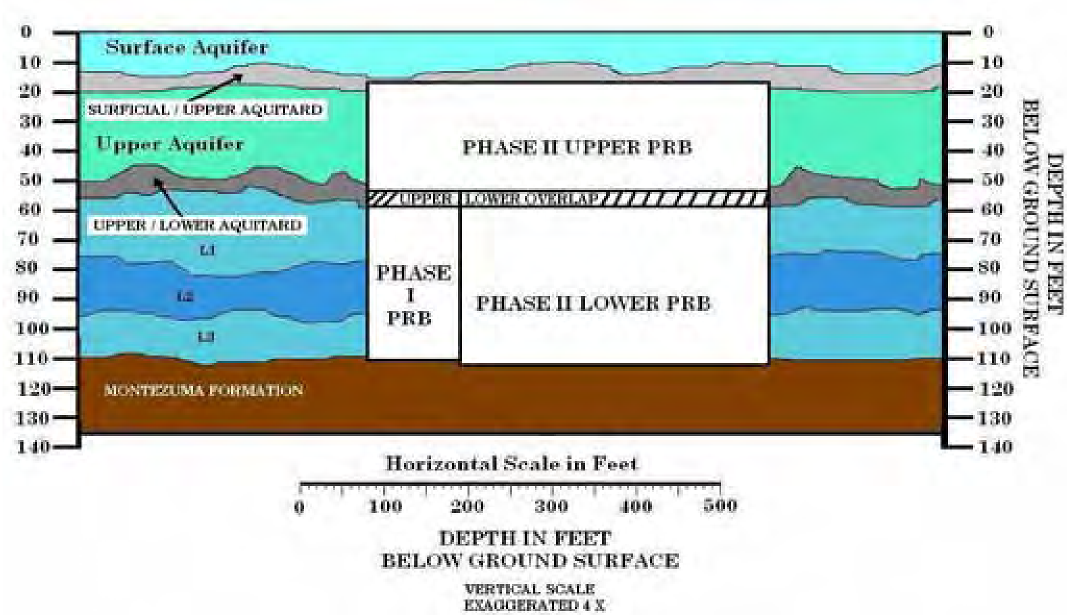
Figure 16 below is a schematic of the Upper and Lower PRBs and their injection well locations. Figure 8 shows a schematic of the PRB projects relative to the aquifers of the area.

Figure 16 DuPont Oakley PRB Project



Taken From: *Completion of Construction Phase II Iron Permeable Reactive Barrier (PRB), February 24, 2006.*

Figure 17 DuPont Oakley Geology and Project Placement



Taken From: *Completion of Construction Phase II Iron Permeable Reactive Barrier (PRB), February 24, 2006.*

PRB Performance Measurements

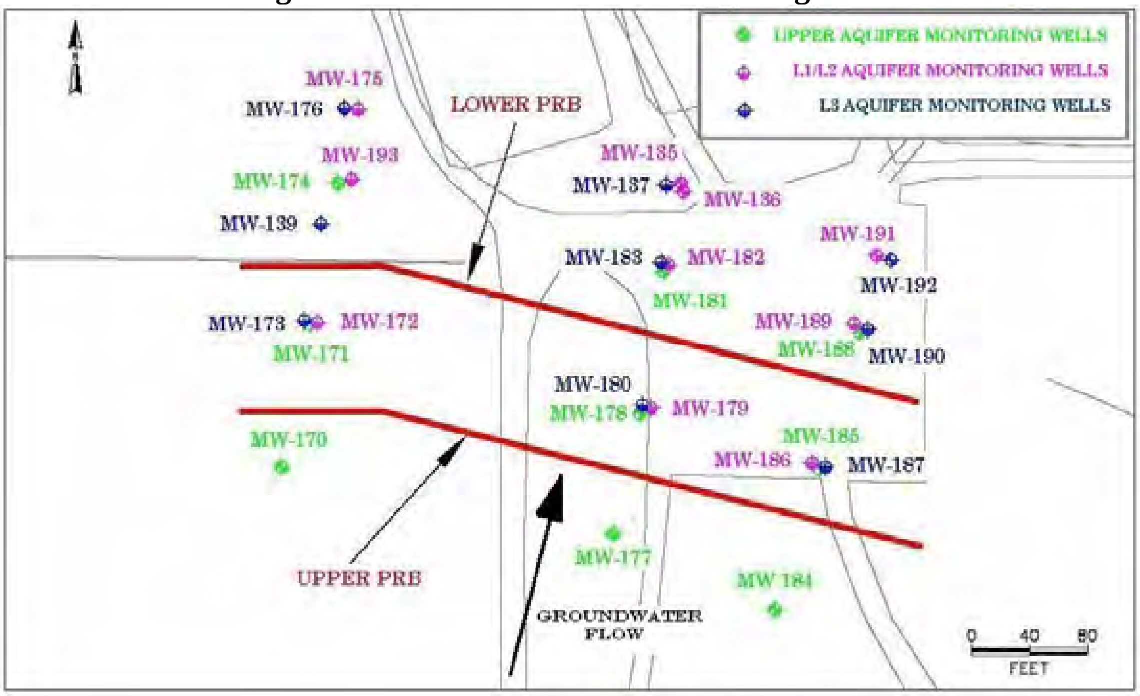
Monitoring wells for the project were installed at three different levels and along three transects. Each transect included one well located 50 feet upgradient and two wells located 50 and 100 feet downgradient of the PRB. Table 9 below lists the wells along with their aquifer levels and transects. The screened intervals for the wells weren't published in the available documentation.

Table 9 DuPont Oakley PRB Monitoring Wells

Aquifer Level	Depth Range (ft. bgs)	Well location with respect to PRB	West Transect 1 Wells	Center Transect 2 Wells	East Transect 3 Wells
Surficial Aquifer	0-15				
Surficial/upper confining unit	10-20				
Upper Aquifer	20-50	50 ft. Upgradient	MW-170	MW-177	MW-184
		50 ft. Downgradient	MW-171	MW-178	MW-185
		100 ft. Downgradient	MW-174	MW-181	MW-188
Upper/Lower confining unit	50-55				
L1/L2 Aquifer	52-90	50 ft. Upgradient	MW-172	MW-179	MW-186
		50 ft. Downgradient	MW-198	MW-182	MW-189
		100 ft. Downgradient	MW-175	MW-135/136	MW-191
L3 Aquifer	90-120	50 ft. Upgradient	MW-173	MW-180	MW-187
		50 ft. Downgradient	MW-139	MW-183	MW-190
		100 ft. Downgradient	MW-176	MW-137	MW-192

Figure 18 below is a diagram of the PRBs and well locations in the Upper, L1/L2 and L3 Aquifers.

Figure 18 PRB Location and Monitoring Wells



Taken From: *Completion of Construction Phase II Iron Permeable Reactive Barrier (PRB), February 24, 2006.*

PRB Performance Analysis

The PRB installation was completed on July 11, 2005. The first groundwater sampling event occurred in January 2006. This performance analysis considers only carbon tetrachloride, the major site contaminant, and chloroform, a biological degradation product from carbon tetrachloride.

The PRB monitoring network includes three transects (Transect 1, Transect 2 and Transect 3) with three locations (upgradient, 50' downgradient and 100' downgradient) in each of the three zones (upper aquifer, L1/L2, and L3). Two monitoring wells of different depth were installed in L1/L2 along Transect 2, so there are a total of 28 monitoring points for evaluating performance.

Ideally, an effective PRB continually reduces contaminant concentrations in the downgradient monitor wells. However, factors other than the PRB treatment may also account for a pattern of contaminant decreases downgradient. These factors include degradation of the parent compound and/or a decrease in the source area itself. Moreover, the highly variable conditions encountered at the DuPont Oakley site

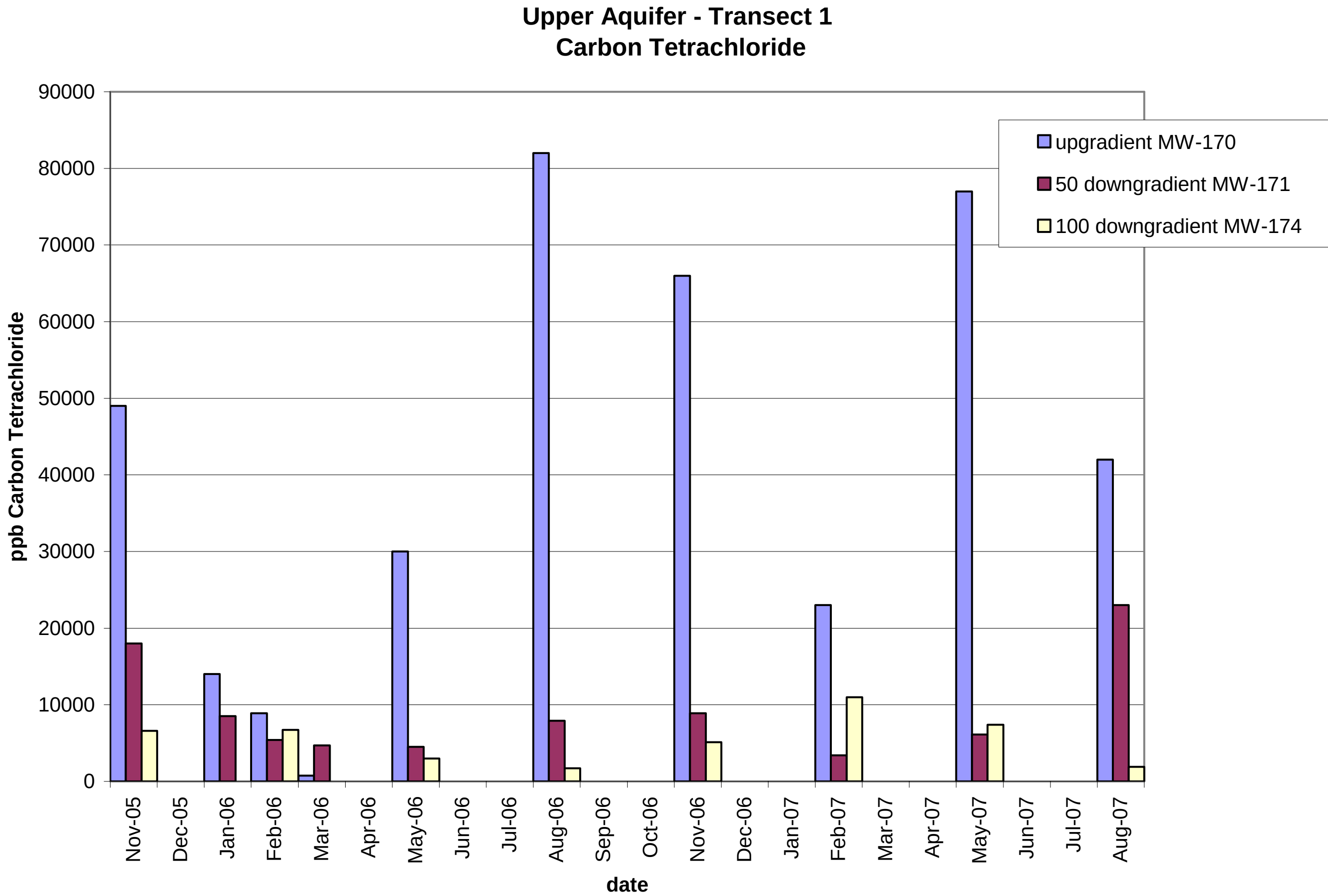
presented a challenge in assessing PRB performance at that site. Thus, rather than presenting results for all 28 sampling locations, the discussion of PRB performance focuses on: (1) those locations that were most demonstrative of treatment, (2) those locations with variable or uncertain results, and (3) those locations with somewhat surprising levels of chloroform. Such patterns are discussed for the monitoring locations in the Upper, L1/L2 and L3 aquifers, since they are the ‘units’ being addressed by the PRBs at this project.

Upper Aquifer

As shown in the previous Figure 11, the upper PRB was installed just behind the 10,000 to 100,000 ppb carbon tetrachloride isoconcentration line. This is reflected in the relatively high (50,000+ ppb) CT concentrations upgradient of the PRB seen in Figure 19 below. The concentration gradient of CT near the plume core is extremely steep and it isn't clear whether the drop in CT concentration from upgradient to the 50 ft. wells is due to the action of the PRB or simply the naturally established concentration gradient. Thus, while there is some apparent continual decrease in concentration below the PRB, it is not completely convincing even after 2 years of monitoring. In part this may be a result of the inherent variability in ground water monitoring data.

It will be interesting to eventually see if the downgradient concentration of 23,000 ppb for CT reported at the 50 ft. downgradient well in August 2007 is an anomaly or an indication that the core concentration of the plume isn't being contained by the PRB. Reductions in CT downgradient of the PRB may also be a result of breakdown into chloroform, as discussed below. In any case, the duration of monitoring necessary to show a conclusive trend – even 50 ft. below the PRB – will be longer than the 2-year period of record available for this report.

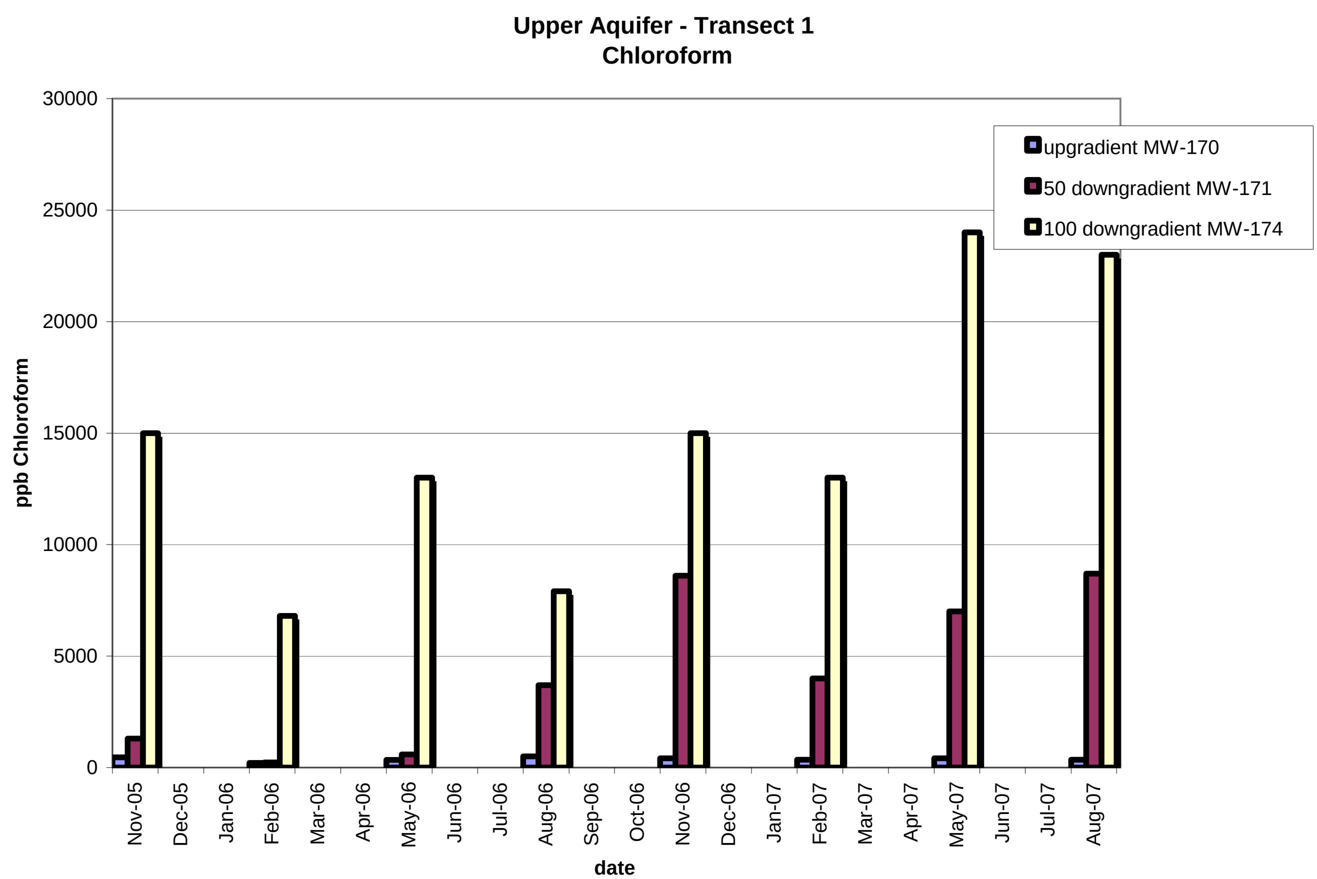
Figure 19 Upper Aquifer (20' – 50' bgs) Transect 1 CT Concentrations



Along Transect 1 in the Upper Aquifer, 100 ft. below the PRB, there is a rise in chloroform concentration. This is shown in Figure 20 (below). Since chloroform is a byproduct of the biological breakdown of CT it is clear that biological attenuation is taking place. For the most part, all of the transects at the various levels show increasing concentrations of chloroform as you go downgradient from the PRB, and this trend is striking along Transect 1 in the Upper Aquifer (Figure 20).

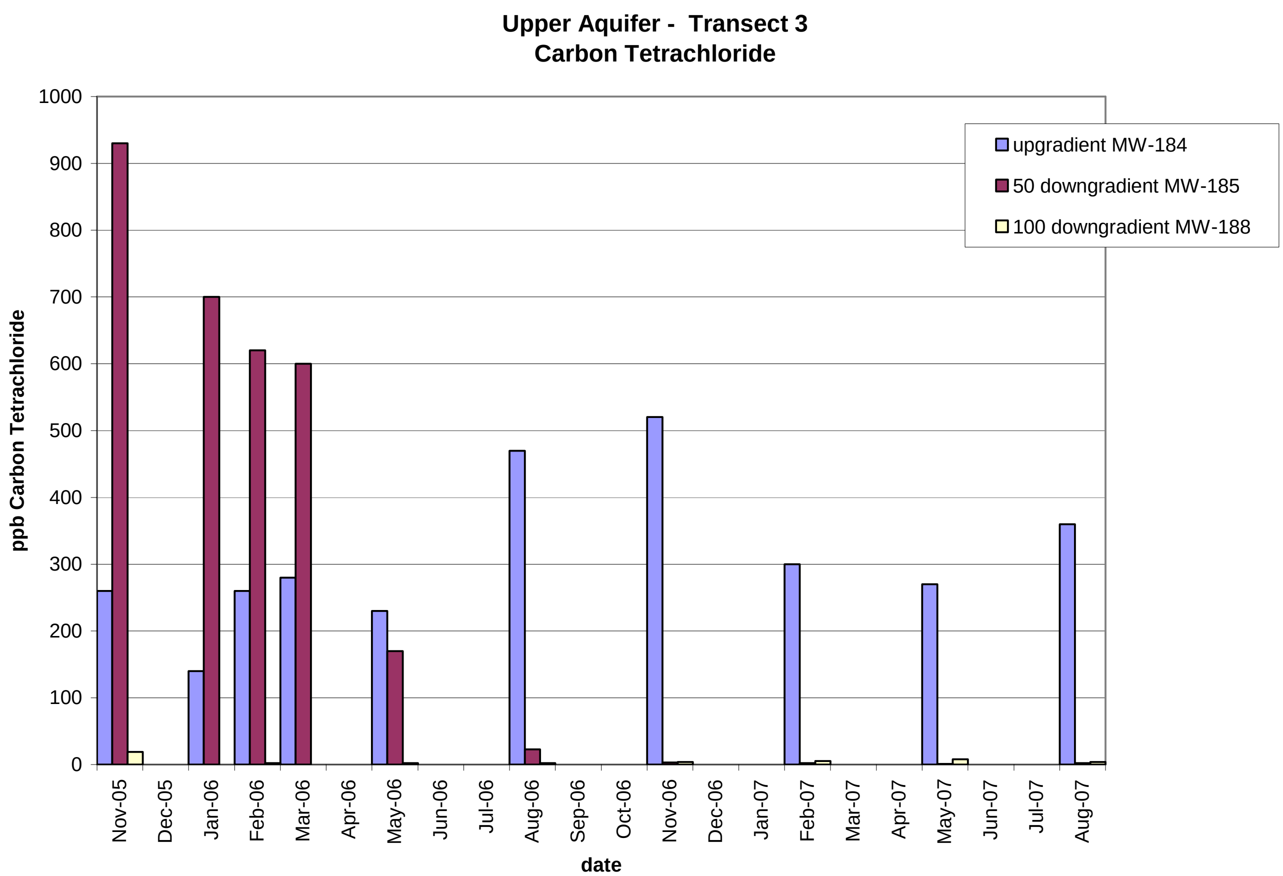
Chloroform is more soluble in water than CT, and may be transported away from the source faster than the parent compound. However, the higher levels seen downgradient are a bit surprising since comparable elevated levels are not seen in the source area. Some unique change may be allowing chloroform to be formed – apparently below the PRB. This would deplete the concentration of CT and give an apparent 'high' estimate of the effect of the PRB.

Figure 20 Upper Aquifer (20' – 50' bgs) Transect 1 Chloroform Concentrations



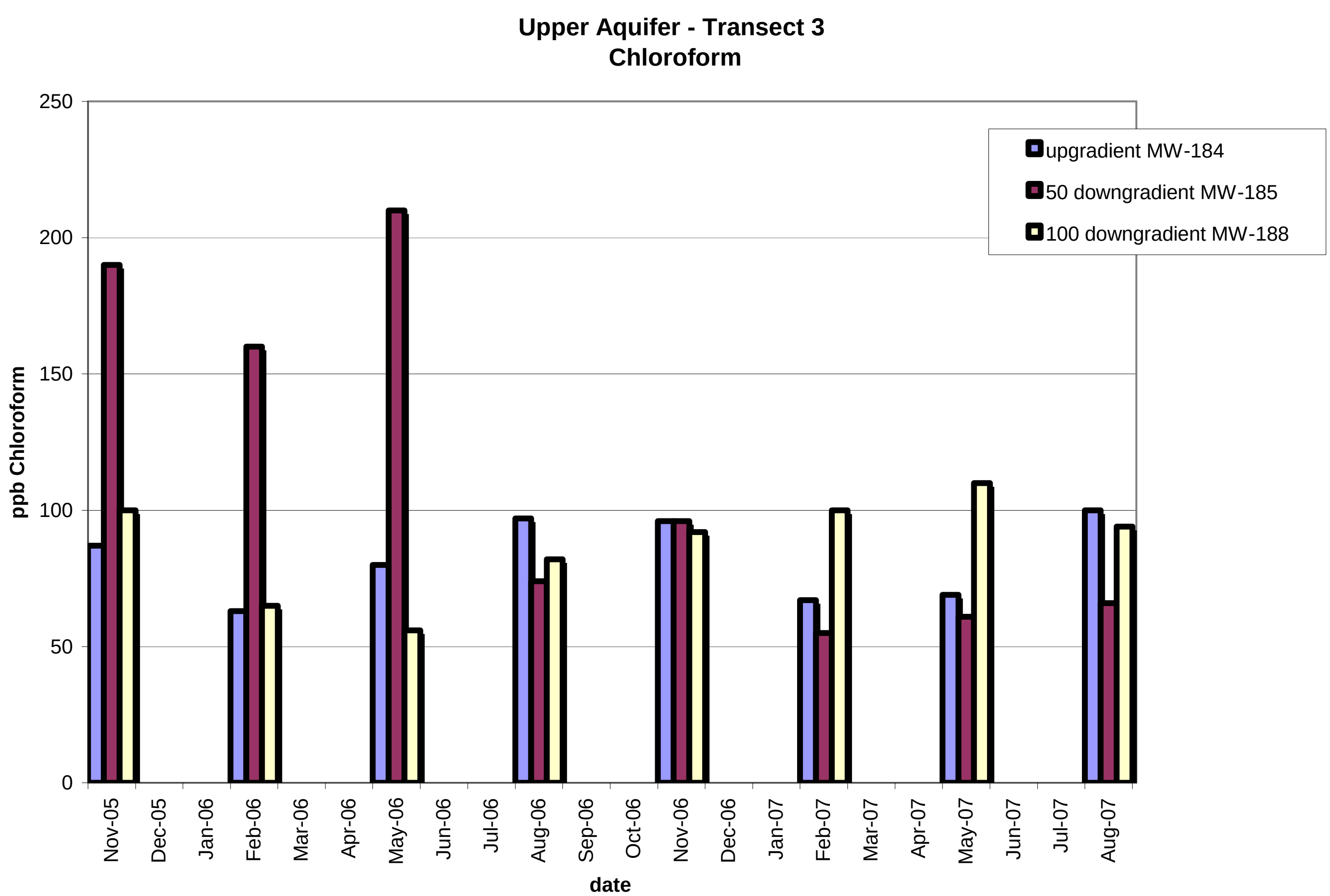
At Transect 3, the 50 ft downgradient CT concentration appears to steadily decrease through November 2006, and then stay quite low. This dramatic drop in downgradient CT concentration over time is what would be ideally expected from a startup PRB project. At the same time, the pattern of chloroform needs to be considered, as is done in Figure 22.

Figure 21 Upper Aquifer (20' – 50' bgs) Transect 3 CT Concentrations



As shown in Figure 22, the chloroform concentrations appear to have fallen at the 50 ft downgradient wells after May 2006. However there doesn't seem to be any further reduction in downgradient chloroform concentration after August 2006. A pattern of reduction in chloroform at the 50 ft. location similar to the pattern of reduction in CT might indicate treatment of both compounds as they pass through the barrier. However, the starting concentrations for both CT and chloroform at Transect 3 are considerably lower (by an order of magnitude) than along Transect 1, so variability in monitoring results may be having a greater influence than at Transect 1. Nonetheless, the constant and dramatic reduction of CT along Transect 3 in the Upper Aquifer is the most convincing evidence of treatment by the PRB.

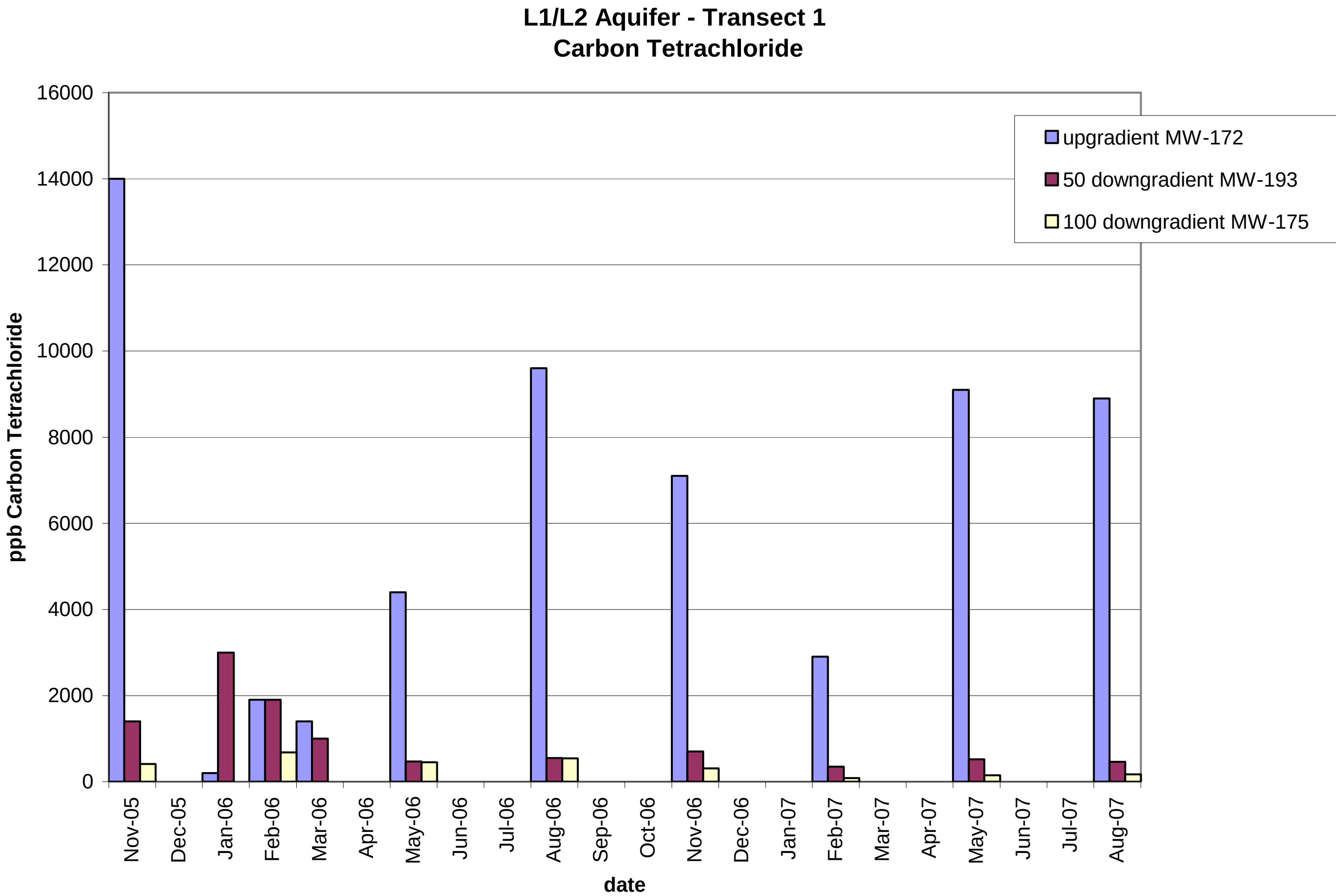
Figure 22 Upper Aquifer (20' – 50' bgs) Transect 3 Chloroform Concentrations



L1/L2 Aquifer

Transect 1 in the L1/L2 Aquifer is the location of the original pilot project PRB installed in 2001. All downgradient CT concentrations are significantly lower than the upgradient well concentrations. This is the performance that would be expected from a PRB which has been in place for 6 years. While the trend for reduction in CT is apparent, it is not as dramatic as along Transect 3 in the Upper Aquifer. The concentrations of CT along Transect 1 are higher in the L1/L2 Aquifer than along Transect 3 in the Upper Aquifer, and this may be influencing the difference in results.

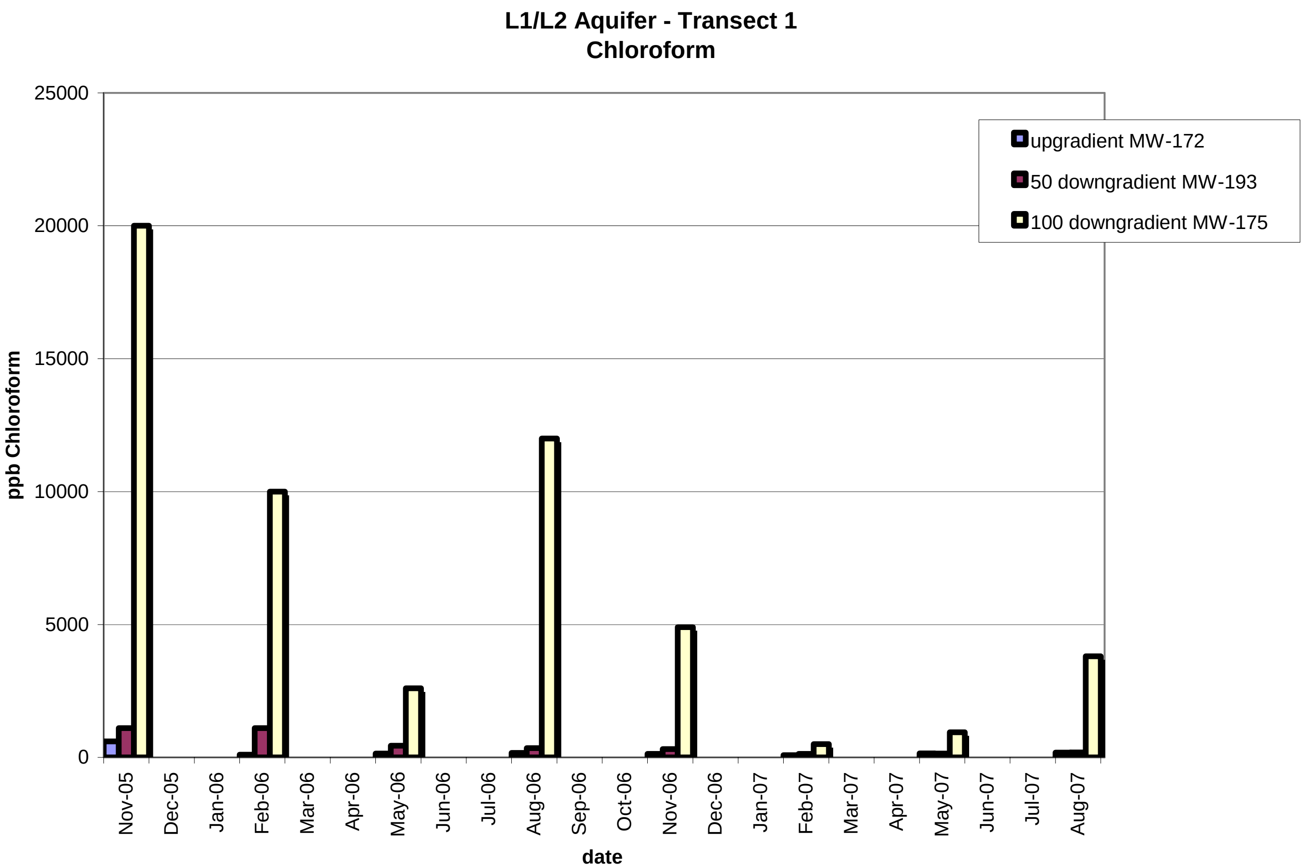
Figure 23 L1/L2 Aquifer (52' – 90' bgs) Transect 1 CT Concentrations



As shown in Figure 24 (below), along Transect 1 in the L1/L2 Aquifer, the 50 and 100 ft downgradient chloroform concentrations appear to be dropping with time. This is a different pattern from the general increase in chloroform with time seen in the Upper Aquifer along this same transect. In addition, upgradient chloroform concentrations are quite low, supporting the view that production of chloroform below the barrier is an important feature of this system.

The trend of chloroform continually declining could be a positive reflection on the performance of the PRB. However, the contrary patterns of increase/decrease in chloroform at different depths along the same transect introduces a complexity to the evaluation.

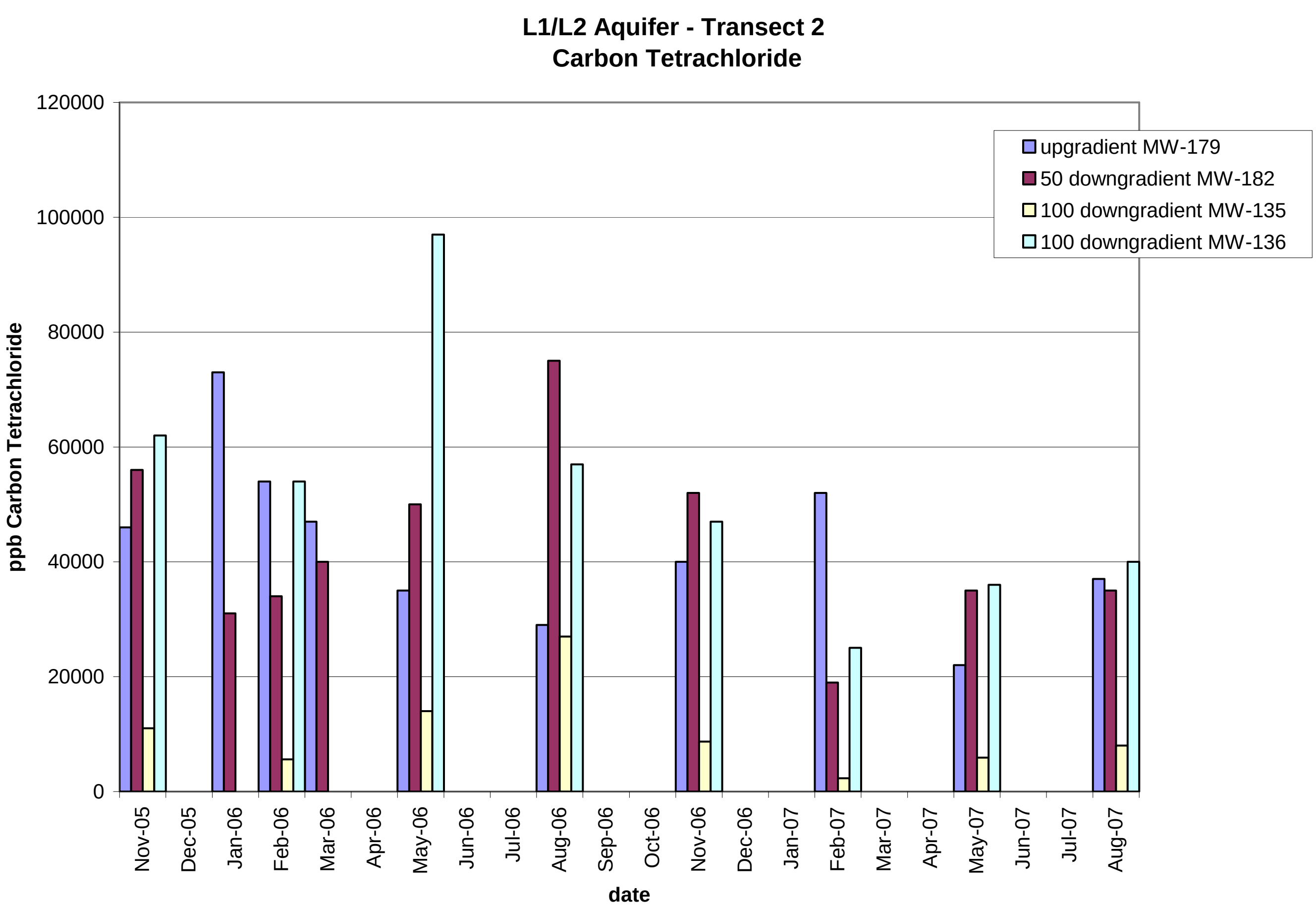
Figure 24 L1/L2 Aquifer (52'-90' bgs) Transect 1 Chloroform Concentrations



Transect 2 in the L1/L2 Aquifer was supplemented with two monitoring wells (MW-135 and MW-136) at the 100' downgradient location. The level of CT at MW-136, the deeper of the two wells is consistently higher than in the shallower well (MW–135). In addition, the level of CT at MW-136 is higher than the upgradient L1/L2 well for Transect 2. The level of CT is also frequently higher at the 50 ft. downgradient location than upgradient (above the PRB). Thus it appears that there may be a complicating 3-dimensional (vertical) character to the distribution of CT in the source area, as well as to the transport of dissolved CT. This complicates analyzing the performance of the PRB far more than would have been the case with monitoring wells located adjacent to the PRB.

