OPPTD Document No. 1218

In-situ Bioremediation of Chlorinated Hydrocarbons

An Assessment of Projects in California

California Department of Toxic Substances Control
Office of Pollution Prevention and Technology Development

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(Appendices for this report are available upon request. Please contact Suzanne Davis at (916) 327-4206 or e-mail your request to sdavis@dtsc.ca.gov)

Acronyms and Abbreviations

cis-1,2-DCE	cis-1,2-dichloroethene
trans-1,2-DCE	trans-1,2-dichloroethene
AFCEE	Air Force Center for Environmental Excellence
AOC	Administrative Order on Consent
bgs	below ground surface
BOD	biological oxygen demand
BW	circulation wells
CCl_4	carbon tetrachloride
CF	chloroform
CFU/mL	colony forming units per milliliter
CM	chloromethane
CO_2	carbon dioxide
COC	contaminant of concern
COD	chemical oxygen demand
CVOC	chlorinated volatile organic compound
DCA	dichloroethane
DCE	dichloroethene
DCP	dichloropropane
DO	dissolved oxygen
DRE	destruction rate efficiency
DTSC	Department of Toxic Substances Control
EISB	enhanced in-situ bioremediation
Fe	iron
GETS	Groundwater Extraction and Treatment System
HCA	hexachloroethane
HCB	hexachlorobenzene
HPC	heterotrophic plate counts
HRC	hydrogen release compound
HVOC	halogenated volatile organic compound
HWMP	Hazardous Waste Management Program
ISB	in-situ bioremediation
ITRC	Interstate Technical Regulatory Council
K	hydraulic conductivity
lbs	pounds
μg/L	micrograms per liter
mg/L	milligrams per liter
MCL	maximum contaminant level
$MeCl_2$	methylene chloride
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
MNA	monitored natural attenuation
NA	not applicable
OPPTD	Office of Pollution Prevention and Technology Development
ORP	oxidation reduction potential or redox

PCE	perchloroethene or tetrachloroethylene
PCP	pentachlorophenol
POC	point of contact
psi	pound per square inch
RPs	responsible parties
RWQCB	Regional Water Quality Control Board
SMPPD	Site Mitigation Properties Project Database
SPEP	School Property Evaluation Program
SVOCs	semi-volatile organic compounds
SWRCB	State Water Resources Control Board
TCA	1,1,1-trichloroethane
TCE	trichloroethene
TOC	total organic content
UPRALSA	Unconfirmed Properties Referred to Another Local or State Agency
U.S. EPA	United States Environmental Protection Agency
UST	underground storage tank
VC	vinyl chloride
VCPP	Voluntary Cleanup Program Properties
VOCs	volatile organic compounds

Executive Summary

The purpose of this report was to investigate the status of in-situ bioremediation (ISB) technology in California by identifying those sites or facilities where pilot or full scale projects have been implemented, and to then evaluate the performance of a selected number of projects. A total of 50 sites were identified based on record searches at several government agencies. Of these 50 sites, ISB was selected as the remediation method at 29 sites while 21 selected monitored natural attenuation (MNA). Based on these results, five (5) sites undergoing bioremediation to reduce chlorinated solvents in groundwater were selected for more detailed evaluation. Of the five sites, most were being remediated for tetrachloroethene (PCE), trichloroethene (TCE) or both. Two of the sites had significant amounts of additional compounds besides PCE and TCE that were targeted for remediation.

A review of the available data at each of these sites found that in-situ biological treatment appears to be more of an emerging than a demonstrated technology. Although it has been considered as a remedial alternative at many California sites and a number of pilot-scale projects have been completed, there are but a few sites where in-situ biological treatment has been implemented full-scale for chlorinated solvents. Field implementation of in-situ biological treatment has shown to be more complicated than the laboratory and bench studies that have been conducted to demonstrate the efficacy of the technology. An analysis of available data for the five case study projects did not find the classic "cascading" series of curves described in the literature for biological reductive dechlorination of chlorinated solvents.

All five sites studied had data that suggested biodegradation was occurring to some degree. However, it was not clear that biodegradation was proceeding in a reliable, demonstrative manner that would be desired for a final remedy. For several sites and many monitoring wells, there was no apparent change in any parameter measured as a result of implementation of the bioremediation system.

At three of the five case study sites there was a build-up of cis-1,2-DCE, and no evident production of subsequent degradation products (e.g., vinyl chloride, ethene). These data indicate that the biodegradation process has "stalled" at these sites. Where "stalling" had occurred, groundwater had not been inoculated with the microorganisms known to effect complete degradation of TCE. As site managers became aware of this problem, there was no contingency program in place to inoculate the site with bacteria capable of degrading the accumulated cis-1,2-DCE. The presence of bacteria capable of reducing the targeted chlorinated compounds is essential for bioremediation technology to be effective. Establishing and maintaining an adequate population of bacteria capable of bioremediation in the subsurface treatment zone (aquifer) is a critical, clear objective of any bioremediation project.

For several of the pilot scale and full-scale applications evaluated, geochemical parameters were not reported. These parameters promote an understanding of the biodegradation pathway at a site, and are necessary to assess that optimum conditions for biodegradation have been established.

For all sites, the specific goals or cleanup objectives for the site were vague or undefined, and monitoring – in terms of well placement based on travel times, degradation rates and compounds to be analyzed – was not clearly based on a pre-implementation analysis of expected results. Well-defined and quantitative goals or benchmarks are needed to guide the development of an adequate monitoring program and serve to establish the success or failure of a project. Without such specific goals, monitoring programs suffer, project success becomes subjective and comparison of the relative success of projects is problematic or not possible.

Based on the review of the five sites included in this report, several recurring issues were observed. The following recommendations made are based on these issues.

- An overall project goal should be established to judge the relative success or failure for the project and be directly related to the overall remediation goals established for the site (e.g., approved Remedial Action Plan).

- Objectives for in-situ bioremediation projects should be clearly defined, measurable and linked to the conditions that promote or enhance biodegradation that the system was designed to achieve.

- An up-front (pre-implementation) analysis of the in-situ biological treatment system and how it will perform over time and over the volume of the contamination plume is essential for developing an adequate monitoring program and assessing the on-going performance of the system.

- Bioaugmentation should be evaluated prior to implementing the project to confirm that the microorganisms present are capable of completely degrading the target compounds to desired environmentally benign end products. If this not the case, the feasibility of a bioaugmentation program should be investigated.

- Areal groundwater contaminant concentration contour plots of the target compounds and expected degradation products should be plotted to allow the comparison with the expected patterns of decrease and increase for the biodegradation pathway being enhanced.

- Groundwater data should be presented for wells and groupings of wells in a manner that illustrates the increase (if any) in biodegradation associated with the project. Typically, this requires graphical presentations that compare and contrast measured concentrations and the trends observed over time. Such results should be compared with predicted and expected ("textbook") results that represent successful attainment of objectives established for the project.

- In-situ bioremediation projects should include a Contingency Plan in the event the biodegradation process appears to have “stalled” or be incomplete. The plan should address methods to correct deficiencies that become apparent after implementation, including bioaugmentation, modification of redox conditions, enhancing electron donor/carbon source distribution, etc.

- Data Accessibility was one hurdle in reviewing these reports. In most cases, the raw data was available but not in an easy to review format for plots and calculations. Electronic copies of datasheets used in data analysis (i.e., spreadsheets, graphs, etc.) should be provided along with the hard copy of the report.

1 Introduction

In-situ bioremediation of chlorinated solvents has received much interest and attention throughout the remediation industry. A number of guidance documents on implementing in-situ biological treatment have been developed by the U.S. EPA, the Interstate Technical Regulatory Council (ITRC), the U.S. Air Force and others. Research, field testing and product development have each targeted biodegradation of chlorinated solvents. The technology has now progressed to where pilot-scale tests have been completed at many different sites, and more importantly a number of full-scale systems have been implemented and are currently in operation.

The purpose of this report was to investigate the status of in-situ bioremediation technology in California by identifying those sites or facilities where pilot or full-scale projects have been implemented, and to then evaluate the performance of a selected number of projects. Review of data developed through field applications is considered the best means to demonstrate how well this technology is being implemented, and how effective the technology has been in achieving its general objective, the destruction of chlorinated solvent contaminants in groundwater.

In 2002, Office of Pollution Prevention and Technology Development (OPPTD) began collecting and analyzing data from projects throughout California where in-situ bioremediation of chlorinated solvents had been implemented. A combination of Internet and database searches, e-mail requests, and personal contacts were used to obtain pertinent data. There were several goals for collecting these data:

- to identify project sites where in-situ bioremediation (ISB) has been implemented (pilot & full-scale)
- to determine the availability and quality of data collected on remediation projects from a variety of locations and agencies that could be used to evaluate the effectiveness of the technology
- to determine if guidance, training and other available resources on implementation of bioremediation are benefiting projects in California
- to assess in a quantitative, or at least a qualitative sense the effectiveness of in-situ bioremediation technology – if it is performing well or poorly at California sites where it is being implemented
- to provide recommendations on the application of bioremediation including monitoring and sampling requirements that are common to most sites

As with many “first of a kind” efforts the collection of data on bioremediation projects was undertaken as a learning experience in and of itself, and to see - in general terms - what lessons (if any) could be learned.

1.1 Bioremediation Basics

Successful bioremediation of chlorinated solvents requires that a sufficient population of microorganisms capable of degrading the compounds of interest be established and maintained for prolonged periods of time. To create the “biological reactor” for destroying the target compounds, chlorinated solvents in the case of this study, requires that an appropriate environment to be created or enhanced that sustains a viable population of the desired microorganisms. Creating an environment conducive to biodegradation of chlorinated solvents typically entails creation of an anaerobic environment, suppression of the redox potential, provision of a carbon (food) source, and even the provision of nutrients (minerals).

Effective biodegradation of chlorinated solvents generally involves the stepwise biodegradation of compounds through reductive dechlorination. For perchloroethene, for example, the most robust pathway for treatment would be:

PCE→ TCE→ cis-1,2-dichlorothene (DCE)→ Vinyl Chloride (VC)→ ethene (ethylene)

With each sequential stage the mixture of the solvents and daughter products in groundwater changes, and so the process of biodegradation can be followed by monitoring compounds that should change in concentration – both absolute concentration and concentrations relative to one another – over time. Where biodegradation is robust and the site well-monitored, treatment (biodegradation) should occur and the field results should mimic the theoretical or predicted results, often described as a “cascade” of intermediates progressing from PCE through ethene.

A key feature of the reductive dechlorination pathway illustrated above is that cis-1,2-DCE is known to occur in significant quantities only as a result of biological activity. Similarly, vinyl chloride is a gas in ambient conditions, and also is a clear marker of biodegradation. Ethene might have other anthropogenic or non-anthropogenic sources, but typically indicates completion of the biodegradation process when found in significant amounts in association with the compounds preceding it in the biodegradation pathway.

An important feature of the pathway from PCE to ethene is that if the biodegradation is incomplete, then one or more of the compounds undergoing treatment should build up. In fact, a crucial step in the above sequence is the reaction that causes transformation of cis-1,2-DCE to vinyl chloride. Where this step is slow or insignificant, conversion stops and cis-1,2-DCE accumulates. This has been referred to as “stalling” and has been observed in the laboratory and in the field.

1.1.1 Monitoring for Target Compounds and Intermediates

Where biodegradation is not robust, or in cases where the monitoring frequency, list of analytes, or monitoring location density are inadequate, field results would be expected to be very different from the idealized or predicted patterns. Where biodegradation is not occurring, no changes in concentrations attributable to biological activity would be apparent.

Figure 1-1 presents are 5 plots of patterns of concentrations expected from the conversion of PCE to ethylene that would provide varying levels of confidence about the biodegradation process. The plots range from “ideal” to “no biodegradation apparent.” Intermediate situations (patterns) that might result from insufficient monitoring, “stalling” of the biodegradation process at cis-1,2-DCE, or patterns resulting from any combination of poor performance and confounding factors are also shown in Figure 1-1.

Plots such as those shown in Figure 1-1 can be constructed from monitoring results where the appropriate compounds are measured. Such plots provide a clear means to monitor the progress – or lack of progress – of biodegradation of chlorinated solvents.

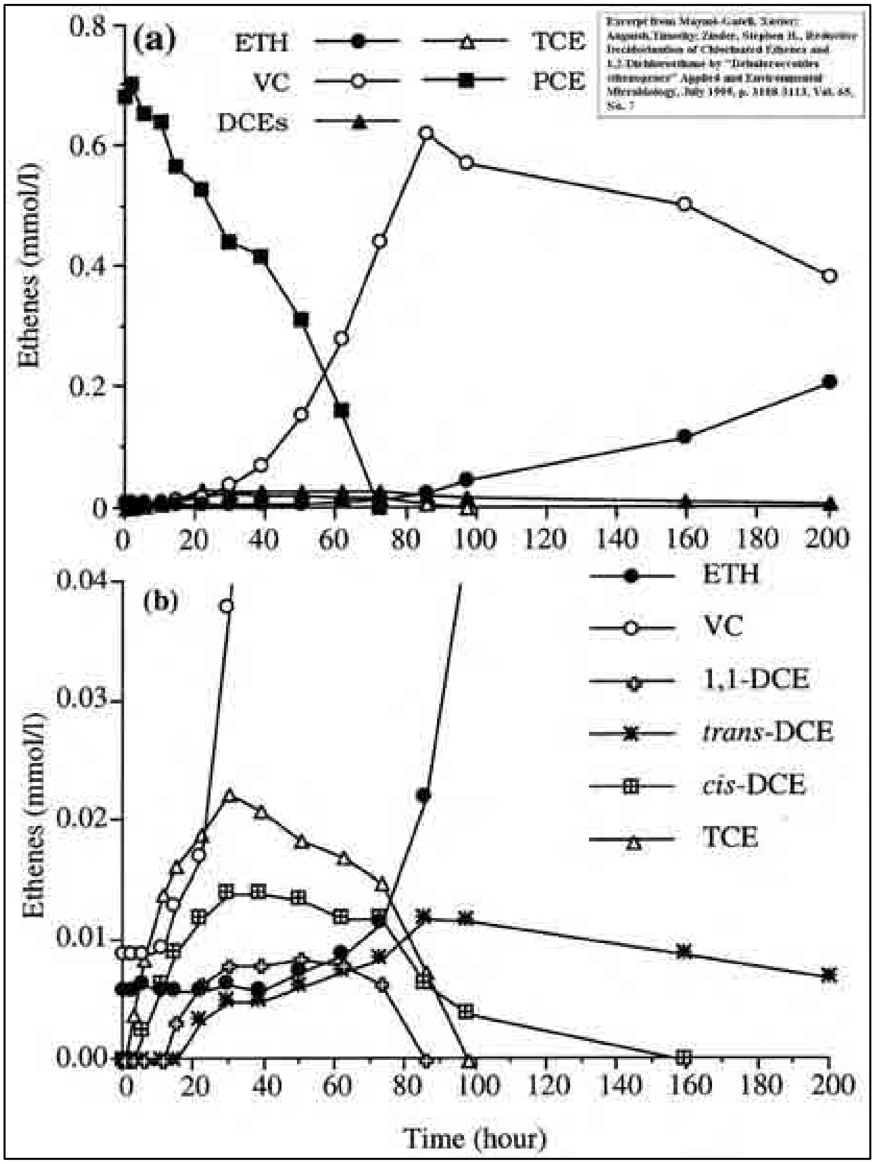
1.1.2 Monitoring for Other Parameters Important to Biodegradation

The idealized (and even unfavorable) patterns shown in Figure 1-1 indicate the degree of treatment that might be occurring during an in-situ bioremediation project. Along with the compounds (solvents and daughter products) being biodegraded, changes in water chemistry can be followed to determine if the environment is favorable or conducive to biodegradation. Redox potential (ORP), dissolved oxygen (DO), alkalinity, metals (notably iron and manganese), anions (nitrate and sulfate, which themselves may be added as nutrients; chloride, which is liberated at each step of the biodegradation process), and pH can all serve to characterize the subsurface environment with respect to biodegradation. Where these parameters respond in a predictable way during the implementation of biodegradation (increases and decreases as expected), there is support for determining that biodegradation is occurring.