Perhaps as a result, as can be seen in Figure 25, along Transect 2 in the L1/L2 Aquifer level, there doesn't seem to be a significant reduction in CT concentrations across the PRB.

Figure 25 L1/L2 Aquifer (52' – 90' bgs) Transect 2 CT Concentrations

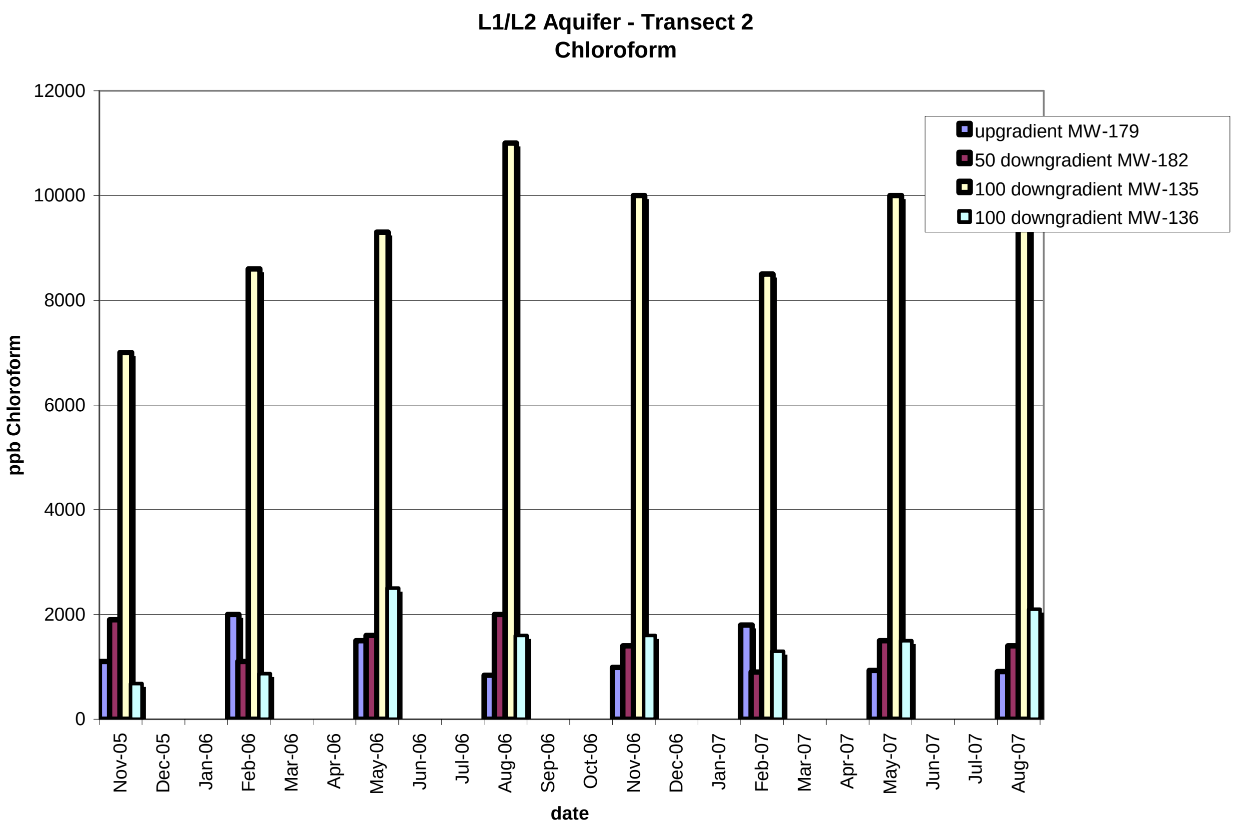


Note: Monitoring well MW-135 is screened from 63 to 65 feet and was drilled to a depth of 65 feet. Monitoring well MW-136 is screened from 85.4 to 87.4 feet and was drilled to a depth of 87.4 feet.

The chloroform concentrations at this transect and level increase from upgradient to 50 ft downgradient to 100 ft downgradient. Unlike the CT concentration – which was higher in the deeper well MW -136 – chloroform is generally higher in the shallow well MW-135. This is likely attributable to biological activity which appears most robust below the barrier, and in this case might be stronger in a shallower zone of the L1/L2 Aquifer as well.

These results again reinforce the confusing effects of the three-dimensional nature of the plume at the DuPont Oakley site. Perhaps the groundwater finding its way downgradient at Transect 2 did not originate at the upgradient well associated with the transect. However, the chloroform concentration seems to be steady with time, which does not allow any positive effect to be attributed to the PRB regardless of the origin of the water.

Figure 26 L1/L2 Aquifer (52'– 90' bgs) Transect 2 Chloroform Concentrations



L3 Aquifer

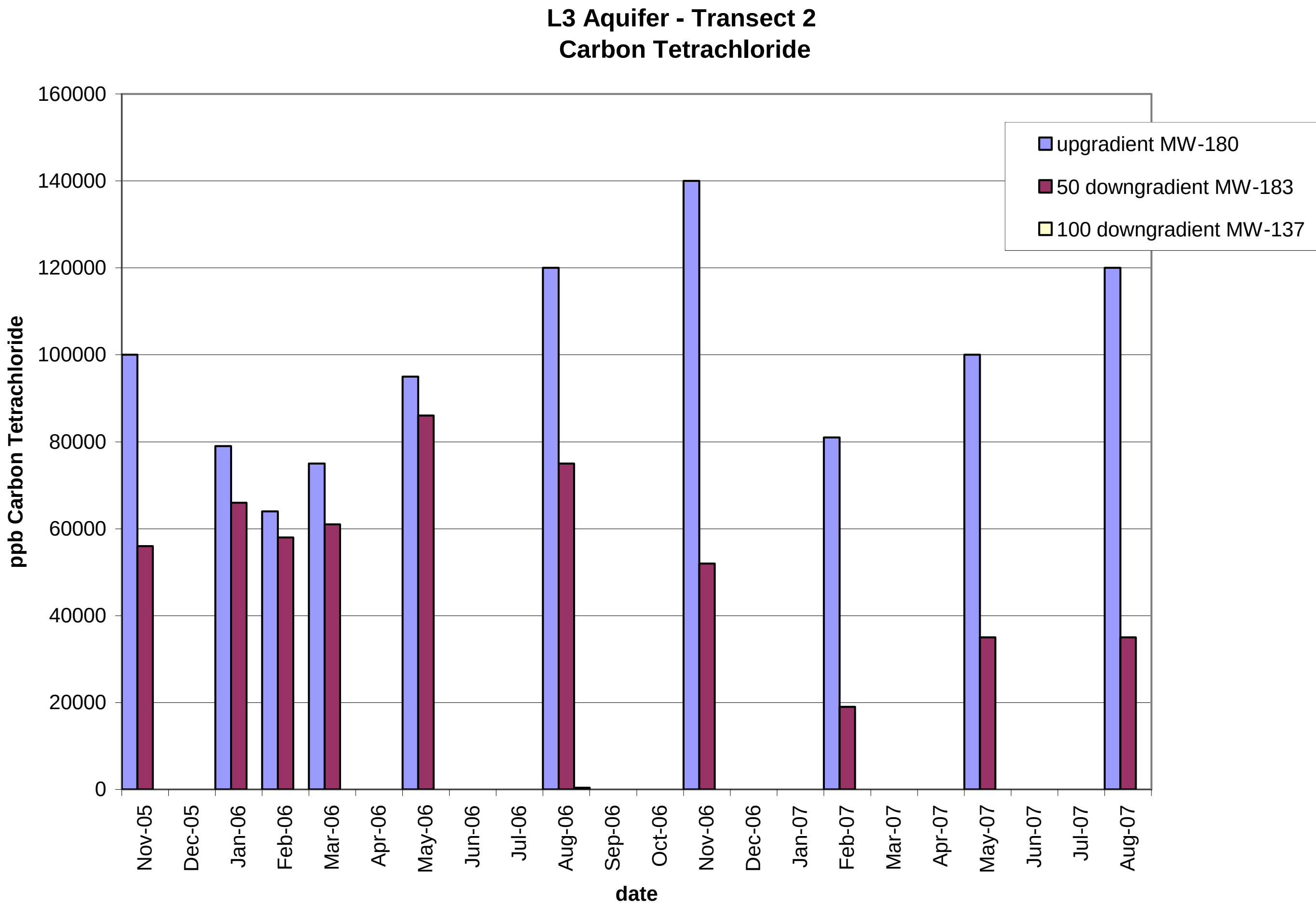
The L3 Aquifer has the highest CT concentrations at the site. The location of the deeper PRB shown in Figure 12 would approximately bisect the 'core' of the CT plume, which is identified by a concentration contour of greater than 100,000 ppb. Thus, in Figure 12 a significant amount of CT is shown to be downgradient of the PRB in the L3 Aquifer.

Figure 27 below shows the upgradient and 50 ft. downgradient CT concentrations along Transect 2 for the L3 Aquifer. CT concentrations at the 100 ft downgradient wells are all below 500 ppb and do not show on the scale of Figure 27.

As can be seen in Figure 27, CT concentrations appear to be falling at the 50 ft. downgradient location in the L3 Aquifer after the May 06 sampling event. This reduction over time may indicate favorable PRB performance. If this were the case, then perhaps the PRB is capturing a significant amount of the CT in the L3.

As observed with other PRBs considered in this report, contaminant levels can persist downgradient of a PRB for extended periods of time. With the levels of CT in the L3 Aquifer sometimes exceeding 100,000 ppb, the same persistence would be expected downgradient of the PRB. It may be that the PRB for the L3 aquifer was installed further downgradient of plume's core than Figure 12 indicates. If this were the case, then the aquifer would be less contaminated at the 50 ft. downgradient monitoring well and a decreasing CT concentration due to the PRB would be more likely. Still, the apparent pattern of decrease of CT has to be viewed cautiously as far as attributing the reduction of CT strictly to the effect PRB.

Figure 27 L3 Aquifer (92'-120' bgs) Transect 2 CT Concentrations



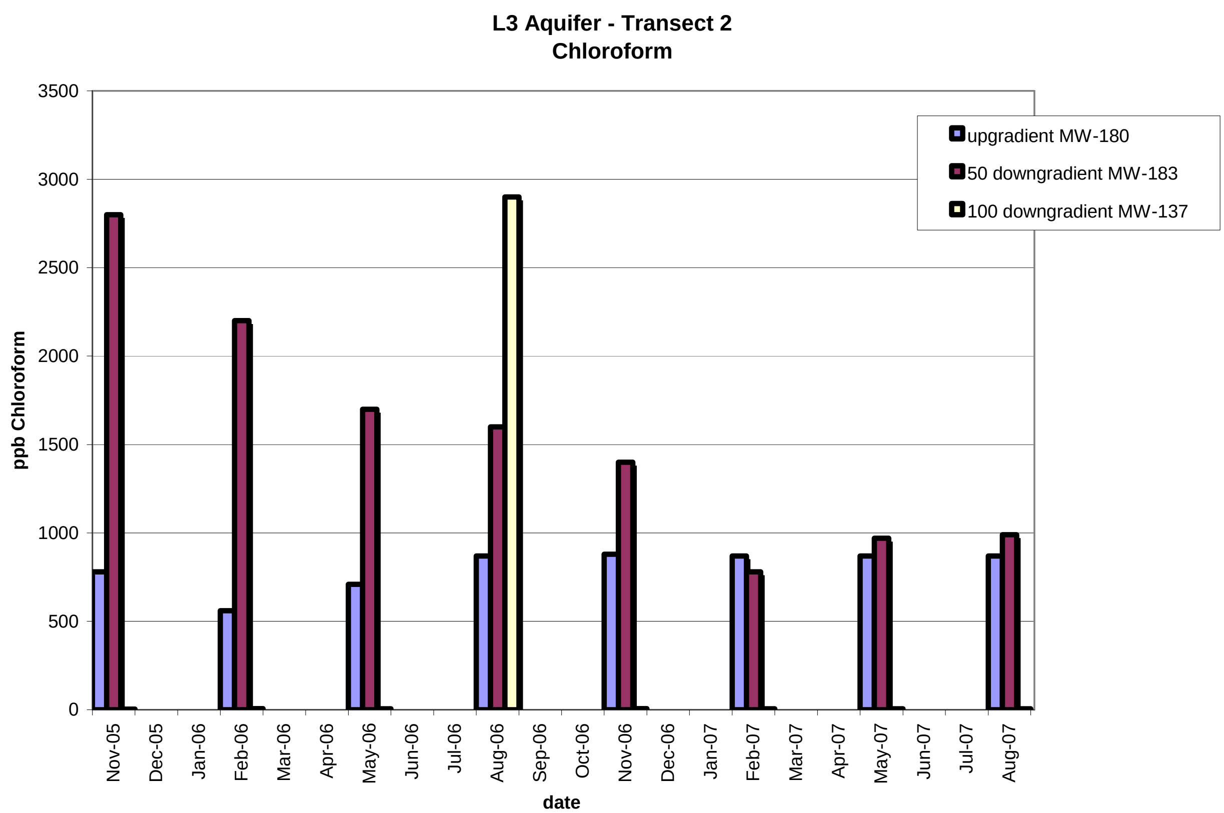
Chloroform concentrations along Transect 2 in the L3 Aquifer are shown in Figure 28. . Upgradient chloroform concentrations appear to be fairly constant and except for the February 2007 sampling event, are always less than the 50 ft downgradient chloroform concentrations. The 50 ft. downgradient chloroform concentrations appear to decline over the period from November 05 to August 07.

The pattern of decrease in both CT and chloroform shown in Figures 27 and 28 indicates that the PRB may be having a beneficial effect. Perhaps the PRB is reducing CT which results in less CT being available for biological production of chloroform by 50 ft. below the barrier. At the same time, chloroform itself may be reduced as it crosses the PRB.

Chloroform is insignificant at MW-137, the 100 ft. downgradient monitoring location, except for one measurement in August 06, which may be an anomaly. While the wells located along Transect 2 in the L3 Aquifer appear to be located along the path of ground water flow, the low levels (generally less than 5 ppb) of chloroform 100 ft. downgradient suggests otherwise. If ground water flow direction does not parallel the transect's alignment, this could significantly influence the results observed for CT and chloroform.

The PRB seems to be having some effect at MW-183, the 50 ft. downgradient well. However ,this possibility is made less certain in light of the patterns of CT and chloroform in the L3 aquifer that are somewhat different than those seen in shallower aquifers.

Figure 28 L3 Aquifer (92'-120' bgs) Transect 2 Chloroform Concentrations



Summary and Conclusions

The PRB installed at the DuPont Oakley site was monitored along three transects in three different aquifer zones. The nearest downgradient monitoring wells were located 50 ft. and 100 ft. below the PRB. As has been seen in other PRB projects, results from monitoring wells installed to monitor performance become more difficult to evaluate with increased distance from the PRB. This was certainly the case for the PRB at DuPont Oakley, where the influence of biological activity (production of chloroform from CT), and three-dimensional dissolved phase transport from an asymmetrical source zone area are apparent.

While some results (patterns) of both CT and chloroform from monitoring wells below the PRB indicate good performance, other results (patterns) are puzzling. Relatively 'good' indications of treatment were observed only along Transect 1 in the L1/L2 Aquifer level and along Transect 3 in the Upper Aquifer level Results for the remaining 7 monitoring transects were difficult to interpret, possibly due to a number of factors:

- Biological activity ongoing at the site (i.e., production of chloroform from CT).
- A complicated 3-dimensional hydrogeologic setting.
- A complex source zone and associated dissolved phase distribution pattern
- The inherent variability in ground water monitoring results.
- The relative distances of monitoring well locations downgradient from the PRB.
- The high residual contamination levels downgradient of the PRB.

In several other projects evaluated in this report, monitoring wells were placed adjacent to – and even placed within (in situ) – the PRB. This allowed a relatively simple analysis of performance, especially where low levels were observed. At the DuPont Oakley site, monitor wells were located at 50 and 100 feet distances downgradient of the PRB. The residual contamination and degradation products (chloroform) downgradient of the PRB coupled with the lag time it takes treated groundwater to reach the monitor wells has made a performance assessment difficult after only two years of operation. While some results downgradient from the PRB at the DuPont Oakley site appear favorable or promising, many downgradient results are inconclusive concerning PRB performance.

The DuPont Oakley project is a large project and covers a wide range of depths and contaminant concentrations. Because of the complexity of the contaminant distribution and other confounding factors, it will take some time before the full effects of the PRB can be demonstrated. This is a similar result to those observed in PRBs installed in simpler hydrogeologic settings, where downgradient water quality patterns do not appear to respond quickly to the function of the PRB, yet monitoring within (in situ) and immediately below the PRB indicates good treatment.

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3.4 Evaluation of the Fairchild / Applied Materials PRB Project

Site History

Fairchild Semiconductor owned the site at 974 East Arques Avenue from 1968 to 1972. Industrial activities at the site included spray painting, photo resist, etching, and alodining (plating with chrome). Trichloroethene (TCE) was used as a cleaning solvent in many of these processes. During this time, an acid waste neutralization sump was located on the western side of the main building.

Hewlett Packard purchased the site in 1972 and conducted manufacturing operations at the site until 1993. HP's operations included parts assembly, metal plating, and painting operations. HP used the acid sump to transfer wastewater to the sanitary sewer from 1978 to 1986.

Site/Hydrology

The geology of the area consists of alluvial deposits consisting of fine grained silt and clay along with fine sand and gravel lenses from 10 to 14 feet bgs. The sand and gravel lenses comprise what is called the A zone aquifer. A layer of low permeability clay exists from 15 to 25 feet bgs and separates the A zone aquifer from the lower B zone aquifer. Groundwater flow in the A zone is from the southwest to northeast at an average rate of around 3 feet/day. The contaminants passing through this area are for the most part, coming from the Mohawk area so the high ratio of cis 1,2-DCE to TCE is also present at this site.

Remediation Activities

In 1986 Hewlett Packard sampled the soil and groundwater at the site and found VOC contamination in the area of the acid sump. HP removed the acid waste sump and excavated 190 cubic yards of contaminated soil. The solvents contaminating the site were primarily TCE, cis-1,2-dichloroethene (cis-1,2-DCE), and tetrachloroethene (PCE).

In 1987, Hewlett Packard began operating a groundwater treatment and extraction system at the site. In 1995, HP excavated another 3000 cubic yards of soil from the acid sump area down to a depth of 26 feet. At this time, an iron filing wall (**Permeable Reactive Barrier**) was installed at the sump area to reduce VOCs in the groundwater.

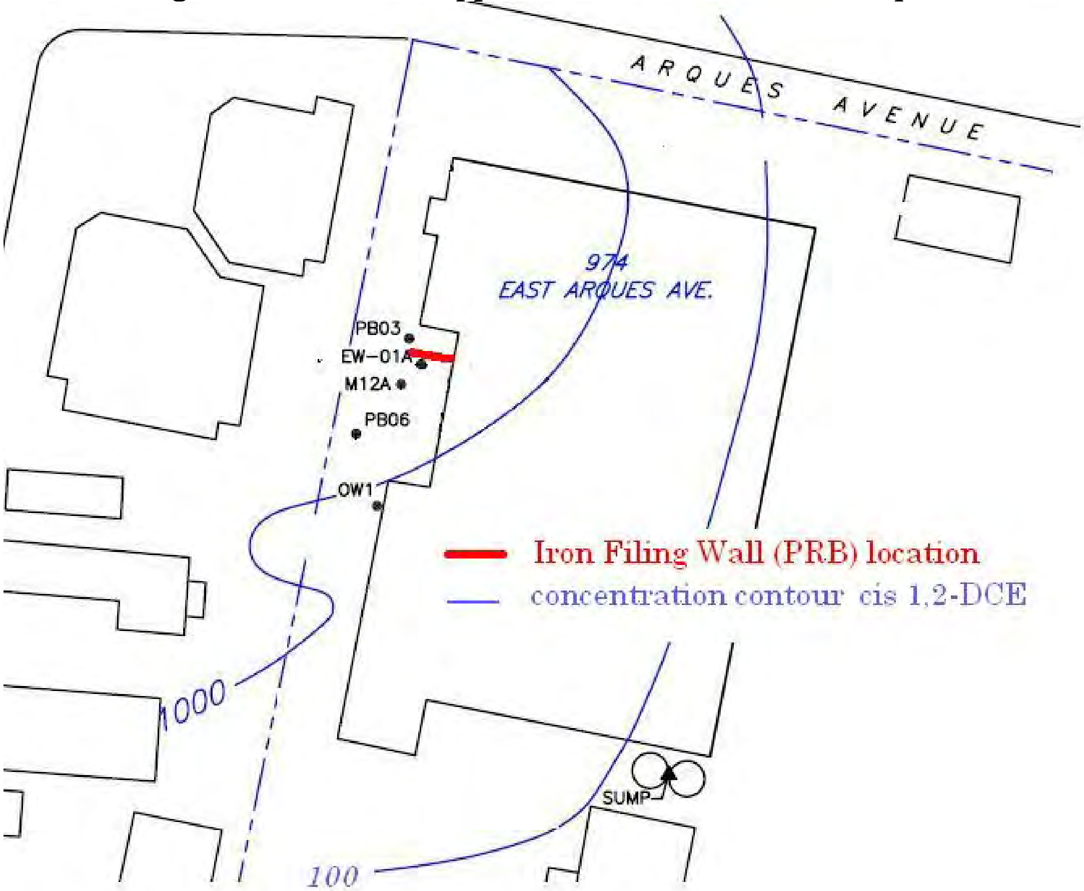
In 1995, Applied Materials Corporation purchased the site from Hewlett Packard. In 1997 the California Regional Water Quality Control Board adopted Site Cleanup Requirements for the site along with the adjacent Mohawk Laboratory site. These 1997 orders established the Commercial Street Operable Unit (CSOU), Subunits 1 and 2). Fairchild, Applied Materials, Mohawk, and NCH Corporation were named as the responsible parties for the site contamination at Subunit 2. In 1998, Fairchild removed the old HP

ground water extraction and treatment system and installed a new treatment system consisting of 2 groundwater extraction wells and a groundwater treatment system.

PRB Installation

An iron filing wall was installed in 1995 across the former acid sump area during the last soil excavation. The intent of the PRB was to reduce any residual chlorinated solvent contamination in the sump area and to prevent groundwater contaminant migration to the north. It was installed with a minimal amount of preplanning, documentation, or regulatory oversight. Figure 29 below shows the position of the PRB relative to the Fairchild property at 974 East Arques Ave. The PRB extends from 20 -25 ft. bgs and is 4.5 ft. wide and 44 ft. long.

Figure 29 Fairchild/Applied Materials at 974 East Arques Ave.

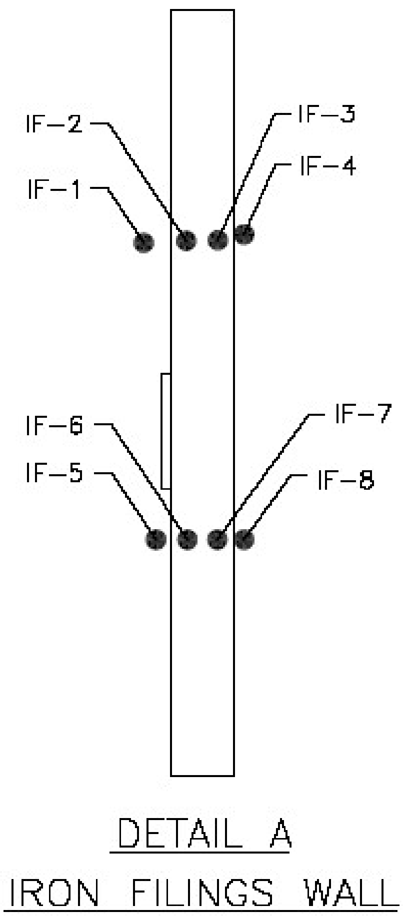


Adapted From: *Five Year Status Report Arques West Side Groundwater Treatment System 974 East Arques Avenue Sunnyvale, California Site Cleanup Requirements Order No. 00-123,*(November 29, 2005)

PRB Performance Measurements

Two transects of monitoring wells were installed across the barrier. The transects include upgradient wells (IF1 and IF5), in-situ wells (IF2, IF3, IF6, IF7), and downgradient wells (IF4 and IF8). The eight monitoring wells are sampled annually to evaluate the performance of the wall. The layout well locations in the barrier wall are diagramed in figure 30 below. The monitoring wells depths and screened intervals are not available.

Figure 30 PRB Monitoring Well Locations



Adapted From: *Five Year Status Report Arques West Side Groundwater Treatment System 974 East Arques Avenue Sunnyvale, California Site Cleanup Requirements Order No. 00-123,* (November 29, 2005)

PRB Performance Analysis

The cis 1,2-DCE and TCE concentrations along both monitoring well transects are graphed in Figures 31 through 34. Similar to other sites reviewed, target contaminant concentrations within the PRB iron wall (in-situ wells) are significantly reduced while downgradient concentrations are higher or similar to upgradient concentrations.

The downgradient cis 1,2-DCE concentration is over 1000 ppb for the majority of the sampling events while the in situ levels are generally less than 50 ppb. The overall reduction in cis 1,2-DCE concentration across the barrier ranges from -15% to 20% for transect 1. The average for transect 1 is about 4%. At transect 2, the reduction in cis 1,2-DCE concentration across the barrier ranges from 14 to 35% with an average around 21%. Figures 33 and 34 show a similar situation with TCE levels upgradient and downgradient of the PRB near 200 ppb and in situ levels generally lower than 10 ppb. The overall reduction in TCE concentration across the barrier is again extremely variable with an average of 10% across both transects.

Figure 31 Fairchild/Applied Material cis 1,2-DCE Concentrations, Transect 1

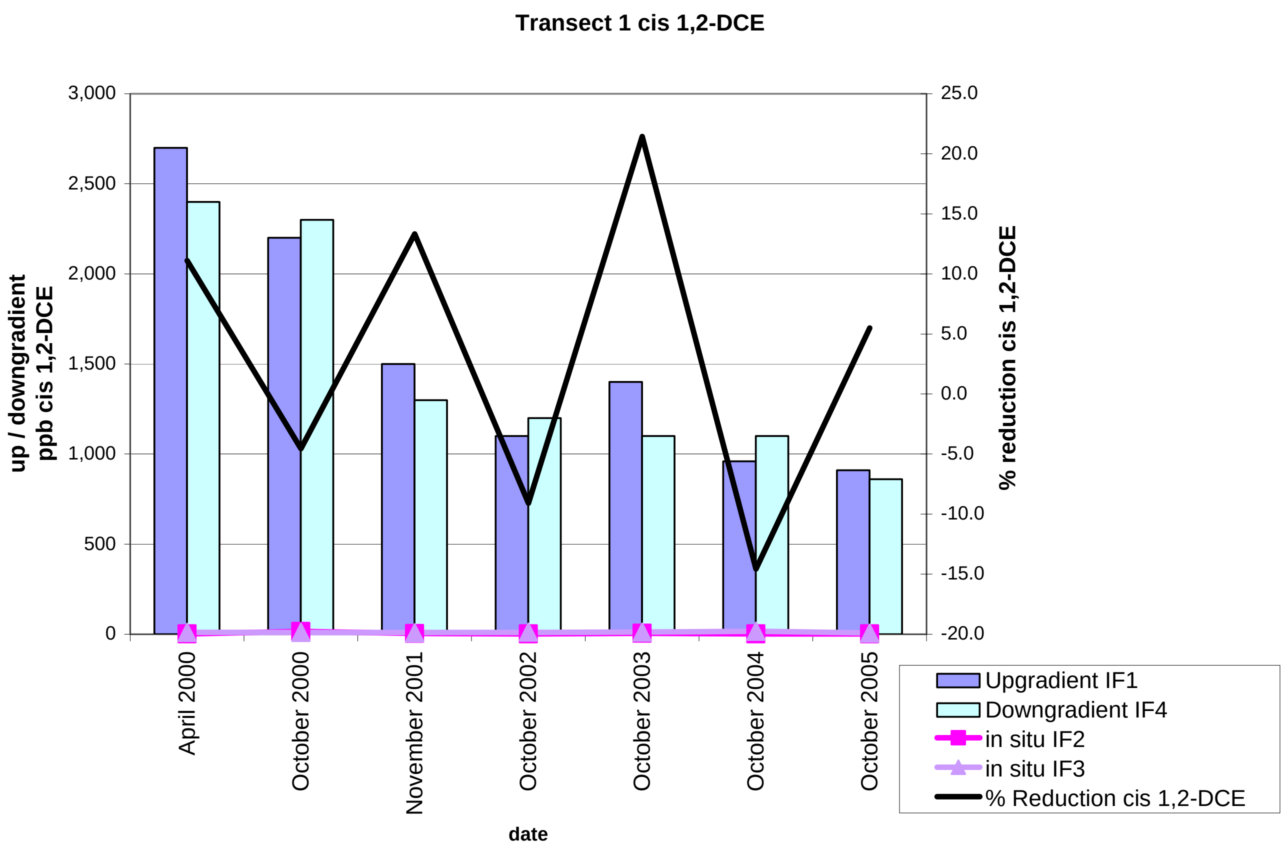


Figure 32 Fairchild/Applied Material cis 1,2-DCE Concentrations, Transect 2

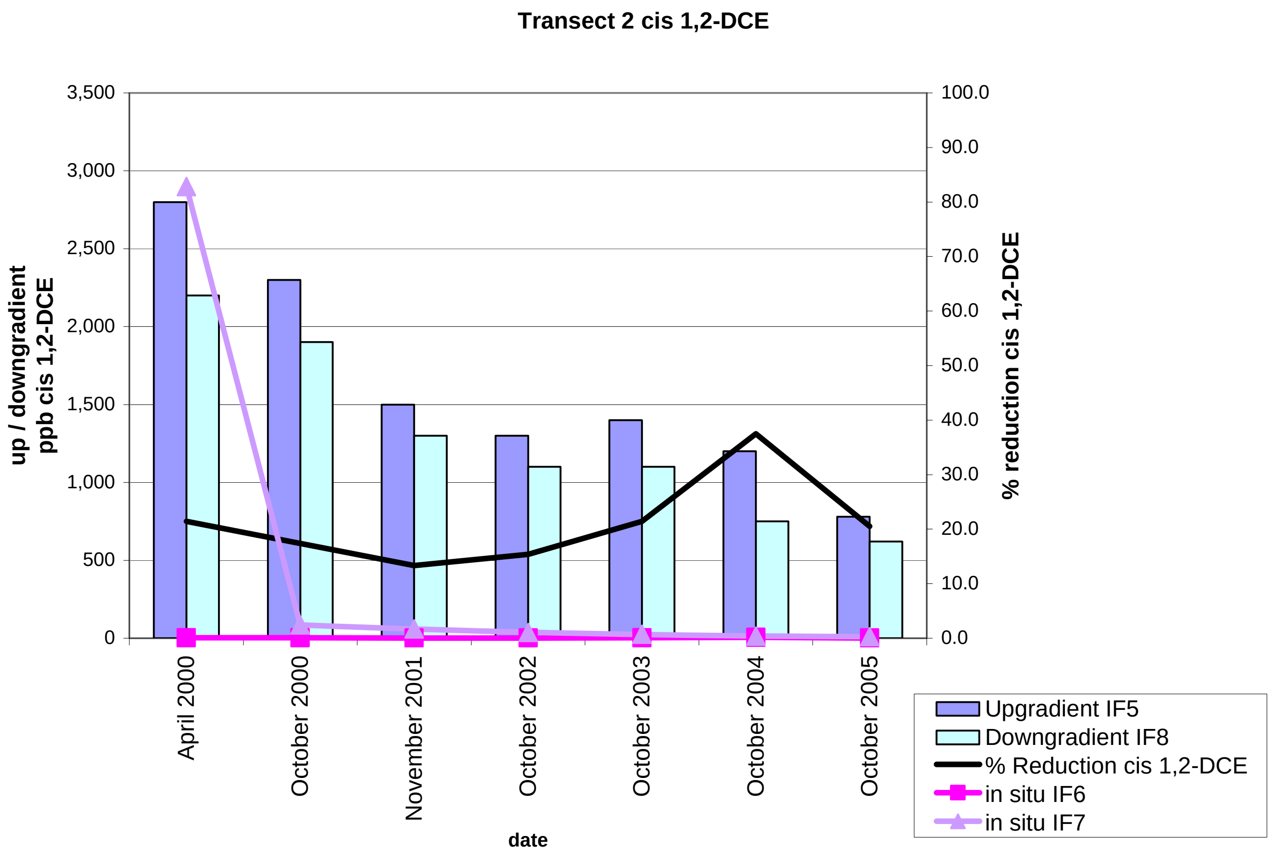


Figure 33   Fairchild/Applied Material TCE Concentrations, Transect 1

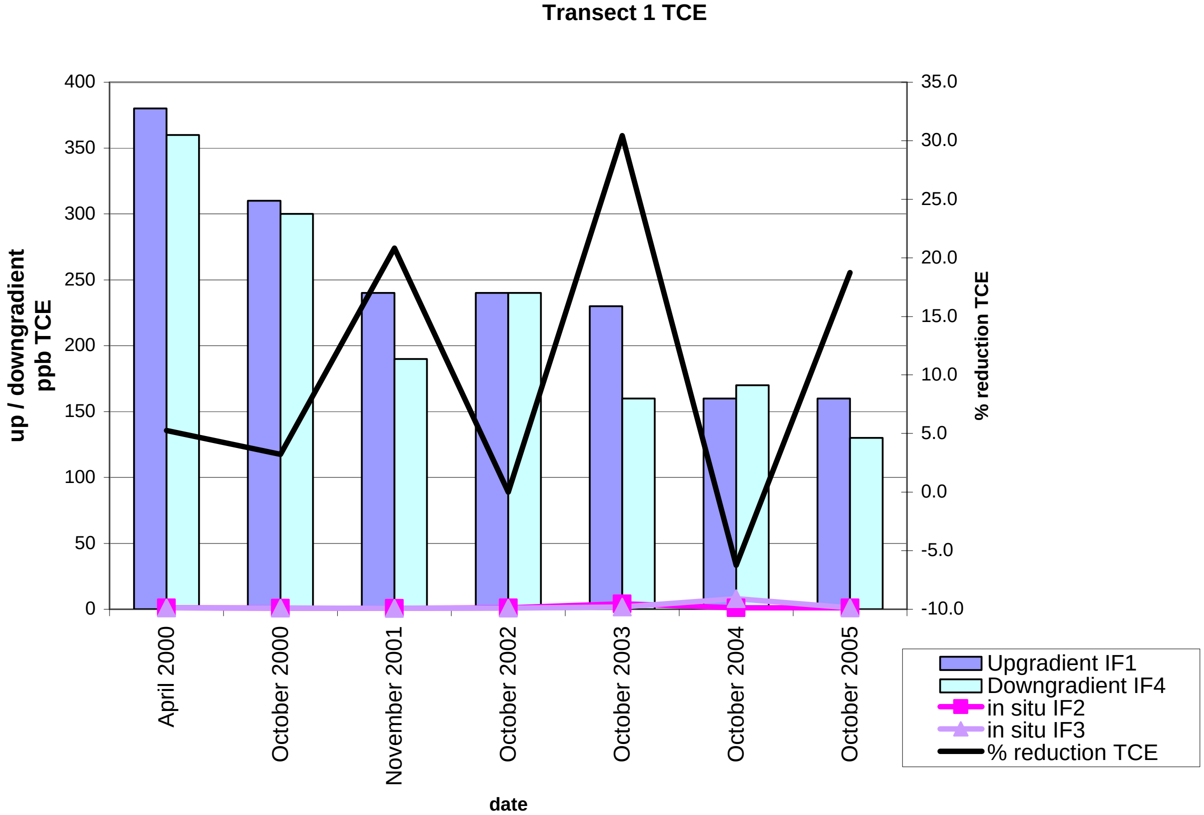
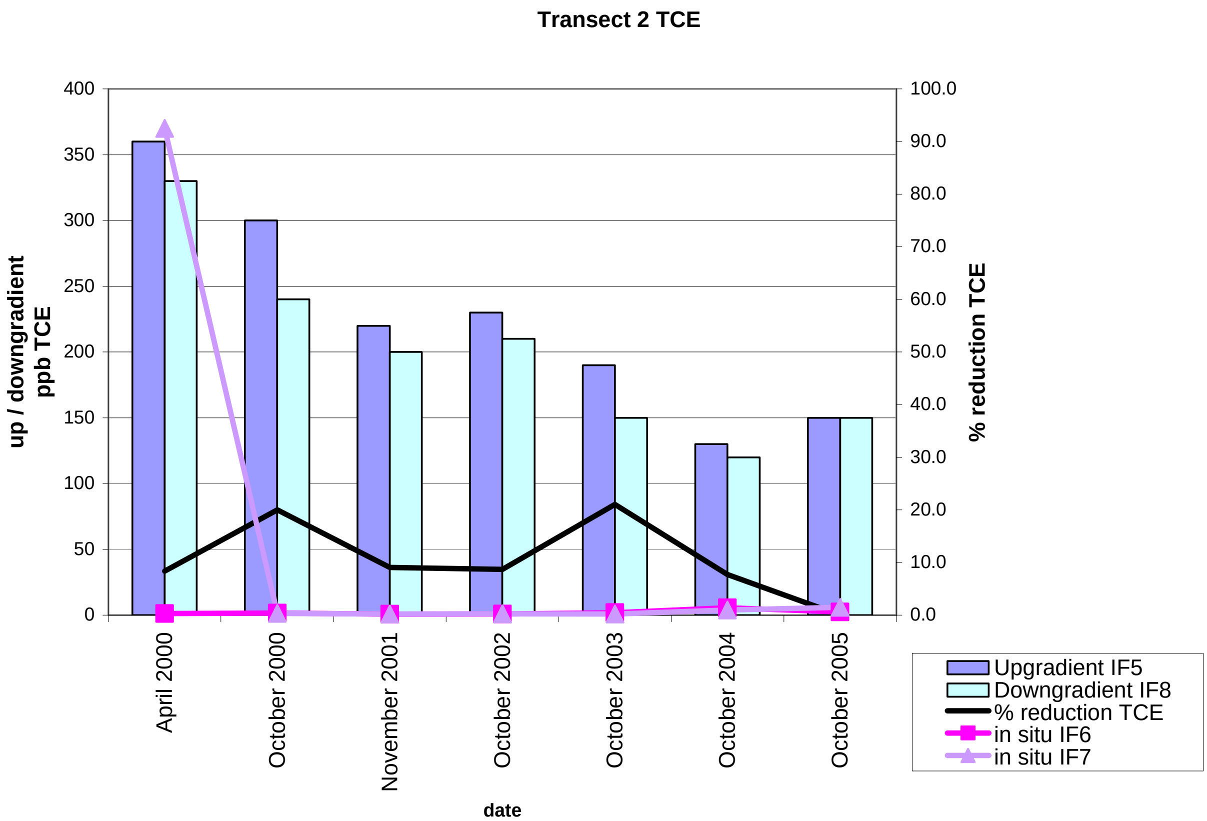


Figure 34 Fairchild/Applied Material TCE Concentrations, Transect 2



Summary and Conclusions

In spite of the significantly low concentrations of both cis 1,2-DCE and TCE measured within the PRB iron wall (in-situ wells), concentrations measured downgradient of the PRB show little reduction. PRB performance appears quite poor when comparing upgradient to downgradient conditions. Contaminant reduction across the PRB wall averaged only 4% and 21% for transect 1 and 2 for cis 1,2-DCE, and averaged 10% across both transects for TCE. This project is downgradient of the much larger Mohawk contamination plume and PRB which may explain the presence of the high ratio of cis 1,2-DCE to TCE. However, the Mohawk PRB achieved a much higher percent reduction that this PRB for both cis 1,2-DCE and TCE.

Here again is a case similar to others reviewed where the in-situ contaminant concentrations are much lower than the downgradient concentrations. Tracer or other hydraulic studies would need to be performed to determine whether this is due to plugging of the PRB, flow channeling, or some other reason.

Little documentation on the design and installation of this PRB was available for this case study review. Important information such iron wall thickness or well screen intervals would have been useful in assessing PRB performance and was not available.

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Schlumberger Limited, *Five Year Status Report Arques West Side Groundwater Treatment System 974 East Arques Avenue Sunnyvale, California Site Cleanup Requirements Order No. 00-123,*(November 29, 2005). Prepared for Fairchild Semiconductor Corporation

Schlumberger Limited, *2005 Annual Groundwater Monitoring Report January through December 2005 974 East Arques Avenue, Sunnyvale, California* (January 27, 2006). Prepared for Fairchild Semiconductor Corporation

3.5 *Evaluation of the Intersil Permeable Reactive Barrier Project*

Site History

Intersil manufactured semiconductors at the site starting in the early 1970's. The company installed an acid neutralization tank system on the eastern side of its facility in 1972 to adjust the pH of wastewater before discharging it to the sewer. In 1982, the California Regional Water Quality Control Board (CRWQCB) requested that Intersil sample and analyze the groundwater around the neutralization tank for possible contamination. The results of sample testing indicated that there were halogenated volatile organic compounds (VOCs) in the groundwater beneath the site. Further sampling was performed at the request of the CRWQCB in 1986 and 1987 to characterize the extent of VOCs in the groundwater and soil in the area of the neutralization tank.

Groundwater Contamination and Hydrology

Prior investigations at the site identified two groundwater zones, one relatively shallow and one much deeper separated by a 65 ft. thick clay and silt layer. No contamination has been detected in the deeper groundwater zone. The shallow contaminated groundwater zone starts at about 10 to 15 feet below ground surface (bgs) and extends down to the lower permeability clay layer at approximately 20 feet bgs. It consists of zones of silty fine grained sand, fine to medium grained sand, and gravelly sand with local clay lenses. The expected groundwater flow rate maximum for the area is 1.2 feet per day in a northwest to northeast direction. The contaminants in the groundwater are Trichloroethene (TCE), cis 1, 2 dichloroethene (cis 1,2-DCE), vinyl chloride (VC), and Freon-113.

Remediation Activities

In 1987 Intersil removed the acid neutralization tank, and excavated and disposed of contaminated soil under the tank. Geomatrix, Intersil's consultant, then performed a detailed analysis of soil and groundwater around the site.

A groundwater extraction well and air stripper treatment system with carbon absorption tanks was installed in November 1987 as a corrective action. Additional sampling in 1986 through 1993 indicated that the Western Microwave facility, adjacent to the Intersil facilities eastern property line, was a source of tetrachloroethene (PCE) and other contaminants. The groundwater extraction system at Intersil was expanded in 1989 and again in 1991. The CRWQCB provided regulatory oversight of the groundwater remediation efforts.

In 1991, Intersil started looking for alternatives to the pump and treat system which had been in operation since 1987. The pump and treat system was operating at 18 gpm and the mass removal rate of contaminants had significantly declined. The system was

beginning to reach the asymptotic limits of what pump and treat could achieve. The pump and treat system was costing over $300,000 a year for operation and maintenance. Intersil was interested in the emerging permeable reactive barrier technology using zero valence iron as an alternative to the costly pump and treat system.

Cleanup Goals/PRB Design

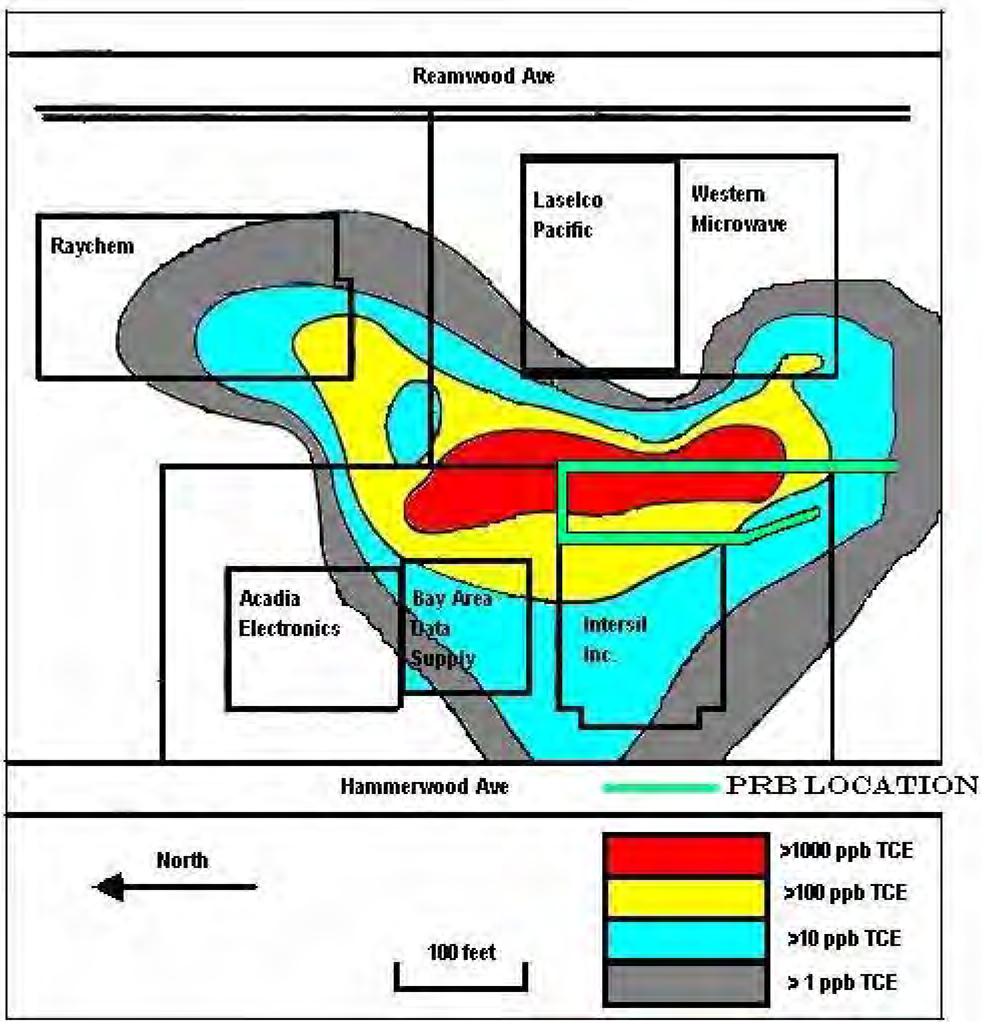
The CRWQCB approved the PRB project at the Intersil site and installation was completed in February 1995. The design goal of the PRB was to contain and treat the portion of the chlorinated solvent plume on the Intersil property, as well as to isolate Intersil property from off-site groundwater contamination. The PRB was not expected to remediate the downgradient plume. The core plume had a TCE concentration near 3000 ppb in 1986. Figure 35 below shows the contaminant plume with the maximum concentration of TCE just west of the Intersil building from a survey taken in 1986. After remedial activities including excavation and the operation of the pump and treat system for 7 years, the highest TCE concentration on the Former Intersil property was 170 ppb in 1994 in an area around well 9A.

A predecessor of EnviroMetal, including researchers at the University of Waterloo, first performed column tests on the contaminated groundwater using reactive media containing 10% iron. These tests showed that the iron was very effective at breaking down the halogenated volatile organic compounds at Intersil. Pilot tests were next done at the site using a fiberglass canister filled with 50% iron and 50% sand. Contaminated groundwater was pumped through the canister at a rate of 4 ft./day for nine months. The iron in the canister proved capable of breaking down the chlorinated compounds without any degradation in performance over nine months

Based on column studies, the project team of EnviroMetal, Geomatrix, and Intersil determined that a two day residence time was needed using the selected zero valent iron to degrade the contaminants at the site to below acceptable levels (California MCLs). This called for a barrier thickness of 4 feet (with 50% iron/sand mix) based on the maximum groundwater flow rate of 1.2 ft./day expected for the site. The PRB was constructed with 100% of iron by weight, which provides an additional safety factor.

The installed PRB wall thickness of 4 feet zero valent iron appears adequate for achieving the treatment goals. Using the EPA Scoping Calculations equation modified for TCE and a groundwater flow rate of 1.2 ft./day, a minimum PRB wall thickness of 2.75 inches of iron would be needed to treat an initial TCE concentration of 210 ppb to the cleanup goal of 5 ppb. For cis 1,2-DCE with an initial maximum concentration of 1415 ppb and a cleanup goal of 6 ppb, the computations would call for a wall thickness of 21 inches.

Figure 35 Intersil Area TCE Plume, 1986



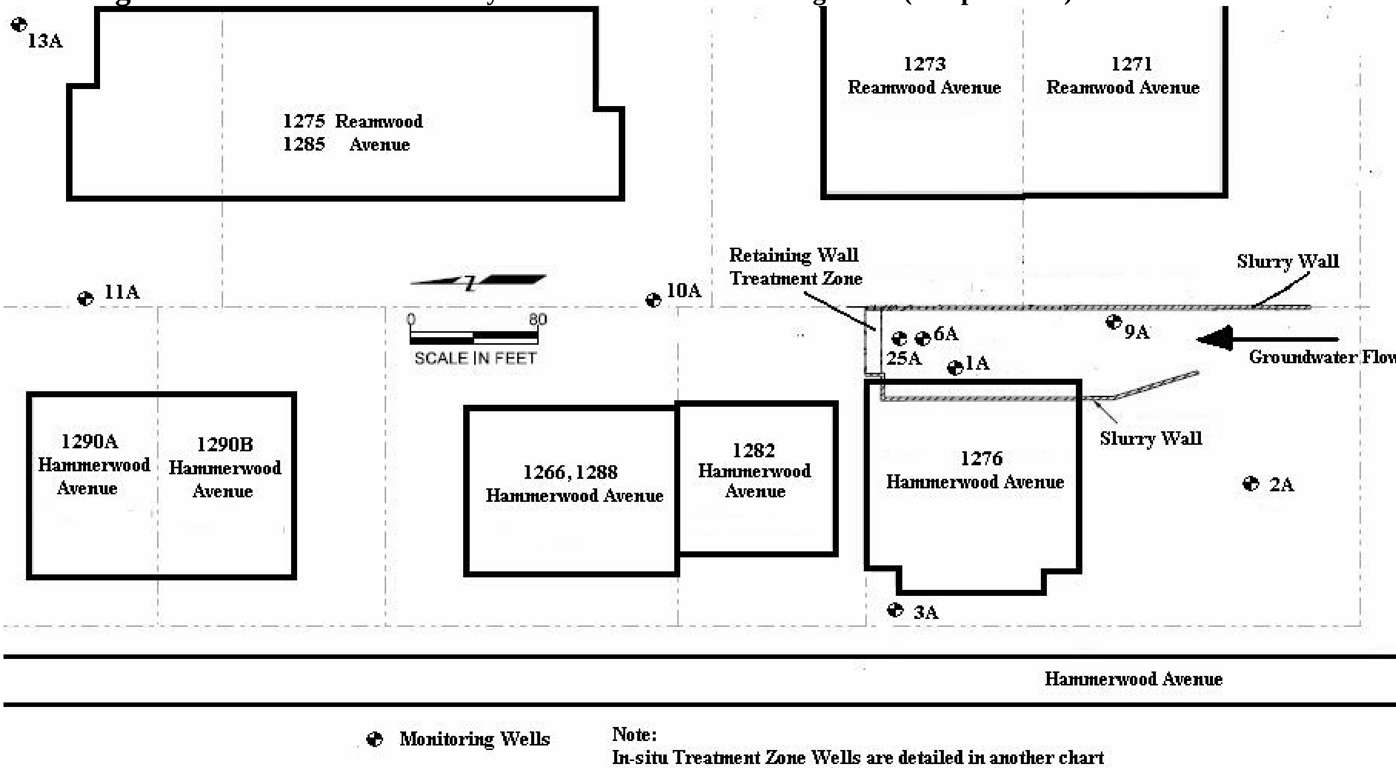
Adapted from: USEPA, *Pump and Treat and Permeable Reactive Barrier to Treat Contaminated Groundwater at the Former Intersil, Inc. Site Sunnyvale, California*, Cost and Performance Report, September 1998

PRB Installation

A funnel-and-gate system PRB was installed using the conventional trench and fill method. Sheet pilling was inserted into the ground at a distance apart of approximately 8 feet. The approximately 40 ft. long trench was excavated down to 20 feet bgs and temporary trench plates were placed 4 feet apart to separate the pea gravel zones from the soon to be filled iron core. The core was filled with 100% granular iron and the 2 foot end zones on each side of the barrier were filled with pea gravel to even out the water

flow through the barrier. The iron barrier was filled to a height of 11 to 14 feet above the clay layer (6 feet bgs) and covered with earthen fill material. Two low permeability slurry walls of 300 ft. and 235 ft. lengths were installed prior to the barrier installation to contain the main area of contamination and to direct groundwater through the PRB. Figure 36 below is a diagram of the PRB along with the main monitoring wells.

Figure 36 **Intersil PRB and Slurry Walls and Main Monitoring Wells (except in-situ)**

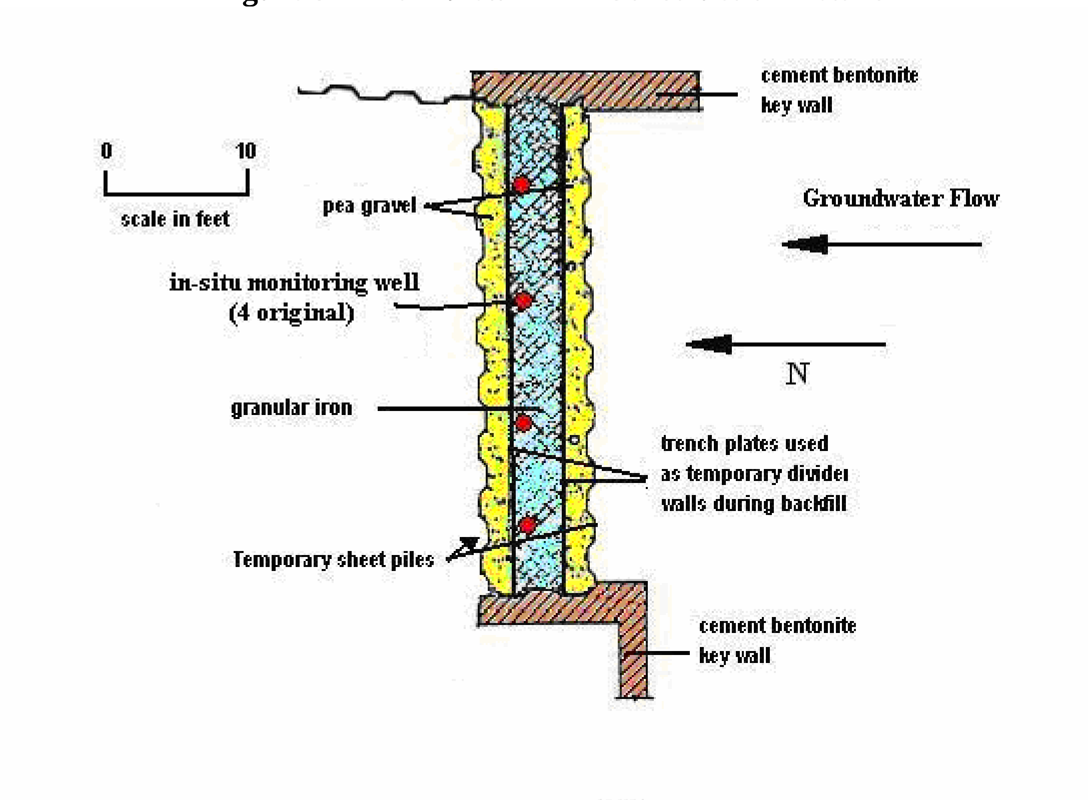


Adapted From:

Geomatrix, *Ten-Year Status Report and Effectiveness Evaluation 1276 Hammerwood Avenue, Sunnyvale, California, Prepared for: General Electric Company.* (February 13, 2006).

Figure 37 below shows how the PRB wall was keyed into the two cement-bentonite slurry walls. It also shows the temporary divider plates used to separate the iron from the pea gravel entrance and exit zones during installation.

Figure 37 Plan View –PRB Construction Details



Adapted from:

US Army Corps of Engineers, *Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents*, (February 1997).

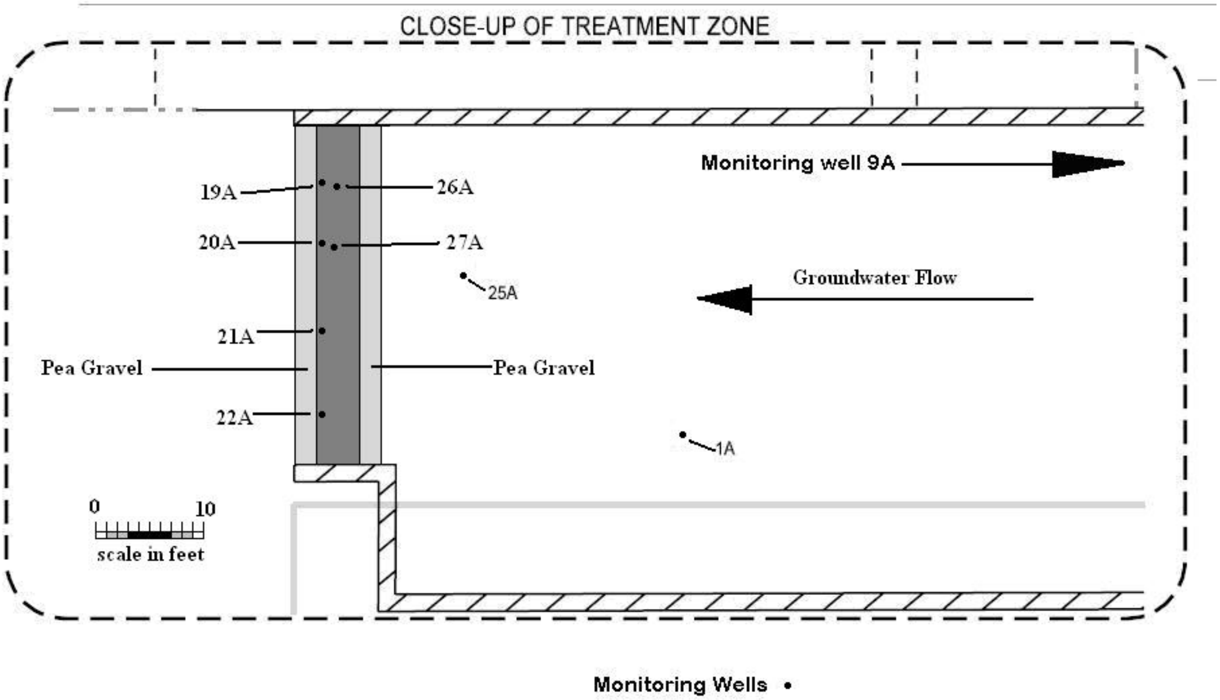
PRB Performance Measurements

Four in-situ monitoring wells were installed in the PRB as primary compliance points within 6 inches of the downgradient edge of the iron barrier. These wells were 19A, 20A, 21A and 22A. In 1997 two more monitoring wells (26A and 27A) were installed in the center of the iron zones adjacent to wells 19A and 20A. These wells were installed because of compliance issues with wells 19A and 20A, when monitoring results indicated MCLs were being exceeded at these locations. Upgradient, the main wells are 1A, 9A, and 25A. 1A and 9A are located on the west and east sides of the area enclosed by the slurry wall gates respectively. Well 25A is located in the center of the gated area just upgradient of the PRB wall.

Quarterly samples were taken from the wells from 1995 through 1998. In 1999 the sampling frequency was dropped to semi-annually.

Figure 38 below diagrams the upgradient and in-situ monitoring well locations.

Figure 38   Intersil Monitoring Well Locations



Adapted from:

Geomatrix, *Ten-Year Status Report and Effectiveness Evaluation 1276 Hammerwood Avenue, Sunnyvale, California, Prepared for: General Electric Company.* (February 13, 2006).

Table 10 below shows the installation dates and screened intervals for the site monitoring wells.

Table 10 Intersil Monitoring Well Specifications

TABLE 3

DEPTH OF SAMPLED PROJECT WELLS

1276 Hammerwood Avenue
Sunnyvale, California

Well I.D.	Date of Well Installation	Well Depth at Time of Installation (feet below MP[1])	Screen Interval (feet below MP)	Depth to Well Bottom[2] (feet below MP)
1A	1983	21.0	5 - 20	19.5
3A	1986	22.0	11 - 21	20.2
6B	1986	90.5	80 - 85	86.0
9A	1986	18.5	8 - 18	13.9
10A	1986	21.0	8 - 18	18.1
11A	1986	19.2	8.5 - 18.5	18.5
19A	01/31/95	17.7	9.1 - 17.7	17.4
20A	01/31/95	18.5	9.4 - 18.5	18.5
21A	01/31/95	18.6	9.5 - 18.6	17.7
22A	01/31/95	17.7	9.2 - 17.7	16.9 [3]
25A	01/31/95	18.5	8 - 18	18.3
26A	01/14/97	18.0	8 - 18	16.7
27A	01/14/97	18.0	8 - 18	17.3 [3]

PRB Performance Analysis

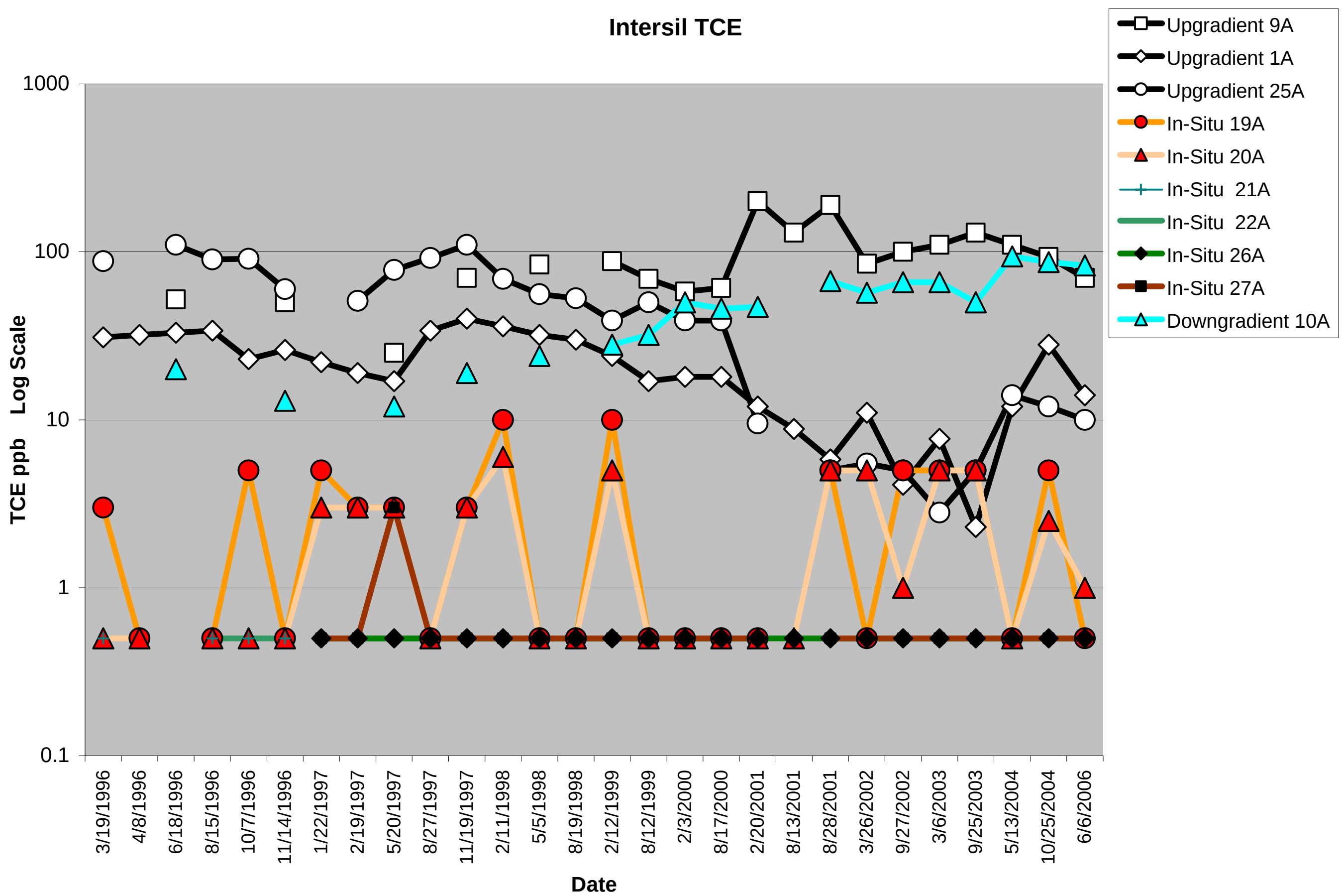
Remediation goals for the PRB were set at the Maximum Contaminant Levels (MCLs) for the contaminants of concern. Charts were developed showing cis 1,2-DCE, TCE concentrations to assess PRB performance and trends in upgradient and downgradient contaminant levels. Freon-113 concentrations mirror the other contaminant trends but are generally below the MCL (near the barrier wall) and therefore not presented in this report. Freon-113 concentration at monitoring wells 1A and 25A upgradient of the PRB have been in the range of 0-50 ppb. Further upgradient at well 9A, Freon-113 concentrations peaked at 24,000 ppb in 1994 and reached a low of 320 ppb in May 2005.

Table 11 California MCLs

TCE	5.0 ppb
cis-1,2-DCE	6.0 ppb
VC	0.5 ppb
Freon-113	1,200 ppb

Figure 39 below shows the upgradient, in-situ, and downgradient TCE concentrations at Intersil. The upgradient TCE concentrations have been extremely variable ranging from 5 to 200 ppb. Two of the in-situ wells, 19A and 20A, have had numerous excursions above the compliance limit of 5 ppb for TCE. The other in-situ wells, 21A, 22A, 26A and 27A, have all been below 5 ppb TCE. Downgradient of the PRB, well 10A has shown a steady increase in TCE concentration from about 15 ppb to over 80 ppb over the period.

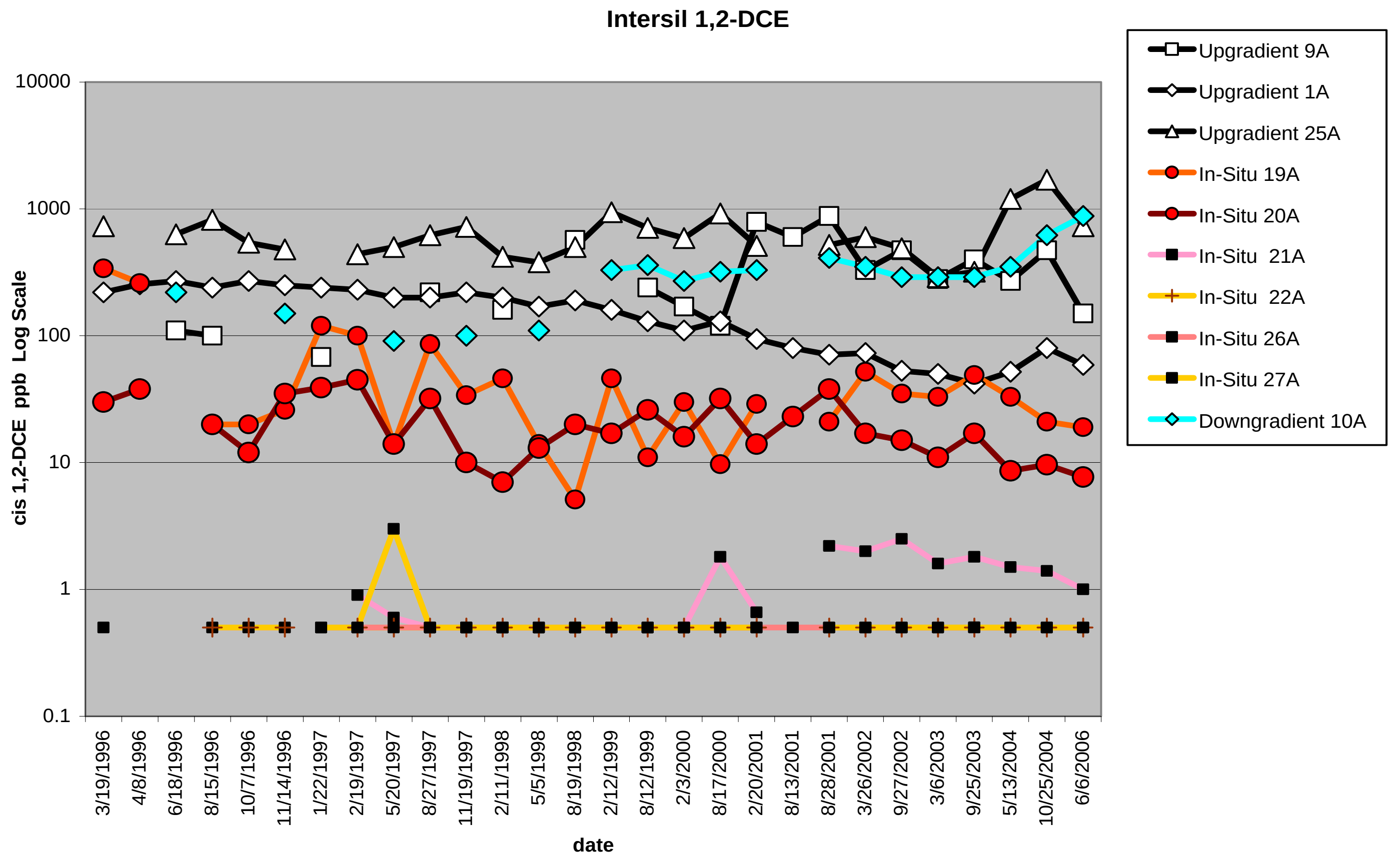
Figure 39 Intersil TCE Concentrations



Note: Non-detect baseline samples were plotted at the detection limits

Figure 40 below shows the cis 1,2-DCE concentrations upgradient, in-situ, and downgradient of the PRB at Intersil. The upgradient cis 1,2-DCE concentrations are also highly variable ranging from a low of 50 to a high of near 2000 ppb. In-situ, wells 19A and 20A are again consistently above the compliance limits of 5 ppb for cis 1,2-DCE. The other in-situ wells, 21A, 22A, 26A and 27A, have all been in compliance through the period. The downgradient well 10A has shown a steady increase in cis 1,2-DCE concentration from 100 to about 1000 ppb over the period.

Figure 40 Intersil 1,2-DCE Concentrations



Note: Non-detect baseline samples were plotted at the detection limits.

VC plots appear similar to the cis 1,2-DCE and TCE charts and have been omitted for the sake of brevity.

Summary and Conclusions

Based on the in-situ monitoring well results, the PRB has met its design goal of preventing off-site migration of contaminated groundwater from the Intersil property.. Even with additional groundwater characterization it would be difficult to assess the effect of this PRB on the downgradient plume due to the contributions from off-site contaminant sources.

The nearest downgradient monitoring well, 10A, is approximately 140 feet downgradient from the PRB. Contamination levels in monitoring well 10A appear to be increasing. This suggests either the PRB is not effective in preventing the downgradient progress of the contamination plume, or that well 10A is located in a portion of the downgradient plume that originates from a source other than the Intersil site.

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USEPA, *Pump and Treat and Permeable Reactive Barrier to Treat Contaminated Groundwater at the Former Intersil, Inc. Site Sunnyvale, California*, Cost and Performance Report, September 1998

US Army Corps of Engineers, Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents, (February 1997).