1.1.3 Showing that Biodegradation Is (or Is Not) Occurring

An objective of any in-situ bioremediation treatment process is not just to show that the treatment occurs (typically the destruction of the target compound) but that the treatment is effectively proceeding toward completion (performance). In the ideal case with sufficient monitoring, the documentation of treatment and robustness of performance can be quantitative as represented by the classical biodegradation pattern in Figure 1-1a. In all cases, at least a qualitative indication of success is expected. Both qualitative and quantitative indications of the biodegradation require sampling for the parent, intermediate and endproducts of the pertinent biodegradation pathway. Perhaps the most useful way of evaluating treatment performance is to plot these data together on the same graph (concentration versus time plots). Preparation of such graphs became the prime method of analysis of groundwater data collected at the five sites selected for further evaluation in this study. Figures 1-1b through 1-1e are examples of patterns where the biodegradation conditions ranged from favorable to not occurring. These graphs are based on data from the case studies presented in Section 4.

Figure 1-1. Five Examples of Different Biodegradation Patterns[1]



(a) Classical biodegradation pattern

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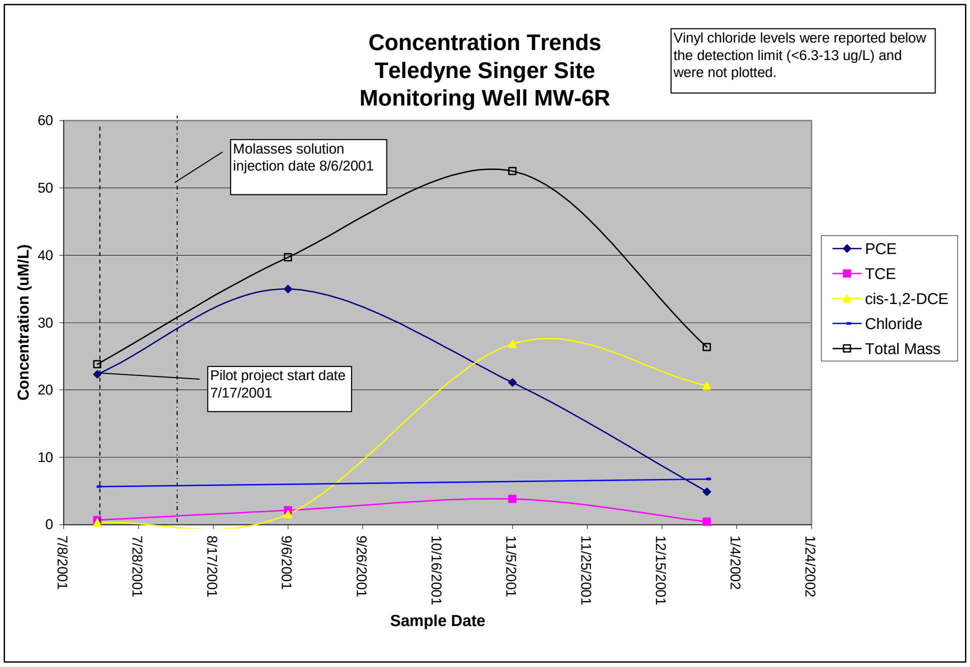
[1] Classical biodegradation graphs are excerpted from Maymó-Gatell, Xavier; Anguish,Timothy; Zinder, Stephen H.**,** Reductive Dechlorination of Chlorinated Ethenes and 1,2-Dichloroethane by "Dehalococcoides ethenogenes", Applied and Environmental Microbiology, July 1999, p. 3108-3113, Vol. 65, No. 7.

Figure 1-1. Five Examples of Different Biodegradation Patterns (cont.)



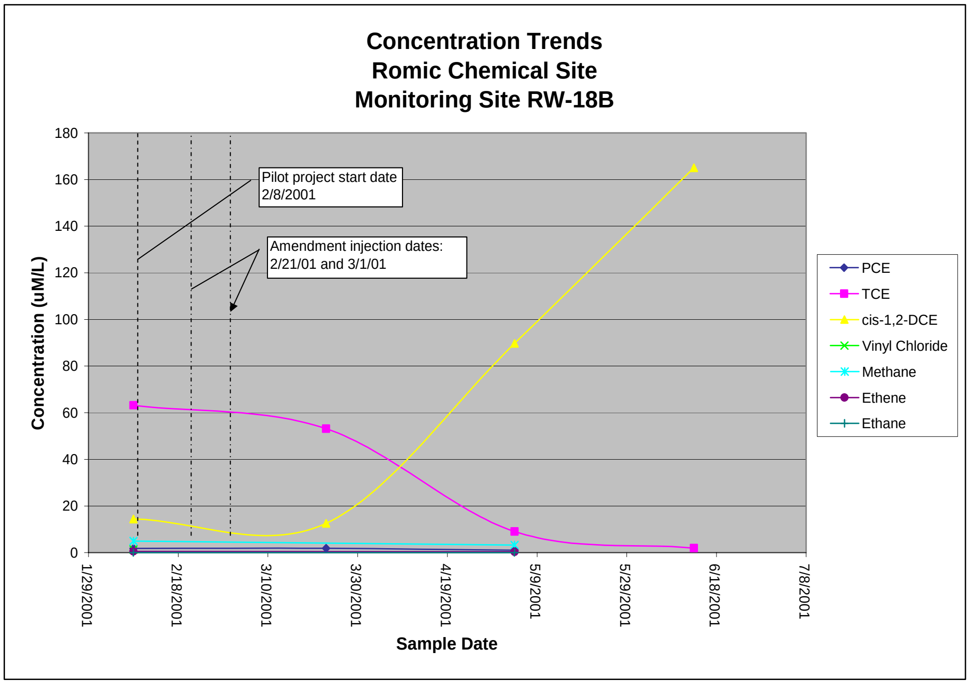
Concentration Trends
Teledyne Singer Site
Monitoring Well MW-6R

Vinyl chloride levels were reported below the detection limit (<6.3-13 ug/L) and were not plotted.

Molasses solution injection date 8/6/2001

Pilot project start date 7/17/2001

(b) Favorable biodegradation pattern



Concentration Trends
Romic Chemical Site
Monitoring Site RW-18B

Pilot project start date 2/8/2001

Amendment injection dates: 2/21/01 and 3/1/01

(c) Inconclusive/stalling at cis-1,2-DCE

Figure 1.-1. Five Examples of Different Biodegradation Patterns (cont.)

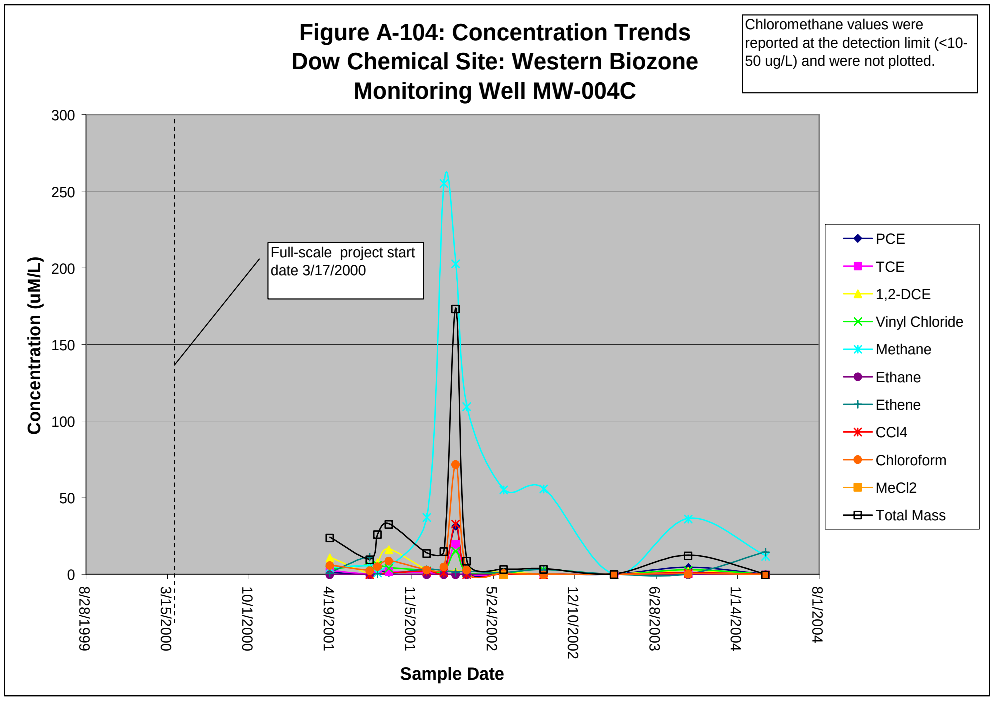


Figure A-104: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-004C

Chloromethane values were reported at the detection limit (<10-50 ug/L) and were not plotted.

Full-scale project start date 3/17/2000

(d) Inconclusive

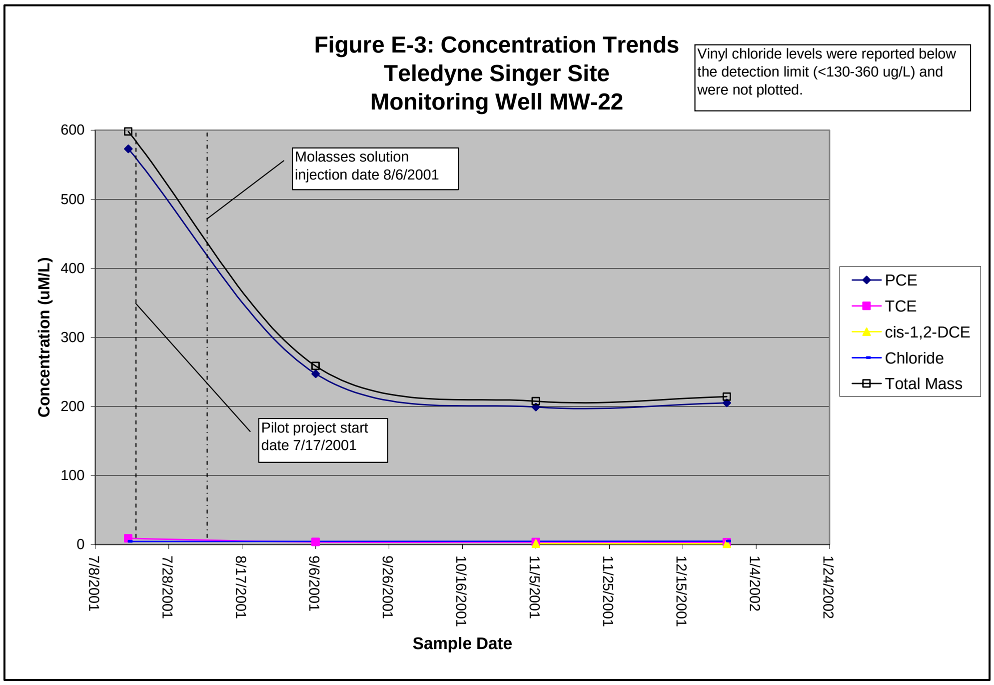


Figure E-3: Concentration Trends
Teledyne Singer Site
Monitoring Well MW-22

Vinyl chloride levels were reported below the detection limit (<130-360 ug/L) and were not plotted.

Molasses solution injection date 8/6/2001

Pilot project start date 7/17/2001

(e) No treatment occurring

2 Data Collection

A total of 50 sites were identified based on information from Department of Toxic Substances Control (DTSC) technical staff, the Calsites database, and searches of the CalEPA, State Water Resources Control Board (SWRCB) and DTSC websites. Of these 50 sites, ISB was selected as the remediation method at 21 DTSC sites, 5 Regional Water Quality Control Board (RWQCB) sites, and 3 U.S. EPA sites while 16 DTSC sites, 3 RWQCB sites, and 2 U.S. EPA sites selected monitored natural attenuation (MNA). Table 2-1 contains a list of all sites identified along with the project status as of March 2003.

2.1 Initial Site Identification

Initially, OPPTD contacted DTSC supervisors in the Site Mitigation and Brownfields Reuse Program (SMBRP) via e-mail requesting the site name and point of contact (POC) for DTSC-lead sites where ISB or MNA was used to remediate groundwater contaminated with chlorinated solvents. OPPTD also contacted the Hazardous Waste Management Program (HWMP) regarding corrective action sites tracked by the permitting section. Approximately 14 DTSC sites were identified by regional DTSC staff.

Next, OPPTD performed a cursory search of the Site Mitigation Property Program Database (SMPPD). Entries within the Calsites, the School Property Evaluation Program (SPEP), the Voluntary Cleanup Program Properties (VCPP), and the Unconfirmed Properties Referred to Another Local or State Agency (UPRALSA) were manually scanned for the following phrases: “in-situ bioremediation”, “monitored natural attenuation”, “enhanced bioremediation”, “chlorinated solvents”, “volatile organic compounds (VOCs)”, and “groundwater contamination”. If the profile’s Site History or Comments section contained one of these phrases, the profile was then reviewed and the site was categorized as an ISB site, a MNA site, a potential ISB or MNA site, or not applicable (NA).

Each site profile was evaluated based on the following criteria: (1) the contaminated media (e.g., groundwater), (2) the type of contamination (e.g., chlorinated solvents), (3) the description of the selected remediation system, and (4) the age of the system. Sites were categorized as ISB or MNA if groundwater was contaminated with chlorinated solvents and either ISB or MNA was identified as the remediation alternative. Sites categorized as potential ISB/MNA sites listed chlorinated solvents, VOCs, or specific chlorinated compound(s) (e.g., TCE, PCE) but had insufficient information on the contaminated media, remediation method, or system age. Sites categorized were excluded from further consideration if information was sufficient to determine: (1) site contamination was not due to chlorinated solvents, (2) site contamination did not affect groundwater, (3) the selected remediation alternative was not ISB or MNA, or (4) another type of remediation system (e.g., pump and treat) was installed recently (within the last two years).

Table 2-1. Summary of Results for Site Search

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
In-Situ Bioremediation						
Abandoned Manufacturing Facility Electro-Coatings, Inc.	RWQCB	In-situ Bioremediation (ISB)	Bioaugmented molasses	Pilot and full-scale	Implemented pilot on 8/95-2/96 and full-scale in 4/97.	1,1,1-Trichloroethane 1,1-Dichloroethane 1,1-Dichloroethene 1,2-Dichloroethane cis-1,2-Dichloroethene Ethane Ethene Hexavalent chromium Methane Tetrachloroethene trans-1,2-Dichlorethene Trichloroethene Vinyl chloride
Aerojet Area 20	DTSC	In-situ Bioremediation (ISB)	Lactate using bioaugmented dehalorespirers (KB-1)	Pilot study	Conducted in June 2001.	1,1-Dichloroethane 1,2-Dichloroethane Carbon tetrachloride Chloroform cis-1,2-Dichloroethene Ethene Perchlorate Tetrachloroethene Trichloroethene Vinyl chloride
Aerojet GET B	DTSC	In-situ Bioremediation (ISB)	Corn syrup	Pilot study	Conducted in August 2001.	Perchlorate
Alameda Naval Air Station Site 4, RABITT Test Cell	RWQCB	In-situ Bioremediation (ISB)	Regenesis HRC	Demonstration project	Implemented 2/2002.	1,2-dichloroethene Tetrachloroethene Trichloroethene Vinyl chloride

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Bay Area Drum	DTSC	In-situ Bioremediation (ISB)	Regenesis ORC	Full-scale	Implemented 3/2002.	1,2-Dichloroethane cis-1,2-Dichloroethene Petroleum hydrocarbons Tetrachloroethene trans-1,2-Dichlorethene Vinyl chloride Volatile Organic Compounds
Boeing	Unknown	In-situ Bioremediation (ISB)	Unknown	Pilot study	Under consideration as a pilot study site as of 2/2002.	Perchlorate
Caterpillar, Inc.	DTSC	In-situ Bioremediation (ISB)	Regenesis HRC	Pilot study	Implemented 11/2001.	Trichloroethene Volatile Organic Compounds
Dow Chemical Company	RWQCB	In-situ Bioremediation (ISB)	30% sodium formate, 60% sodium lactate, with a 56% ammonium polyphosphate microbial nutrient solution	Full-scale	Implemented 3/99.	Carbon tetrachloride Chlorinated solvents Chloroform Tetrachloroethene Trichloroethene Vinyl chloride
Edwards Air Force Base	DTSC	In-situ Bioremediation (ISB)	Unknown	Demonstration project	Unknown	Perchlorate
Edwards Air Force Base Site 19	DTSC	In-situ Bioremediation (ISB)	Toluene and hydrogen peroxide	Demonstration project	Conducted in 1998.	Trichloroethene
FMC Corporation East Brokaw Road	RWQCB	In-situ Bioremediation (ISB)	Regenesis HRC	Full-scale	Implemented 5/2000.	cis-1,2-Dichloroethene Tetrachloroethene trans-1,2-Dichlorethene Trichloroethene Vinyl chloride
Former Moffett Airfield Stationwide	U.S. EPA	In-situ Bioremediation (ISB)	Methane, toluene, phenol, oxygen, and hydrogen peroxide	Demonstration project	Implemented 3/96 - 3/97.	cis-1,2-Dichloroethene Tetrachloroethene trans-1,2-Dichlorethene Trichloroethene Vinyl chloride