3.6 Evaluation of the Moffett Field PRB Project

Site History

Operations at Moffett Field started in 1933 when the area was commissioned as a base to support dirigible operations. In 1935 the base was transferred to the Army Air Corps for use in training air cadets. The Ames Aeronautical Laboratory was established at the site during the Army's tenure and later became the NASA Ames Research Center.

In 1942, the station was given back to the Navy and the base again started supporting dirigible and blimp operations as well as fighter aircraft support. The station eventually became the largest naval air transport base on the west coast. In July 1994, the airfield was closed and Moffett Field was transferred to The NASA Ames Research Center.

Groundwater Contamination and Hydrology

In the early 1990's the site was tested for soil and groundwater contamination. Various contaminants were found including waste oils, solvents, cleaners, and jet fuels, originating from above and underground storage tanks, a dry cleaning facility, and sumps. The chlorinated solvents, trichloroethylene (TCE), dichloroethylene (both cis and trans) (1, 2-DCE), and perchloroethylene (PCE) were found with maximum concentrations of 2,990 ppb TCE, 280 ppb 1, 2-DCE, and 26 ppb PCE. The plume of contaminated groundwater was more than 10,000 ft. long and 5000 ft. wide.

The site consists of a complex mixture of alluvial clay, silt, sand, and gravel sediments which form a series of lens shaped, interbraided channel deposits that are divided into three separate aquifers, A, B, and C. Aquifer A is approximately 65 feet thick and is further divided into an A1 and A2 zone. The Al zone extends from 5 to 25 feet bgs. The A2 Zone is 25 feet thick and lies beneath the A1 zone. The A1 and A2 zones are separated by a 0 to 15 ft. thick semi-confining clay layer. The groundwater contamination is primarily confined to the A1 aquifer.

Cleanup Goals/PRB Design

The Moffett PRB was part of a larger study involving several other PRB designs at other facilities The PRB demonstration project at Moffett was designed to assess the lifespan of a PRB made from granular iron and how long would iron remain reactive when exposed to chlorinated hydrocarbons and mineral contaminants in groundwater. The project was also designed to look for any hydraulic changes in the PRB over time and evaluate the potential for plugging. Another goal of the larger study was to assess the hydraulic performance of various PRB designs (at various sites across the US) in terms of their ability to meet the desired groundwater capture zone and residence time requirements.

An iron sample from Peerless Metal Powders Inc. which had demonstrated the greatest treatment efficiency for TCE and PCE was the only sample used in the column tests. The half-lives calculated from the column tests were 0.87 to 1.0 hr for TCE, 0.29 to 0.81

hr for PCE, 3.1 hr for 1, 2 DCE, 9.9 hr for 1, 1-DCA, and 4.7 hr for vinyl chloride. Based on these half-lives and the maximum contaminant concentrations expected, the design thickness for the PRB was determined to be 6 feet thick.

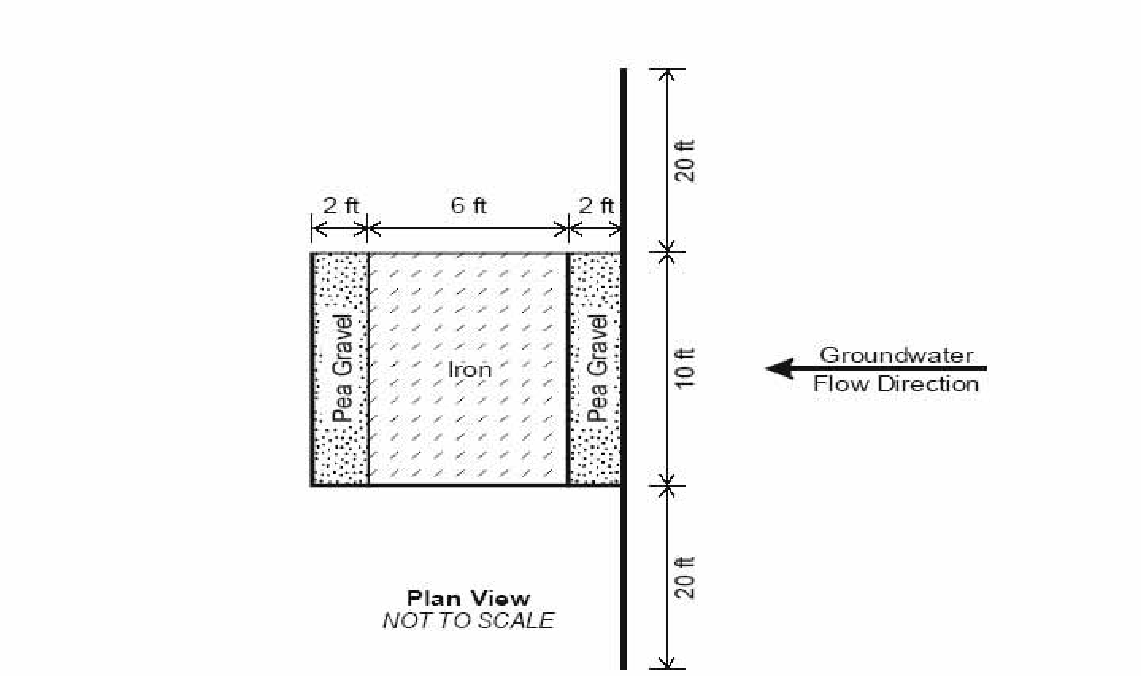
Using the EPA Scoping Calculations equation modified for TCE with a groundwater flowrate of 1.5 ft./day and an initial TCE concentration of 3000 ppb and a cleanup goal of 5 ppb, the computations call for a design thickness of 0.5 inches of iron. The EPA Scoping Calculations equation modified for cis 1,2-DCE with a maximum cis 1,2-DCE concentration of 300 ppb and a cleanup goal of 5 ppb results in a wall design thickness of 1.7 feet. The actual PRB thickness of 6 feet is a very robust design.

PRB Installation

In April 1996, a funnel and gate PRB was installed at Moffett NAS using standard trench and fill techniques. The iron cell, composed of 100% iron, was 6 ft. thick by 10 ft. wide and 22 ft. deep. Two foot thick pea gravel sections were installed on either side of the reactive cell. Finally, funnel walls of sheet piling were installed extending 20 feet to either side of the gate. The system was installed at the core of the contaminant plume. It was not keyed into the underlying semi-confining clay layer to avoid the possibility of breaking through this layer.

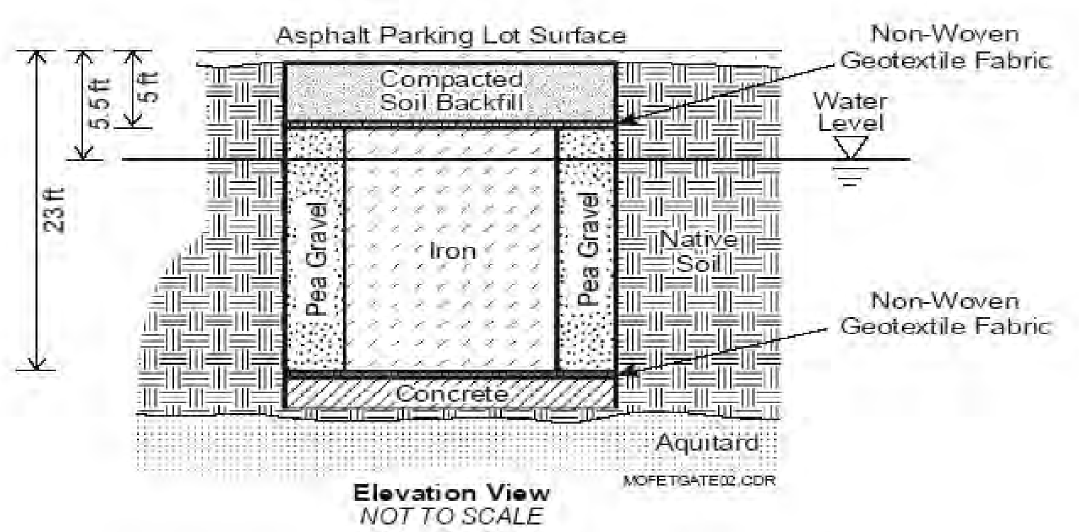
Figures 41 and 42 below are schematics of the PRB installation. Figure 41 is a top view of the installation and figure 41 is a cross sectional side view.

Figure 41 Top View Moffett PRB



Source ESTCP - **LONG TERM PERFORMANCE ASSESSMENT OF A PERMEABLE REACTIVE BARRIER AT FORMER NAVAL AIR STATION MOFFETT FIELD- June 24, 2005**

Figure 42 Side View Moffett PRB



Source: ESTCP - **LONG TERM PERFORMANCE ASSESSMENT OF A PERMEABLE REACTIVE BARRIER AT FORMER NAVAL AIR STATION MOFFETT FIELD- June 24, 2005**

PRB Performance Measurements

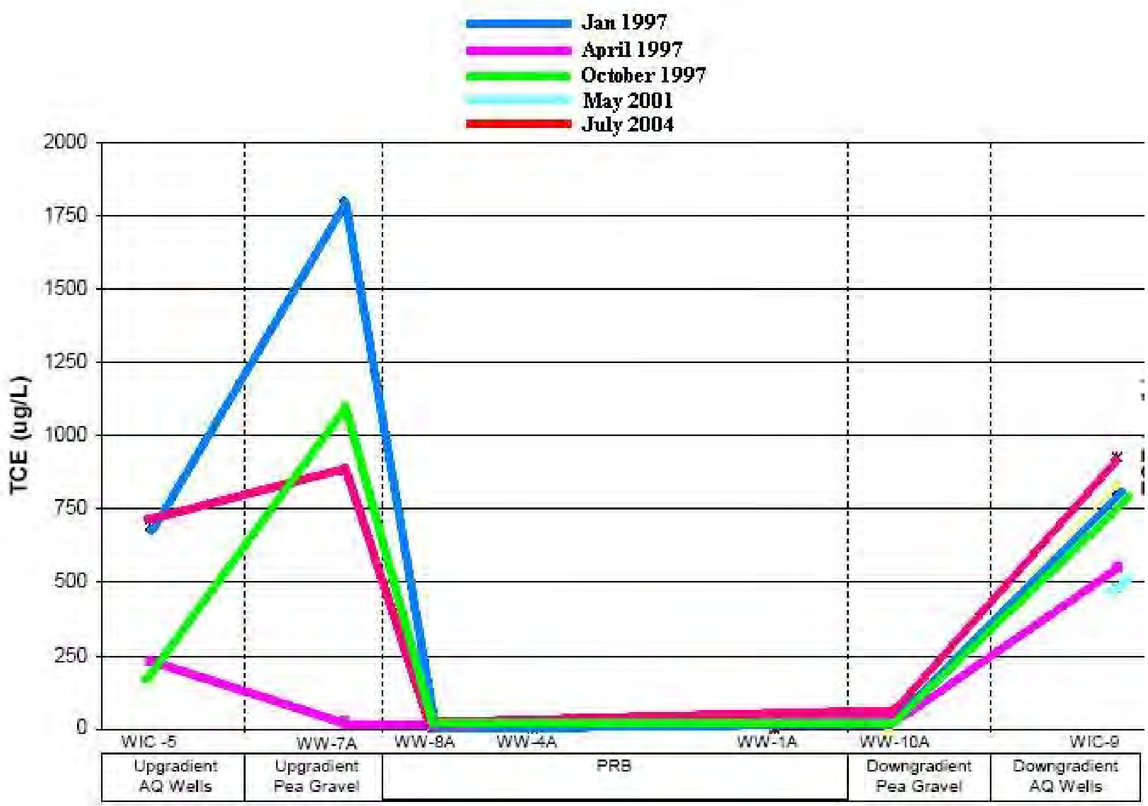
Ten monitoring wells were installed within the iron cell of the PRB. Four monitoring wells were installed within each pea gravel section of the system. Two upgradient and three downgradient wells were installed in the A1 Aquifer. The wells were monitored quarterly for VOCs along with other chemicals and properties.

PRB Performance Analysis

The chlorinated solvents, trichloroethylene (TCE), dichloroethylene (1, 2-DCE), and perchloroethylene (PCE) are all reduced to below Maximum Contaminant Levels (MCLs) within the first 3 feet of the reactive cell. Tracer tests showed that the flowrate ranged from 0.5 to 1.5 ft./day through the PRB during the testing period from 1996 through 1997. The flow patterns were heterogeneous with higher groundwater flowrates at the lower depths of the PRB.

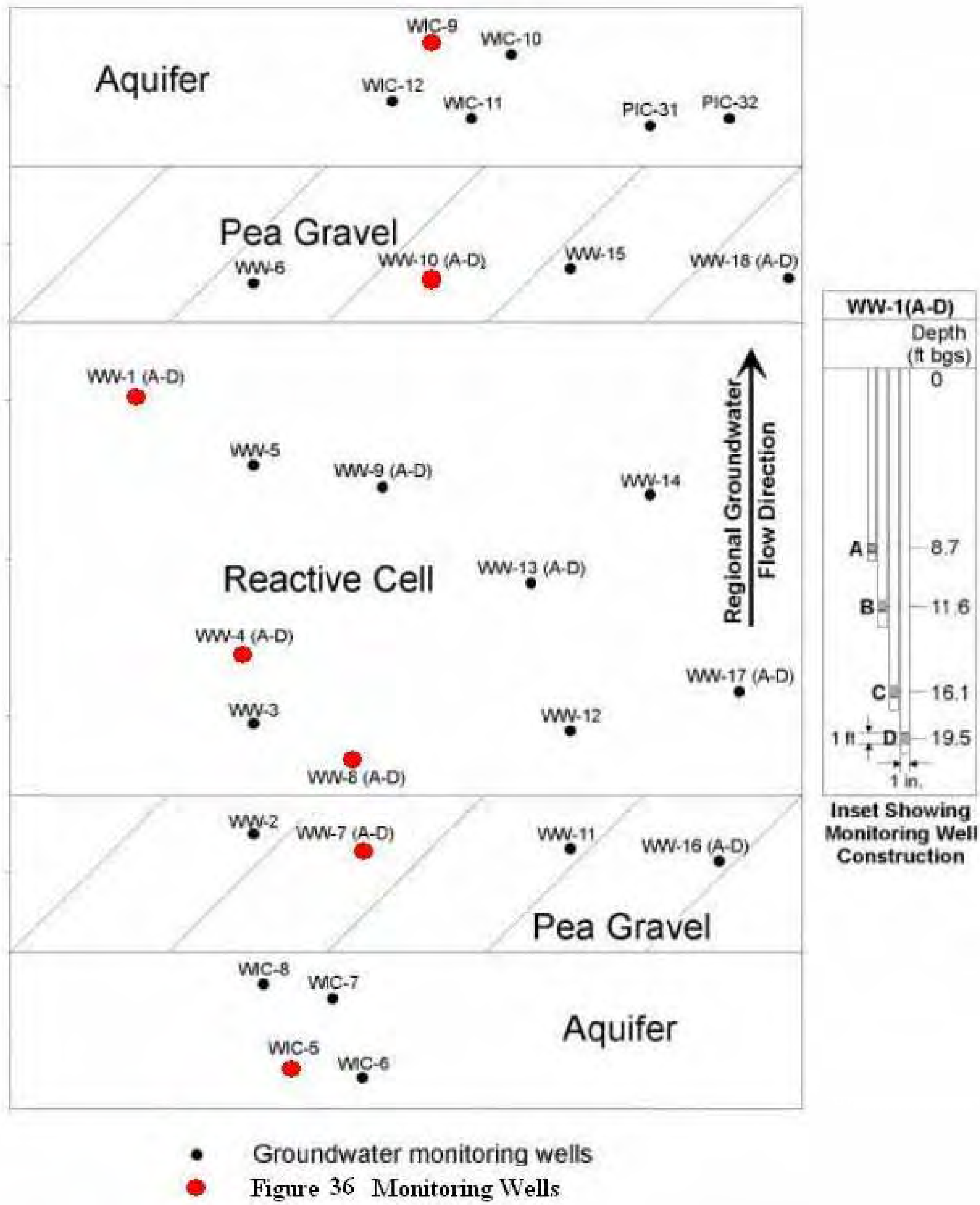
Figure 43 below is a graph of the upgradient, in-situ, and downgradient TCE levels at various quarterly test intervals at the site. The graph shows the results of monitoring events for the shallow monitoring wells. Of note is the high TCE level downgradient of the PRB.

Figure 43 Moffett TCE Concentrations



Source: ESTCP - **LONG TERM PERFORMANCE ASSESSMENT OF A PERMEABLE REACTIVE BARRIER AT FORMER NAVAL AIR STATION MOFFETT FIELD- June 24, 2005**

Figure 44 Monitoring Wells associated with Figure 42 TCE graphs



Adapted from: Figure 3.5. *Planar View of Coring Locations and Groundwater Monitoring Wells*: ESTCP, *Permeable Reactive Wall Remediation of Chlorinated Hydrocarbons in Groundwater*, July 1999.

Summary and Conclusions

Monitoring at Moffett and other sites of the study determined that it would take over 30 years to reduce the reactivity of iron in a PRB by a factor of two (the definition used as the useful life of a PRB). Additionally, the hydraulic performance of the funnel-gate design proved to be successful.

Although the PRB performance appeared effective within the constructed barrier, water quality immediately downgradient of the barrier has shown little, if any, signs of improvement. This is a significant problem with not only this particular project, but also with other systems reviewed in this report. When the PRB was installed at Moffett, the expectation was for a clean front of groundwater to sweep across the downgradient contamination plume. Five years later, there was no noticeable improvement in downgradient water quality.

This lack of downgradient improvement was carefully studied. Several explanations were proposed in the June 2005 ESTCP report (footnote to bibliography) to explain this phenomena that plagues many PRB projects. The absence of downgradient improvements in contaminant concentration in spite of very low in-situ contaminant concentrations:

•Less groundwater may be flowing through PRB than was expected.

• Cleaner effluent from the PRB may be mixing with contaminated groundwater flowing under or around the PRB.

• CVOCs trapped in the silty clay layers surrounding the sand channel may be diffusing back into the cleaner PRB effluent.

• Groundwater may be channeling through preferential pathways in the iron causing overloading of the PRB and breakthrough of contaminants.

References

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, *Field Applications of In-Situ Remediation Technologies: Permeable Reactive Barriers* (EPA 542-R-99-002) (April 1999).

Tri-Agency Permeable Reactive Barrier Initiative and ITRC, *Evaluation of Permeable Reactive Barrier Performance Revised Report* (December 9, 2002).

Battelle, *Long Term Performance Assessment of a Permeable Reactive Barrier at Former Naval Air Station Mofffett Field* June 24, 2005).

US Department of Defense - ESTCP, *Evaluating the Longevity and Hydraulic Performance of Permeable Reactive Barriers at Department of Defense Sites* (January 2003).

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, *Cost Analyses for Selected Groundwater Cleanup Projects: Pump and Treat Systems and Permeable Reactive Barriers* (February 2001)

ESTCP, *Permeable Reactive Wall Remediation of Chlorinated Hydrocarbons in Groundwater*, July 1999.

3.7 Evaluation of the Mohawk Laboratory PRB

Site History

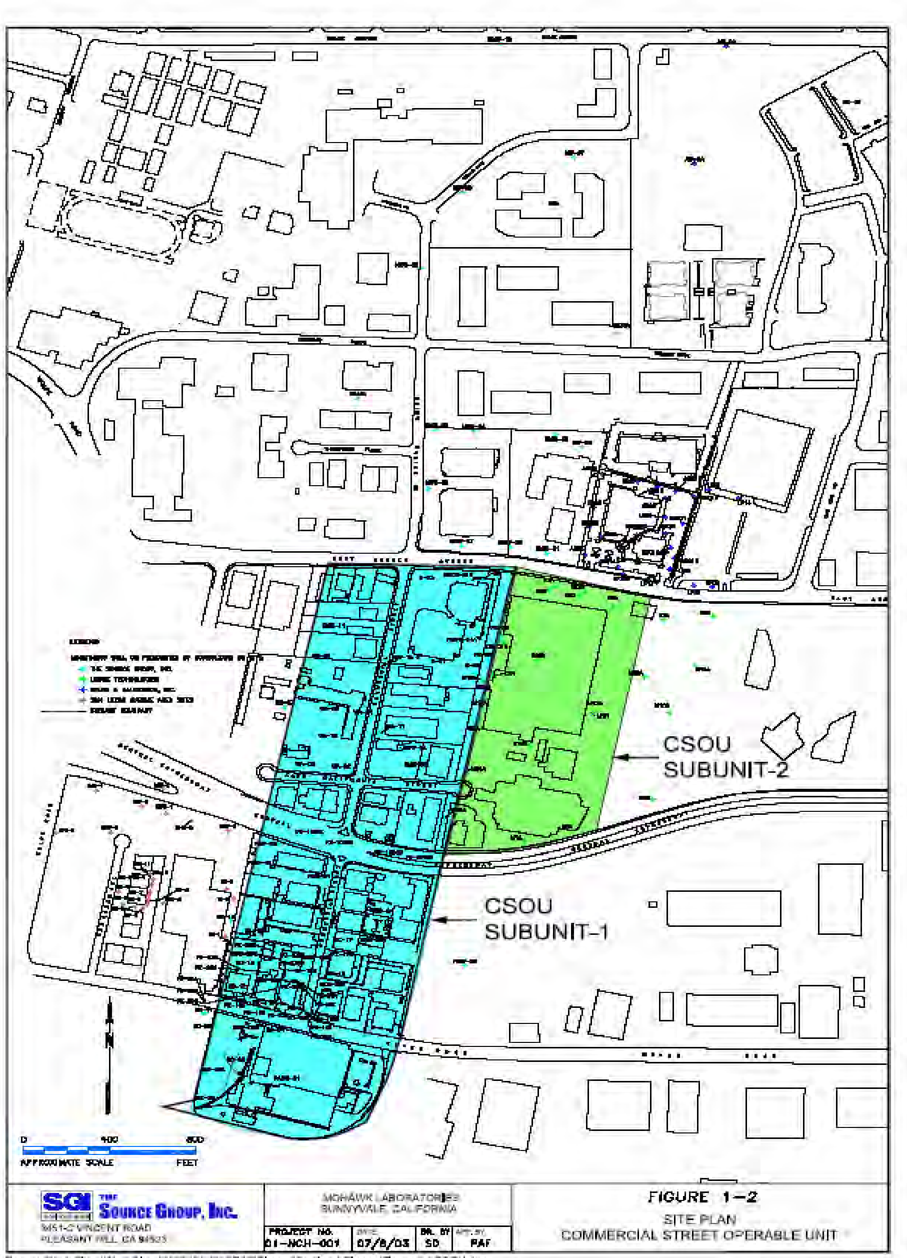
The Mohawk Laboratory site is located at 932 Kifer Road in Sunnyvale, California. The first owner of the site operated an above ground storage tank farm from the 1950's until Mohawk took over the site in 1967. The tank farm had a capacity of over 150,000 gallons and stored mineral spirits, kerosene, xylenes, isopropanol, and various chlorinated solvents. The chemicals stored in the tank farm were transferred to a warehouse, blended into mixtures and packaged for sale.

After purchasing the property, Mohawk continued using the tank farm and warehouse for a blending operation. Mohawk removed the tank farm in 1988 and began storing all chemicals within the warehouse. At the request of the Regional Water Quality Control Board, Mohawk sampled the ground beneath the site for contamination in 1987. The initial testing showed that there was soil contamination beneath the site. Further investigation revealed a plume of chemical contamination extending northward from the original tank farm site. Mohawk Laboratories next completed two extensive studies of the onsite contamination and of the extent and composition of the offsite plume. The on-site study identified the area directly underneath the tank farm and an area next to the main laboratory building as the source areas for the contamination.

Other nearby industrial sites were also found to have contributing contamination sources. The California Regional Water Quality Control Board - San Francisco Bay Region (SFRWQCB) designated the area as the Commercial Street Operational Unit (CSOU).

Figure 45 below is a map of the CSOU, including Subunit 1 and Subunit 2. Subunit 1 covers the Mohawk Lab site and the property owned by Applied Materials to the north/northeast, while Subunit 2 covers the Schlumberger site to the east.

Figure 45 Commercial Street Operational Unit



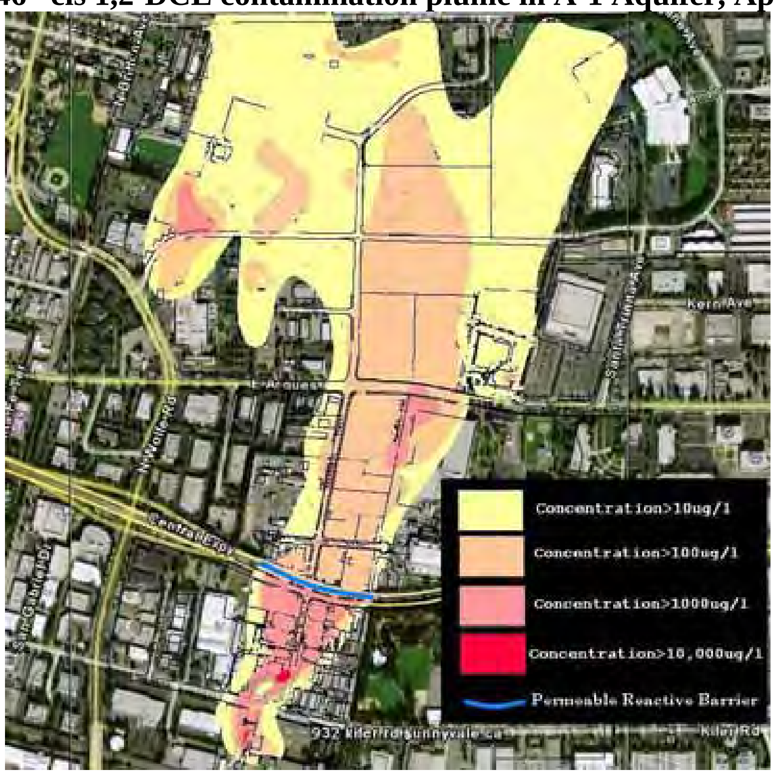
Taken from: The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

To characterize the extent of soil and groundwater contamination, the companies of the Commercial Street Operational Unit (CSOU) performed over 500 cone penetration tests and soil borings, and installed over 100 monitoring wells and piezometers. The primary contaminants detected in soil and groundwater at the site include:

- Tetrachloroethylene (PCE)
- Trichloroethylene (TCE)
- Cis-1, 2- Dichloroethylene (cis 1,2-DCE)
- Trans-1, 2- Dichloroethylene (trans 1,2-DCE)
- Vinyl chloride (VC)
- Chlorobenzene
- 1, 2-Dichlorobenzene (1, 2 DCB)
- 1, 3-Dichlorobenzene (1, 3 DCB)
- 1, 4-Dichlorobenzene (1, 4 DCB)
- Total Petroleum Hydrocarbons (TPH)

Figure 46 is an isoconcentration map showing the main offsite plume contaminant, cis 1,2-DCE in 2006 in the A-1 aquifer. The plume extends over 5000 feet to the north of the Mohawk Laboratory site.

Figure 46 cis 1,2-DCE contamination plume in A-1 Aquifer, April 2006



Adapted From: The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

Groundwater Contamination and Hydrology

The groundwater hydrology at the site has been characterized as containing 2 permeable zones identified as A (shallow) and B (deeper). The upper aquifer zone (Zone A) has been studied extensively and further subdivided in two zones. The A1-Zone extends from ground surface to approximately 22 feet below ground surface (ft.-bgs). The A2-Zone extends from 22 to 35 ft.-bgs.

The A-Zone divisions are based primarily on the characteristics of the sand/gravel deposits. See figure 3. The A1-Zone and A2-Zone distinctions exist south of East Arques Avenue. Farther downgradient of the PRB, north of East Arques Avenue, there are no characteristic differences between the A1 and A2 zones and they should be considered as a single A-Zone.

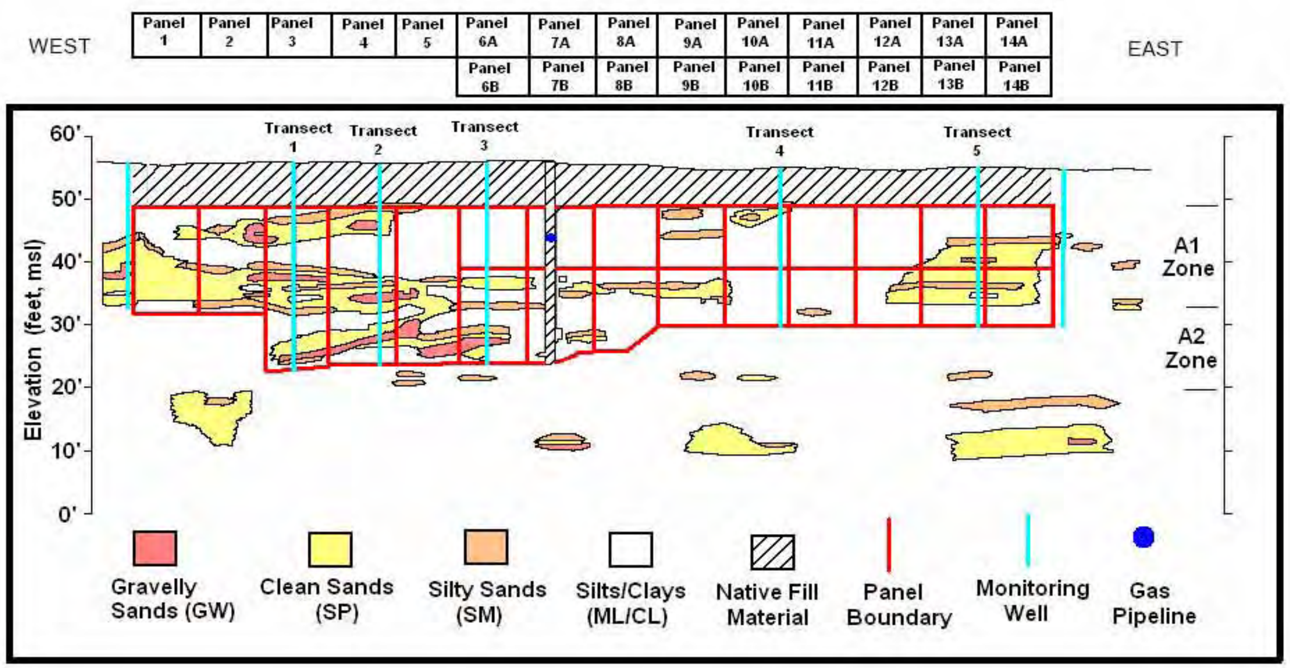
Beneath the A-Zone, a B-Zone has been identified which extends from the bottom of A2 to at least 100 ft.-bgs. A B-Zone investigation in 2002 concluded that the A-Zone plumes do not significantly impact the B-Zone aquifer due to a fairly continuous silt/clay layer at approximately 35 ft.-bgs.

Groundwater is generally encountered between 6 and 11 ft.-bgs and flows to the north/northeast. Groundwater velocities have been estimated to range from 3 to 9 feet per day (ft. /day) based on tracer tests. The average velocities based on this data are as follows:

- A1-Aquifer Zone (upper sands) average 3 ft. /day
- A2-Aquifer Zone (lower gravels) average 5.75 ft. /day
- Clay/Silt Zones with an estimated negligible flow contribution

The groundwater flow in the "A" aquifer is predominantly through preferential flow pathways in the sand and gravel channels. Figure 47 shows a cutaway diagram of the sand and gravel channels and the clay/silt zones at the PRB location. It also shows the individual PRB panels and transect locations which will be described later in this report.

Figure 47   Mohawk Geology and PRB Placement



Adapted from:

The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

Remediation Activities

A number of remedial actions have been undertaken at the site since discovery of the contamination in 1987. These include groundwater extraction, soil vapor extraction (SVE), ozone injection, a well recirculation system, an enhanced anaerobic biodegradation (EAB) injection program, a monitored natural attenuation program (MNA), and finally a permeable reactive barrier (PRB). Currently, the ozone injection, SVE, EAB, MNA, and PRB are active remediation programs. These past and currently on-going remedial activities are located upgradient and do not affect performance of the PRB evaluated in this report.

Table 12 below summarizes the remediation activities at the Mohawk site.

Table 12 Mohawk Remedial Activities

Remedial Technology	Years in Service	Activities
Groundwater Extraction and Treatment /Soil Vapor Extraction	1993-2001	27,000 lbs VOCs removed
Ozone Injection	2002 – current	200 lb ozone injection/day capacity
Recirculation Wells	1997-2000	87 lbs VOCs removed
Enhanced Bio Degradation	2005 - current	5000 gal Edible Oil Substrate injected, PCE and TCE concentrations dropped by 70% at selected wells.
Soil Vapor Extraction	2001 - current	1260 lbs VOCs removed in Q2/2006
Monitored Natural Attenuation	1993-current	Total VOCs down 50% in 4 of 8 wells monitored over 5 years
Permeable Reactive Barrier	2003 - current	Reduction in total VOCs across barrier > 70% on average

Compiled from:

Quarter 1 and Quarter 2, 2006 (Q1/Q2 2006) Semi-Annual Self-Monitoring Report for the Mohawk Laboratories property (the Site), dated July 30, 2006.

And Draft Final Remedial Action Plan (FRAP, Volume I)

And Draft Revised Human Health and Ecological Risk Assessment Report (Risk Assessment, Volume II) for the Mohawk Laboratories site in Sunnyvale, California. Dated January 16, 2006

Initial Cleanup Goals and PRB Design Approach

The PRB was initially planned to treat the major contaminant at the site, cis 1,2-DCE, down to a level of 2.5 ppb. Column studies were performed using contaminated water from the site and several available zero valent iron samples from different vendors. Determined rate constants were then applied to the numerical model used to design the PRB. The numerical model calculated that a 5.8 foot thick wall would be needed to treat a plume with an initial concentration of cis 1,2-DCE of 3000 ppb and an average groundwater flowrate of 3.0 ft./day, . (See appendix A for column study parameters and equations)

For a 5.8’ thick PRB extending from 8 ft. bgs to 25 ft. bgs and with a capture length of 1000 ft., the volume of iron required would be 1000 x (25-8) x 5.8 = 98,600 ft^3. One brand of bulk granular iron has a bulk density of 137.4 lb/ft^3 and a cost of $375/ton in 2003. Using this source, the PRB would require 6773 tons of zero valent iron and cost over iron $2,500,000.

To reduce cost, the overall length of the barrier was reduced to 700 feet to more closely match the plume width. The length of the PRB was also divided into sections and each section analyzed separately to determine the minimum amount of iron required for remediation.

Additionally a plan was presented to the SFRWQCB for the design of the PRB to treat groundwater to less than 600 ppb total VOCs instead of the much lower drinking water maximum contaminant levels (MCLs) which are 6 ppb for cis 1,2-DCE and 5 ppb for TCE. The plan incorporated natural attenuation to further reduce the contaminant levels downstream of the PRB to acceptable levels over a period of 20 years.

PRB performance goals:

The Mohawk site’s groundwater contamination plume is over a mile in length. The plume has been around for many years, long enough for significant natural attenuation to have occurred. Evidence of natural attenuation can be seen in the high concentrations of cis 1,2-DCE and vinyl chloride in the plume which are breakdown products of PCE and TCE.

At one central monitoring well point in the contamination plume (PZ-1009A), the concentration of the breakdown product cis 1,2-DCE was 1700 ppb while the TCE concentration was 120 ppb in the first quarter of 2006. This indicates that 90% of the original TCE was transformed to cis 1,2-DCE through biological breakdown. The final design of the PRB at Mohawk incorporated natural attenuation as an integral part of the remediation process. Instead of trying to treat contaminants down to California MCL cleanup levels, the PRB at Mohawk targeted reducing the total VOC (predominantly PCE, TCE, cis 1,2-DCE, and vinyl chloride) concentration to 600 ppb. This would be an 80-85% reduction of the total VOC concentration upstream of the PRB. Under this remedial design, the PRB would reduce contamination down to a level where natural attenuation would be sufficient to reach target goals. Computer flow and attenuation modeling predicted there would be a gradual reduction of the downgradient contaminant plume to below MCLs over 20 years with the PRB in place.

PRB Design

Laboratory column studies were performed on water collected from monitoring wells at the site using several different sources of granular iron. The source of iron eventually chosen for the PRB was Connelly 8/50 mesh iron. This decision was based on the iron’s performance in column testing performed by Prima Environmental and advice from

Environmetal Technologies Inc (ETI), the patent holder of the zero valent iron technology.

To check PRB design, iron wall thicknesses were calculated for each PRB panel using the EPA Scoping Calculations equation modified for cis 1,2-DCE. The rate constant for reaction of cis 1,2-DCE with zero valent iron is much less than that for TCE, making it a controlling factor in determining the required wall thickness for the PRB. Table 14 presents calculated and actual wall thicknesses along with the concentration and flow parameters for each PRB panel. In every case the iron flow through thickness actually used in each panel is slightly larger than Equation 1 would require.