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Former Moffett Naval Air Station Area North of Hangar 1	U.S. EPA	In-situ Bioremediation (ISB)	Propionic acid	Pilot study	Ongoing	BTEX cis-1,2-Dichloroethene Tetrachloroethene Trichloroethene Vinyl chloride
Jet Propulsion Laboratory OU-1/3	DTSC	In-situ Bioremediation (ISB)	Corn syrup	Pilot study	Workplan under development.	Carbon tetrachloride Perchlorate Tetrachloroethene Trichloroethene
Lemoore NAS Site 14	DTSC	In-situ Bioremediation (ISB)	Unknown	Unknown	RI/FS under development.	Trichloroethene
Long Beach Naval Complex IRP Site 14	DTSC	In-situ Bioremediation (ISB)	Regenesis HRC	Pilot study	Ongoing. Implemented in 7/2002.	cis-1,2-Dichloroethene Tetrachloroethene trans-1,2-Dichlorethene Trichloroethene Vinyl chloride
McClellan Air Force Base Site 22	DTSC	In-situ Bioremediation (ISB)	Toluene	Pilot study	Proposed. Workplan under development in 8/94.	Chlorinated solvents
McKesson Chemical Company	DTSC	In-situ Bioremediation (ISB)	Sucrose/yeast	Pilot study	Discontinued 5/2000.	1,1,1-Trichloroethane 1,1-Dichloroethane 1,1-Dichloroethene 1,2-Dichloroethane 1,2-dichloroethene Trichloroethene Vinyl chloride
Mercury Dry Cleaners	DTSC	In-situ Bioremediation (ISB)	Regenesis HRC	Pilot study	Implemented 11/2002.	1,2-Dichloroethane cis-1,2-Dichloroethene Petroleum hydrocarbons Tetrachloroethene trans-1,2-Dichlorethene Vinyl chloride

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Myers Drum	DTSC	In-situ Bioremediation (ISB)	Regenesis HRC	Full-scale	Implemented 5/2000.	1,1,1-Trichloroethane 1,1-Dichloroethane 1,1-Dichloroethene 1,2-Dichlorobenzene 1,2-Dichloroethane 1,2-dichloroethene 1,2-Dichloropropane Chlorobenzene Chloroethane Dichloromethane Tetrachloroethene Trichloroethene Vinyl chloride
Point Mugu Naval Weapons Station Site 24	DTSC	In-situ Bioremediation (ISB)	Lactic acid/oxygen/methane	Pilot study	Conducted Phase II 3/2002 and Phase I in 12/98.	Dichloroethene Ethene Methane Trichloroethene Vinyl chloride
Point Mugu Naval Weapons Station Site 6	DTSC	In-situ Bioremediation (ISB)	Lactic acid	Pilot Study	Implemented 9/2000.	1,1-Dichloroethane 1,1-Dichloroethene cis-1,2-Dichloroethene trans-1,2-Dichlorethene Trichloroethene Vinyl chloride
Raley Field	RWQCB	In-situ Bioremediation (ISB)	Lactic acid	Full-scale?	Ongoing	Trichloroethene
Rocket Manufacturing Plant	Unknown	In-situ Bioremediation (ISB)	Unknown	Unknown	Unknown	Perchlorate

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Romic Environmental Technologies	U.S. EPA	In-situ Bioremediation (ISB)	Molasses/cheese whey	Pilot study	Implemented 2/2001.	1,1-Dichloroethane Acetone BTEX cis-1,2-Dichloroethene Methyl ethyl ketone Methyl isobutyl ketone Tetrachloroethene Tetrahydrofuran Trichloroethene Vinyl chloride
San Leandro Regional Plume	DTSC	In-situ Bioremediation (ISB)	Regenesis HRC	Pilot study	Workplans under review.	Dichloroethene Tetrachloroethene Trichloroethene
Stauffer Chemical	DTSC	In-situ Bioremediation (ISB)	Soybean oil	Pilot study	Workplan under review.	1,2-Dichloroethane Vinyl chloride
Teledyne Singer	DTSC	In-situ Bioremediation (ISB)	Molasses	Pilot study	Implemented 8/2001.	1,1,1-Trichloroethane Dichloroethene Freon Tetrachloroethene Trichloroethene
Vandenberg Air Force Base IRP Cluster Site 32/35	DTSC	In-situ Bioremediation (ISB)	Molasses	Pilot study	Ongoing. Implemented	cis-1,2-Dichloroethene trans-1,2-Dichlorethene Trichloroethene
Vandenberg Air Force Base IRP Site 19	DTSC	In-situ Bioremediation (ISB)	Hydrogen peroxide	Unknown	RI/FS under development	Chlorinated hydrocarbons
Monitored Natural Attenuation						
Bay Area Drum	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Ongoing	1,2-Dichloroethane cis-1,2-Dichloroethene Petroleum hydrocarbons Tetrachloroethene trans-1,2-Dichlorethene Vinyl chloride
Beale Air Force Base Site 17	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Pilot study	Discontinued in 1999.	POL/Solvents

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Britz Fertilizer-Five Points	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Full scale clean up	Ongoing. Implemented in 6/99.	Benzene DDT Dibromochloropropane Dieldrin DNBP Prometryn Sodium chlorate Toluene Total petroleum hydrocarbons Toxaphene Xylene
Camp Pendleton OU 1, Site 9	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Implemented 1/97.	1,2,3-Trichlorobenzene 1,2-Dichloroethane 2-Butanone Acetone Antimony Bromomethane cis-1,2-Dichloroethene Mercury Naphthalene Nickel Tetrachloroethene Toluene Total petroleum hydrocarbons Trichloroethene
Chatham Brothers Barrel Yard	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Implemented ?	1,1,1-Trichloroethane Chlorinated solvents cis-1,2-Dichloroethene Polychlorinated Biphenyls Tetrachloroethene Trichloroethene Vinyl chloride
Chemcentral Corporation	RWQCB	Monitored natural attenuation (MNA)	Not Applicable	Unknown	Unknown	1,1,1-Trichloroethane Tetrachloroethene Toluene Total xylenes Trichloroethene
Edwards Air Force Base	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Pilot study	Unknown	Solvents

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Former Golden Eagle Refinery	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Implemented 12/2000.	BTEX Vinyl chloride
Fort Ord Army Base	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Pilot study	Ongoing. Implemented in 3/2000.	Carbon tetrachloride Chloroform
Foster-Gardner Chemical	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Implemented 3/97.	1,2-Dibromoethane 1,2-Dichloroethane 1,2-Dichloropropane Ammonia Benzene DDT Vinyl chloride Volatile Organic Compounds
General Electric-Oakland	DTSC	Monitored natural attenuation (MNA)	Unknown	Pilot study	Conducting the RI phase.	Volatile Organic Compounds
Jones-Hamilton Company	RWQCB	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Ongoing	1,1-Dichloroethane 1,2-Dichloroethane Benzene Pentachlorophenol Tetrachlorophenol Toluene Total xylenes
Lawrence Livermore National Laboratory Site 300, Landfill OU, Pit 6	U.S. EPA	Monitored natural attenuation (MNA)	Not Applicable	Full-scale	Ongoing.	Nitrate Perchlorate Trichloroethene Tritium
Lawrence Livermore National Laboratory Site 300, OU2, Bldg. 834 area	U.S. EPA	Monitored natural attenuation (MNA)	Not Applicable	Bench study	Not selected.	1,2-dichloroethene Nitrate Tetra-butyl-orthosilicate Tetra-kis-2-ethylbutylorthosilicate Trichloroethene
Linfinity Microelectronics, Inc.	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Unknown	Under evaluation	Volatile Organic Compounds

Site Name	Lead Agency	Remediation Type	Substrate Used	Project Scale	Project Status	Contaminant Name
Naval Telecommunication Station	RWQCB	Monitored natural attenuation (MNA)	Not Applicable	Unknown	Proposed verbally.	Solvents
North Island Naval Air Station Site 5	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Pilot study	Implemented 3/97.	1,1-Dichloroethene BTEX cis-1,2-Dichloroethene Ethene Tetrachloroethene trans-1,2-Dichlorethene Trichloroethene Vinyl chloride
SP-Purity Oil	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Unknown	Under consideration as part of RI/FS	1,2-dichloroethene Chlorinated solvents
Tracy Defense Depot San Joaquin BASWS	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Unknown	Updated RAP/ROD under development.	Tetrachloroethene Trichloroethene
Travis Air Force Base SD036	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Unknown	Unknown	Solvents
Vandenberg Air Force Base Cluster Sites 13/14/28	DTSC	Monitored natural attenuation (MNA)	Not Applicable	Pilot study	Implemented 5/2002.	1,1-Dichloroethene Carbon disulfide cis-1,2-Dichloroethene trans-1,2-Dichlorethene Vinyl chloride
Groundwater Monitoring						
Hunters Point Naval Shipyard Parcel B	DTSC	Groundwater Monitoring	Not Applicable	Unknown	RI/FS under development.	1,1,1-Trichloroethane BTEX Polychlorinated Biphenyls Tetrachloroethene Total petroleum hydrocarbons Trichloroethene

A list of potential ISB/MNA sites was then developed and DTSC project managers for each site on this list were contacted via e-mail to confirm the database information. OPPTD scheduled visits to each DTSC regional office to review available project files for each confirmed ISB and MNA site. File review consisted of but was not limited to reports (e.g., remedial investigation and feasibility studies, groundwater monitoring reports, five-year review reports, ISB or MNA project reports, etc.), work plans, and correspondence files available from regulatory agencies. Information pertaining to the site history, hydrogeology, groundwater sampling and monitoring results, fate and transport, etc., was collected for later evaluation.

Most DTSC sites were found to be either pilot studies or demonstrations. Only two DTSC sites implemented full-scale ISB systems while 6 DTSC sites implemented full-scale MNA systems. OPPTD expanded the site survey to identify additional full-scale ISB or MNA projects including those overseen by the RWQCB and U.S. EPA. Thirteen non-DTSC sites were identified where either ISB or MNA was implemented.

2.2 Characteristics and Commonalities of Sites Selected

Based on the results from the data collection effort, five (5) sites undergoing bioremediation to reduce chlorinated solvents in groundwater were selected for more detailed evaluation. All of the five sites were being remediated for tetrachloroethene (PCE), trichloroethene (TCE) or both. Two of the sites had significant amounts of additional compounds besides PCE and TCE that were targeted for remediation.

The plume size at these sites ranged from 0.06 acres to 18 acres. In most cases, the portion of the plume where bioremediation was implemented was far less than ½ the total plume. In one case the bioremediation was implemented as a “barrier” before groundwater reached a surface water body. Despite the various design configurations for implementing bioremediation, the biological process to be enhanced (reductive dechlorination) was the same in all cases, and so on this basis the sites are comparable.

The geological settings of the 5 sites varied from inland alluvial deposits to Bay Muds. However, all of the sites were being remediated for rather shallow groundwater in low permeability deposits. In some cases, there was little if any apparent gradient across the groundwater system. The overall groundwater flow velocities for the 5 sites were estimated to range from 0.01 ft/day to 0.3 ft/day. A groundwater velocity of 0.01 ft/day is essentially a “stagnant” system, accounting for less than 4 ft/yr movement.

Despite geographic variability, all sites were similar in that shallow, slow-moving groundwater resident in low-permeability deposits was being remediated. Thus, it was hoped that the adequacy of monitoring well networks (well spacing, density) and the relative success of various designs for amending groundwater could be evaluated for these general conditions.

A variety of carbon sources were used at the five sites included for detailed evaluation. While every carbon source has unique properties and - possibly - unique advantages, most practitioners of bioremediation recognize that bacteria can utilize a wide range of carbon sources. Therefore the results should be comparable between sites that utilize different carbon sources.

The general characteristics and conditions of the 5 sites evaluated are presented in Table 2-2. Raw data and trend graphs for each of the sites included in this report are available in Appendices B thru F.

Table 2-2. General Characteristics and Conditions at Five Selected Sites

Site Name	Site Size (acres)	Plume Size (acres)	ISB Design	Carbon source	GW Depth (ft bgs)	Hydraulic Gradient (ft/ft)	GW Velocity (ft/day)
Dow Chemical Co. (Pittsburg, Ca)	993	Western: 12 Central: 18 Northern: 8	Barrier	Propylene glycol/ ammonium polyphosphate	2-13	--	U: 0.01* D: 0.02-0.3*
Electro-Coatings (Emeryville, Ca)	0.9	--	Injection grid	Molasses	3.5-8	0.008	0.02
Myers Drum (Oakland, Ca)	1.6	0.06	Injection grid	Regenesis HRC	9-16	--	--
Romic Chemical (East Palo Alto, Ca)	14	--	Injection ring	A: Molasses B: Cheese whey	A: 4-25 B: 20-50	A: 0.001 B: 0.001	--
Teledyne-Singer (Palo Alto, Ca)	2.6	0.8	Barrier	Molasses	65	0.03-0.4	0.03

Note: U = Upgradient, D = Downgradient, -- = Not available
*Natural groundwater velocity

3 Data Evaluation

Many biological pathways have been identified and described that transform or degrade chlorinated solvents. The most robust and effective biological pathway – particularly the 2-carbon chlorinated solvents prevalent at many sites - is reductive dechlorination. As described in the literature, guidelines developed by the U.S. EPA, ITRC, and Air Force Center for Environmental Excellence (AFCEE), research studies and many field applications, the classical pattern of degradation of PCE through reductive dechlorination is:

PCE→ TCE→DCE→ VC→ ethene

Successful inducement or enhancement of reductive dechlorination can cause chlorinated solvents such as PCE and TCE to biodegrade to innocuous end products such as ethene. Ethene (or ethylene), is a harmless gas used to ripen bananas and other fruit that is readily degradable in the environment to carbon dioxide (CO_2) and water.

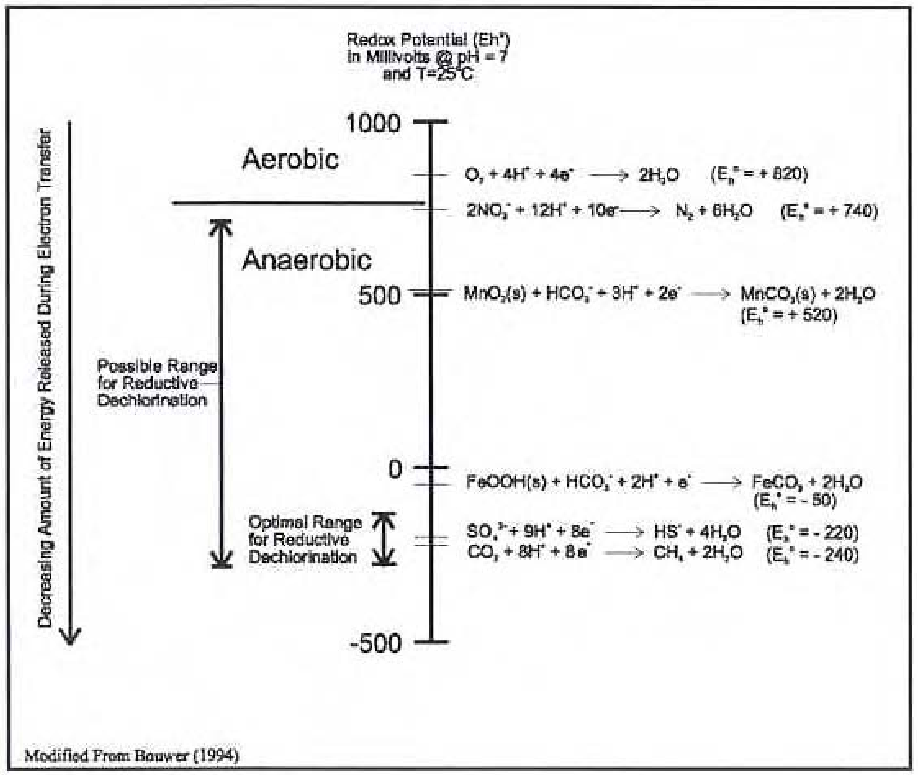
To successfully induce or enhance this process in groundwater, an anaerobic environment, moderate to strong reducing conditions, and the presence of microorganisms (bacteria) capable of carrying out the biochemical reactions are required. In many cases, the appropriate environmental and microbiological conditions are produced by adding a carbon source and nutrients. In some cases, the addition or augmentation with dechlorinating bacteria may be necessary.

Successful implementation of reductive dechlorination has been shown in small-scale pilot studies and to a lesser extent in larger-scale applications. A key aspect to these demonstrations is clear and focused objectives for the monitoring program to allow evaluation of the rates of degradation. Typically the monitoring on such projects includes more data collection points (wells), and frequent sampling at those monitoring points for a wide range of organic and inorganic analytes.

Reductive dechlorination may not be possible where groundwater conditions are not conducive for these biological reactions to occur. Highly aerobic aquifers are very poor candidates for reductive dechlorination of chlorinated solvents. At many sites, the dechlorination process can only proceed up to production of cis-1,2-DCE, and proceed no further. This phenomenon, “stalling,” has been the subject of considerable discussion in bioremediation circles.

The classical pattern of biological reductive dechlorination of PCE involves a cascading of concentration curves from PCE through ethene, with each subsequent daughter product being produced in stoichiometrically equivalent amounts to the parent compounds. The “cascade” proceeds through the eventual production of ethene, which is a harmless compound that is readily biodegradable.

Figure 3-1. Oxidation-Reduction Potentials for Various Reactions[1]



Modified From Bouwer (1994)

Commensurate with the pattern of biodegradation of the solvents is a pattern of uptake and production of inorganic compounds/ions, constituents, and geochemical parameters that are part and parcel of the biological reactions causing biodegradation. Recommended key parameters to monitor - but which may not be practical in all cases to measure - include oxygen, redox, carbon dioxide, alkalinity, chloride ion, iron, sulfate, pH, and nitrate. The "classical" pattern of geochemical parameters associated with reductive dechlorination is shown in Figure 3-1.

Readily available guidances can assist project managers recognize the patterns of chlorinated solvent biodegradation and geochemical indicators. However, while these patterns are often made apparent in highly-instrumented research projects, obtaining similar results is more of a challenge in full-scale remediation projects with specific objectives - where the distribution of contaminants can be very complex, where variables can be far more difficult to control, and where resources can be limited.

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[1] From the U.S. EPA, Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater, EPA600/R-98/128, September 1998, Appendix B, pg B3-34.

3.1 Evidence of Biodegradation

There are several indicators available to show that biodegradation of chlorinated solvents is occurring: (1) reduction in concentration/mass, (2) geochemical evidence, and (3) presence of desired biodegradation endproducts. Available data were evaluated in terms of these indicators in combination to assess the effectiveness of biodegradation for each of the five sites selected for detailed evaluation. Another indicator, microbial (laboratory) evidence, is also recommended in the bioremediation literature but a discussion is not included in this report since 4 of the 5 case study sites did not attempt to speciate the microbes at their particular sites.

3.1.1 Loss of Contaminant Mass

One indication that biodegradation may be taking place *in-situ* involves the presence, concentration, and distribution of the parent compound and daughter products. For example, if TCE is the parent compound, an increase in concentration of cis-1,2-DCE in groundwater (a daughter product of TCE), along with a decrease in TCE concentrations can be used as an indicator that biodegradation is occurring.

The presence of VC (a degradation product of cis-1,2-DCE) and ethene (a degradation product of VC) can also be used as indicators of the biodegradation process. Cis-1,2-DCE, VC and ethene are particularly important since they are indications that the biodegradation pathway is going to completion. They are also important in that they result from biological activity, whereas parent compounds (PCE and TCE) can occur from co-disposal or for TCE from degradation. Cis-1,2-DCE, vinyl chloride, and ethene thus are direct measures of biological activity, and their presence (compared to non-detect) is encouraging. For parent compounds (PCE and TCE), any number of confounding patterns of concentration may occur due to disposal patterns, degradation or dilution through pumping/recirculation.

The breakdown pathway for PCE and carbon tetrachloride are provided below as a reference. Degradation pathways have been identified for other chlorinated compounds (e.g., TCA, DCA), and are presented in available guidances on in-situ bioremediation.

PCE and daughter product breakdown mechanism:

PCE: $C_2Cl_4 + H^+ + 2e^- \rightarrow C_2Cl_3H + Cl^-$
TCE: $C_2HCl_3 + H^+ + 2e^- \rightarrow C_2Cl_2H_2 + Cl^-$
cis-1,2-DCE: $C_2Cl_2H_2 + H^+ + 2e^- \rightarrow C_2ClH_3 + Cl^-$
VC: $C_2ClH_3 + H^+ + 2e^- \rightarrow C_2H_4 + Cl^-$

Carbon tetrachloride and daughter product breakdown mechanism:

Carbon tetrachloride: $CCl_4 + 2e^- + H^+ \rightarrow CHCl_3 + Cl^-$
Chloroform: $CHCl_3 + 2e^- + H^+ \rightarrow CH_2Cl_2 + Cl^-$
Methylene chloride: $CH_2Cl_2 + 2e^- + H^+ \rightarrow CH_3Cl + Cl^-$
Chloromethane: $CH_3Cl + 2e^- + H^+ \rightarrow CH_4 + Cl^-$

For this evaluation effort, contaminant concentration data were plotted and evaluated for decreasing trends in the parent compounds (i.e., PCE and carbon tetrachloride (CCl_4)). The data were also evaluated for corresponding increasing/decreasing trends of daughter products similar to the classic biodegradation pattern expected for the particular parent product.

Looking for the presence (especially the increase) of the final products (ethene, ethane, methane) was a focus of the evaluation. As discussed, clear increases in these compounds would provide support that biodegradation is occurring, even through the patterns of concentrations of parent compounds may be confounding.

Note that in the reduction reactions presented above chloride ions are produced. Evolution of chloride is a geochemical marker of biodegradation. Geochemical indicators of biodegradation are discussed below.

3.1.2 Geochemical Indicators

The another indication evaluated the presence of enhanced geochemical conditions based on the following criteria: (1) depletion of ferric iron and manganese (Mn^{4+}), (2) reduction of sulfate to sulfide, and nitrate to nitrite, (3) low dissolved oxygen concentrations (< 2 mg/L), (4) redox conditions <750 mV, (5) increased alkalinity, (6) pH between 6.0 and 8.5, (7) reduction of phosphate and ammonia, and (8) evolution of chloride ions. Many of these geochemical indicators can be blurred by background conditions where concentrations of various inorganic constituents are orders of magnitude higher than any change that would result from biodegradation.

After depletion of dissolved oxygen (DO), anaerobic microbes will use nitrate as an electron acceptor, followed by iron (III), then sulfate, and finally carbon dioxide (methanogenesis). Each sequential reaction drives the groundwater redox conditions (ORP) downward into the range within which reductive dechlorination can occur. Reductive dechlorination is most effective in the ORP range corresponding to sulfate reduction and methanogenesis, but dechlorination of PCE and TCE also may occur in the ORP range associated with denitrification or iron (III) reduction. Dehalogenation of DCE and VC generally are restricted to sulfate reducing and methanogenic conditions (U.S. EPA, September 1998).

An increase in the alkalinity of ground water above background may be produced when carbon dioxide produced by biological activity reacts with carbonate minerals in the aquifer. Field indications of biological activity may be identified by increased alkalinity, compared to background wells, from carbon dioxide due to biodegradation of the pollutants (U.S. EPA, September 1998).

Carbon dioxide, although not measured at each of the study sites, provided an additional indication of biodegradation activity. As with the hydrocarbon gases that are endproducts of biodegradation, increases in the concentration of carbon dioxide may be attributable to biodegradation. Carbon dioxide measurements can help to resolve confounding patterns that can occur for other geochemical indicators.

3.1.3 Data Trends

3.1.3.1 Data Trends – Qualitative Analysis

The biodegradation activity at each well selected was evaluated based on the presence of the following conditions: (1) contaminant mass loss with daughter products, (2) enhanced geochemical conditions, and (3) elevated dissolved gases (i.e., methane/ethane/ethene). The biodegradation activity was then rated: (1) highly enhanced (HE) if the data showed all three conditions were present, (2) moderately enhanced (ME) if two of the 3 conditions were present, (3) slightly enhanced (SE) if one condition was present, (4) not enhanced (NE) when none of these conditions were present, and (5) unknown if there was insufficient data.

3.1.3.2 Data Trends – Quantitative Analysis

For plotting purposes and subsequent analysis, concentration data were converted from micrograms per liter (µg/L) to micromoles per liter (µM/L) for each parent and daughter product compound. This allowed results to be analyzed on a stoichiometric basis. The total contaminant mass was determined by adding the molar concentrations for the parent and daughter products in each sample (i.e., adding molar concentration of PCE, TCE, cis-1,2-DCE, and VC).

Hydrocarbon end products were not included in the calculation of the “total” mass for two reasons: (1) as a practical matter, they were rarely measured, and (2) “treatment” is undertaken to remove the parent (chlorinated) compounds. It was hoped that tracking “total contaminant mass” as defined might smooth out spurious results that arise from variability due to sampling.

The data were reviewed on the whole to determine if a trend could be established. In some cases establishing a trend was problematic due to highly fluctuating detection limits. If the detection limits were below the last actual reported concentration value, then the data point was plotted at the detection limit. Otherwise the data point was left blank if the detection limit was higher than the previous data point or all sample data were reported at the detection limit.

Biodegradation was considered to be occurring if: (1) the overall parent compound (PCE, TCE, CCl4) concentration trend decreased over time, (2) the overall daughter product (i.e., 1,2-DCE, vinyl chloride, methylene chloride, and chloroform) concentration trend increased, and (3) the overall end product (ethene, ethane, methane) concentration trend increased as daughter product concentrations decreased. Decreases in parent compound concentrations with no observed increases in daughter product and end product concentrations alone were not considered sufficient evidence of biodegradation occurring since other site conditions such as dilution may have influenced the results.

3.1.4 Summary of Data Evaluation

Four separate analyses were performed on groundwater monitoring data from the five sites included in this study:

(1) daughter products,
(2) geochemical indicators,
(3) dissolved hydrocarbon end products (gases), and
(4) trend analysis (mass destruction).

Collectively these analyses provide a means of measuring and quantifying the performance of bioremediation of chlorinated solvents in groundwater. Where possible, the level of enhancement was ranked (HE, ME, SE), and calculation of a rate of destruction of a parent compound was calculated.

By looking for several possible indicators of biodegradation, it was hoped that a “better” or “preferred” approach for reporting on biodegradation projects could be determined. It was also intended to look for every reasonable indication that biodegradation was occurring, and that treatment (complete, destruction of the targeted compounds) could be attributed to the remediation project. In short, every effort was made to credit the bioremediation process with being effective in treating chlorinated solvents.

4 Selected In-Situ Bioremediation Sites Evaluated

4.1 Myers Drum

Summary

A pilot study was conducted at the former Myers Drum site in the groundwater formation, located 14-19 feet bgs. One-hundred and five (105) injection points were installed in a grid pattern over a 163-foot by 124-foot area where 4,230 lbs of HRC was injected during one injection event in May 2000. Seven monitoring wells were sampled over a 6-month period for PCE, TCE, cis-1,2-DCE, VC and select geochemical parameters.

After 262 days, concentrations of PCE, TCE and cis-1,2-DCE in monitor well OW-1, had decreased 89%, 77%, and 47%, respectively, while vinyl chloride concentrations increased 32%. OW-1 was located in the "core" area of the plume with highest vinyl chloride concentration prior to the pilot study. By the time the pilot was started vinyl chloride concentrations at this well location had decreased substantially. At monitor well OW-2 which had the highest reported concentrations during the pilot study, PCE concentrations were increased by 39% while TCE, cis-1,2-DCE and VC concentrations were reduced by 4%, 10%, and 11%, respectively.

Site Background

The Myers Drum site was a drum recycling facility located in a commercial, industrial and residential area. The site is situated along the East Bay Plain of the San Francisco Bay in the Berkeley Plain subarea at approximately 35 feet above mean sea level. The nearest surface water body is the San Francisco Bay, which is approximately 4,000 feet west of this site. Due to poor drum recycling practices, there were periodic, massive releases of hazardous wastes at the site.

Soils at the site were contaminated with metals (lead, zinc, and arsenic); volatile organic compounds (toluene, xylene, and propanol); semivolatile organic compounds (naphthalene and phenol); and total petroleum hydrocarbons. Two localized groundwater plumes were also identified at the site. In May 1996, a remedial action plan was approved, which included building demolition, soil removal and the installation of a groundwater remediation system. As part of the March 31, 1999 Phase I remedial action, approximately 22,500 tons of contaminated soil was excavated and disposed of off-site to satisfy the residential cleanup level requirements. About 20,000 gallons of water were generated during excavation and were transported off-site.

As part of the Remedial Alternatives Analysis, an in-situ bioremediation pilot study using the Regenesis Hydrogen Releasing Compound (HRC) was conducted from May 2000 to February 2001. According to the consultant's report, the HRC technique was able to reduce contamination levels, but the groundwater cleanup goal of the MCL was not achieved.

In November 2002, Myers Drum backfilled an excavation that was located over an area of shallow localized groundwater contamination. More than 57,000 gallons of groundwater was periodically pumped from the excavation into a tank for approximately two months in an effort to remove volatile organic compound contamination. The last round of sampling indicated that groundwater cleanup levels were not achieved. Prior to backfilling the excavation with pea gravel, piping was installed and more than 74,000 gallons of groundwater in the excavation was pumped. In October 2003, some of the pea gravel was removed and replaced with clay soil to minimize vapor migration from the groundwater to the soil surface. The RAP was then modified to allow for on-going groundwater monitoring at 2 monitoring wells. Groundwater sampling results indicated that VOC concentrations had been reduced greatly even though the concentration did not meet the RAP goals. The groundwater was to be either monitored for 5 years, until monitored natural attenuation reduces VOC concentrations to 1996 RAP groundwater cleanup goals, or until DTSC determines groundwater monitoring can cease.

Site Geology/Hydrogeology

The top layer consists of 3.5 to 7 feet of engineered fill placed as part of the soil removal action conducted at the site. Underlying the engineered fill is a sequence of alluvial deposits that fall into three broad categories: (1) a fine-graded clay and clayey sand soils with a thickness ranging from 9 to 16 feet that comprises the water table aquifer, (2) a low permeability clay and sandy clay aquitard ranging in thickness from 2 to 4 feet, and (3) a medium to coarse-grained sand and clayey sand with gravel interbeds, that comprises the underlying semi-confined aquifer.

As part of the Remedial Investigation, a slug test was performed on the shallow groundwater aquifer and yielded a hydraulic conductivity ranging from 4.9×10^{-2} cm/sec to 9.8×10^{-3} cm/sec. Since the slug test only measures a small volume of the aquifer, an aquifer pump test was performed in 2000 to verify the aquifer hydraulic characteristics.

Aquifer pump tests were conducted around PW-1 where the flow rate was determined to be 0.89 gpm. PW-1 was dewatered after approximately 20 minutes of pumping with no appreciable responses observed in OW-2 thru OW-4. The water level rose about 3 inches in OW-1, which is 10.4 feet downgradient from PW-1. After 100 minutes, the water table recovered 7-inches (0.57 feet) in PW-1. Additional pump tests were not conducted due to the low permeability and slow recovery observed in the shallow groundwater aquifer.

Project Description

Pilot Study

Regenesis designed the HRC injection grid to overlay an area 163 feet by 124 feet where the vinyl chloride plume concentration was 1.0 µg/L. This grid is presented in Figure 4-1. The vinyl chloride plume area was divided into two areas; (1) the core area where vinyl chloride concentrations exceeded 100µg/L, and (2) the area where vinyl chloride concentrations were between 1.0 and 100 µg/L. The HRC injection grid consisted of 105 injection points:18 points in the core area, 2 points in the vicinity of Well W-6 (not shown in Figure 4-1), and the remainder in the area where vinyl chloride concentrations were less than or equal to 100 µg/L.

Each injection point was installed by advancing 1⅛" probe to a depth of 14 to19 feet bgs using the Geoprobe 6600 direct-push technology. The total depth of each push was based on the groundwater measured at each location during the direct-push operation. Once the desired depth was reached, the probe was pulled back and HRC was injected up to a depth of 6 feet bgs. HRC was injected into each push-hole using a 1,500-psi prototype Geoprobe pump developed specifically for injecting HRC. Due to its high viscosity, the HRC required heating so it could be pumped and injected into the formation. Approximately 90 pounds (9 pounds per foot) of HRC were injected into each of the push-holes located in or near the core area. For all other injection points, approximately 30 pounds (3 pounds per foot) of HRC was injected. It was estimated a total of 4,230 lbs of HRC was injected. Back pressure was observed at injection points where more than 30 pounds of HRC was injected. HRC injections over the grid were initiated and completed on May 22, 2000.