After the first two panels were installed, a decision was made to standardize the actual wall thickness to either 2 feet or 4 feet, and to adjust the sand/iron ratio as needed to effectively meet the iron flow through requirements. By adjusting the iron mass for the expected contaminant mass loading, and reducing the length of the PRB from 1000 to 700 feet, the total amount of iron needed for the PRB project was reduced from 6773 tons to 2325 tons. The cost of iron for the project was reduced from $2,500,000 to around $872,000.

Table 13 Panel Design Parameters and Calculations

Panel #	actual trench width	water flow rate ft/day	percent iron by volume	initial [cDCE] expected	final [cDCE] expected	$Ln(P_o/P)$	iron wall thickness needed by calculation Appendix A	iron flow through thickness actually used	Envirometal Technologies Inc. estimated total VOC'S downgradient from PRB from modeling
1	1.7	3.0	100%	3000	433	1.9	1.6	1.7	557
2	2.2	3.1	100%	4600	441	2.3	2.0	2.2	568
3	4	5.6	100%	4600	443	2.3	3.6	4	603
4	4	5.6	100%	4600	440	2.3	3.6	4	537
5	4	5.6	100%	4600	457	2.3	3.5	4	793
6A	4	3.0	20%	Clay/Silt Zones estimated to contain negligible flow contribution.				0.8	
6B	4	5.6	100%	4600	445	2.3	3.6	4	653
7A	4	3.0	20%	Clay/Silt Zones estimated to contain negligible flow contribution.				0.8	
7B	4	5.6	100%	4600	436	2.4	3.7	4	492
8A	4	3.0	20%	Clay/Silt Zones estimated to contain negligible flow contribution.				0.8	
8B	4	5.6	100%	4600	442	2.3	3.6	4	566
9A	2	3.1	20%	0	396			0.4	406
9B	2	3.1	55%	1700	489	1.2	1.0	1.1	546
10A	2	3.1	20%	600	396	0.4	0.4	0.4	620
10B	2	3.1	55%	1700	488	1.2	1.0	1.1	552
11A	2	3.1	20%	600	396	0.4	0.4	0.4	406
11B	2	3.1	55%	1700	489	1.2	1.0	1.1	564
12A	2	3.1	20%	Clay/Silt Zones estimated to contain negligible flow contribution.				0.4	
12B	2	3.1	20%	250	166	0.4	0.3	0.4	228
13A	2	3.1	20%	100	66	0.4	0.4	0.4	88
13B	2	3.0	85%	3000	497	1.8	1.5	1.7	585
14A	2	3.1	20%	100	66	0.4	0.4	0.4	78
14B	2	3.1	28%	1000	574	0.6	0.5	0.56	594

Adapted from Table 1 and Table 2:
The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

PRB Installation

Mohawk Lab installed the zero-valent iron PRB in 2003 in the median of the Central Expressway, near its intersection with Commercial Street. The PRB was installed using conventional trenching methods with a biopolymer backfill to support the trench walls. The zero valent iron/sand mixture was tremmied into the trenches as the polymer slurry was removed.

A “sectionalized” approach was used in the construction due to the large variations in contaminant loading expected across the plume. The PRB consists of 14 sections that are roughly 50 feet long each, yielding a PRB with an overall length of 700 feet. Except for the first 2 sections which were 1.7 feet and 2.2 feet thick respectively, each section is either 2 or 4 feet thick. The sections generally extend from 6 ft.-bgs to approximately 24

or to 33 ft.-bgs. The first 5 sections consist of one panel each while sections 6 through 14 are divided into upper and lower panels. Each panel consists of either 100 percent zero valent iron or a zero valent iron and sand mixture depending on the expected contaminant concentration and loading.

Two design changes were made during the construction of the PRB. First, the trench was made shallower by a few feet in the central portion of the PRB when a lower clay zone was encountered. Second, an 8-foot gap was left in the PRB (through panels 7A and 7B) due to the presence of a PG&E natural gas line at 10 ft.-bgs.

The previously referenced Figure 47 shows the panel placement and subsurface geology at the PRB location. Table 14 below lists the composition and dimensions of each panel of the PRB as installed.

Table 14 Mohawk PRB Panel Specifications

PRB Iron/Sand Quantities By Panel
Mohawk Laboratories, Sunnyvale, CA
November 2003

Panel No.	Depth to Top (ft)	Depth to Bottom (ft)	Trench Width	Iron Flow Through Thickness (ft)	Percent Iron by Volume	Panel Volume (ft3)	Percent Sand by Volume	Percent Iron by Weight	Percent Sand by Weight
1	6	24	1.7	1.7	100%	1530	0%	100.0%	0.0%
2	6	24	2.2	2.2	100%	1980	0%	100.0%	0.0%
3	6	33	4	4	100%	5400	0%	100.0%	0.0%
4	6	33	4	4	100%	5400	0%	100.0%	0.0%
5	6	33	4	4	100%	5400	0%	100.0%	0.0%
6A	6	16	4	0.8	20%	2000	80%	25.1%	74.9%
6B	16	33	4	4	100%	3400	0%	100.0%	0.0%
7A	6	16	4	0.8	20%	2000	80%	25.1%	74.9%
7B	16	33	4	4	100%	3400	0%	100.0%	0.0%
8A	6	16	4	0.8	20%	2000	80%	25.1%	74.9%
8B	16	29	4	4	100%	2600	0%	100.0%	0.0%
9A	6	16	2	0.4	20%	1000	80%	25.1%	74.9%
9B	16	24	2	1.1	55%	800	45%	62.1%	37.9%
10A	6	16	2	0.4	20%	1000	80%	25.1%	74.9%
10B	16	24	2	1.1	55%	800	45%	62.1%	37.9%
11A	6	16	2	0.4	20%	1000	80%	25.1%	74.9%
11B	16	24	2	1.1	55%	800	45%	62.1%	37.9%
12A	6	16	2	0.4	20%	1000	80%	25.1%	74.9%
12B	16	24	2	0.4	20%	800	80%	25.1%	74.9%
13A	6	16	2	0.4	20%	1000	80%	25.1%	74.9%
13B	16	24	2	1.7	85%	800	15%	88.4%	11.6%
14A	6	16	2	0.4	20%	1000	80%	25.1%	74.9%
14B	16	24	2	0.56	28%	800	72%	34.3%	65.7%

Taken from: The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

PRB Performance Measurements

The contaminants of interest in the offsite plume are a reduced set of the total contaminant list as many of the contaminants have not migrated far from their source or have broken down before reaching the PRB in significant quantities.

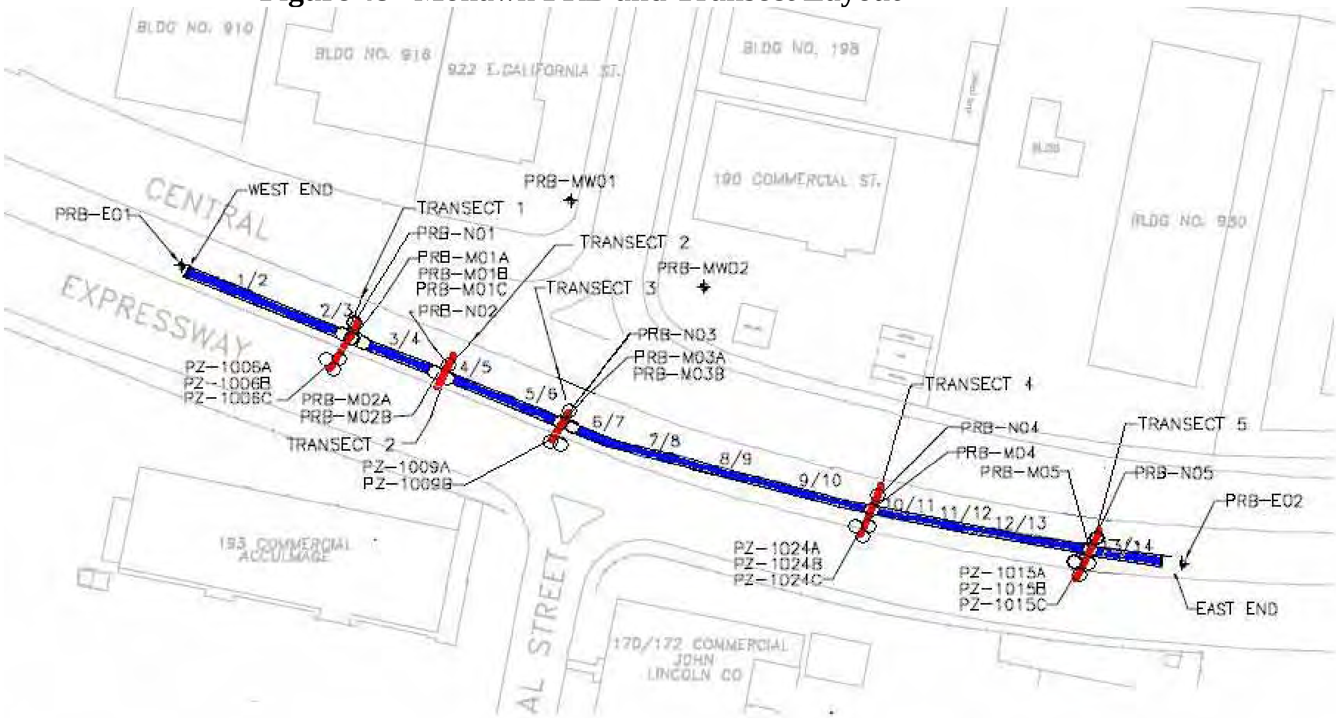
The major contaminants of interest (COI) in the offsite plume are:

PCE
cis 1,2-DCE
TCE
TPH

This report exams the primary contaminants cis 1,2-DCE and TCE to assess performance of the PRB. TPH for the most part is confined to the area south of the PRB and is not routinely tested for during the PRB monitoring well sampling events and will not be considered in the analysis of the PRB performance. PCE concentrations and degradation behavior across the PRB closely mirrors that of TCE and for the sake of brevity is not presented in this report.

Performance monitoring wells along five transects were included in the PRB design. Figure 48 below shows the transect well locations. Four of the transects (1, 3, 4, 5) were aligned with pre-existing monitoring wells so that the data could be compared with historic measurements. Transect wells are located upstream, within (center of the PRB wall), and on the downstream edge of the PRB. Additionally, two wells were installed on the east and west edges of the PRB and 2 wells were installed approximately 105 feet downgradient of the PRB.

Figure 48   Mohawk PRB and Transect Layout



Adapted from: The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

Table 15 below lists the monitoring wells associated with evaluating the performance of the PRB along with their construction details.

Table 15 Mohawk Monitoring Well Specifications

PRB Effectiveness Monitoring Well Construction Details
Mohawk Laboratories, Sunnyvale, CA
November 2003

Well Location	PRB Location	Well Type	Top of Casing Elevation (ft/msl)	Diameter (inches)	Screen (ft-bgs)
Offsite Wells					
PRB-MW-01	NA	HS	54.32	2	8-28
PRB-MW-02	NA	HS	54.74	2	8.5-28.5
End Wells					
PRB-E01	West End	HS	55.54	2	8-25
PRB-E02	East End	HS	54.41	2	7-24
Transect 1					
PRB-S01A/PZ-1006A	Upgradient	PZ	55.24	1.25	9-12
PRB-S01B/PZ-1006B		PZ	55.29	1.25	17-22
PRB-S01C/PZ-1006C		PZ	55.40	1.25	28-32
PRB-M01A	In-Situ	NFP	55.68	2	8-13
PRB-M01B		NFP	55.68	2	17-22
PRB-M01C		NFP	55.69	2	28-33
PRB-N01	Downgradient	HS	55.31	2	8-33
Transect 2					
PRB-M02A	In-Situ	NFP	55.47	2	18-23
PRB-M02B		NFP	55.37	2	25-30
PRB-N02	Downgradient	HS	54.92	2	7-29
Transect 3					
PRB-S03A/PZ-1009A	Upgradient	PZ	55.50	1.25	18-20
PRB-S03B/PZ-1009B		PZ	55.57	1.25	27-31
PRB-M03A	In-Situ	NFP	55.03	2	18-23
PRB-M03B		NFP	55.03	2	26-31
PRB-N03	Downgradient	HS	55.54	2	7-32
Transect 4					
PRB-S04/PZ-1024B	Upgradient	PZ	54.91	1.25	19-23
PRB-M04	In-Situ	NFP	55.49	2	20-25
PRB-N04	Downgradient	HS	54.74	2	8-25
Transect 5					
PRB-S05/PZ-1015C	Upgradient	PZ	54.53	2	20-22
PRB-M05	In-Situ	NFP	54.97	2	17-21
PRB-N05	Downgradient	HS	54.35	2	8-25

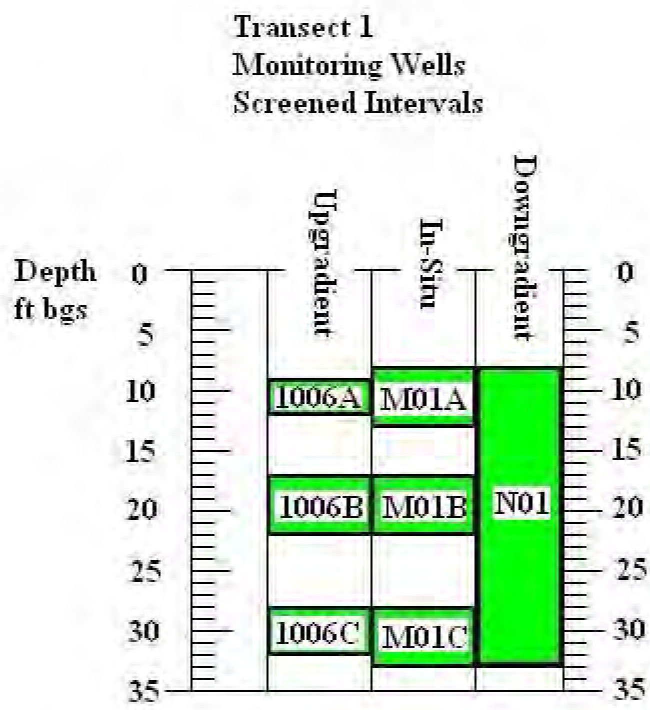
PRB = PERMEABLE REACTIVE BARRIER
E = END OF PRB
S = SOUTH OF PRB
M = MIDDLE OF PRB
N = NORTH OF PRB

HS = Hollow Stem Auger
NFP = Non-Filter Pack (in-situ)
PZ = Existing Piezometer

Taken from: The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

In the following analysis, results for the different sampling depth intervals at each multiple well cluster location have been averaged for each sampling event. Figure 49 below illustrates the screened intervals (shaded in green) of transect 1. In this case, sample results from the upgradient wells 1006A, 1006B, and 1006C are averaged together to get a single result for a given date. The in-situ monitoring well results from M01, M02, and M03 are also averaged for a given sampling date. No averaging is performed on downgradient results as there is only one well at each transect screened for the entire height of the PRB.

Figure 49   Mohawk Transect 1 Monitoring Well Screened Intervals



PRB Performance Analysis

This report evaluates PRB performance primarily using percent reduction in concentration of selected contaminants (total VOCs, TCE, cis 1,2-DCE, and TCE) across the barrier along each of the 5 transects. The overall attainment of the compliance goal over time across all sections of the PRB is also considered. Lastly, hydrologic conditions that potentially impacted PRB performance are noted.

<u>Transect 1</u>

Transect 1 crosses through the middle of Panel 3. The effluent total VOC concentration has been above the 600 ppb target level for most of the period of operation. The last 2 quarterly monitoring results however, have been below the 600 ppb compliance target for total VOCs.

Also of note are the results for the performance monitoring well located inside the PRB. Results for this mid-PRB monitoring well are all below the 600 ppb target level compared to downgradient concentrations greater than the target level.

The upstream cis 1,2-DCE concentrations have all been less than the 4600 ppb expected in the design for panels 2 through 4. The reduction in cis 1,2-DCE concentration has averaged 76 % for this transect since the installation of the barrier. The reduction of TCE concentration across the barrier has averaged 95% since the first year of operation.

Figures 50, 51, and 52 show concentrations of total VOCs, cis 1,2-DCE, and TCE across transect 1. For most sampling events, the in-situ concentrations of total VOCs, cis 1,2-DCE, and TCE were significantly lower then the downgradient concentrations.

Figure 50 Mohawk Transect 1 Total VOC Concentrations

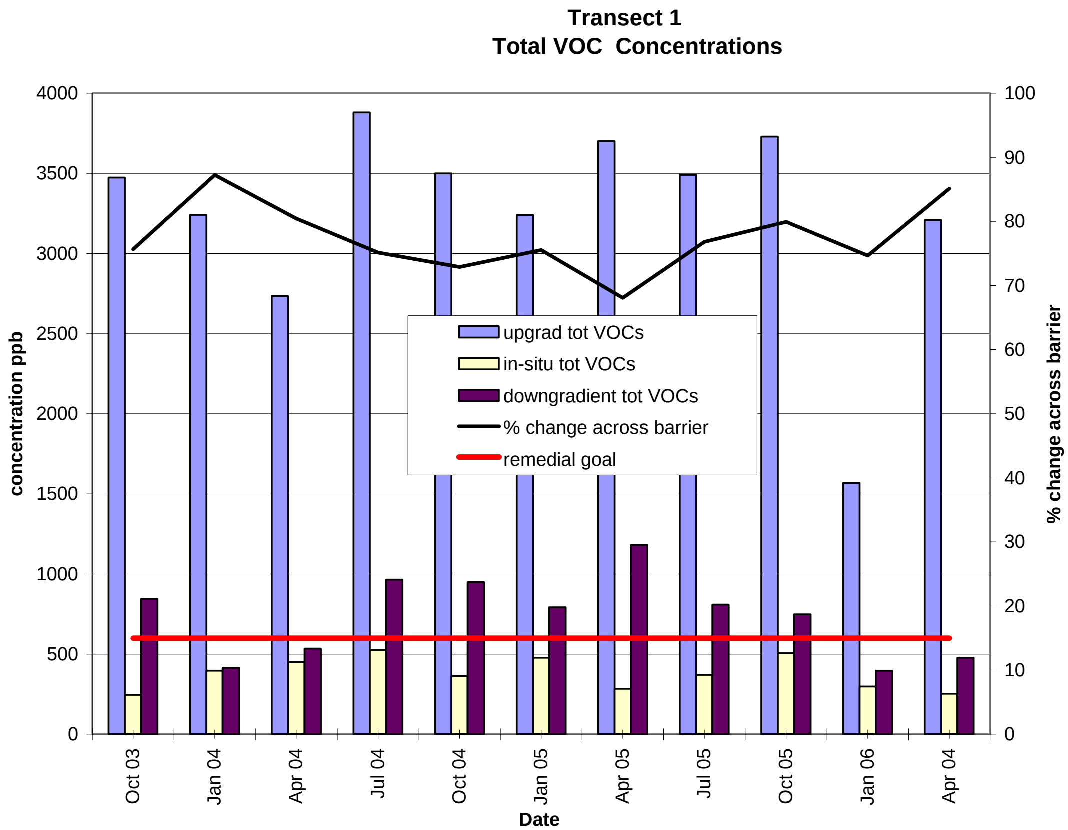


Figure 51 Mohawk Transect 1 cis 1,2-DCE Concentrations

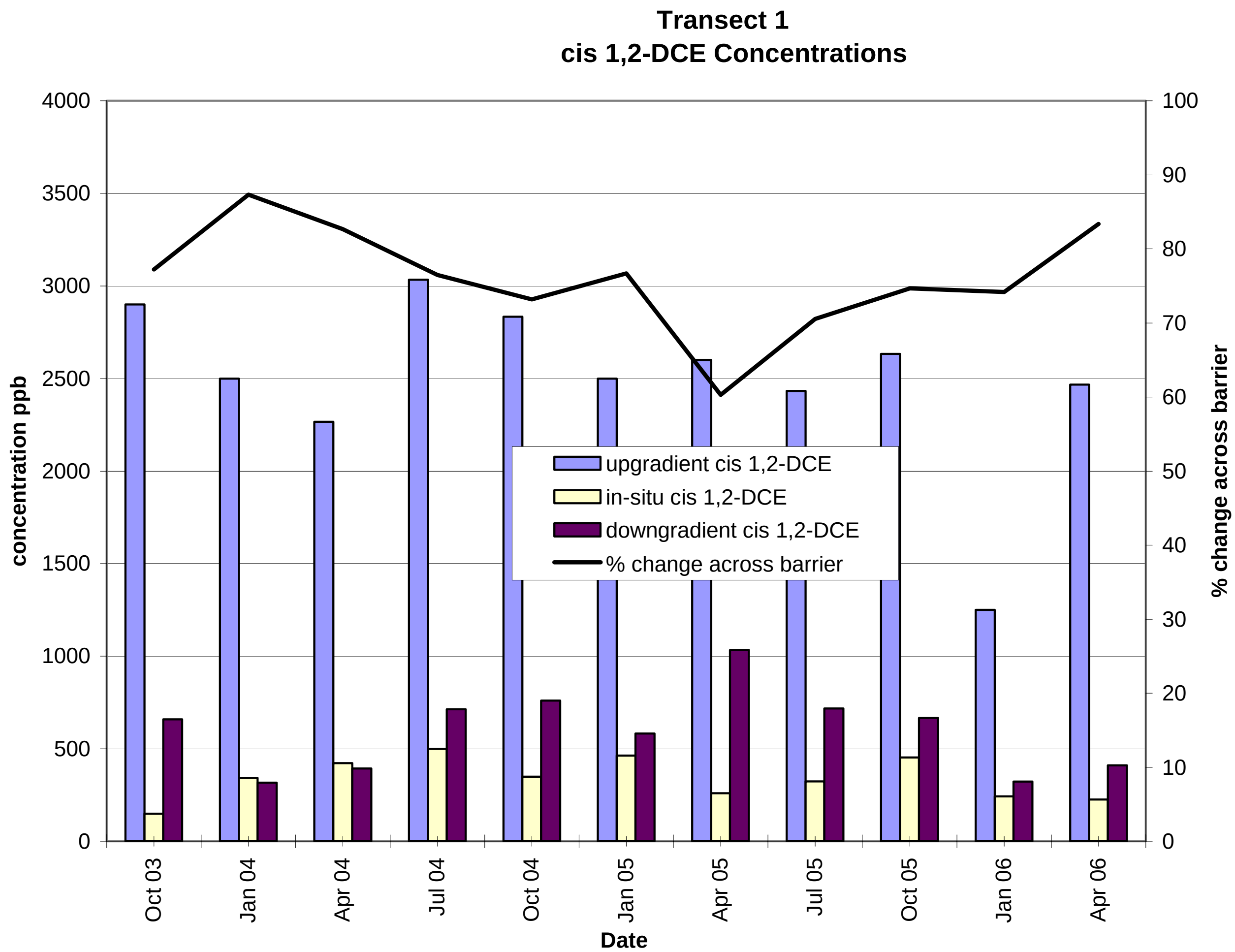
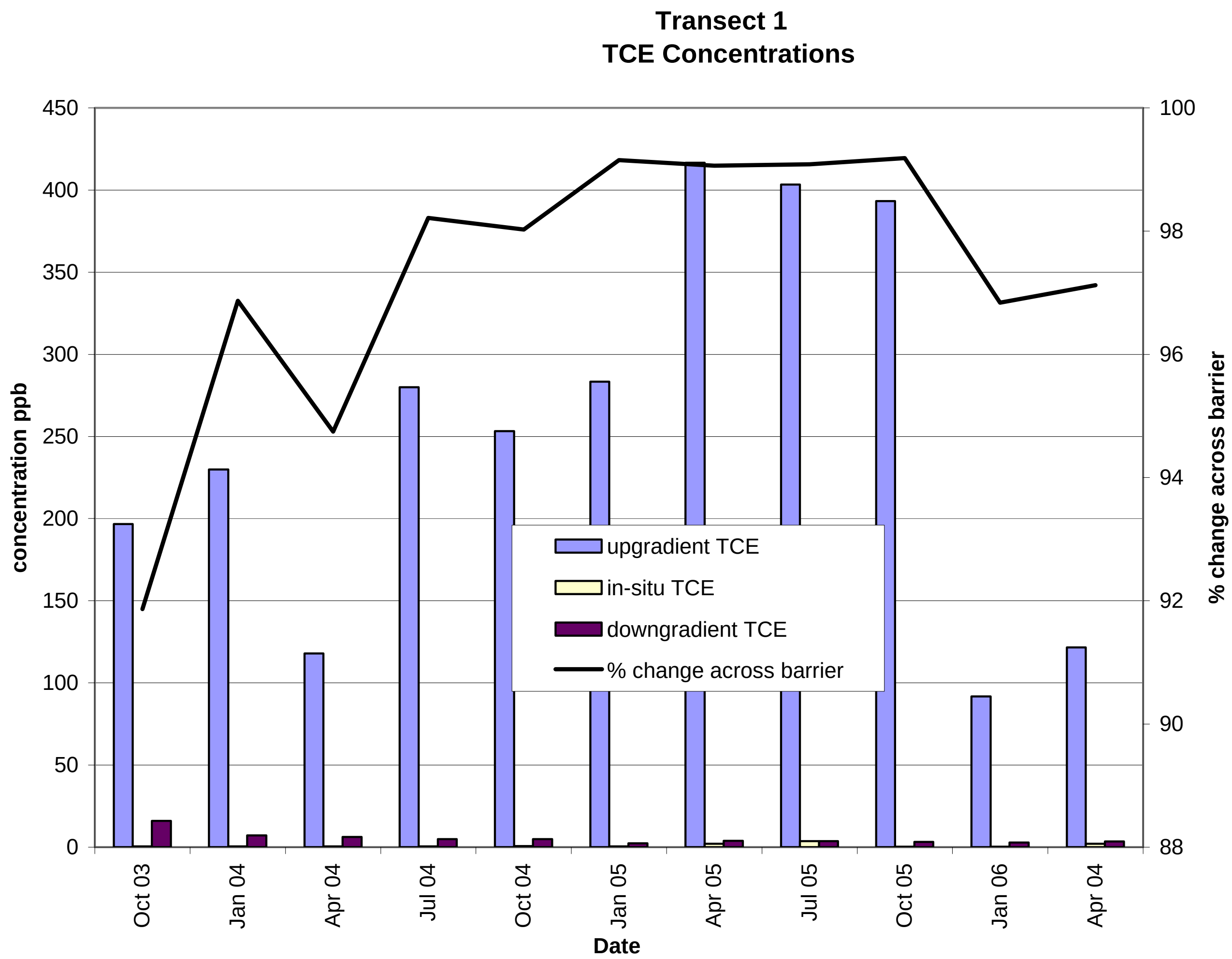


Figure 52   Mohawk Transect 1 TCE Concentrations



Transect 2

Transect 2 is located in panel number 4 close to the side bordering panel 5. This transect doesn't have an upstream monitoring well. This transect reached the compliance target of 600 ppb for total VOCs in January 2004 and has been in compliance since.

The PRB panels adjacent to this transect are all 4 feet thick and are composed of 100% iron. They were designed for the highest cis 1,2-DCE concentration (4600 ppb) and the highest groundwater flow rate (5.6 feet per day) expected to be encountered by any panel.

Transect 2 appears to be performing up to expectations since its installation. Notable in the results is the frequent condition where the downgradient concentration is higher than the in-situ concentrations of a given contaminant.

Figures 53, 54, and 55 show concentrations of total VOCs, cis 1,2-DCE, and TCE across transect 2.

Figure 53 Mohawk Transect 2 Total VOC Concentrations

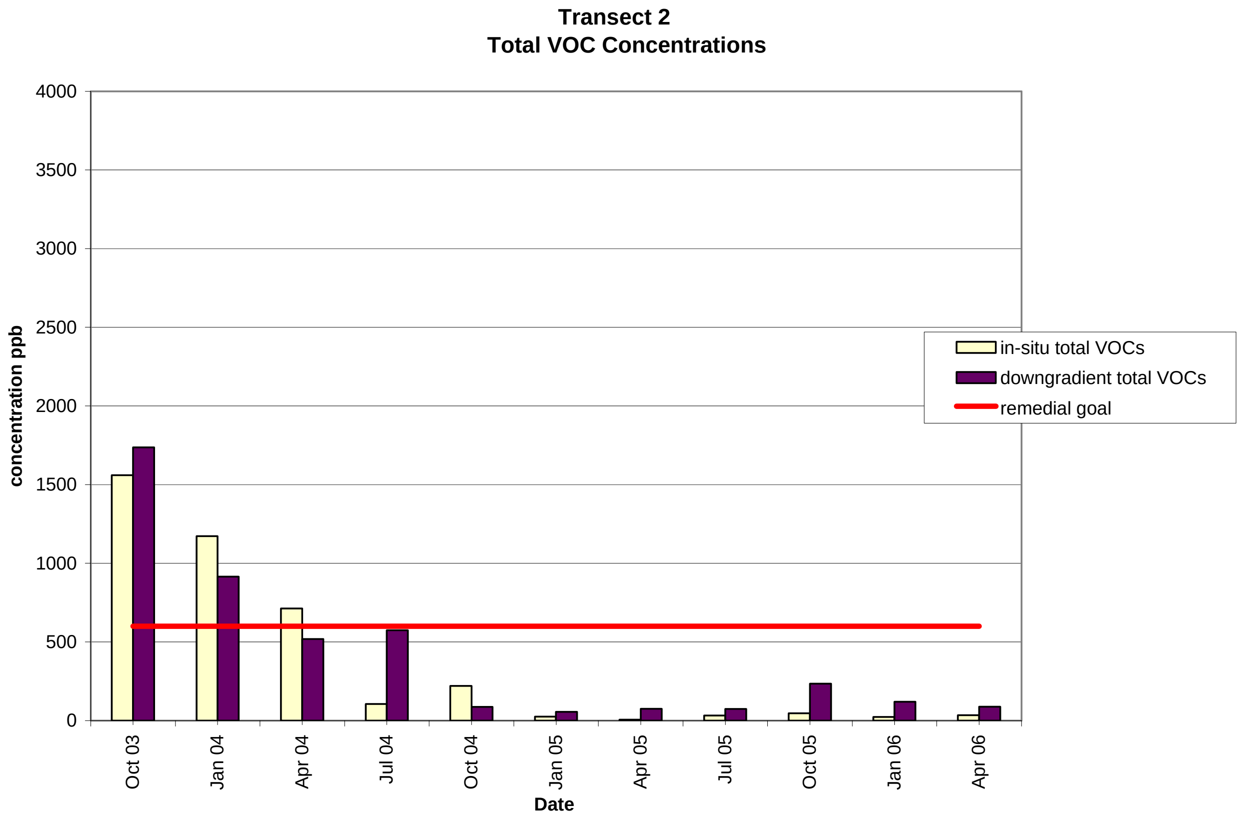


Figure 54 Mohawk Transect 2 cis 1,2-DCE Concentrations

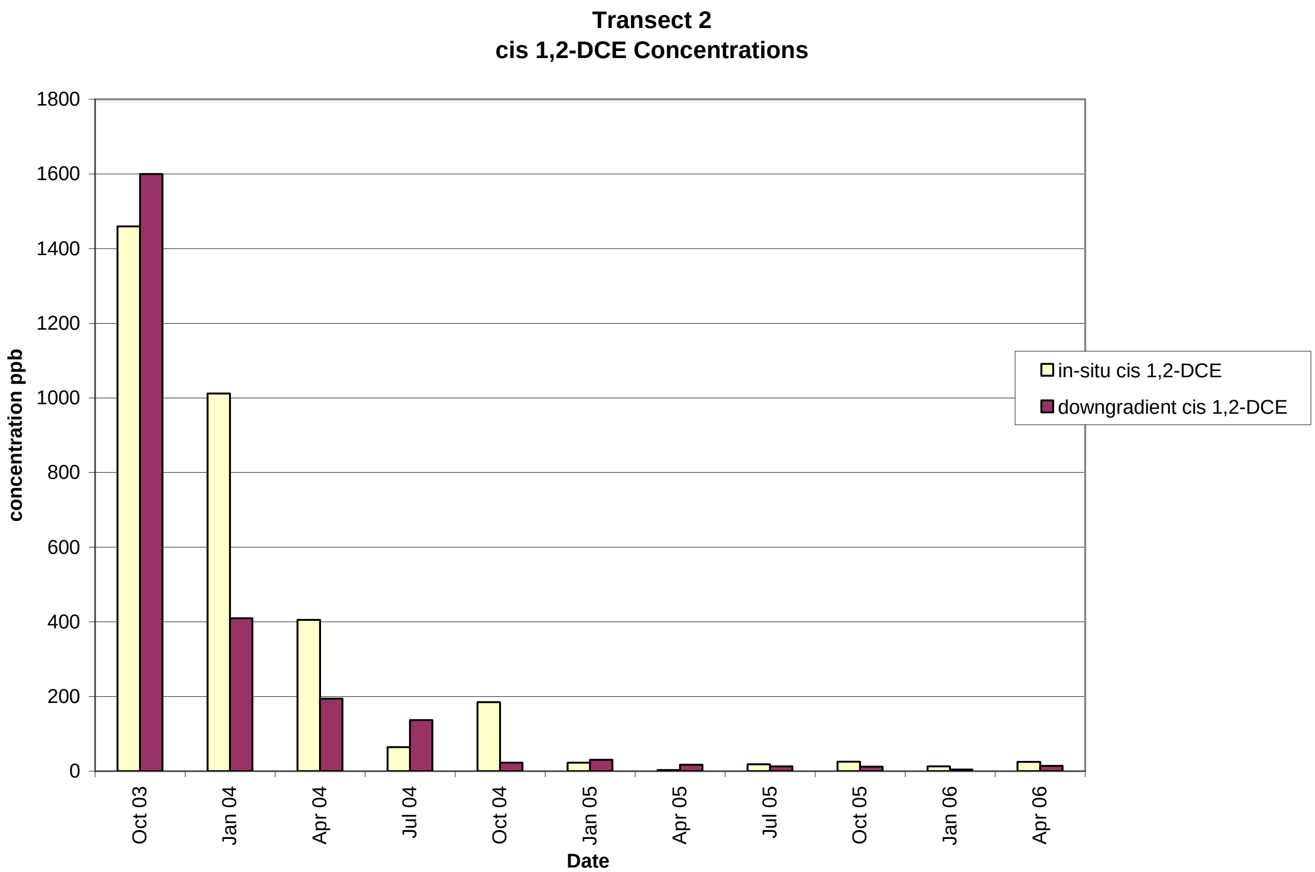
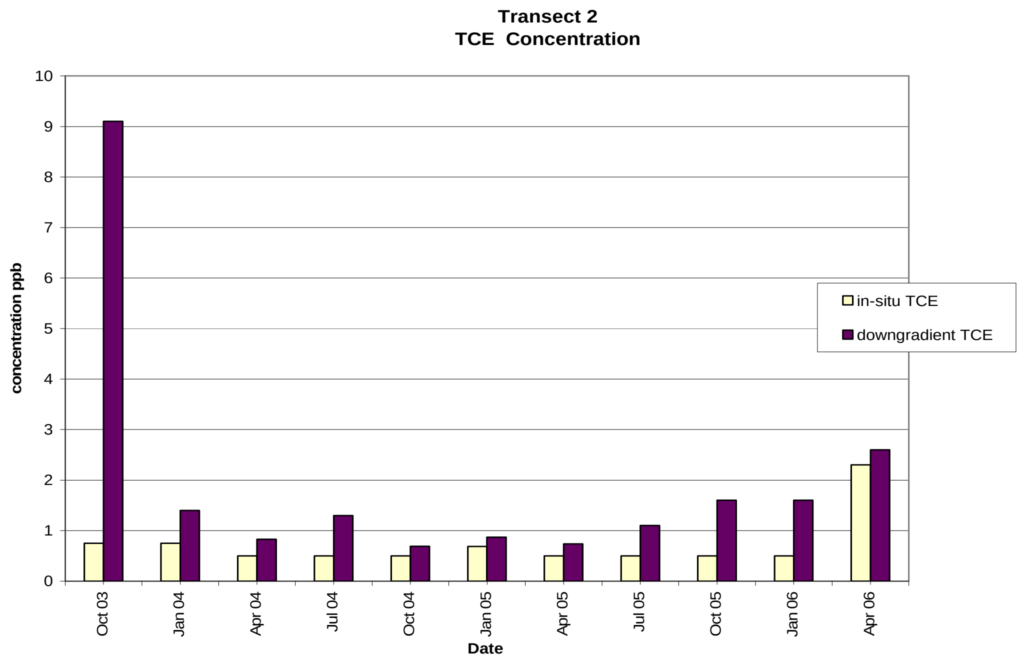


Figure 55 Mohawk Transect 2 TCE Concentrations



Transect 3

Transect 3 passes through panels 6A and 6B. Upper Panels 6A and 7A are designed for minimal contaminant loading (2 feet thick and 20% iron content) as the area is comprised of low permeability silt/clay with no sand or gravel channels. Other panels associated with this transect (5, 6B and 7B) are designed for the highest flow rate and contaminant level (5.6 feet/minute flow and 4600 ppb cis 1,2-DCE) and are 4 feet thick and 100% iron.