Baseline groundwater samples were collected from seven on-site monitoring wells (W-6, W-10, PW-1, OW-1, OW-2, OW-3 and OW-4) on May 11 and 12, 2000. These seven on-site monitoring wells were then sampled six times over a 7-month period between June 27, 2000 and February 8, 2001. Groundwater samples collected were analyzed for the parameters listed in Table 4-1 below unless otherwise noted.

Table 4-1. Groundwater Analyses By Well at the Former Myers Drum Facility

Well No.	Field Parameters	U.S. EPA Analytical Methods							
		8260	300.0[a]	376.2[b]	415.2[c]	6010[d]	300.0[e]	310.1[f]	RSK175[g]
W-6	x	x							
W-10	x	x							
PW-1	x	x	x	x	x	x	x	x	x
OW-1	x	x	x	x	x	x	x	x	x
OW-2	x	x	x[i]	x[i]	x[i]	x[i]	x[i]	x[h]	x[h]
OW-3	x	x	x	x	x	x	x	x	x
OW-4	x	x	x	x	x	x	x	x	x

Field parameters consist of pH, temperature, specific conductivity, and dissolved oxygen. No ORP values were available.

[a] Analysis for nitrates, sulfate, chloride

[b] Analysis for sulfide

[c] Analysis for total organic carbon

[d] Analysis for total and dissolved iron and manganese

[e] Analysis for metabolic acids (acetate, burate, lactate, and propiate)

[f] Analysis for alkalinity

[g] Analysis for dissolved gases (methane, ethane, and ethene)

[h] Only one sample from this well was analyzed by this method.

[i] Two samples from this well were analyzed by this method.

Project Performance

Appendix C contains tables and graphs of the groundwater monitoring results for all seven wells monitored as part of the pilot study including baseline concentrations. Figures 4-2 through 4-8 present graphs with concentration and select geochemical parameter trends. These figures also present tables with qualitative and quantitative indications of biodegradation conditions at each well.

Over the nine month monitoring period for the pilot project, HRC injections didn’t appear to enhance biodegradation at any well except OW-1. PCE concentrations decreased in wells where concentrations were either initially low (PW-1 at <25 µg/L) or moderate (OW-1 at 360 µg/l and OW-3 at 170 µg/L). At the highest concentration well, OW-2, PCE concentrations fluctuated between 5,400-13,000 µg/L. Increases in daughter product concentrations (TCE, cis-1,2-DCE, and vinyl chloride) appeared independent of reduced PCE concentrations at all wells.

Anaerobic conditions were present based on DO values (<2.0 mg/L) at all wells with pH values ranging between 6.5 and 8.5 except at OW-2 which ranged from 9.33 -11.28. ORP values were not recorded for any monitoring well during the pilot study. Total and ferrous iron concentrations in most wells decreased except at OW-3 where they increased. Sulfate concentrations remained constant in OW-1 and OW-4; increased in OW-3; decreased in PW-1; and was not determined in OW-2. Total organic content (TOC) concentrations decreased in all wells except OW-3. Alkalinity appeared to fluctuate independent of the TOC. At OW-3, a sulfide peak was observed which didn’t correspond to a decrease in sulfate concentrations. For W-6 and W-10, geochemical data was not available for many parameters making it difficult to assess whether enhanced conditions were present. (Refer to Figure C-8 thru Figure C-21 in Appendix C).

After 262 days, PCE, TCE, cis-1,2-DCE and vinyl chloride concentrations were compared to the 5/11/2000 baseline concentrations. Concentration trend graphs for W-6, W-10, PW-1, OW-1, OW-2, OW-3, and OW-4 are presented in Figures 4-2 thru 4-8. Concentrations in OW-1, one of the “core” area wells had decreased 89% for PCE, 77% for TCE, and 47% for cis-1,2-DCE, while vinyl chloride concentrations increased 32%. For OW-2, TCE, cis-1,2-DCE, and vinyl chloride concentrations decreased 4%, 10%, and 11%, respectively while PCE concentrations increased 39%.

It should be noted that prior to the pilot study vinyl chloride concentrations at PW-1 and OW-1 decreased substantially. This reduction is based on comparing the October 29, 1999 data to the May 11, 2000 data which are presented in Table 4-2 below. TCE and cis-1,2-DCE concentrations also decreased greatly in both these wells while they increased in OW-3 and OW-4. PCE concentrations in OW-1 and OW-3 increased. However, a trend for PCE in OW-4 and PW-1 could not be determined. The cause of these changes was not documented.

Table 4-2. Comparison of October 1999 and May 2000 Sample Results at the Former Myers Drum Facility

	PCE			**TCE**			**cis-1,2-DCE**			**Vinyl Chloride**		
Well Number	**10/29/99 (µg/L)**	**5/11/00**	**% Diff**	**10/29/99 (µg/L)**	**5/11/00**	**% Diff.**	**10/29/99 (µg/L)**	**5/11/00**	**% Diff.**	**10/29/99 (µg/L)**	**5/11/00**	**% Diff.**
OW-1	82	360	-339%	970	520	46%	2300	580	75%	1500	190	87%
OW-3	150	170	-13%	68	91	-34%	150	140	7%	18	35	-94%
OW-4	4.1	<10	--[a]	44	64	-45%	33	240	-627%	5.2	10	-92%
PW-1	<100	<25	--[a]	19000	<25	99.9%	15000	<25	99.8%	7800	<13	99.8%

[a] The percent difference was not calculated because the baseline or final sample concentration was below the detection limit.

Project Costs

The following costs were provided as part of the remedial alternatives analysis prepared by TRC in the document entitled “Groundwater Aquifer Evaluation Report, Remedial Alternatives Analysis, HRC Injection Pilot Study Workplan”. The estimated cost was a total capital cost of $145,000 and a total operation and maintenance cost of $22,000 over three years that included:

- Injecting HRC initially into 103 borings, installed on a 10-to-20 foot grid,
- Injecting HRC into 35 additional borings in the hot spot area if the COC concentrations were in excess of the proposed cleanup goals after one year of groundwater monitoring, and
- Monitoring the groundwater for three years that includes collecting groundwater samples every 6 weeks for the first 6 months at existing wells and analyzing for

contaminants of concern, and then collecting groundwater samples every 3 months for one year.

The project manager estimated the costs for this project were to be $25,000 for drilling, $35,000 for the HRC injections, and $30,000 for chemical analyses and reporting.

Summary Observation and Lessons Learned

Technology performance is generally measured with respect to a technology's ability to achieve pre-established goals or objectives. Neither the pilot project workplan nor report identified project objectives. The overall site goals such as groundwater clean-up levels and timeframe would have been useful in assessing how well the technology performed and its ultimate applicability to this specific site. Also lacking were specific objectives on concentrations of total organic compounds in downgradient monitoring wells to assess whether conditions were being maintained to enhance in-situ bioremediation.

Detection limits used in the first VOC sampling round and subsequent VOC sampling rounds were higher than the baseline values collected approximately a month prior to the HRC injections. The report does not explain this. Due to the high detection limit, it is difficult to analyze for trends especially when the detection limits are greatly raised between sampling events.

The data analysis in the report does not provide a discussion on how key parameters influence or affect the biological process and may have differed from initial assumptions. The data analyses only reports favorable biological results on a well by well basis. Not discussed are data that provide questionable or inconclusive evidence that the technology was effective.

Reference

Department of Toxic Substances Control (DTSC), Calsites Site Mitigation Program Properties Database (SMPPD) Profile Report, no date.

Department of Toxic Substances Control (DTSC), Fact Sheet: Former Myers Drum Site Proposed Change to the Remedial action Plan, Oakland, CA, November 2003.

TRC, HRC Injection Pilot Study Report Myers Container Corporation Former Drum Reconditioning Facility, 6549 San Pablo Avenue, Oakland, CA, June 2001.

TRC, Groundwater Aquifer Evaluation Report Remedial Alternatives Analysis HRC Injection Pilot Study Workplan, April 2000.

Figure 4-1. HRC Injection Grid for the Former Myers Drum Facility

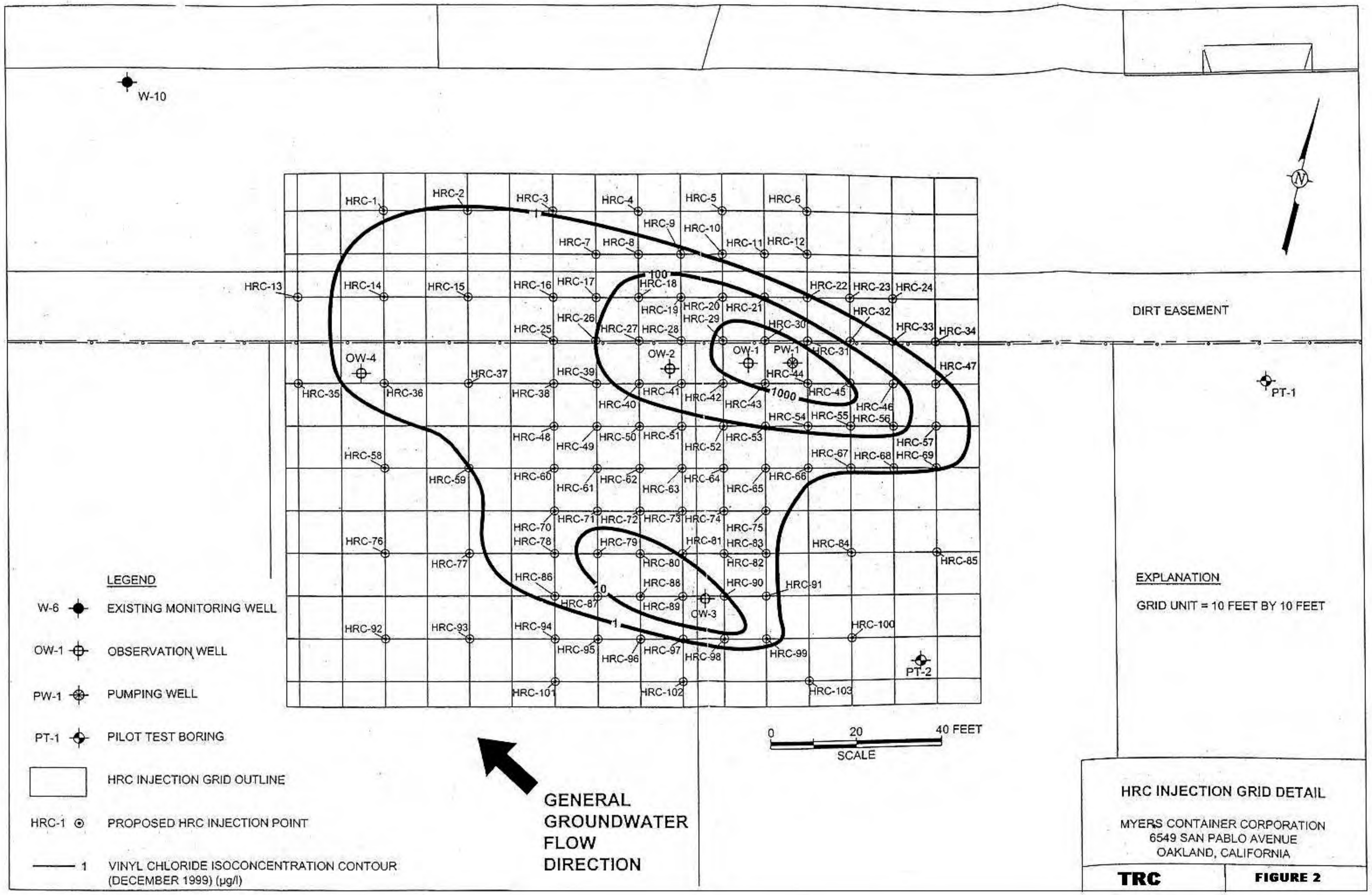
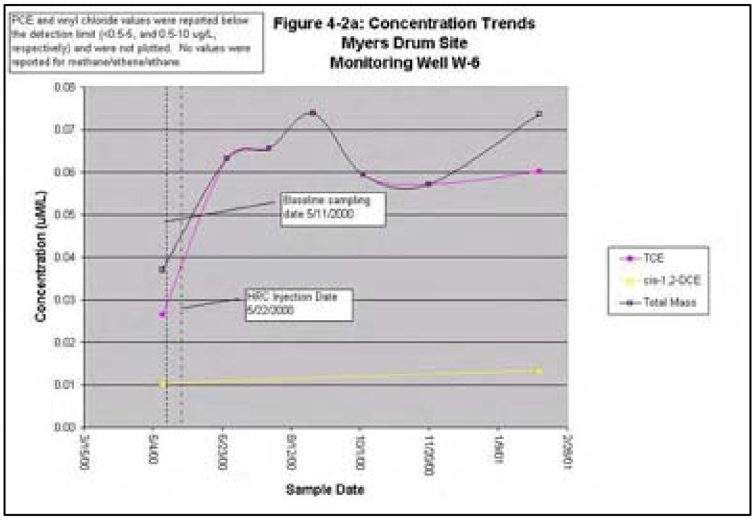
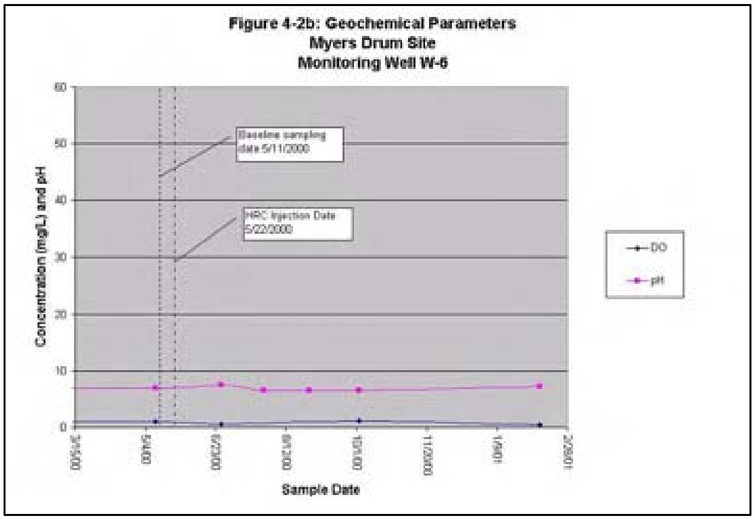


Figure 4-2. Data Analyses for Monitoring Well W-6 at the Myer Drum Facility





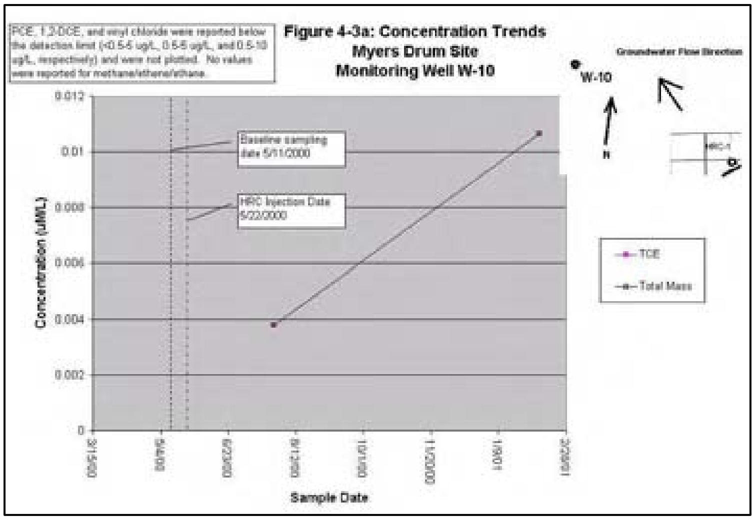
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
W-6		-	-				NE

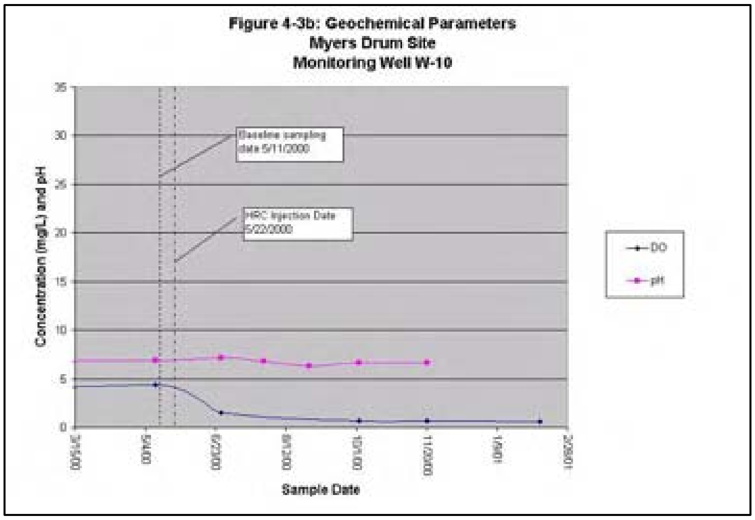
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{262}	% reduced	C_o (µg/L)	C_{262}	% reduced	C_o (µg/L)	C_{262}	% reduced	C_o (µg/L)	C_{262}	% reduced
W-6	<1	<0.5	--	3.5	7.9	-126%	<1	1.3	--	<0.5	<0.5	--

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. "Core" area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

Figure 4-3. Data Analyses for Monitoring Well W-10 at the Myers Drum Facility



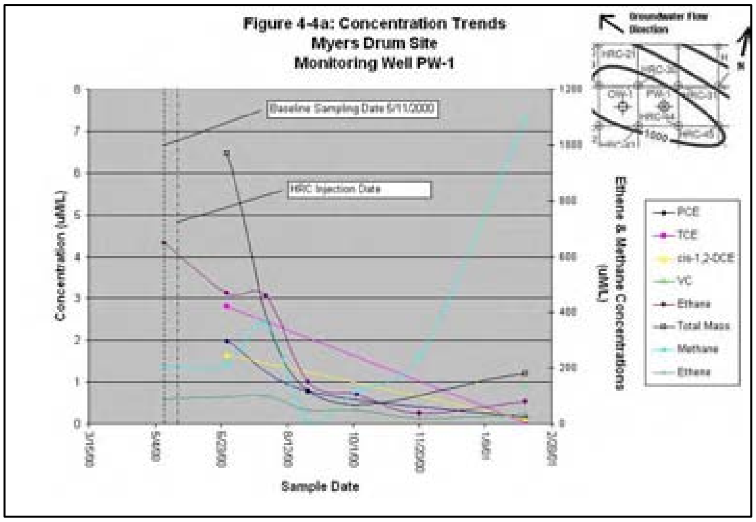


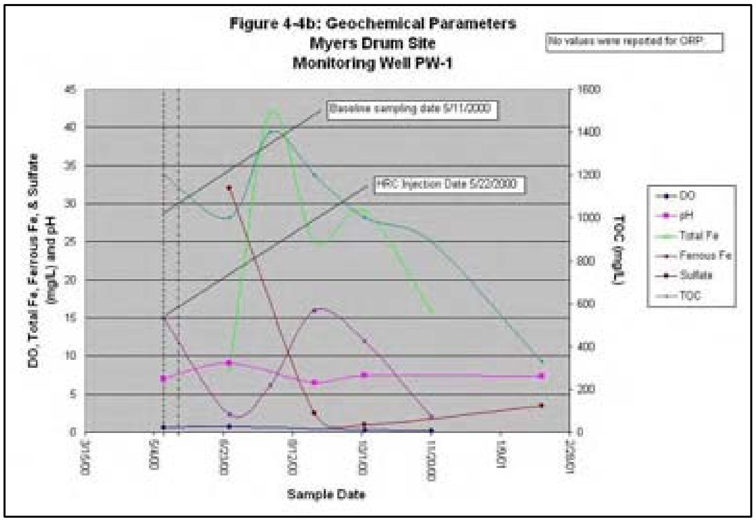
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
W-10		-					NE
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced							

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced
W-10	<5	<5	--	<5	1.4	--	<5	<5	--	<10	<0.5	--

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. "Core" area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

Figure 4-4. Data Analyses for Monitoring Well PW-1 at the Myers Drum Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
PW-1	+	+	-		+	-	ME

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced
PW-1	<25	<25	--	<25	4.2	--	<25	11	--	<13	56	--

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. "Core" area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

Figure 4-5. Data Analyses for Monitoring Well OW-1 at the Myers Drum Facility

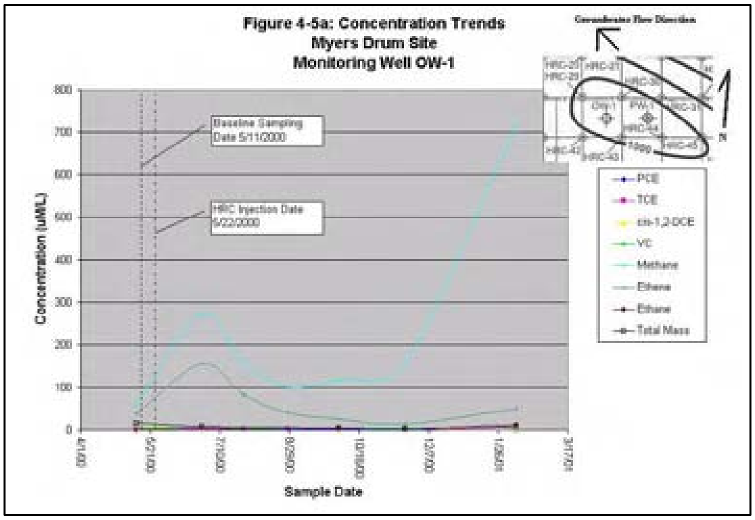


Figure 4-5a: Concentration Trends
Myers Drum Site
Monitoring Well OW-1

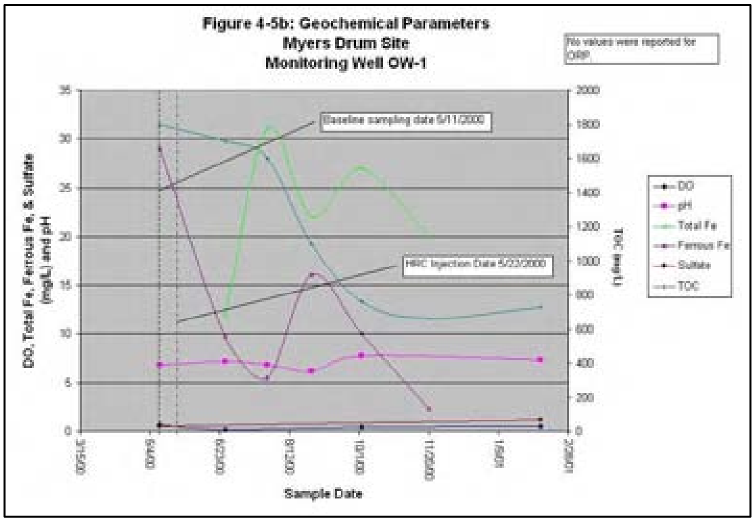


Figure 4-5b: Geochemical Parameters
Myers Drum Site
Monitoring Well OW-1

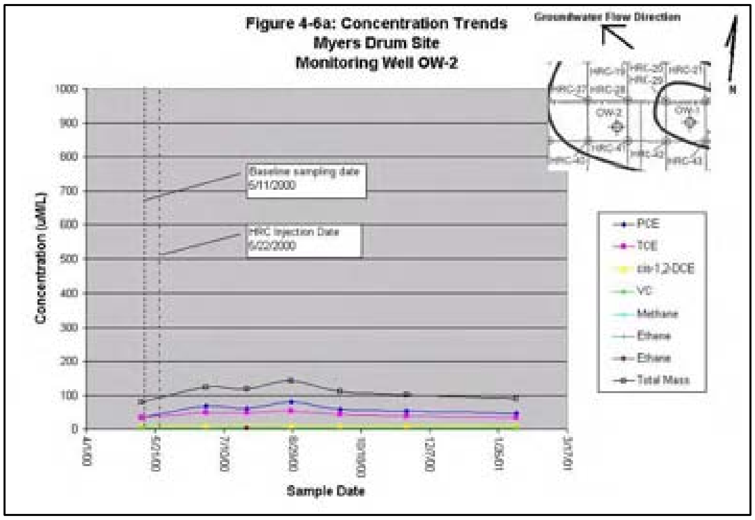
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
OW-1	+	+	+	+	-	+	ME

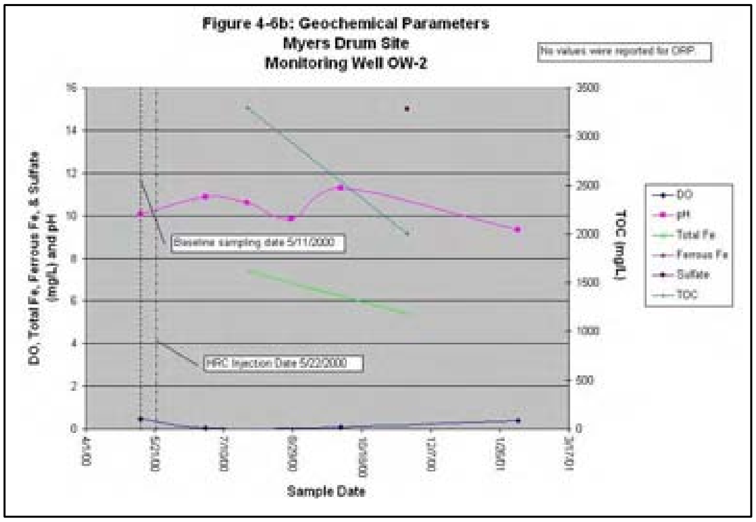
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{262}	% reduced	C_o (µg/L)	C_{262}	% reduced	C_o (µg/L)	C_{262}	% reduced	C_o (µg/L)	C_{262}	% reduced
OW-1	360	38	89%	520	120	77%	580	310	47%	190	250	-32%

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. "Core" area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

Figure 4-6. Data Analyses for Monitoring Well OW-2 at the Myers Drum Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
OW-2	-	0	0	0			NE
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced							

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o	C_{262}	% reduced	C_o	C_{262}	% reduced	C_o	C_{262}	% reduced	C_o	C_{262}	% reduced
	(µg/L)			(µg/L)			(µg/L)			(µg/L)		
OW-2	5400	7500	-39%	4500	4300	4%	960	860	10%	180	160	11%

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. “Core” area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

Figure 4-7. Data Analyses for Monitoring Well OW-3 at the Myers Drum Facility

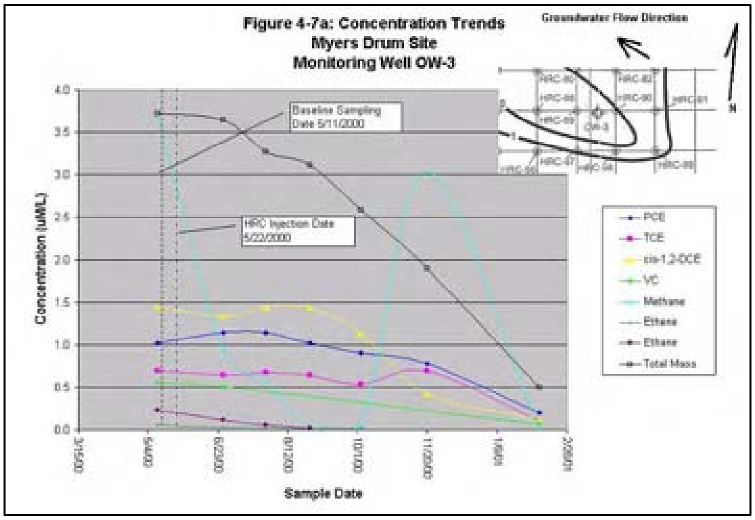


Figure 4-7a: Concentration Trends
Myers Drum Site
Monitoring Well OW-3

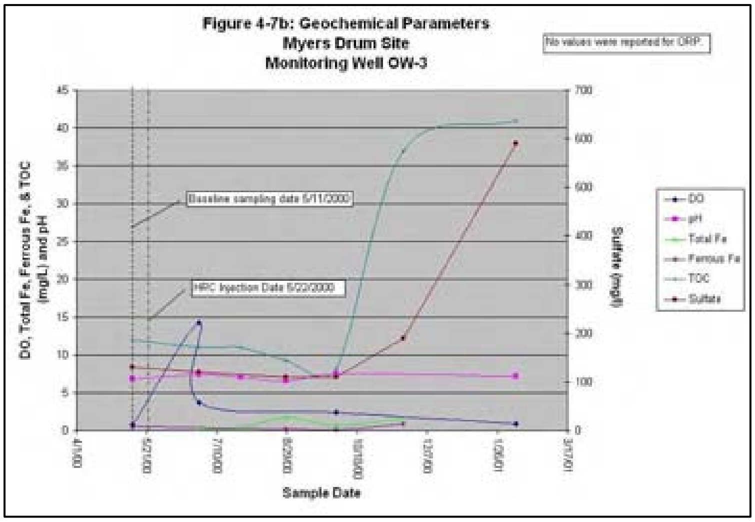


Figure 4-7b: Geochemical Parameters
Myers Drum Site
Monitoring Well OW-3

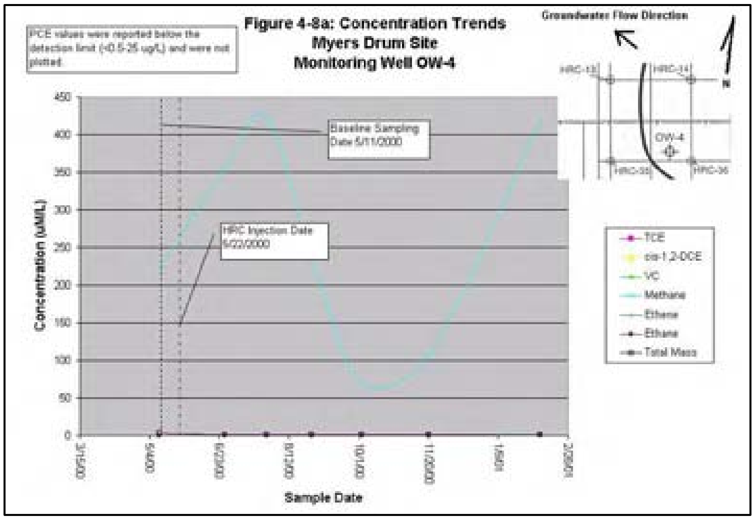
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
OW-3	+	+	-	0	-	-	SE

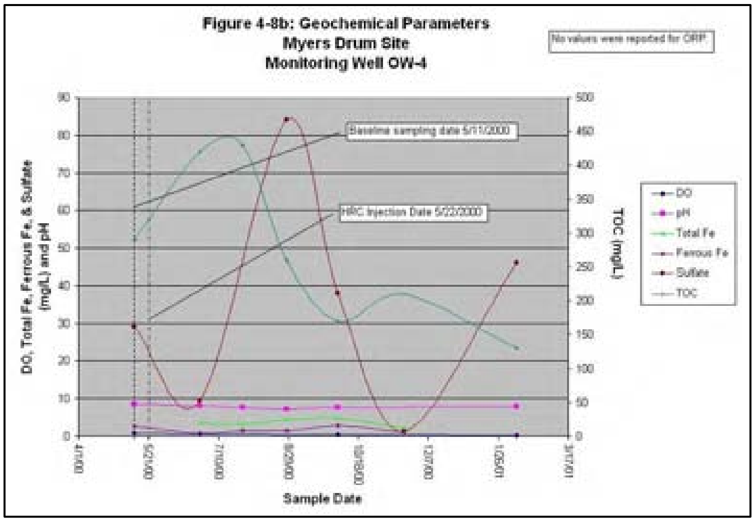
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced
OW-3	170	33	81%	91	14	85%	140	12	91%	35	4.3	88%

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. "Core" area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

Figure 4-8. Data Analyses for Monitoring Well OW-4 at the Myers Drum Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
OW-4		-	-	0		+	SE

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced	C_o (µg/L)	C_{262} (µg/L)	% reduced
OW-4	<10	<0.5	--	64	11	83%	240	60	75%	10	10	0%

Note: C_o is the baseline concentration for samples collected on 5/11/2000.
C_{262} is the concentration for samples collected on day 262 (2/8/2001).
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day 262. "Core" area wells consist of OW-1 and OW-2, which are located within the groundwater plume where concentration are greater than 1000 µg/L and 100 µg/L, respectively.