Except for the first quarter, the reduction in total VOCs across this transect has ranged from 75 to 95%. The compliance target of 600 ppb total VOCs was met for 7 out of 11 sampling events. This is in spite of the fact that there is a gap in panel 7A and 7B due to a natural gas pipeline through the PRB.

As in Transects 1 and 2, contaminant levels in the in-situ wells are occasionally lower than observed in downgradient wells.

Figures 56, 57, and 58 show concentrations of total VOCs, cis 1,2-DCE, and TCE across transect 3.

Figure 56   Mohawk Transect 3 Total VOC Concentrations

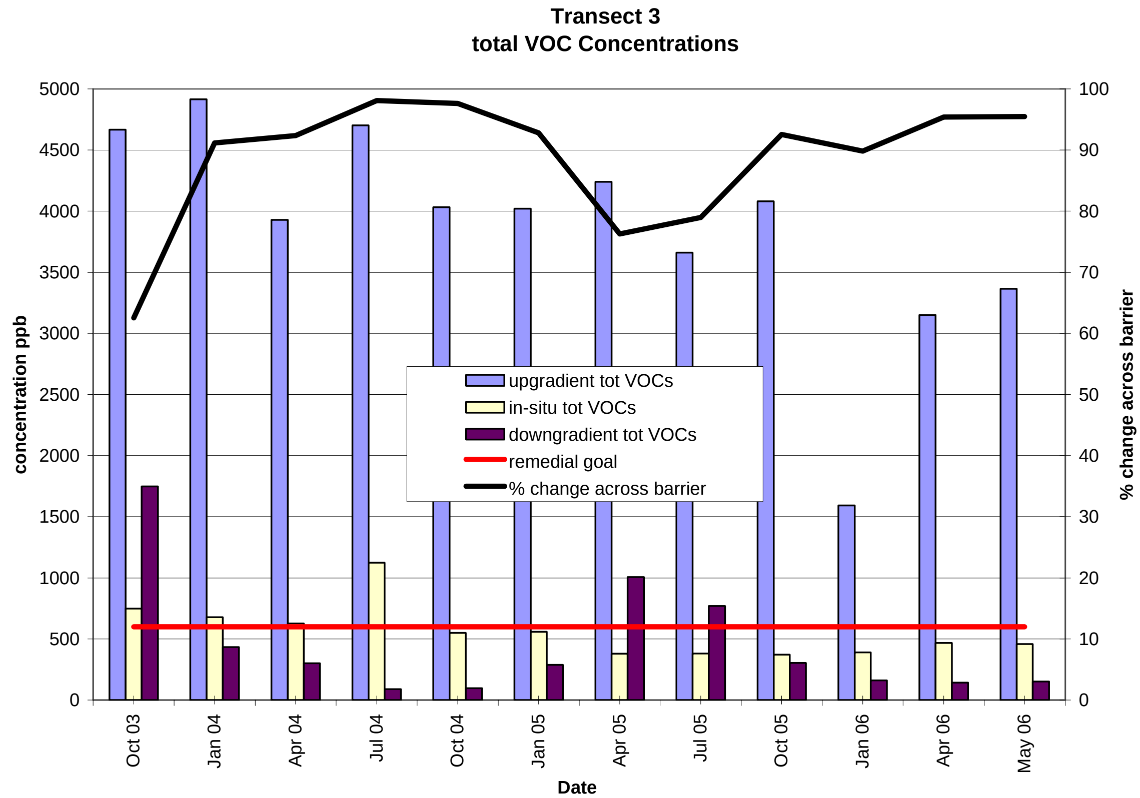


Figure 57 Mohawk Transect 3 cis 1,2-DCE Concentrations

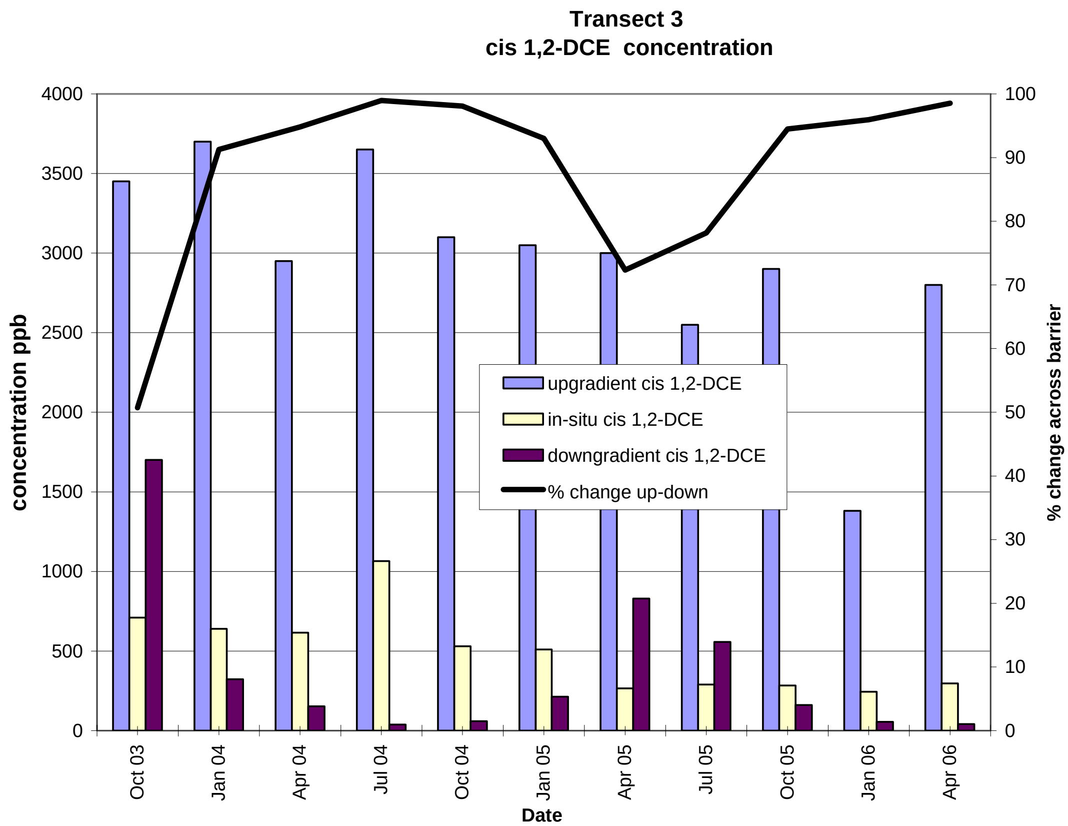
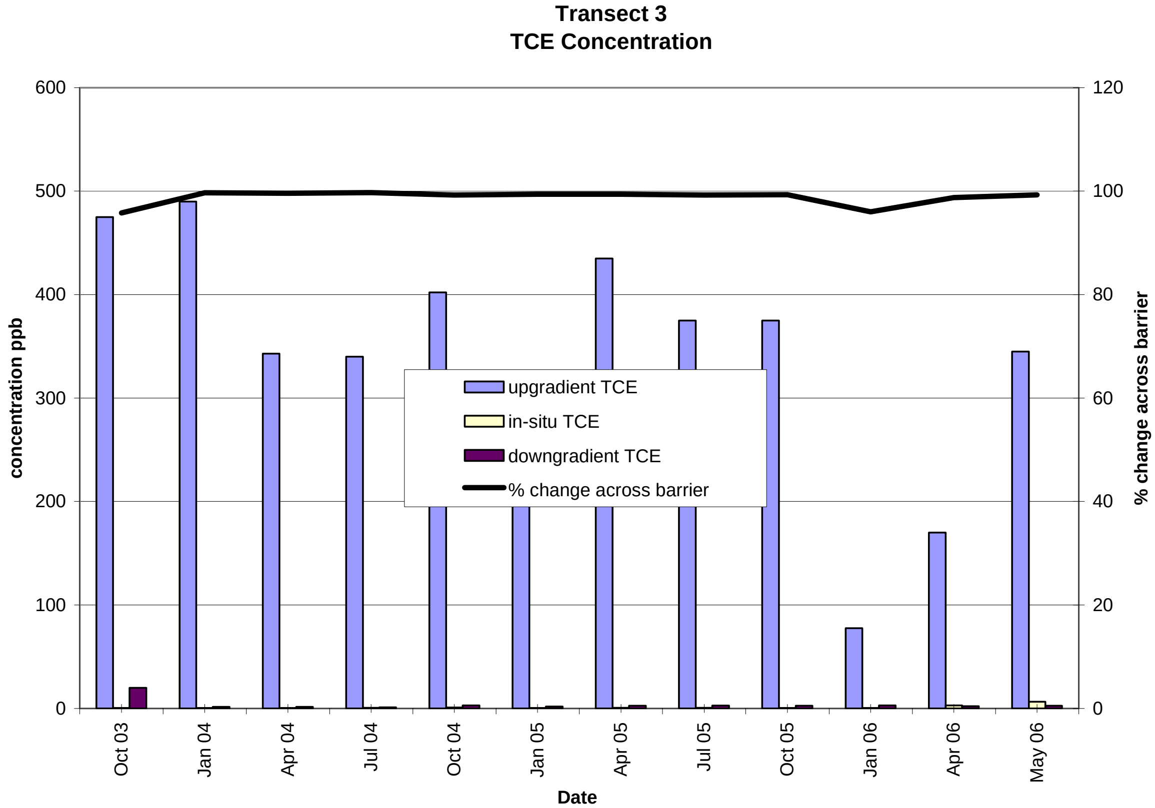


Figure 58   Mohawk Transect 3 TCE Concentrations



Transect 4

Transect 4 passes through the east side of panels 10A and 10B. All of the upper panels near the transect (9A, 10A, 11A) were designed for minimal flow rates and contaminant levels, and all are 2 feet thick with 20% iron. The lower panels near the transect were designed for low flow rates and moderate contaminant levels (3.1 feet per minute and 1700 ppb cis 1,2-DCE).

Evaluation of PRB performance along this transect is difficult because the upgradient, in-situ and downgradient PRB monitoring wells are not all screened at the same depth interval. The upgradient monitoring well, PZ-1024B, is screened from 19-23 feet bgs. The down gradient well, screened from 8-25 ft. bgs, may sample a contaminated zone that the upgradient well, screened from 19 thru 23 ft. bgs, does not see. The in-situ well is screened from 20 to 25 ft. bgs.

Other upgradient wells of this multi-depth well cluster are infrequently sampled (PZ-1024A screened from 9-12 ft. bgs and PZ-1024C screened from 26-29 ft. bgs) and show relatively low cis 1,2-DCE, total VOC and TCE levels.

The downgradient well was below the compliance level of 600 ppb total VOCs for 6 of 11 sampling events. Transect 4's performance on reducing the total VOC concentration has varied periodically over time, ranging from highs of 90% (Oct. 2004; Oct. 2005) to lows of < 50% (Jan 2005; Jan 2006).

Contaminant levels in the in-situ wells are consistently higher than those of the downgradient wells. There were also two instances where the upgradient contaminant levels were lower than the in-situ well levels.

Figures 59, 60, and 61 show concentrations of total VOCs, cis 1,2-DCE, and TCE across transect 4.

Figure 59 Mohawk Transect 4 Total VOC Concentrations

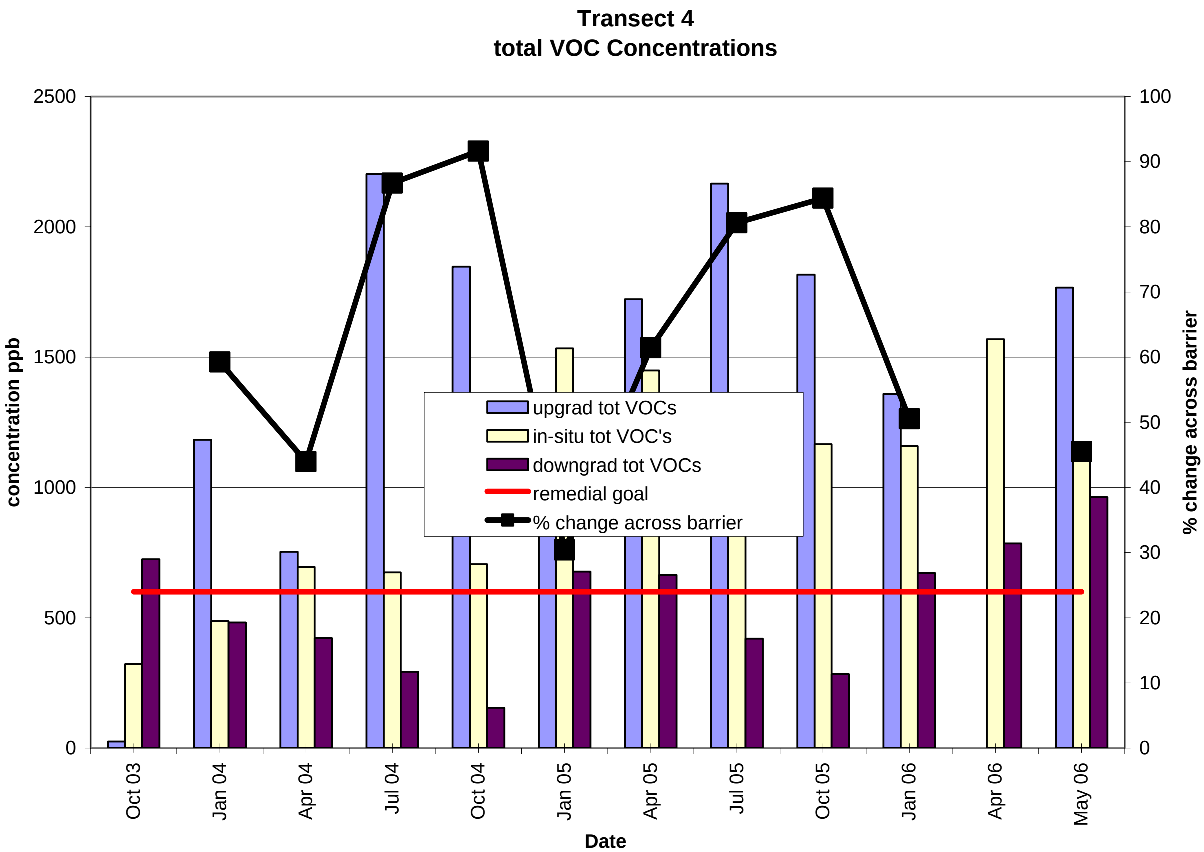


Figure 60 Mohawk Transect 4 cis 1,2-DCE Concentrations

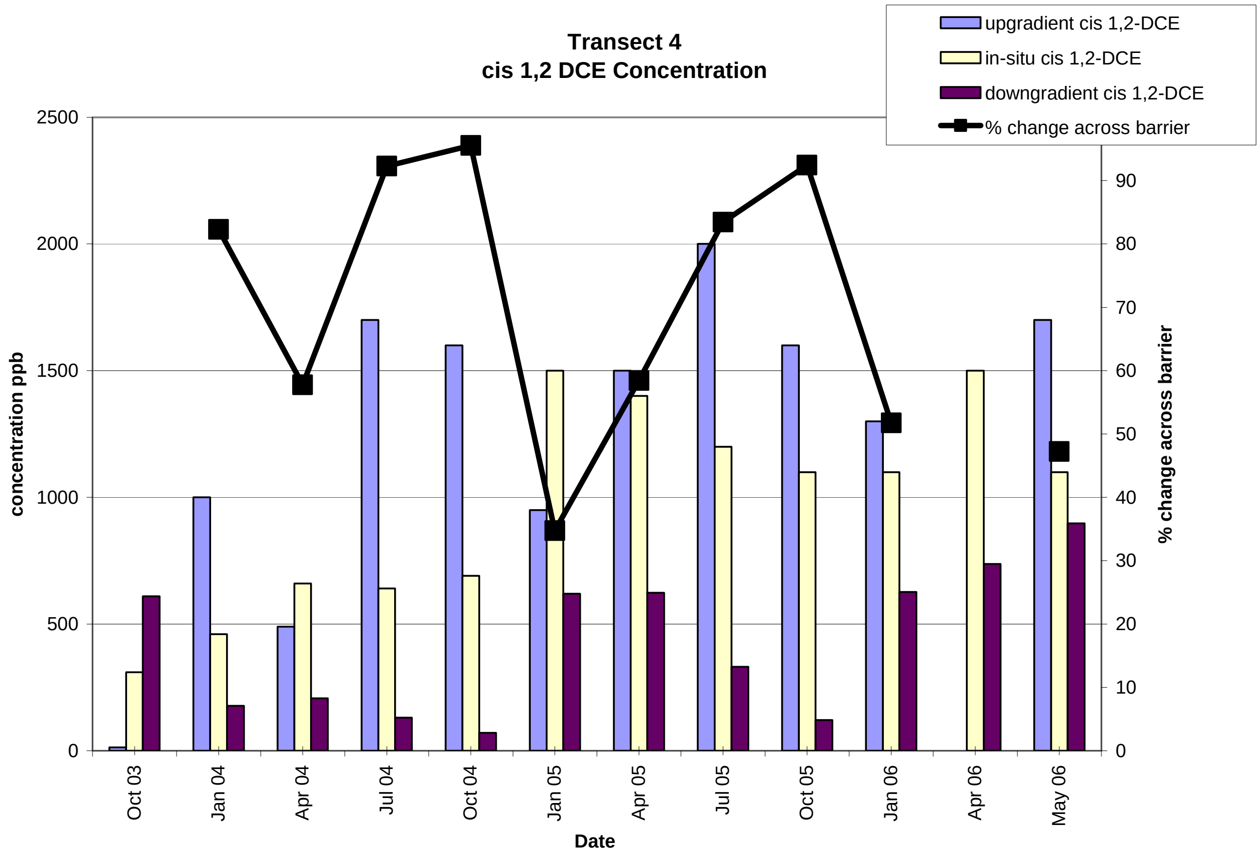
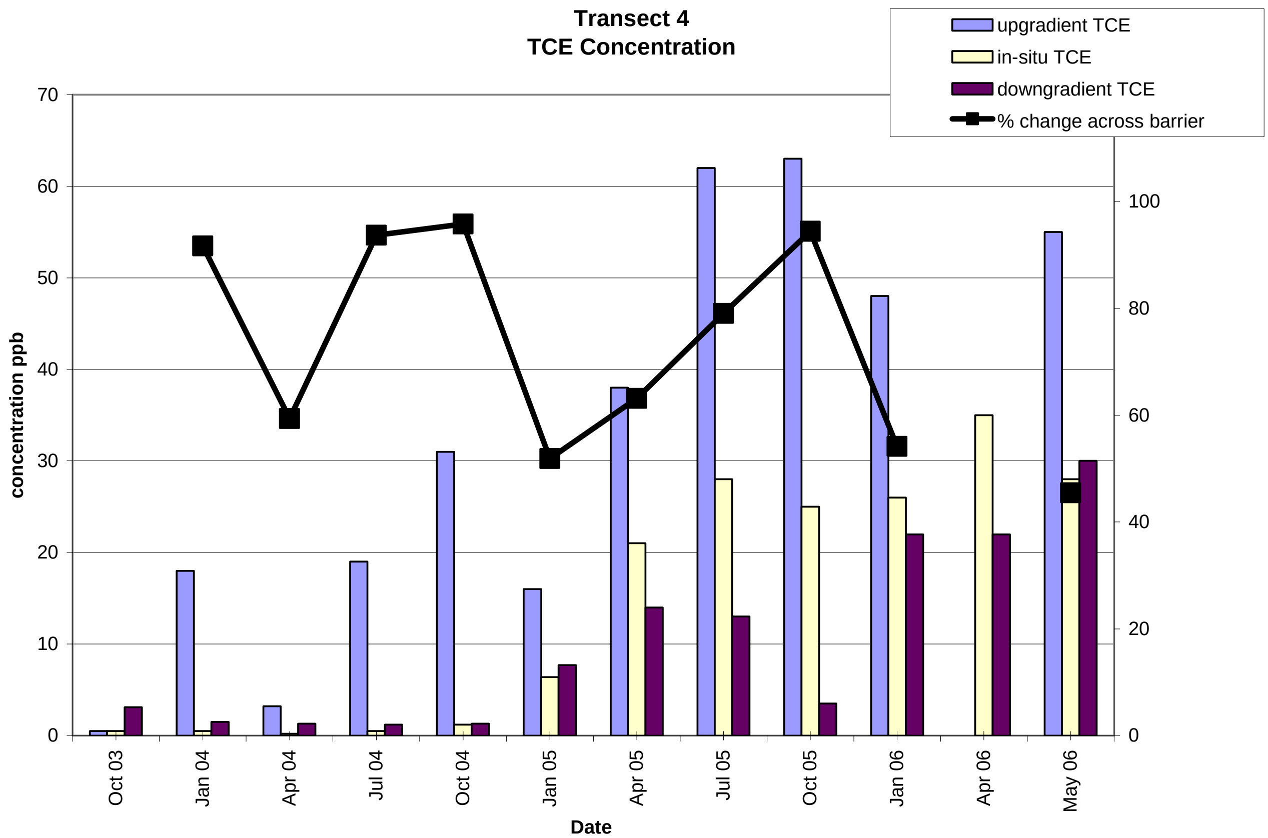
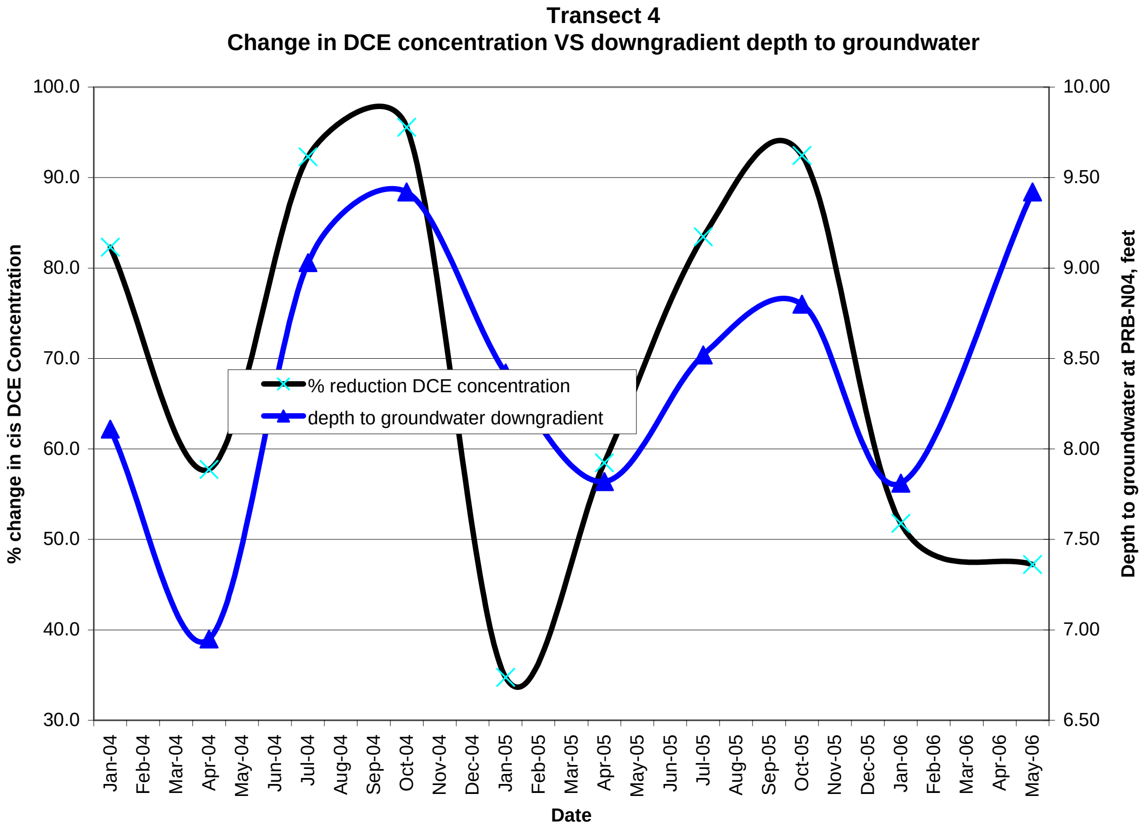


Figure 61 Mohawk Transect 4 TCE Concentrations



It is possible that changes in contaminant flowrate and concentrations due to seasonal changes in groundwater flow may have adversely impacted PRB performance at transect 4. Figure 62 is a graph of the cis 1,2-DCE % reduction in concentration across the barrier at transect 4 plotted against the depth to groundwater at well PRB-N04 over time. The other transects do not show this relationship between depth to water and % change in contaminant concentration across the PRB.

Figure 62 Mohawk Transect 4 Downgradient Depth to Water



Transect 5

Transect 5 passes through the east side of panels 13A and 13B next to panels 14A and 14B. All of the upper panels were designed for upstream cis 1,2-DCE levels of less than 250 ppb. The lower panels, 13B and 14B, were designed for 3000 ppb and 1000 ppb cis 1,2-DCE concentrations, respectively.

During the first three quarters, the transect 5 effluent cis 1,2-DCE concentrations were higher than the upgradient concentrations. This could be a result of diffusion from a residual cis 1,2-DCE source downstream of the PRB. Another possibly might be the presence of high contamination levels passing through the PRB that the upstream monitoring well does not intercept/detect.

Since July 2004, transect 5 has met the target remediation goal of 600 ppb total VOCs for 6 of 8 monitoring events. For the last two monitoring events, upgradient well concentrations were below the target remediation goal.

Again, as in other transects, the in-situ contaminant levels are often lower than those measured in the wells just downgradient of the PRB. On two occasions the levels measured at the in-situ wells are higher than measured upgradient.

Figures 63, 64 and 65 show concentrations of total VOCs, cis 1,2-DCE, and TCE across transect 5.

Figure 63 Mohawk Transect 5 Total VOC Concentrations

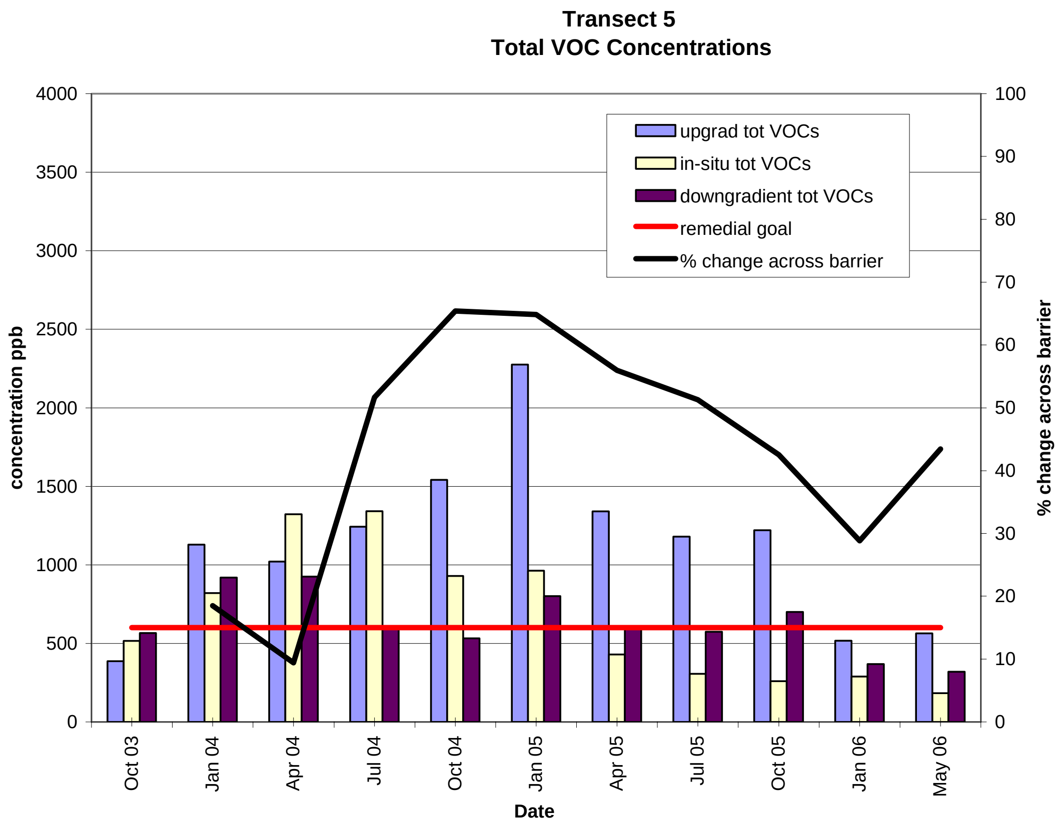


Figure 64 Mohawk Transect 5 cis 1,2-DCE Concentrations

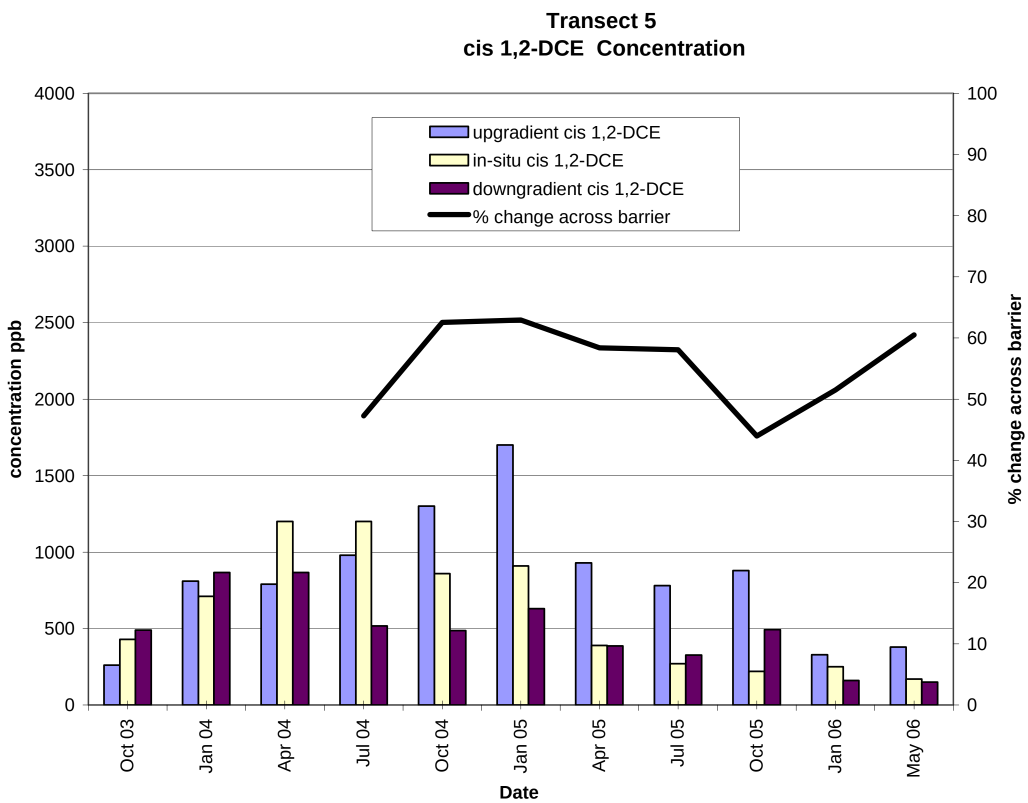
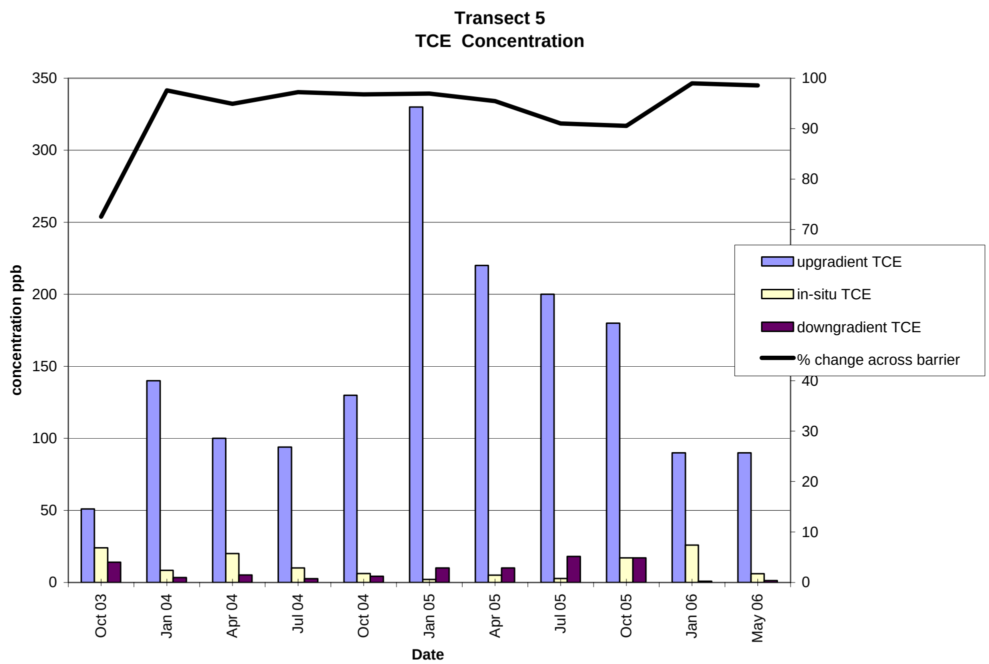


Figure 65 Mohawk Transect 5 TCE Concentrations



All Transects

Table 16 shows the transect downgradient VOC results by date. The primary VOCs were cis-1,2-DCE, TCE, and Vinyl Chloride. Since 2004, transect monitoring results were 400 ppb higher than the design level on only two occasions. During the first 2 quarters of 2006, only transect 4 was above the 600 ppb VOC target. During this same period, however, the overall VOC concentration reduction across transects 4 and 5 was less than 52%.

Overall, based on the transect monitoring well results, the PRB has performed at generally acceptable levels, although there have been numerous of instances of total VOC concentration above the design target of 600 ppb

Table 16 Transect Performance against Design Targets

	transect 1	transect 2	transect 3	transect 4	transect 5
	voc ug/l	voc ug/l	voc ug/l	voc ug/l	voc ug/l
October 2003	845	1737	1748	724	566
Jan 2004	413	915	434	482	920
April 2004	534	518	300	422	925
July 2004	965	574	89	293	601
October 2004	949	86	96	155	533
January 2005	793	56	289	677	800
April 2005	1181	75	1006	664	590
July 2005	810	74	770	420	575
October 2005	749	235	304	284	701
January 2006	397	120	162	672	368
April 2006	477	88	144	785	248

within 600 ug/l design limit

above 600 ug/l design limit by less than 400 ug/l

above the 600 ug/l design limit by more than 400 ug/l

The predominant contaminant with the highest concentration in the plume is cis-1,2-DCE. Cis 1,2-DCE is a significantly more difficult compound to break down with zero valent iron than TCE. As illustrated in Table 17 below, the concentration reduction for cis-1,2 DCE, averages over 80% for transects 1 and 3, and below 70% for Transects 4 and 5. The TCE concentration reduction across all transects is over 95% except for transect 4 where it averages 73%. Concentration change across transect 2 cannot be evaluated since there is no upgradient monitoring well.

Table 17 % Reduction TCE, DCE Across Barrier – Jan 2004 through April 2006

PRB upgradient vs. down gradient concentration reduction in % for TCE and DCE

	transect 1		transect 3		transect 4		transect 5	
	TCE	DCE	TCE	DCE	TCE	DCE	TCE	DCE
Jan-2004	96.9	87.3	99.7	91.3	91.7	82.3	97.6	*
Apr-2004	94.7	82.7	99.6	94.8	59.4	57.8	94.9	*
Jul-2004	98.2	76.5	99.7	99.0	93.7	92.3	97.2	47.2
Oct-2004	98.0	73.2	99.2	98.1	95.8	95.6	96.8	62.5
Jan-2005	99.2	76.7	99.4	93.0	51.9	34.7	97.0	62.9
Apr-2005	99.1	60.3	99.4	72.3	63.2	58.5	95.5	58.4
Jul-2005	99.1	70.5	99.3	78.2	79.0	83.5	91.0	58.1
Oct-2005	99.2	74.7	99.3	94.5	94.4	92.4	90.6	44.0
Jan-2006	96.8	74.2	96.0	95.9	54.2	51.8	99.0	51.5
Apr-2006	97.1	83.4	98.8	98.5	45.5	47.2	98.6	60.5
Average	**97.8**	**75.9**	**98.8**	**88.6**	**72.9**	**69.6**	**95.8**	**55.7**

Data from 2006 Q1 Q2 Self Monitoring Report by The Source Group

In addition to the performance monitoring wells installed along transects, two monitoring wells, MW01 and MW02, were installed approximately 125 feet downgradient of the PRB. Figures 66 and 67 show the TCE and cis 1,2-DCE levels for these two wells since the PRB was installed. Both wells show substantial reductions of both TCE and cis 1,2-DCE over time.