4.2 Romic Chemical Company, East Palo Alto Facility

Summary

A pilot study was conducted at the Romic Chemical facility where groundwater is encountered in 2 aquifer zones; the A-zone from 7.5-21 feet bgs and B-zone from 20-49.7 feet bgs. A total of 6 monitoring wells and 8 injection wells were installed: 3 monitoring wells and 4 injection wells in the A-zone, and 3 monitoring wells and 4 injection wells in the B-zone. A total of 1,600 gallons of a 1:10 molasses:water solution was injected into the A-zone while 800 gallons of a 3:1 cheese whey:water solution was injected into the B-zone. Six monitoring wells were sampled over a 4-month period and monitored for PCE, TCE, cis-1,2-DCE, VC and select geochemical parameters.

Biodegradation in the B-zone which had the highest reported concentrations reported decreases in PCE from 17-70% and TCE from 78-97%, respectively. However, the biodegradation process appears to have stalled at cis-1,2-DCE where the concentration was reported to increase from 400-1043%.

Site Background

Romic Chemical Company (Romic) is a 14-acre treatment/storage facility located in East Palo Alto, California near the western shore of the San Francisco Bay, and bordered by tidal sloughs that are tributary to the Bay. Romic has received hazardous waste from industries and household hazardous waste collection programs that it either recycled for reuse on-site, or treated for off-site disposal. Most of Romic's business involved processing solvent wastes and wastewater from a variety of sources including paint, ink, recording tape, adhesive, automotive, and electronics industries.

In 1988, Romic entered into an Administrative Order of Consent (AOC) with EPA that required Romic to investigate the nature and extent of groundwater contamination. The investigation found that shallow groundwater was primarily contaminated with VOCs. The highest VOC concentrations in the subsurface are associated with three areas: the former pond area beneath the northern drum storage buildings, the central processing area in the center of the facility, and the southwestern portion of the site. Figure 4-9 shows the potential source areas and the wells at the site. About 50 to 60 percent of the contaminants detected were chlorinated solvents including PCE, TCE, cis-1,2-DCE, 1,1-DCA and vinyl chloride. Other contaminants detected included aromatic VOCs (benzene, toluene, and ethylbenzene), ketones (acetone, MEK, and MIBK), and tetrahydrofuran. SVOCs have also been detected but to a lesser extent and at lower concentrations than VOCs.

Although the contaminated groundwater was not used as a source of drinking water, limited off-site sampling suggested that contaminated groundwater had migrated off-site potentially affecting protected wetlands. Romic installed a pump-and-treat system which has been in place since 1993.

Site Geology/Hydrogeology

Romic is located in an area underlain by 500 to 1,000 feet of alluvial and estuarian sediments, and is capped by up to 8 feet of heterogeneous fill. Beneath the fill are three water-bearing zones named A-, B-, and C-zone which are vertically separated by generally continuous silt and clay units. A thick clay unit separates the C-zone from a fourth water-bearing zone identified as D-zone.

A-zone is comprised of interbedded clays, sands, and gravel. The sand and gravel and overlying sediments range in thickness from 7.5 to 21 feet. Monitoring wells in the A-zone are screened from 4 to 25 feet bgs. The groundwater gradient is relatively flat at approximately 0.001 ft/ft.

B-zone is a semi-confined aquifer composed of fine sands and silts with minor localized clay lenses. Monitoring wells in the B-zone are screened between 20 to 49.7 feet bgs. The B-zone groundwater gradient is also relatively flat at approximately 0.001 ft/ft. C-zone is a confined aquifer consisting of poorly to well-sorted sands, silty sands, and clays. C-zone monitoring wells are screened between 57 to 82 feet bgs. The groundwater gradient in C-zone is relatively flat at approximately 0.002 ft/ft. The pilot study report did not provide data on the groundwater velocity or indicate that a tracer test was conducted. However, the groundwater pump and treat system at the site has an estimated extraction rate of 3 gpm.

Project Description

Pilot

A pilot study was conducted to provide information on using in-situ bioremediation as a potential remedy for contaminated groundwater at the site. The pilot study involved two test areas; the southwestern portion of the site (A-zone aquifer) and the central process area (B-zone aquifer). In the A-zone aquifer test area, four injection wells (IP-1 thru IP-4) along with three monitoring wells (RW26A, RW-27A, and RW-15A) were employed. All injection wells were screened from 10-15 feet bgs. Monitoring wells RW-26A, RW-27A, and RW-15A were screened from 8.5-18.5 feet bgs, 10-20 feet bgs, and 5.5-15.5 feet bgs, respectively. The B-zone aquifer test area also used four injection wells and three monitoring wells. Injection well IP-5 was screened from 31-36 feet bgs while injection wells IP-6 thru IP-8 were screened from 32-42 feet bgs. Monitoring wells MW-17B and MW-18B were screened from 33-43 feet bgs while RW-8B was screened from 20-40 feet bgs.

On February 8, 2001, baseline samples were collected from the six monitoring wells and analyzed for VOCs, TOC, total iron, dissolved gases (CO_2, CO, ethene, ethane, methane, nitrogen, and oxygen), chloride, nitrate, nitrite, and sulfate. Table 4-3 lists the analyses performed on the baseline and monitoring groundwater samples.

Table 4-3. Groundwater Analyses by Well at the Romic Facility

Well Number	Field Parameters	U.S. EPA Analytical Methods					
		8260[a]	300.0[b]	415.1[c]	200.7[d]	6000/70000[e]	AM15/AM18[f]
MW-15A	x	x	x	x	x	x	x
MW-26A	x	x	x	x	x	x	x
MW-27A	x	x	x	x	x	x	x
MW-8B	x	x	x	x	x	x	x
MW-17B	x	x	x	x	x	x	x
MW-18B	x	x	x	x	x	x	x

Field parameters consist of pH, temperature, specific conductivity, dissolved oxygen, oxidation reduction potential, ferrous iron, and turbidity.

[a] Analysis for volatile organic compounds (VOCs)

[b] Analysis for nitrate, nitrite, sulfate, and chloride

[c] Analysis for total organic carbon

[d] Analysis for total iron performed on pilot study samples only.

[e] Analysis for total iron performed on baseline samples only.

[f] Analysis for dissolved gases (CO_2, CO, methane, ethene, ethane, nitrogen, and oxygen)

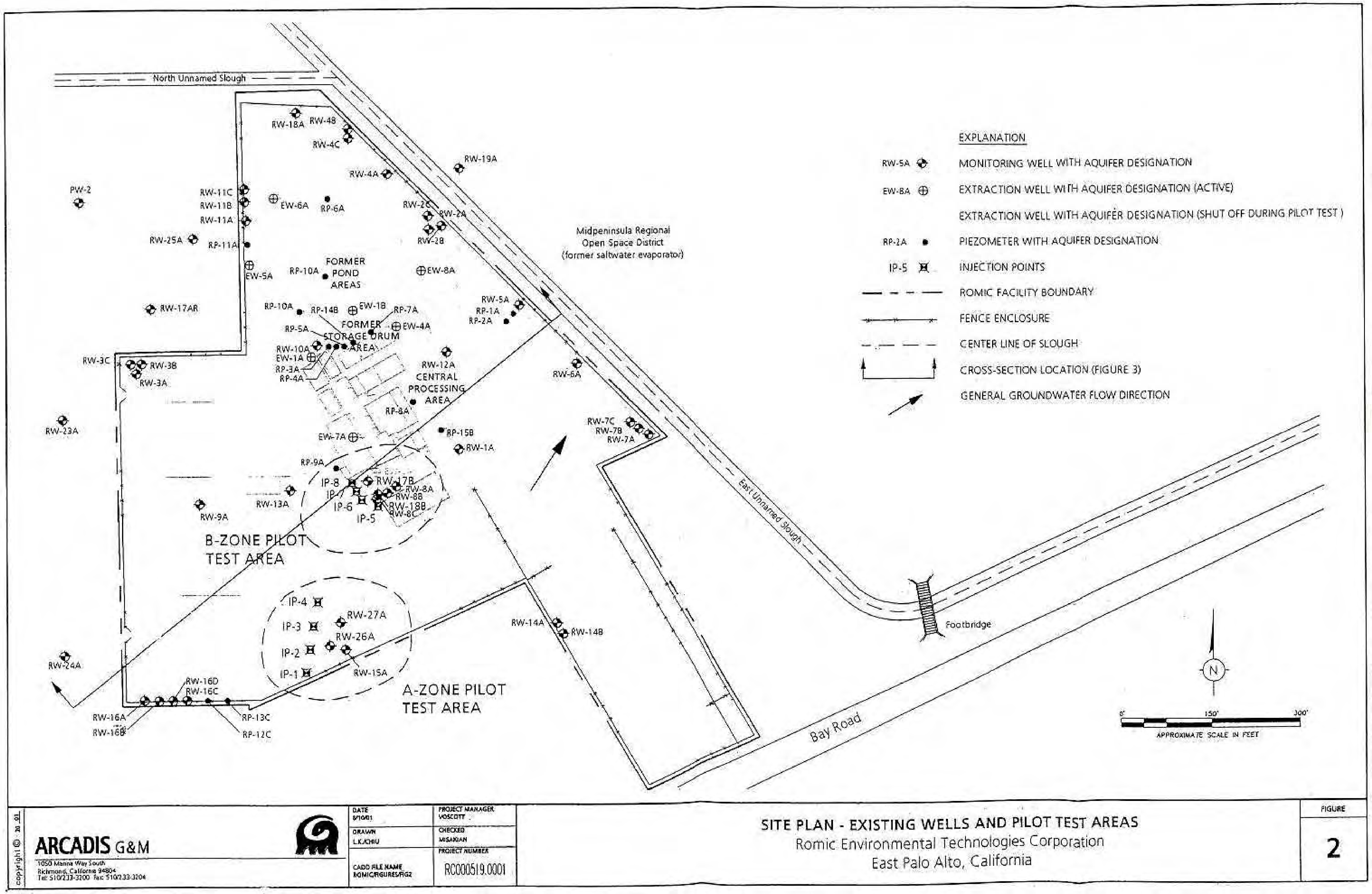
Two injection events were performed at both test areas: one on February 22, 2001, and one on March 1, 2001. A third injection event was conducted on June 13, 2001 in the A-zone aquifer test area to address low TOC values detected in the monitoring wells. The A-zone injection events used a 1:10 mixture of molasses:water, while a 3:1 mixture of cheese whey:water was used in the B-zone injection events. Table 4-4 lists the amount and ratio for each injection event conducted at the site.

Table 4-4. Injection Events at the Romic Facility

Pilot Test Area	Injection Well	Injection Date	Ratio	Amount (gallons)	
				Per well	Total
A	IP-1 IP-2 IP-3 IP-4	2-21-01	1:10 molasses: water	100	400
		3-1-01	1:10 molasses: water	100	400
		6-13-01	1:10 molasses: water	200	800
B	IP-5 IP-6 IP-7 IP-8	2-21-01	3:1 cheese whey: water	100	400
		3-1-01	3:1 cheese whey: water	100	400

The injection system consisted of a trailer mounted injection tank unit. A centrifugal pump was used to inject the molasses or cheese whey mixture into the injection well via a manifold. Injection pressures were monitored at the well head while the flow rate was measured via trailer-mounted flow-meters. The injection rates varied between 6 gpm to as high as 14 gpm with injection pressures as high as 20 psi.

Figure 4-9. Monitoring and Injection Wells at the Romic Facility



Based on the results of the pilot study, U.S. EPA has installed ISB injection wells in the area of RW-2A/2B/2C as an interim remedy. The area around RW-2A/2B/2C is considered a hot spot for chlorinated and non-chlorinated solvents. Twelve injection wells have been installed around RW-2A/2B/2C with six wells in the A-zone and six wells in the B-zone. The proposed substrate will be a mixture of molasses, cheese whey, and water. The ratio of each component was not available. As of 8/11/2003, no injection events have been conducted at the site.

Project Performance

Appendix D contains tables and graphs of the groundwater monitoring results for all seven wells monitored as part of the pilot study including baseline concentrations. Figures 4-10 through 4-15 present graphs with concentration and select geochemical parameter trends. These figures also present tables with qualitative and quantitative indications of biodegradation conditions at each well.

In Pilot Test Area A, PCE biodegradation in RW-15A did not appear to be enhanced after 125 days while it appeared slightly enhanced in RW-26A and moderately enhanced in RW-27A. TCE and 1,2-DCE concentrations remained fairly constant in RW-15A and RW-26A. At RW-27A, TCE and 1,2-DCE concentrations appeared to fluctuate where an increase in TCE corresponded to a decrease in 1,2-DCE and vice versa. Concentration trend graphs for these wells are presented in Figures 4-10 thru 4-12. Anaerobic conditions (DO <2 mg/L) existed for approximately three months after the second amendment injection but changed to aerobic (DO>2 mg/L) by the third amendment injection. Nitrate was reduced in all wells and was supported by ORP values (< 750 mV) indicative of nitrate reducing conditions. RW-27A had one ORP value on 5/4/2001 which was less than -200 mV indicating sulfate reducing conditions. Sulfate in all wells was reduced slightly. The sulfate decrease in RW-27A did not correspond with the ORP drop and may be due to fluctuations in background concentrations that were not available for this review. Ethene was detected in very low concentrations. A trend for dissolved gases could not be determined since only two data points were available.

For Pilot Test Area B, PCE degradation was moderately enhanced in RW-8B, RW-17B, and RW-18B. Decreases in TCE concentrations corresponded to increases in 1,2-DCE concentrations at all wells. Vinyl chloride was reported below the detection limit (< 100-250 µg/L) in most samples. Concentration trend graphs for these wells are presented in Figures 4-13 thru 4-15. Anaerobic conditions existed in all wells up to one month before the end of the pilot test based on DO values (<2 mg/L). Amendments appeared to affect a decrease in ORP levels in all three monitoring wells. After the second injection event, ORP ranged from <-200 mV to 0 mV in RW-8B and RW-17B, and between <-200 mV to 200mV for RW-18B. Nitrate was reduced in RW-8B and RW-18B and not detected in MW-17B which is supported by the ORP values. However, sulfate and total iron were observed to either remain constant or increase which is contrary to what is expected based on the ORP values. Dissolved methane/ethene/ethane concentrations did not appear to increase based on the results of only two samples. (Refer to Figure D-7a thru Figure D-18b in Appendix D).

Figure 4-10. Data Analyses for Monitoring Well RW-15A at Romic Chemical

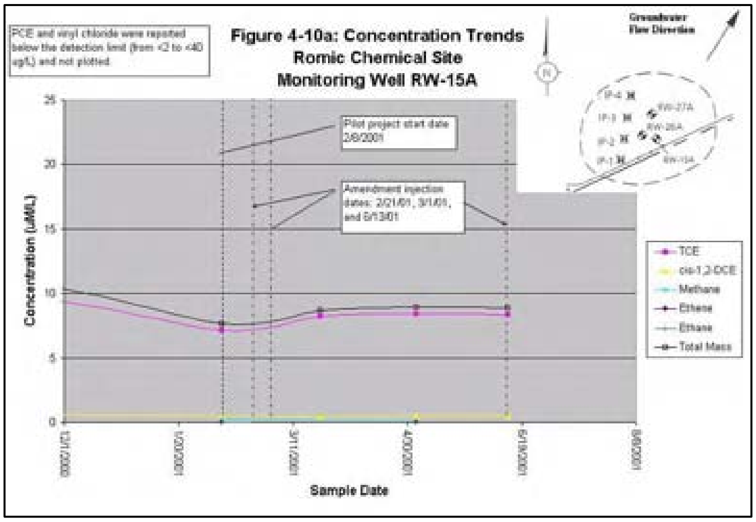


Figure 4-10a: Concentration Trends
Romic Chemical Site
Monitoring Well RW-15A

PCE and vinyl chloride were reported below the detection limit (from <2 to <40 ug/L) and not plotted.