Figure 66 Offsite Well MW01 TCE and cis 1,2-DCE Concentrations

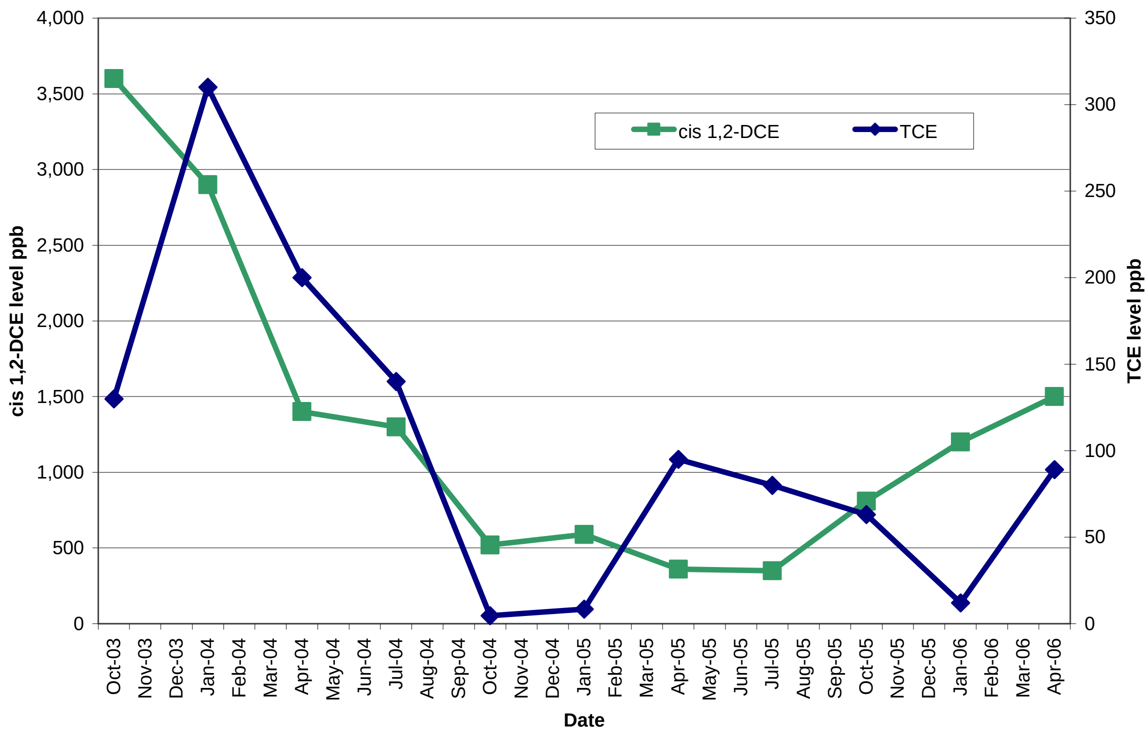


Figure 67 Offsite Well MW02 TCE and cis 1,2-DCE Concentrations

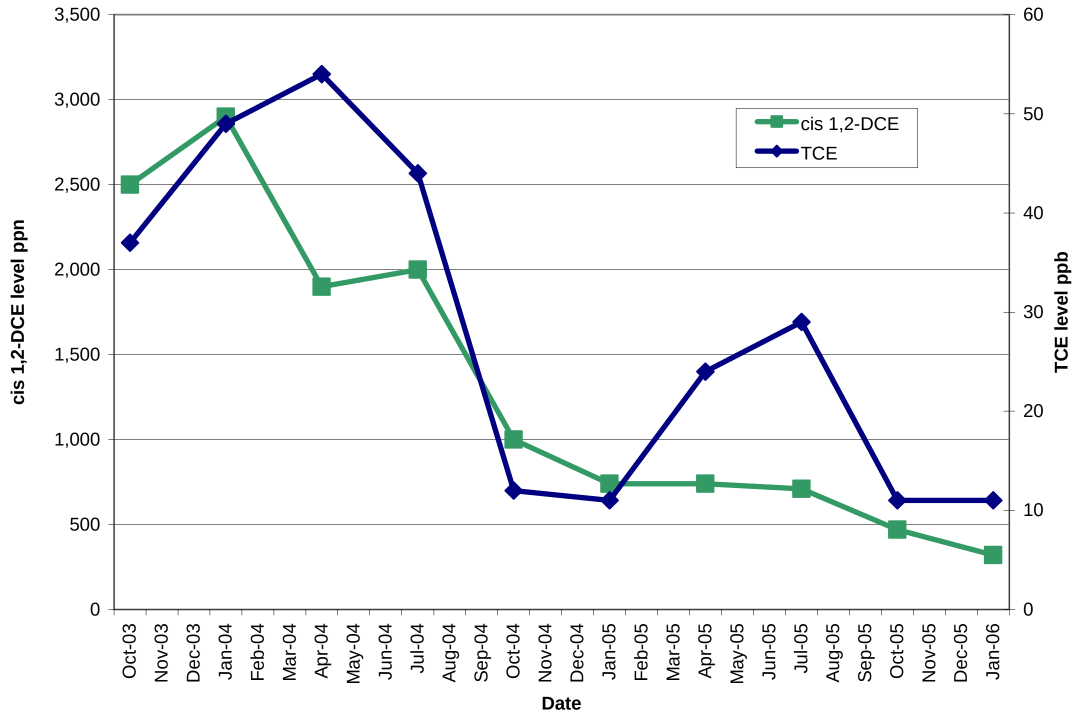
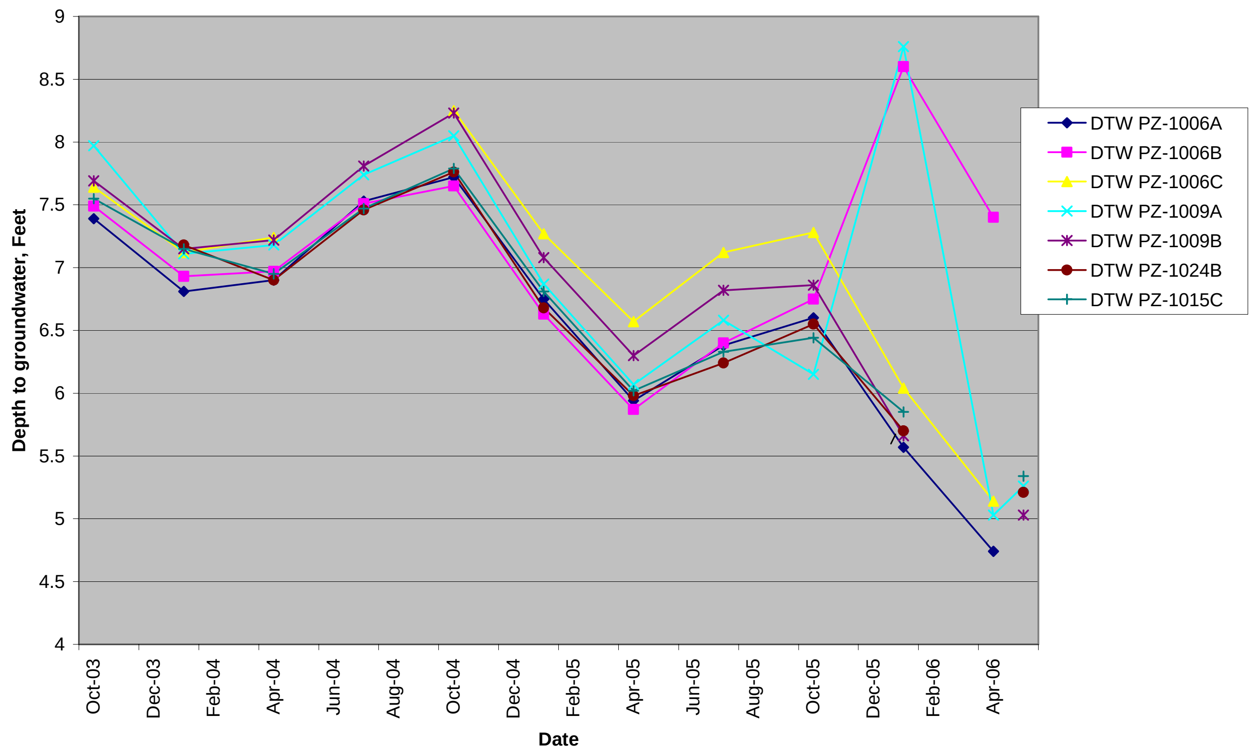


Fig 61 below shows the upgradient well depth to groundwater trend. Along with the expected seasonal variations, there seems to be a general trend toward rising water levels behind the barrier. The last two sampling events for January and May 2006 show that the depth to groundwater is less than 6 feet for four of the six upgradient monitoring wells. The barrier panels were reportedly only filled with iron up to 6 feet bgs as the groundwater depth was expected to always be below this level.

Figure 68 Upgradient Depth to Water



Summary and Conclusions

The transect data and downgradient well data show that there has been a substantial reduction in contaminant levels across the PRB. Overall, the PRB is working even though individual transects aren't meeting the design goal of 600 ppb total VOCs at all times.

This plume is composed of one of the harder compounds to degrade with iron, cis 1,2-DCE. The plume extends over a mile from the source, and the groundwater flowrate is high at 3-5 feet per day. All of these factors combine to make Mohawk a difficult project.

The project began with a goal of treating the cis 1,2-DCE down to 2.5 ppb downgradient but the cost of over $2,500,000 was prohibitive. The design treatment goal was modified to reduce the cost of the project to a more reasonable level with the final downgradient remediation targets expected to be reached through natural attenuation and other remedial actions.

A remaining regulatory concern over the project involves the west side. Recent data suggests that some of the groundwater on the west side may be bypassing the PRB. There are plans to address this in the future with an alternative remedial action, possibly injection of a bioaugmentation agent.

Table 18 below shows compliance goals for various locations downgradient of the PRB along with their timeframes. These goals were based on computer modeling results taking into account the expected performance of the PRB along with natural attenuation expected to take place downgradient of the PRB.

Table 18 Mohawk Performance Monitoring Criteria

Proposed Performance Monitoring Criteria
Mohawk Laboratories , Sunnyvale California
November 2003

Compliance Area	California Street		Arques Ave.					Stewart Drive				Duane Ave.
Aquifer Zone	A1/A2		A1		A1	A1	A2	A1	A1	A2	A2	A1
Compliance Wells	WA-11		NMW-07		RW-1	E-03	NRCW-02B	New Well NMW-12A	46-S	New Well NMW-12B	S-38B	NMW-10
Years	Total VOC Concentrations, ug/L											
	Actual	**Goal**	**Actual**	**Goal**								
2003 Baseline	3814	3814	2160	2160	2300	455	2016	1640	507	-		75
2005	2573	2100	1550	2000	-	310	954	340 1250	550	500		ND <0.5
2006	2200		1163				724	370		345		
2007	600		1500					1050				Continued Reduction
2009	400		800					800				
2011	300		450					700				
2013	250		275					650				
2015	220		200					550				
2017	200		150					400				

Adapted from: The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, November 2003.

The Mohawk PRB appears close to meeting the compliance goals set through computer modeling for the site for its first 2 years. The total VOCs measured at well WA-11 during the April 2006 sampling event was 2200 ppb which is close to the year 2 target of 2100 ppb set for California Street. The total VOCs measured at wells NRCW-02B and NMW-07 during the April 2006 sampling event were 724 ppb and 1163 ppb respectively. These results are well below the year 2 target value of 2000 ppb for Arques Ave. The total VOCs measured at wells NMW-12A and NMW-12B during the April 2006 sampling event were 370 ppb and 345 ppb respectively, well below the year 2 target value of 1250 ppb for Stewart Ave. Ultimately, it will take over 10 additional years to see if the above VOC goals are reached with the help of the PRB project.

References

The Source Group, *Semi-Annual Self-Monitoring Report – Quarter 3, 2004 and Quarter 4, 2004 Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, 94086* (January 30, 2005).

The Source Group, *Semi-Annual Self-Monitoring Report – Quarter 3 and Quarter 4, 2005 Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California, 94086* (January 30, 2006).

The Source Group, Semi-Annual Self-Monitoring Report – Quarter 1 and Quarter 2, 2006 Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California 94086 (July 28, 2006)

The Source Group, Permeable Reactive Barrier Completion Report, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California 94086 (November 15, 2003).

The Source Group, *Draft Final Remedial Action Plan (FRAP, Volume I)*, Mohawk Laboratories, 932 Kifer Road, Sunnyvale, California 94086 (January 18, 2006).

3.8 Evaluation of the Sierra Army Depot PRB Project - GeoSierra

Site History

Sierra Army Depot (SIAD) is located in Honey Lake Valley of Lassen County in northeast California. The total area of the main depot is over 30,000 acres.
The PRB project was located in the Building 210 Area near the southeast corner of SIAD. From 1942 until 1949 this area served as a vehicle maintenance facility. Additional activities included sand blasting, spray painting, steam cleaning, powder packaging, and tank engine fogging. Wastes generated at this site included degreasing solvents, oils, sludge. Buildings adjacent to Building 210 were also used for vehicle maintenance from the 1940s until 1973.

Groundwater Contamination and Hydrology

Trichloroethylene (TCE) was first detected in the groundwater in the Building 210 area in 1995. Site investigations found that the contamination plume had migrated off post to the south and is now greater than 3,500 feet long. The maximum TCE concentration in core of the plume is approximately 2500 ppb. Figure 69 below shows the TCE contaminant plume as it extends to the southeast of the SAID property boundary.

Figure 69   SAID TCE Plume

Adapted From:
Arcadis, *First Quarter November 2003 through January 2004 Treatment System Monitoring Report for the Building 210 Area Sierra Army Depot Herlong California*(April 14, 2004).

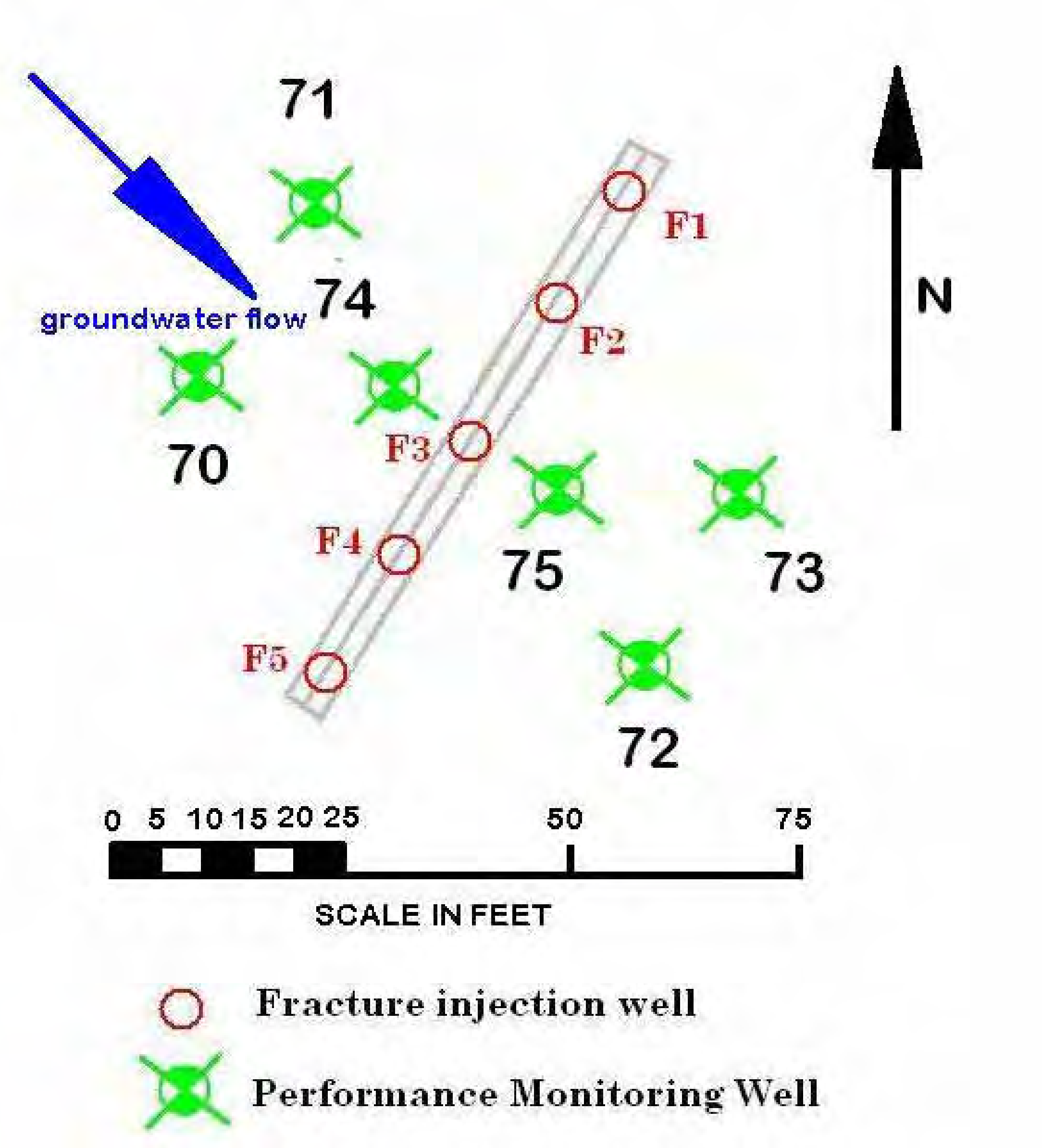
Groundwater is generally encountered as a shallow layer at a depth of 80 to 115 feet. At depths below 115 ft bgs a layer of impermeable clay/silt is encountered which acts as an aquitard to the contaminated ground water layer. Water flow in the area is to the southeast at 0.2 to 0.5 ft/day.

PRB Design & Installation

Using the EPA Scoping Calculations equation modified for TCE and a groundwater flowrate of 0.5 ft. /day, a minimum PRB design thickness of 2.4 inches of iron is needed to treat an initial TCE concentration of 2500 ppb to the cleanup goal of 5 ppb. The installed PRB with 4.5 inches should be sufficient to achieve this goal.

In April 2003 GeoSierra installed a PRB at the site by using their patented hydrofracturing technology. The barrier was installed from 95 to 115 ft bgs, and was 75 feet long by 4.5 inches thick. Five (5) injection points spaced 15 feet apart were used to install a total of 53 tons of zero valent iron. Below is a diagram of the PRB location along with the monitoring well locations.

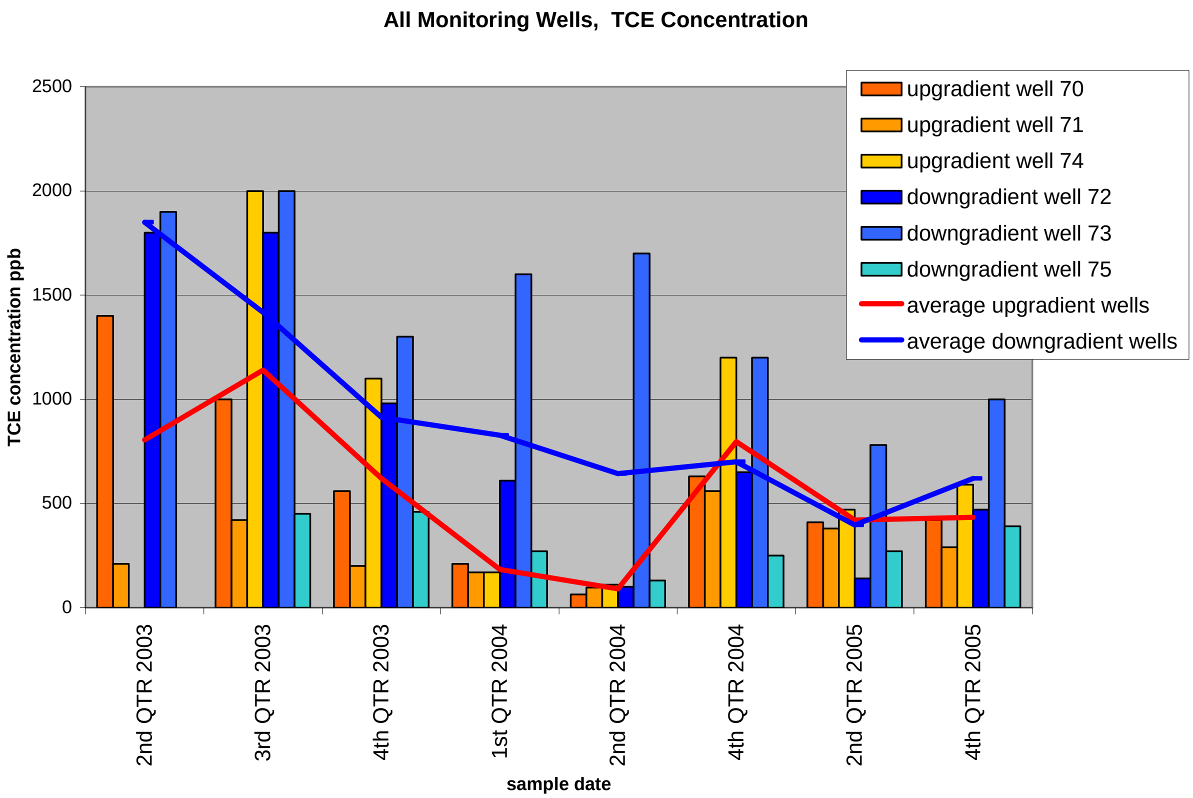
Figure 70 GeoSierra SAID PRB Injection Points and Monitoring Wells



PRB Performance Analysis

Monitoring wells 70 through 75 were sampled quarterly for various hydrocarbons. TCE is the only compound significantly above California MCLs. Figure 71 below is a chart of the upgradient and downgradient TCE levels from the PRB monitoring wells. Until the 4th Quarter 2004, the average of the TCE concentrations in the upgradient wells has been lower than the average TCE concentrations of the downgradient wells. From the 4th Quarter 2004 and on, the average upgradient and downgradient TCE concentrations are virtually the same.

Figure 71 Sierra Army Depot Monitoring Well TCE Concentration



Summary and Conclusions

Based on the above monitoring well results there appears to be little reduction in TCE concentration across the PRB. The northward extent of the contaminant plume suggests that groundwater flow had reversed in the past due to groundwater extraction and treatment activities in the area. Such groundwater flow reversal would certainly have impacted PRB performance. However, an examination of the potentiometric published in Annual Treatment System Monitoring Reports of the area from 2003 through 2005 shows

a consistent groundwater flow gradient from the northwest to the southeast. In all, the available results do not support installing a full scale PRB treatment wall at the site.

The contractor that installed the PRB, GeoSierra has suggested that wells 74 and 75 may be mislabeled, and that based on a fall 2005 groundwater elevation survey, the groundwater flow is to the northwest. These issues related to well mislabeling and groundwater flow gradient need to be resolved before making final conclusions on the performance of this PRB project.

References

Arcadis, *Fourth Quarter (August 2005 through October 2005) and 2005 Annual Treatment System Monitoring Report for the Building 210 Area*. Prepared for: Sierra Army Depot, Herlong California. (January 12, 2005**).**

Arcadis, *Second Quarter (February 2006 through April 2006 Treatment System Monitoring Report for the Building 210 Area*. Prepared for: Sierra Army Depot, Herlong California. (July 14, 2006).

3.9 *Evaluation of the Sierra Army Depot PRB Project - ARS Technologies*

Site History

Sierra Army Depot (SIAD) is located in the Honey Lake Valley of Lassen County, in California. The total area of the main depot is over 30,000 acres. The Building 210 Area is located near the southeast corner of SIAD and includes the areas adjacent to Buildings 208, 209, and 210. Building 210 was used as a vehicle maintenance facility from 1942 until 1949. Additional activities in the area included sand blasting, spray painting, steam cleaning, powder packaging, and tank engine fogging. Wastes generated at this site included degreasing solvents, oils, and sludges. Buildings adjacent to Building 210 were also used for vehicle maintenance from the 1940s until 1973. The Building 210 area at SIAD has been the host of 2 permeable reactive iron barrier projects along with numerous other remediation activities.

Groundwater Contamination and Hydrology

Trichloroethylene (TCE) was first detected in the groundwater at the site in 1995. Further investigation showed that a plume of TCE contamination had migrated off post to the south in the Building 210 area. The Building 210 TCE plume, above 1,000 ppb at its core, is now greater than 3,500 feet long. Other contaminants detected in the plume include 1,1-Dichloroethane (0-6 ppb), 1,2-Dichloroethane (0-2 ppb) and cis 1,2-Dichloroethene (0-500 ppb). Figure 72 below shows the location of the ARS Technologies PRB project with respect to the TCE plume which extends to the southeast of the site.

Figure 72 Sierra Army Depot TCE Plume

Adapted From:
Arcadis, *First Quarter November 2003 through January 2004 Treatment System Monitoring Report for the Building 210 Area Sierra Army Depot Herlong California*(April 14, 2004).

Groundwater is generally encountered as a shallow layer at a depth of 80 to 115 feet. At depths below 115 ft. bgs a layer of impermeable clay/silt is encountered which acts as an aquitard to the contaminated ground water layer. Water flow in the area is to the southeast at 0.2 to 0.5 ft. /day.

Cleanup Goals/PRB Design

The project goals were to demonstrate that the Ferox injection technology could emplace iron efficiently into the ground at depths of up to 120 feet bgs, and to assess performance and overall viability of the PRB treatment system at this depth.

PRB Installation

In July 2002, ARS Technologies installed an iron PRB at the site using their patented Ferox technology. In this technology, an injector assembly is inserted into a predrilled well and zero valent iron powder slurry is injected into the ground using nitrogen or compressed air as a carrier. The PRB was installed using a grid of 9 injection wells spaced 40 feet apart. Approximately 42,000 pounds of ZVI were injected into the subsurface at the site between a depth of 95-115 bgs. The geology and depth of the site presented several challenges to ARS. The drilling method had to be modified due to running sand and the depth at the site. The 42,000 lbs of iron is the equivalent of a 1 inch thick iron barrier behind the 4000 sq ft. facial area of the PRB. The installed thickness does not appear adequate for achieving treatment to desired MCL levels. Using the EPA Scoping Calculations equation modified for TCE and a groundwater flowrate of 0.5 ft. /day, a minimum PRB design thickness of 2.4 inches of iron would be needed to treat an initial TCE concentration of 2500 ppb to the cleanup goal of 5 ppb.

Figure 73 below shows a schematic of the injection setup. Figure 73 shows the orientation of the injection and monitoring wells at the site.

Figure 73   Ferox Iron Injection Setup

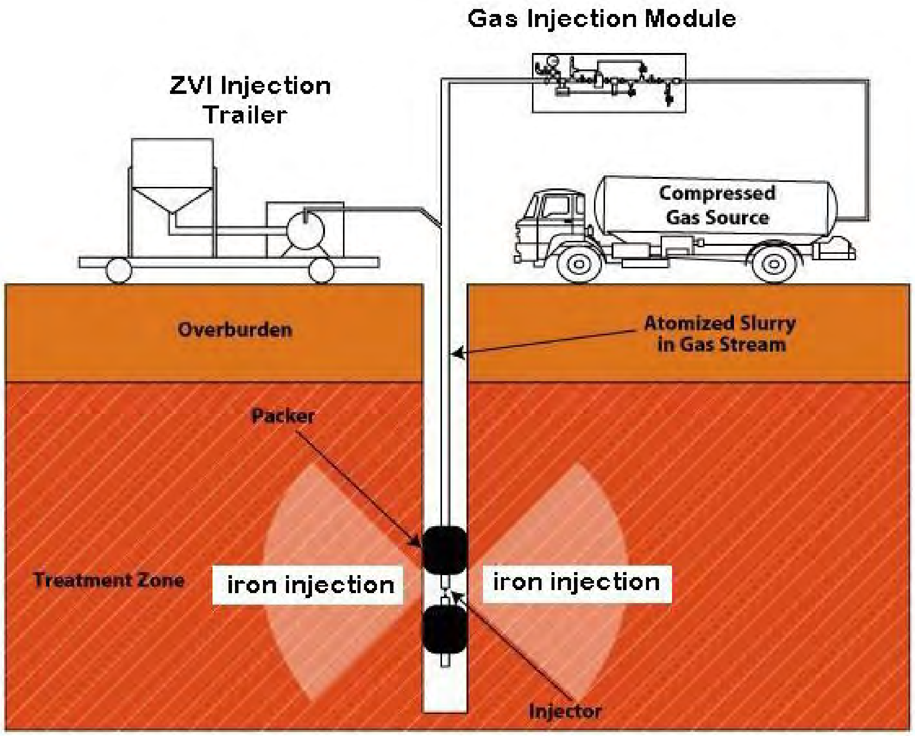
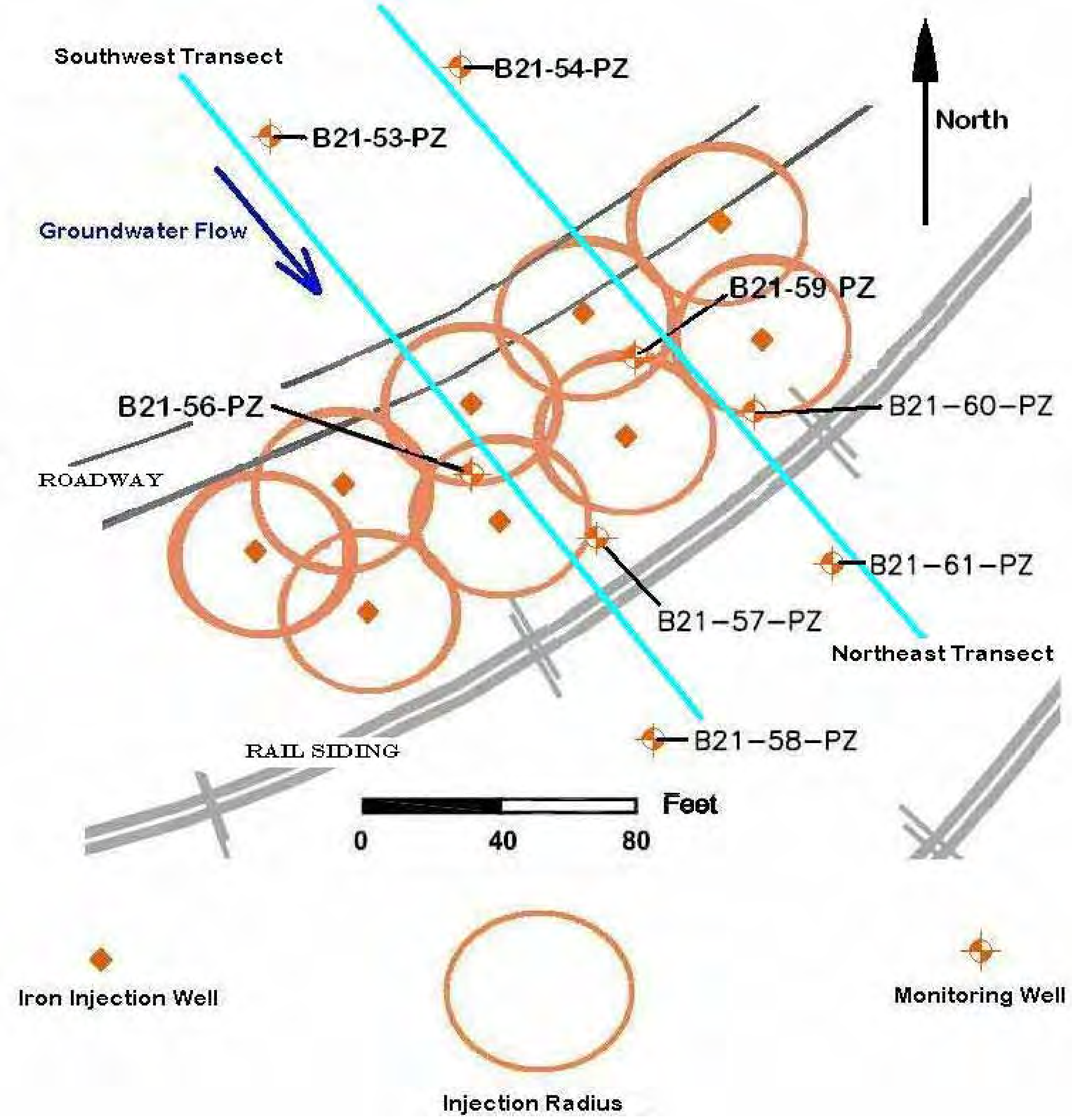


Figure taken from   http://www.arstechnologies.com/ferox_zero_valent_iron.html

Figure 74 SAID Injection and Monitoring Wells



PRB Performance Measurements

The monitoring wells are arranged roughly along two transits as described in the table below. The screen intervals for the wells are not documented.

Table 19 Sierra Army Depot Monitoring Wells - ARS Technologies

Well location	Southwest Transit	Northeast Transit
50 feet upgradient PRB	B21-53-PZ	B21-54-PZ
In-situ PRB	B21-56-PZ	B21-59-PZ
Downgradient edge PRB	B21-57-PZ	B21-60-PZ
50 feet Downgradient PRB	B21-58-PZ	B21-61-PZ

These monitoring wells were initially monitored monthly for 4 months, then quarterly, and finally on a semiannual basis.

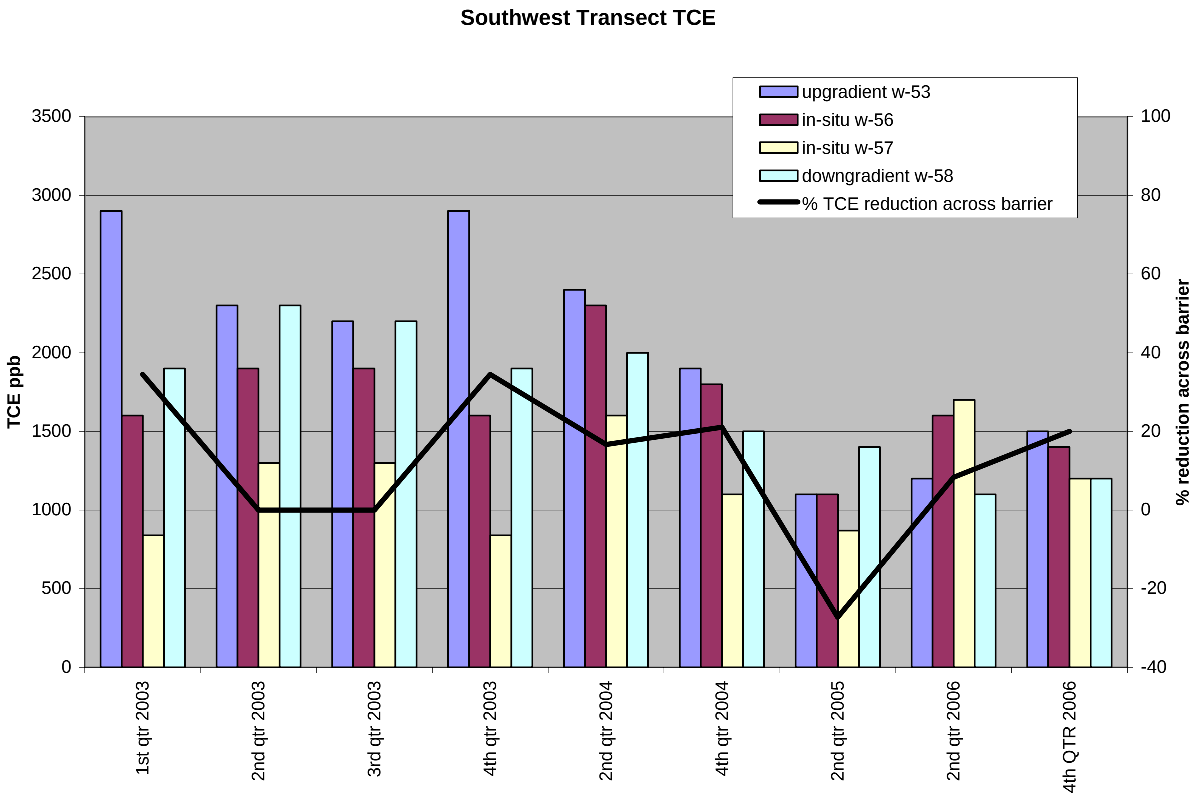
PRB Performance Analysis

Below are two charts showing the TCE concentrations in the groundwater along each transect. Only TCE will be considered in the performance analysis of the PRB. Cis 1,2-dichloroethelene is present, but at fairly low and inconsistent levels (0-150 ppb) in the PRB monitoring wells

<u>Southwest Transect Analysis</u>

The first quarter 2003 results look favorable in that there is a reduction in TCE concentration from 2900 ppb at the upgradient well to 1600 ppb at the in-situ well. There seems to be a further concentration reduction to 840 ppb by the end of the PRB reaction zone. This is a 71% reduction in concentration from the upgradient well. However, there is a return to 1900 ppb at the downgradient well. This pattern is repeated on this transect for the next 5 quarterly monitoring events. In the second quarter 2005, the downgradient well concentration exceeds the upgradient concentration while little or no or TCE reduction is observed in the in-situ and downgradient edge wells. In the second quarter of 2006, TCE concentrations of the in-situ and downgradient edge wells are actually higher than the upgradient well results. Finally, the last recorded results of the fourth quarter 2006 show a 20% reduction in the downgradient TCE levels when compared to the upgradient well.

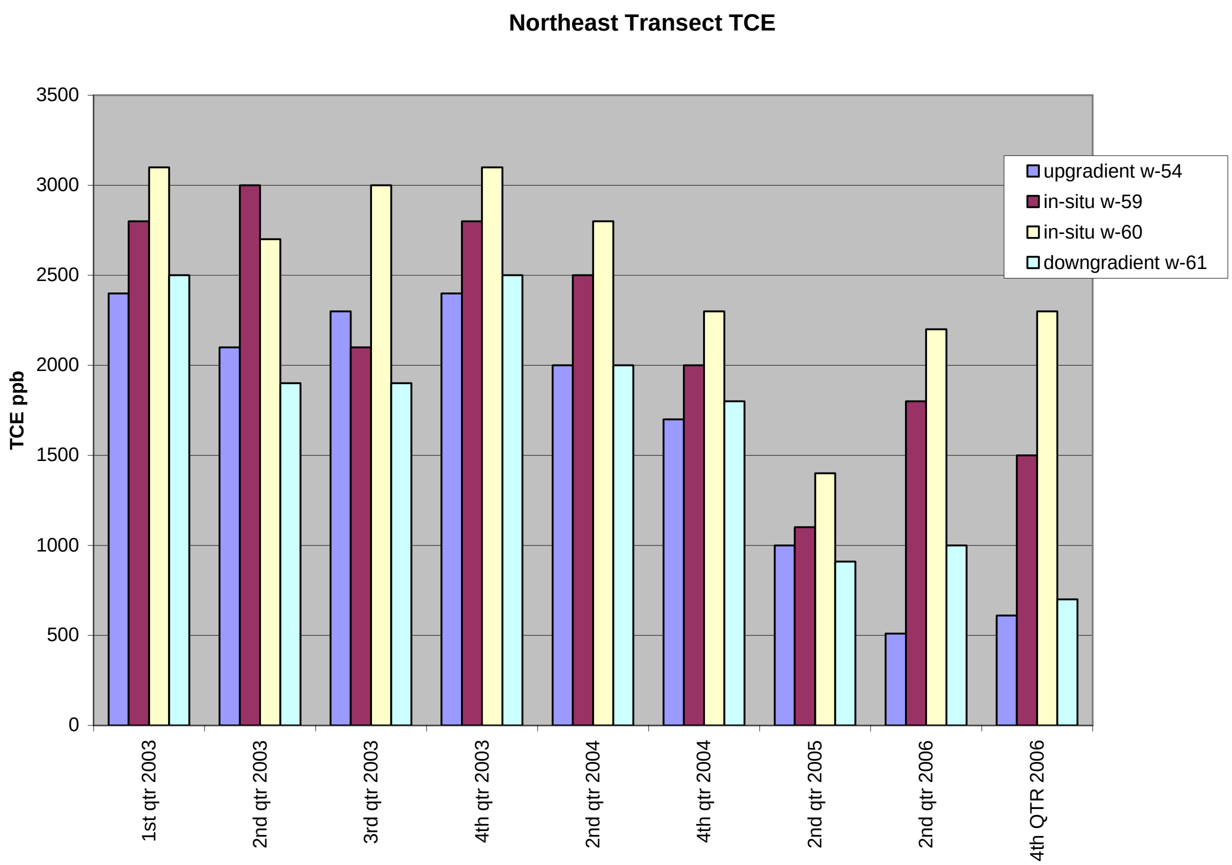
Figure 75   Sierra Army Depot SW Transect TCE Concentrations - ARS



Northeast Transect

The performance of the PRB along the Northeast Transect is perplexing. The in-situ wells show higher TCE concentrations than the upgradient or downgradient wells for most of the sampling events. For six out of nine sampling events, the downgradient TCE concentration is higher than the upgradient concentration.

Figure 76 Sierra Army Depot NE Transect TCE Concentrations - ARS



Summary and Conclusions

Although ARS demonstrated that iron could be injected into the ground using their Ferox Technology, the PRB failed to perform as expected. The poor performance to date of the PRB does not support expanding on the original pilot project.

The Southwest Transit shows highly variable and modest reductions in TCE concentrations across the PRB. Comparing upgradient and downgradient well results, TCE reduction ranged from less than 40% to a minus 20%, and averaged about 12%. Comparing upgradient well results with results for monitoring wells at the downgradient edge of the PRB, TCE reduction appeared greater, but averaged only 33%.

The Northeast Transect results are baffling in that all of the in-situ measurements within the PRB iron wall are higher than the upgradient concentrations of TCE. These results are an anomaly with respect to the other PRBs reviewed and are very hard to rationalize. TCE concentrations measured within the iron wall (in-situ wells) should not be consistently higher than the concentrations measured in both the upgradient and downgradient wells as occurred along the Northeast Transect. One explanation would be for these wells to have somehow been mislabeled.

References

http://www.arstechnologies.com/ferox_zero_valent_iron.html

Arcadis, *Fourth Quarter (August 2005 through October 2005) and 2005 Annual Treatment System Monitoring Report for the Building 210 Area*. Prepared for: Sierra Army Depot, Herlong California. (January 12, 2005).

Arcadis, *Second Quarter (February 2006 through April 2006 Treatment System Monitoring Report for the Building 210 Area*. Prepared for: Sierra Army Depot, Herlong California. (July 14, 2006).

Arcadis, First Quarter November 2003 through January 2004 Treatment System Monitoring Report for the Building 210 Area Sierra Army Depot Herlong California(April 14, 2004).

3.10 Evaluation of the Travis AFB PRB Project

Site History

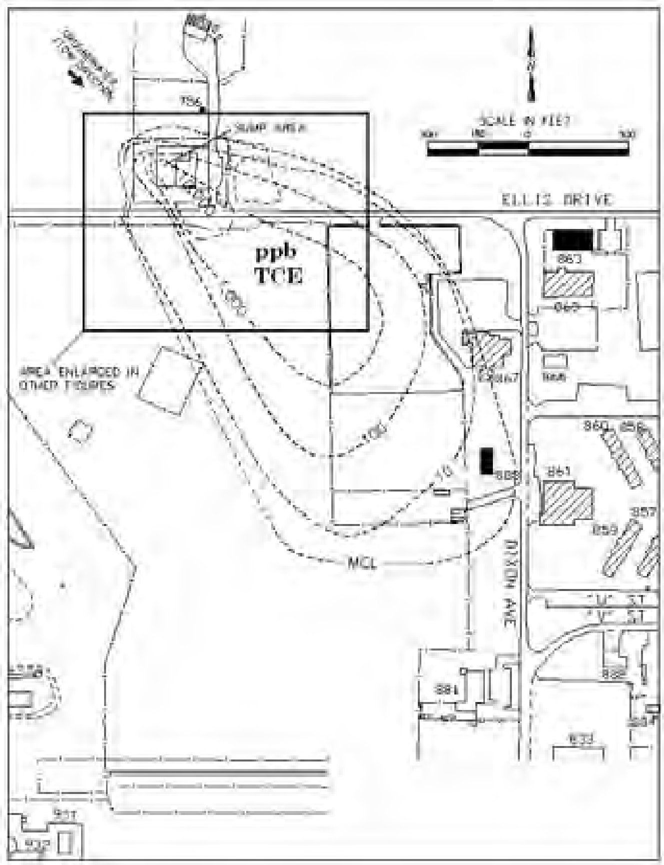
Building 755 at Travis Air Force Base was used for cleaning generators, recharging and dismantling lead-acid and nickel cadmium batteries, and testing rocket engines. Lead-acid solutions were pumped to a sump located northwest of the building. The sump was discharged to a leach field to the west until it was piped to the sanitary sewer in 1978. In 1993, the sump was removed and backfilled with clean fill.

Site/Contaminant Hydrology

In the mid 90's, investigations showed that the sump area was contaminated by chlorinated hydrocarbons and that a plume composed primarily of trichloroethylene (TCE) and 1, 1-dichloroethylene (1, 1-DCE) and vinyl chloride (VC) extended from the site to the southeast.

The lithology in the plume area consists of a 50 ft. deep layer of alluvial silts, sands, and gravels which overlie a layer of stiff micaeous clays and fine-grained sandstone considered part of the Tehama Formation. The groundwater contamination was found to be confined to the upper 50 ft. alluvial layer. Groundwater flow rates based on pump test data ranges from 0.16 to 0.38 ft./day, with a mean of 0.27 ft./day. Figure 77 below shows the concentrations of TCE in the Building 755 plume as it was defined in 1999.

Figure 77   Building 755 TCE Plume in 1999



Adapted from:
AFCEE Project, *Demonstration of Columnar Wall Jet Grouting—Final Report/ Travis AFB* (June 2002).

Site Cleanup Activities

Past cleanup activities at the site included the installation of a Dual-Phase Extraction (DPE) system, the installation of a groundwater extraction system, and monitored natural attenuation. In 1999 Travis installed a pilot zero valence iron (ZVI) permeable reactive barrier (PRB) at the Building 755 site.

PRB Goals/Design

The pilot project at Travis AFB was designed to:

1. Determine if columnar jet grouting could be used to emplace a PRB at Travis Air Force Base, and, if successful, to provide data to transfer this technology to other locations.

2. Document costs to provide general cost comparisons with other groundwater remediation technologies.
3. Meet the maximum contaminant levels (MCLs) for trichloroethene [TCE], 1, 1-dichloroethene [1,1-DCE], and vinyl chloride [VC] immediately downgradient of the PRB.

Peerless iron with a mesh size of –30/+70 and a bulk density of 160 lb/ft^3 was selected for this pilot study. Based on column testing results, 0.1 ft. of 50 percent zero valent iron (ZVI) would be sufficient to remediate the groundwater down to the MCls. The final design was for the equivalent of 1 ft. of 100 percent ZVI (20 percent ZVI in 5-ft. diameter columns). The design provided for a safety factor of 20.

PRB installation

The PRB was constructed in June, 1999 using the double-rod columnar jetting process. This process has been widely used to install cement-bentonite barriers, but had never been used to install an operational PRB

In this process, a hole is drilled and the injection rig is connected to a high pressure pumping system. The system injects the grout (guar gum and zero valence iron granules) under high pressure through one set of nozzles. Air is simultaneously injected through a separate set of nozzles to induce additional turbulence to aid in displacing soil. To break down the viscous gel and regain permeability, an enzyme is added to the guar gum/ZVI suspension as it is injected into the ground. The injection assembly is slowly raised while being rotated through 360 degrees to form the zero valence iron column.

After considerable trial and error, the PRB was installed. The PRB consisted of 24 overlapping columns, and was 91-ft. long by approximately 5-ft. wide. The top of the wall was 15 ft. below ground surface (bgs) or 5 ft. higher than the water table. The bottom of the PRB was keyed approximately 2 ft. into Tehama Foundation bedrock located 50 ft. bgs. With these dimensions, the required amount of ZVI was:

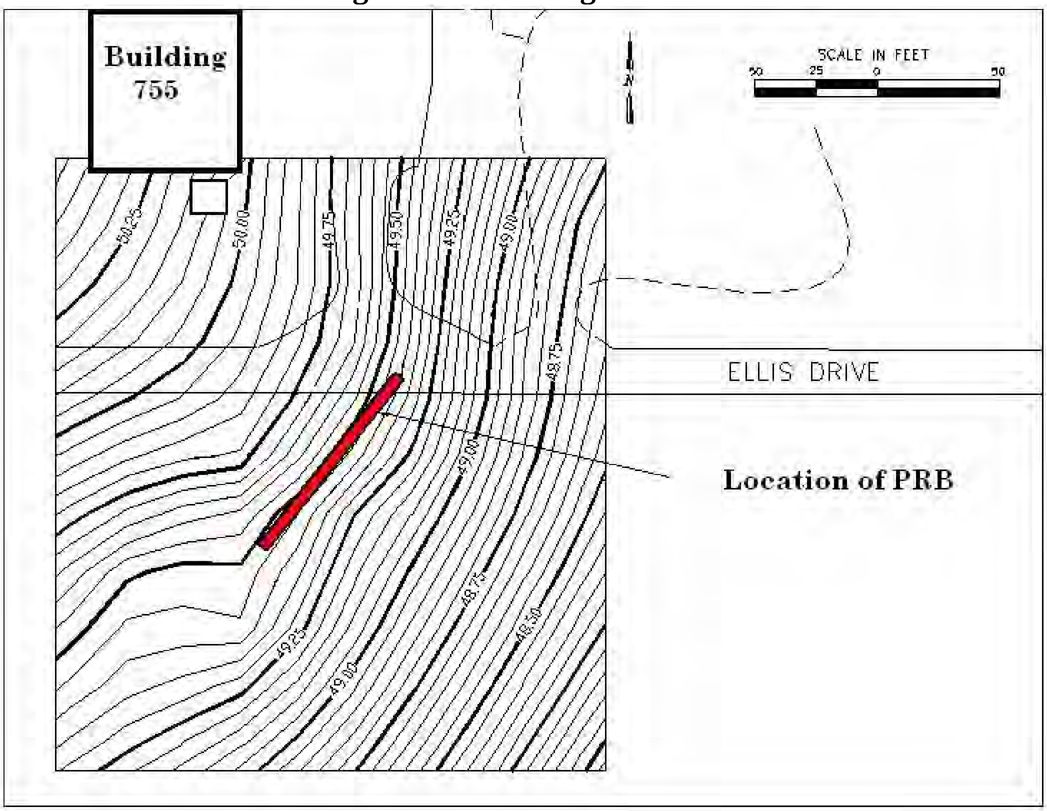
$$\text{Volume} = 5\text{ ft.} \times 35\text{ ft.} \times 90\text{ ft. x } 20\% = 3{,}150\text{ ft}^3$$
$$\text{Mass Iron} = 3{,}150\text{ ft}^3 \times 160\text{ lbs/ft}^3 \times 2{,}000\text{ lb/ton} \approx 250\text{ tons.}$$

For the entire PRB, 303 tons of ZVI was jetted into the subsurface. About 161 tons or 53 percent remained in the formation. Distributed evenly, this quantity is equivalent to 0.65

ft. wall thickness of ZVI. About 48 percent of the ZVI returned to the surface as spoils and was wasted.

Figure 78 below shows the layout of the PRB relative to Building 755 and Ellis Drive.

Figure 78 Building 755 PRB

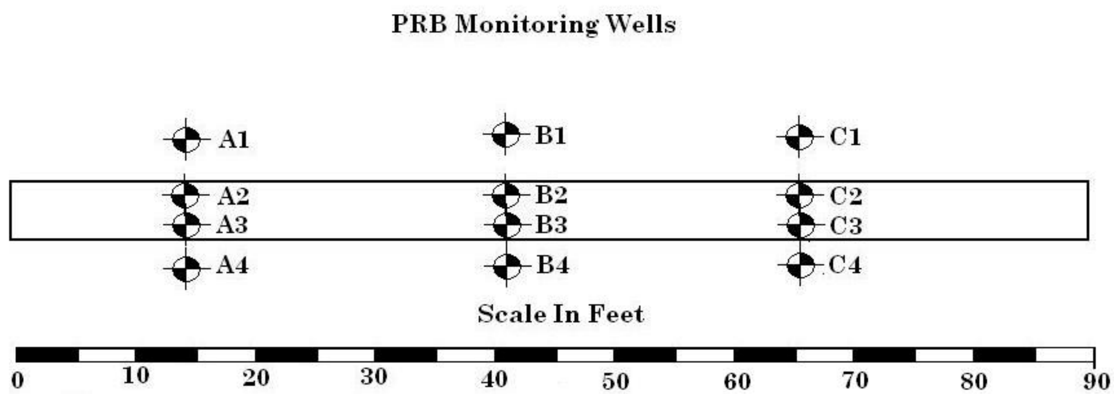


Adapted from:
AFCEE Project, *Demonstration of Columnar Wall Jet Grouting—Final Report/ Travis AFB* (June 2002).

PRB Performance Measurements

Twelve monitoring wells were installed along three transects (see Figure 79). The wells were screened over the same depth interval along a given transect in the zone that exhibited the highest concentrations of TCE and 1, 1-DCE Placement of the wells was based on an extensive site characterization study using a cone penetrometer with a laser induced fluorescence sensor, and groundwater samples from 24 piezometers in the area.

Figure 79 Travis AFB PRB Monitoring Well Layout

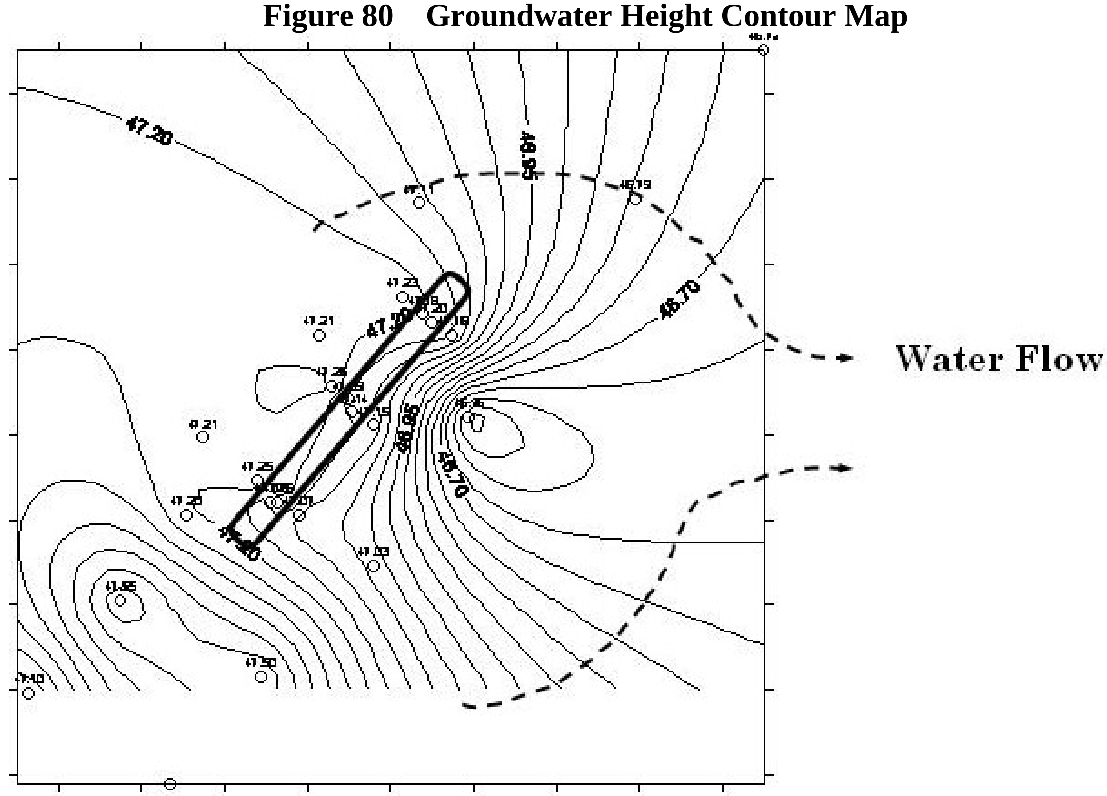


PRB Performance Analysis

Upgradient TCE and 1, 1-DCE concentrations were about 8000 and 1500 ppb respectively just after the PRB installation. These values decreased to about 10 ppb inside the PRB. Unfortunately, TCE and DCE concentrations in the downgradient wells were not significantly reduced.

The groundwater elevations showed that groundwater mounded upgradient of the PRB. It is now believed that groundwater generally flows around the PRB rather than through it. The groundwater elevation contours in the figure 80 below illustrate this mounding phenomena and the resulting water flow around the PRB.

Figure 80 Groundwater Height Contour Map



Adapted from:
AFCEE Project, *Demonstration of Columnar Wall Jet Grouting—Final Report/ Travis AFB* (June 2002).

Summary and Conclusions

The project did not achieve any of its established goals. This failure is largely due to the resultant low permeability of the emplaced PRB, causing groundwater to flow around rather than through the barrier.

Little, if any, impact was seen in the downgradient walls. The chlorinated hydrocarbons did appear to degrade inside the PRB, likely the result of high groundwater residence times within the PRB.

Using the columnar jetting process, about half of the ZVI iron injected to construct the PRB was returned to the surface as waste spoils. This would be unacceptable for an actual project, especially with current iron costs around $600.00/ton. There is also a hazardous waste disposal issue with the contaminated spoils.

As of 2006, the cause for the low permeability across the PRB remains undetermined. This problem may be due to the columnar injection process itself, or failure of enzyme additive to effectively break down the guar gum.

References

AFCEE Project, *Demonstration of Columnar Wall Jet Grouting—Final Report/ Travis AFB* (June 2002).

4 Findings

4.1 Design

Zero Valent Iron (ZVI) works as predicted in field applications to degrade TCE, Carbon Tetrachloride and cis-1,2-DCE in ground water.

Scoping-level calculations to determine the thickness of a permeable reactive barrier (PRB) – and quantify the amount of ZVI necessary – were found generally reliable based on reductions observed within the PRB wall in the “in situ” wells. PRBs created with the injection well and hydro-fracturing method should be comparably adequate. For this type of installation, placement of in-situ monitoring wells is problematic, and downgradient monitoring for such projects has not demonstrated treatment effectiveness in many cases in California. The DuPont Oakley project has shown success using hydrofracture technology.

A major design challenge for ZVI PRBs is ensuring that the contaminated groundwater plume is captured, flows uniformly through the reactive barrier to provide adequate treatment, and does not somehow bypass or short-circuit through the reactive barrier.

4.2 Performance

For only two projects, the Mohawk site and DuPont Oakley, were there even modest improvements in groundwater quality downgradient of the PRB. For the remaining projects reviewed, downgradient groundwater quality improvement was not observed or monitored, or was insignificant when compared to the upgradient water quality measurements.

The 10 PRBs considered in the report all bisect existing plumes. This complicates assessing PRB performance for these sites. None were placed downgradient of an advancing plume in clean ground water. All sites evaluated had persistent high chlorinated solvent contamination downgradient of the PRBs. Leaching or a ‘back diffusion” of contaminants into the groundwater flow likely persists due to the elevated contaminant levels stored in aquifer materials.

Virtually all TCE contaminated ground water plumes also contained cis 1,2-DCE and vinyl chloride. These compounds are daughter products of biological activity, and indicate that biodegradation is a significant component of many- if not most- ground water plumes with TCE. Similarly, chloroform, a biological degradation product of carbon tetrachloride, was present at high levels in the Dupont Oakley plume. Importantly, cis 1,2-DCE is more difficult to treat than its parent compound, TCE, and consequently requires more ZVI and a longer residence time to adequately treat.

There were confounding factors observed for several projects. At Travis AFB the wall was not permeable. At Intersil the wall was breached, and other nearby sites complicate

analysis of ground water hydrology and downgradient water quality measurements. At one site where the wall was installed by injection, the actual direction of ground water is probably opposite of that considered in design and installation. At one site wells used to assess performance may have been a mis-numbered, which would explain the highly anomalous results.

4.3 Monitoring

To assess effectiveness, a number of the projects relied on "in-situ" monitor wells placed within the PRB's iron matrix near the downgradient side of the PRB wall. Most chlorinated solvent measurements taken from these "in-situ" monitor wells reported levels below MCLs.

Several sites lacked adequate downgradient monitoring to evaluate the PRB's ability to cleanup the contaminated groundwater plume.

Of the 10 sites studied, few actually compared upgradient with downgradient contaminant levels in a graphical presentation that would readily allow a determination of PRB wall performance.

Baseline data and trends for the groundwater contaminant plume were not available for many of the PRBs reviewed. PRB performance is not easily assessed without knowing baseline conditions prior to installation and upgradient trends throughout the life of the project.

Some sites had widely varying concentrations of contaminants of concern both upgradient and downgradient of the PRB throughout the periods of record. In one case, the upgradient TCE concentration varied by over an order of magnitude between sampling events. This variability in monitoring results confounded the analysis of the PRB performance at several sites.

4.4 Cost

Capital cost of installing PRBs is a concern, especially with the increasing cost of zero valent iron. Additionally, although PRBs may be considered a passive technology (no required O&M after installation), installation and ongoing costs of an adequate monitoring program can be significant.

5 Recommendations

5.1 Design

Numerical models and other predictive tools should be considered in the design of a PRB. Models can predict how the PRB design will perform over time with respect to downgradient water quality, as well as the overall time to achieve cleanup goals. Models can provide a more realistic understanding of the number of pore volumes and time that may be required to flush out residual contamination contained in downgradient aquifer materials.

Column tests are a recommended feature of the design process, focusing on water chemistry that might lead to plugging of the wall and as well as determining the target contaminant reaction rates with the selected source(s) of zero valent iron. Column testing should address parent compound reaction rates as well as the formation of reaction byproducts and their respective rates.

5.2 Performance

Only modest downgradient water quality improvement should be expected in the near term (time for several pore volumes to sweep the downgradient portion of the plume). The obscuring effects of aquifer/contaminant interactions - notably back diffusion – precludes any of the optimistic hopes for recovery of downgradient water quality that was anticipated when PRBs were first introduced.

Trenching has been shown to be a reliable method for installing PRBs to specified thickness and depth. The same finding has yet to be confirmed for injection-installed PRBs. Increased performance monitoring and analysis would be required for injection-installed PRBs, compared with one installed via trenching and backfill.

5.3 Monitoring

A well designed monitoring system should be an integral component of any PRB project. In general, monitoring wells should be placed along transects in parallel with groundwater flow and across the PRBs. Transects should include both upgradient and downgradient monitoring, as well as in situ wells (if the PRB wall is sufficiently thick).

Some downgradient monitor wells should be placed at a distance such that there is a reasonably short transit time (~ 1 week) for treated groundwater that passes through the PRB to reach the monitor well. The PRB's effectiveness in remediating groundwater contamination downgradient of the barrier can then be evaluated in a timely manner, versus waiting for an extended period for a minimum number of treated groundwater pore volumes to pass the monitoring point.

In-situ well results are useful to show that contaminant reductions are occurring within the PRB.

Groundwater flow and contaminant contour maps are useful to verify groundwater flow patterns through the barrier and to show improvements in the groundwater contaminant plume due to the PRB. Baseline trends – both for ground water hydrology and contaminant levels – need to be evaluated in advance of PRB installation and taken into account in assessing performance of PRBs.

Tracer tests are recommended. Tracer tests can determine that established groundwater flow patterns are consistent with PRB design, and that the PRB is not short circuited or bypassed. Tracer tests can also validate the travel time for groundwater to pass the PRB and reach downgradient monitoring point.

Tracer tests can also substantiate that the ground water monitoring network is adequate, and that ground water exiting a PRB is actually captured in monitoring wells downgradient. Where there are significantly thick panels of ZVI and the potential for vertical migration, and/or where vertical movement of ground water is a potentially complicating issue, tracer tests may be very useful in demonstrating and assessing the performance of the PRB and in quantifying improvements in downgradient water quality.

Appendix A. Scoping Calculations

Cost-effective use of permeable reactive barriers for ground-water treatment requires proper estimation of the amount of reactive material required and choosing the best means of emplacing it in the ground. The weight of reactive material per unit cross-section of the plume may be estimated from laboratory reaction kinetics data and basic knowledge of the plume and the remediation goals. The value of this parameter has implications regarding the choice of permeable barrier design and emplacement method. The use of tremie tubes, trenching machines, high pressure jetting, and deep soil mixing may be appropriate for different situations, depending on the amount of reactive material required, the dimensions of the plume, and other factors. The specific application considered here is granular iron to treat ground water contaminated with chlorinated solvents, but the principles are applicable to other types of media and contaminants.

Reaction rate parameters from laboratory studies of iron-mediated degradation of a variety of chlorinated solvents have appeared in the literature in the past several years (Johnson et al., 1996; Shoemaker and al., 1996). The work of Johnson et al. (1996) has been especially helpful in establishing the high degree of consistency between kinetics data obtained from batch and column studies. By expressing rate data in a way that accounts for the iron surface area concentration, it was demonstrated that results reported in the literature varied by less than had previously been thought. This makes it possible to obtain a fairly reliable estimate of the iron requirement for a potential application even before site specific laboratory feasibility tests are conducted. The bulk of the data reviewed by Johnson et al. suggest a surface-area-specific rate parameter (k_{SA}) of about 0.2 $cm^3\ h^{-1}\ m^{-2}$ for TCE and of about 0.04 $cm^3\ h^{-1}\ m^{-2}$ for cDCE. For the examples considered here, 1.0 m^2/g will be used for the specific surface area, a value typical of the granular irons which currently appear to be the most practical for permeable barrier applications. Further, the rate of reaction will be decreased by 50% to adjust for subsurface temperatures being lower than room temperature (Sivavec and Horney, 1995). Therefore, the effective rate parameter to be used is 0.1 $cm^3\ g^{-1}\ h^{-1}$ for TCE and 0.02 $cm^3\ g^{-1}\ h^{-1}$ for DCE.

Two example cases are considered below. The first and simplest involves degradation of a chlorinated compound (e.g., TCE) where the levels of intermediate products (e.g., DCE) are low enough that they do not influence the iron requirement. The second case involves significant generation of an intermediate product that degrades more slowly than the parent and thereby determines how much iron is required.

Case 1: Parent Products Only

The rate of reaction may be expressed as

$$\frac{dP}{dt} = -k_1 \rho_m P \tag{39}$$

where P is the concentration of dissolved chlorocarbon, t is the contact time between the dissolved chlorocarbon and iron particles, k_1 is the first-order rate parameter, and ρm is the mass of zero-valent iron particles per solution volume. This equation may be integrated to give

$$\ln\left(\frac{P_0}{P}\right) = -k_1 \rho_m t \tag{40}$$

where P_0 is the initial concentration of dissolved chlorocarbon. In a batch laboratory experiment, k_1 may be derived from the slope of a semi-log plot of P_0/P vs. time.

For the case of steady-state flow in a packed bed reactor, an expression analogous to Equation 40 may be derived by expressing the residence time (t) as the product of the bed void fraction (ε) and the reactor volume (V), divided by the liquid flowrate through the bed, yielding

$$\ln\left(\frac{P_0}{P}\right)=\frac{k_1\rho_m \varepsilon V}{Q} \tag{41}$$

The term $\rho_m \varepsilon V$ is the mass of zero-valent iron, W, that the fluid encounters as it flows through the bed. With this substitution, and by representing the flowrate as the product of the cross-sectional plume area (A), the soil porosity (n), and the average flow velocity (u), the amount of iron required per unit cross-section of plume to effect a desired decrease in chlorocarbon concentration may be expressed as

$$\frac{W}{A}=\frac{un}{k_1}\ln\left(\frac{P_0}{P}\right) \tag{42}$$

This is a useful expression because it allows estimates to be made without assuming a particular design (such as funnel-and-gate) or calculating parameters such as residence time, but rather expresses a key aspect of the design (W/A) in the most fundamental terms. However, it does not reflect uncertainties and fluctuations in parameter values that must be considered in any design. These can be accounted for in terms of a factor of safety (F) which increases the amount of reactive material employed:

$$\frac{W}{A}=F\frac{un}{k_1}\ln\left(\frac{P_0}{P}\right) \tag{43}$$

A Monte-Carlo simulation has been developed to estimate appropriate factors of safety for permeable reactive barrier systems (Eykholt, 1997). With influent concentrations varying 10%, the reaction rate parameter varying 30%, and the ground-water velocity varying 100%, achieving a 1000-fold decrease in contaminant concentration with 95% confidence was found to require a safety factor of 3.5.

As shown in Table 9, calculations based on a safety factor of 3.5 and a range of practical values for reaction rate parameters and ground-water velocities suggest that W/A should be expected to vary from as little as about 20 lb/ft^2 to perhaps 1,000 lb/ft^2.

The values for the constants used in equation 43 to product the results in table 2 are as follows:

F=4

n=0.3 from soil tests

ρ iron = Density of bulk iron = 2.2 g/cm^3

Temperature compensated value for k_1 = 2.0 cm^3/g day from column studies on cis 1,2-DCE.

$$\frac{W}{A\ \rho_{iron}} = L$$

Where **L** is the width of the barrier needed in feet.

After substituting the above values and relations into equation 43 and rearranging the equation becomes:

$$L = 0.27\, u\ \mathrm{Ln}(P_o / P)$$

Where ***u*** is the ground water flowrate expressed in feet/day.

This equation is used to evaluate the design and performance of the Mohawk, Fairchild, and Intersil barrier projects in this report.

Equivalent equations for the other contaminants listed in Table 5 are based on the half lives of the contaminants in zero valent iron column studies.

The above discussion and calculations were taken from:

US EPA/RTDF (Sept 1998), *PERMEABLE REACTIVE BARRIER TECHNOLOGIES FOR CONTAMINANT REMEDIATION*, Appendix C, Scoping Calculations, EPA/600/R-98/125

Appendix B. Acronyms

AFB	Air Force Base
B	bulk density
bgs	below ground surface
BTEX	benzene, toluene, ethyl benzene, and xylenes
CCl4	carbon tetrachloride
cis-1,2-DCE	cis-1,2-dichloroethene
COC	contaminant of concern
CPT	cone penetrometer testing
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DNAPL	dense, non aqueous -phase liquid
DRE	destruction rate efficiency
DTSC	Department of Toxic Substances Control
EISB	enhanced in-situ bioremediation
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ETI	EnviroMetal Technologies, Inc.
Fe	iron
GETS	Groundwater Extraction and Treatment System
HRC	hydrogen release compound
HVOC	halogenated volatile organic compound
ISB	in-situ bioremediation
ITRC	Interstate Technical Regulatory Council
JAG	jet-assisted grouting
K	hydraulic conductivity
K aquifer	aquifer hydraulic conductivity
lbs	pounds
MCL	maximum contaminant level
MNA	monitored natural attenuation
n	porosity
NAS	Naval Air Station
NASA	National Aeronautics and Space Administration
O&M	operating and maintenance
OSHA	Occupational Safety and Health Administration
PCE	perchloroethylene
PRB	permeable reactive barrier
PRP	potentially responsible party
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RTDF	Remediation Technologies Development Forum
SERDP	Strategic Environmental Research and Development Program
T	temperature
TCA	trichloroethane
TCE	trichloroethylene
U.S. EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VC	vinyl chloride
VOC	volatile organic compound

Appendix C. Chlorinated Compounds Degraded by Zero Valence Iron

Common name	abbreviation	Other	CAS
Ethenes			
Tetrachloroethene	PCE	Perchloroethylene	127-18-4
Trichloroethene	TCE	Ethylene trichloride	79-01-6
cis-1,2-Dichloroethene	cis-1,2-DCE	cis-1,2-Dichloroethylene	540-59-0
trans-1,2-Dichloroethene	trans-1,2-DCE		540-59-0
1,1-Dichloroethene	1,1-DCE	Vinylidene chloride	75-35-4
Vinyl chloride	VC	Chloroethene	75-01-4
Ethanes			
Hexachloroethane	HCA	Carbon hexachloride	67-72-1
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA		630-20-6
1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	Acetylene tetrachloride	79-34-5
1,1,1-Trichloroethane	1,1,1-TCA	Methyl chloroform	71-55-6
1,1,2-Trichloroethane	1,1,2-TCA	Vinyl trichloride	79-00-5
1,1-Dichloroethane	1,1-DCA		75-34-3
1,2-Dibromoethane	1,2-DBA	Ethylene dibromide	106-93-4
Methanes			
Tetrachloromethane	CT, PCM	Carbon tetrachloride	56-23-5
Trichloromethane	TCM	Chloroform	67-66-3
Tribromomethane	TBM	Bromoform	75-25-2
Propanes			
1,2,3-Trichloropropane	1,2,3-TCP	Allyl trichloride	96-18-4
1,2-Dichloropropane	1,2-DCP	Propylene dichloride	78-87-5
Other Chlorinated			
N-Nitrosodimethylamine	NDMA	Dimethylnitrosamine	62-75-9
Dibromochloropropane	DBCP		96-12-8
Lindane	Benzene hexachloride		58-89-9
1,1,2-Trichlorotrifluoroethane	Freon 113		76-13-1
Trichlorofluoromethane	Freon 11		75-69-4

Appendix D. References

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