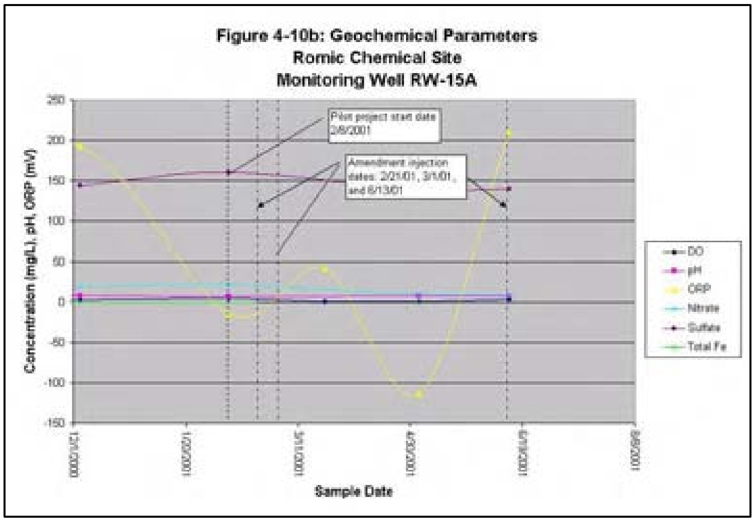


Figure 4-10b: Geochemical Parameters
Romic Chemical Site
Monitoring Well RW-15A

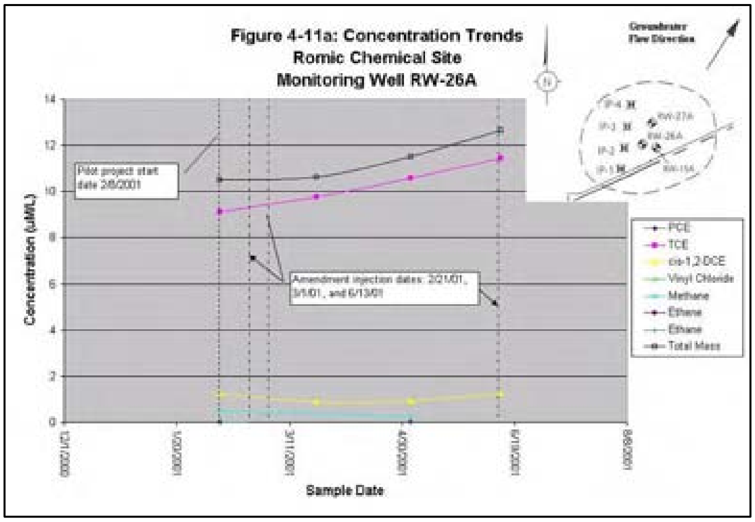
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
RW-15A		-	0		-	-	NE

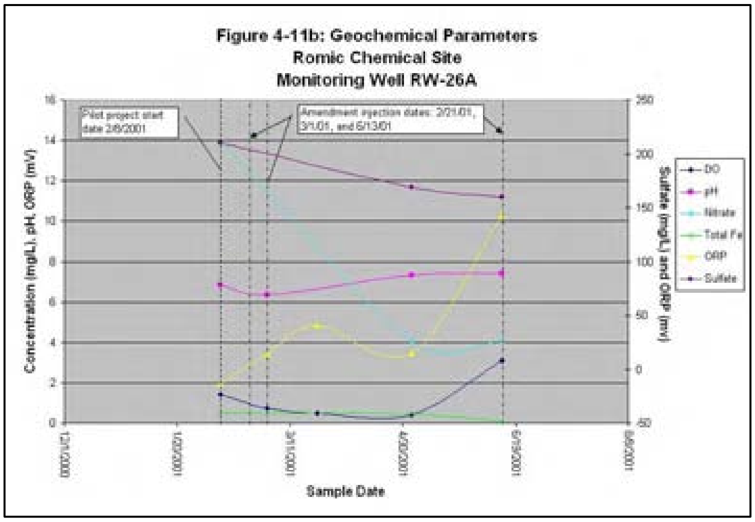
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{125}	% reduced	C_o (µg/L)	C_{125}	% reduced	C_o (µg/L)	C_{125}	% reduced	C_o (µg/L)	C_{125}	% reduced
RW-15A	<2	<40	--	940	1100	-17%	48	49	-2%	<2	<40	--

Note: C_o is the baseline concentration for samples collected on 2/8/2001.
C_{125} is the concentration for samples collected on 6/13/2001.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-11. Data Analyses for Monitoring Well RW-26A at Romic Chemical





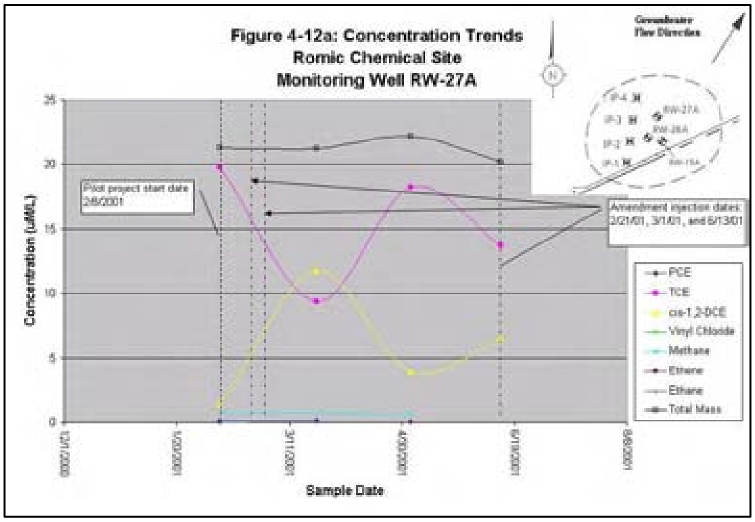
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
RW-26A	-	-	0		+	-	SE

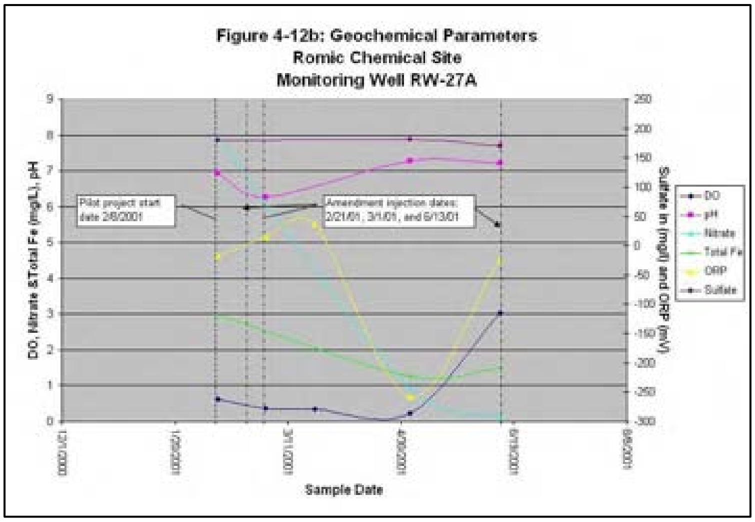
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced
RW-26A	2	<29	--	1200	1500	-25%	120	120	0%	6.9	<29	--

Note: C_o is the baseline concentration for samples collected on 2/8/2001.
C_{125} is the concentration for samples collected on 6/13/2001.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-12. Data Analyses for Monitoring Well RW-27A at Romic Chemical





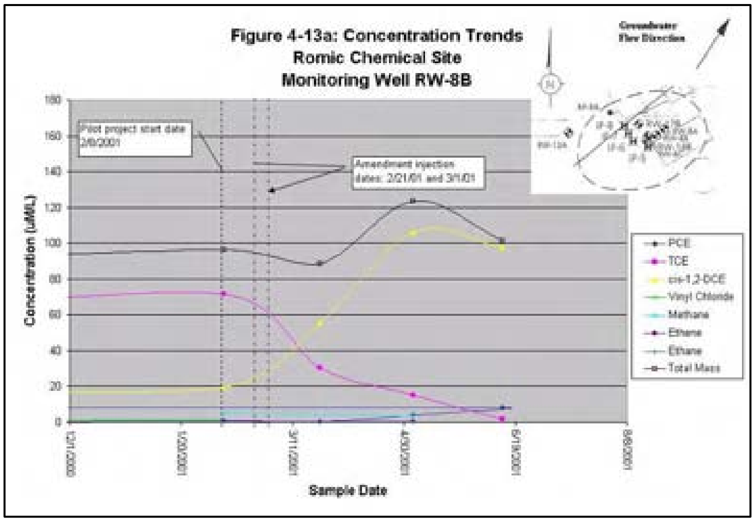
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
RW-27A	0	+	+		+	-	ME

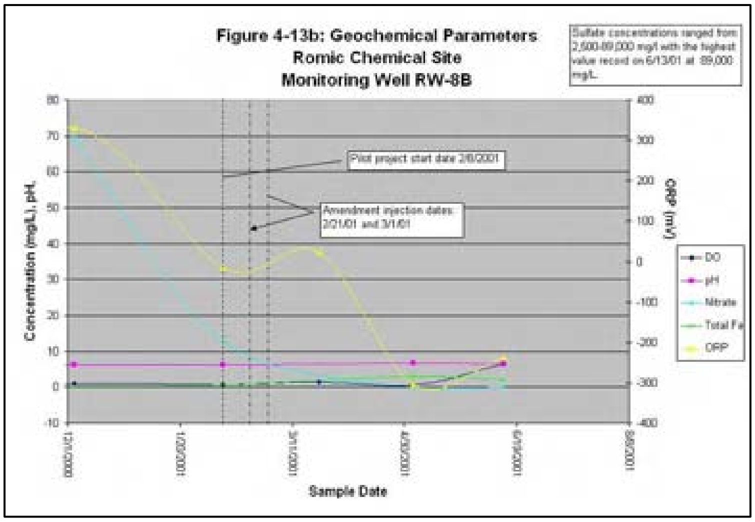
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced
RW-27A	21	<25	--	2600	1800	31%	130	630	-385%	4.5	<25	--

Note: C_o is the baseline concentration for samples collected on 2/8/2001.
C_{125} is the concentration for samples collected on 6/13/2001.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-13. Data Analyses for Monitoring Well RW-8B at Romic Chemical





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
RW-8B	0	+	+	0	+	-	ME
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced							

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced
RW-8B	660	<200	70%	9400	270	97%	1900	9500	-400%	88	<200	--

Note: C_o is the baseline concentration for samples collected on 2/8/2001.
C_{125} is the concentration for samples collected on 6/13/2001.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-14. Data Analyses for Monitoring Well RW-17B at Romic Chemical

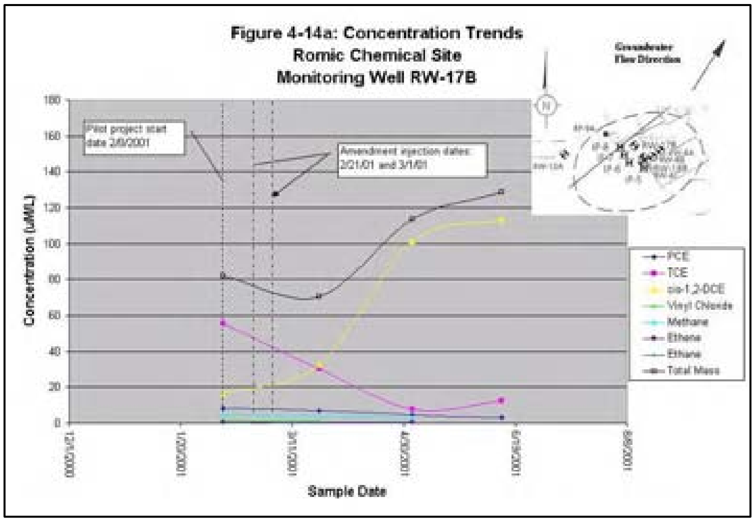


Figure 4-14a: Concentration Trends
Romic Chemical Site
Monitoring Well RW-17B

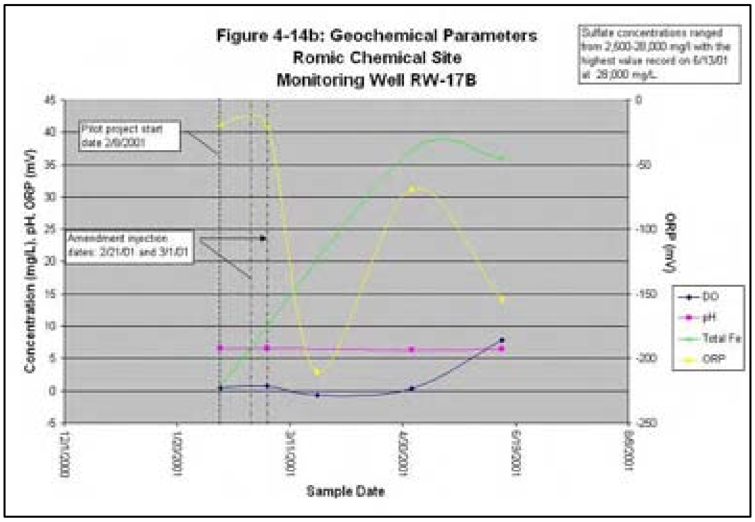


Figure 4-14b: Geochemical Parameters
Romic Chemical Site
Monitoring Well RW-17B

Sulfate concentrations ranged from 2,600-28,000 mg/l with the highest value record on 6/13/01 at 28,000 mg/L.

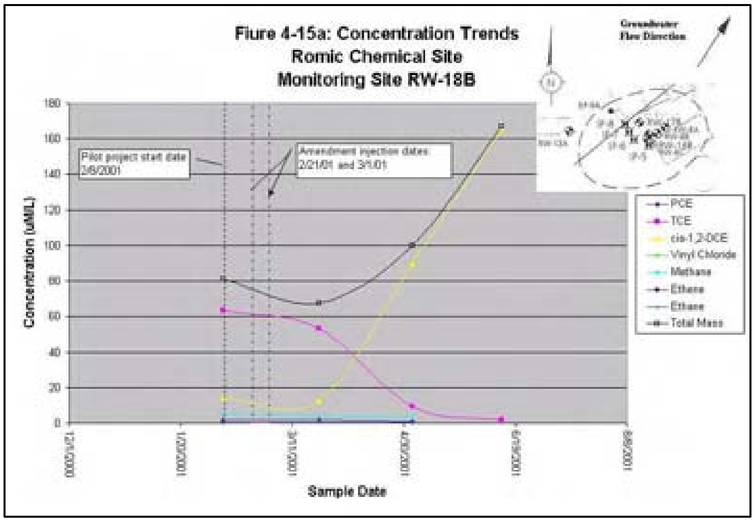
Well Number	**Contaminant Mass Loss**				**Enhanced Geochemical Conditions**	**Increased Dissolved Gases**	**Evaluation Rating**
	PCE	**TCE**	**DCE**	**VC**			
RW-17B	0	+	+	0	+	-	ME

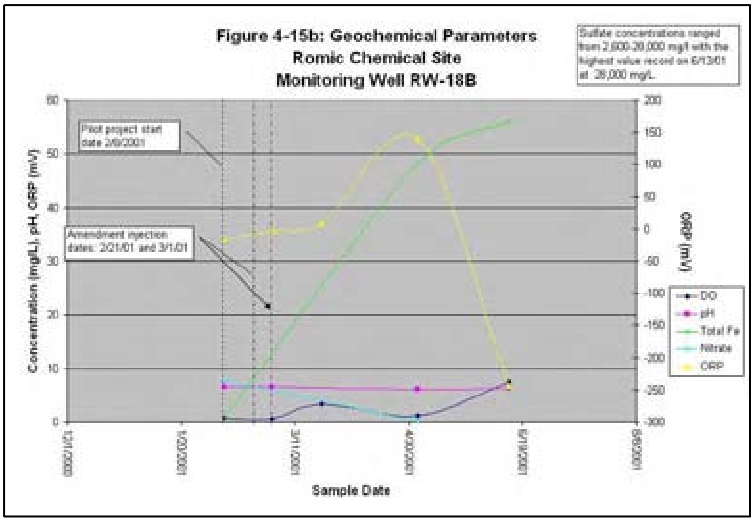
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	**PCE**			**TCE**			**cis-1,2-DCE**			**Vinyl Chloride**		
	C_o	**C_{125}**	**% reduced**	**C_o**	**C_{125}**	**% reduced**	**C_o**	**C_{125}**	**% reduced**	**C_o**	**C_{125}**	**% reduced**
	(µg/L)			**(µg/L)**			**(µg/L)**			**(µg/L)**		
RW-17B	1400	510	64%	7300	1600	78%	1600	11000	-588%	100	<250	--

Note: C_o is the baseline concentration for samples collected on 2/8/2001.
C_{125} is the concentration for samples collected on 6/13/2001.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-15. Data Analyses for Monitoring Well RW-18B at Romic Chemical





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
RW-18B	0	+	+		+	-	ME

Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced	C_o (µg/L)	C_{125} (µg/L)	% reduced
RW-18B	300	<250	17%	8300	<250	97%	1400	16000	-1043%	82	<250	--

Note: C_o is the baseline concentration for samples collected on 2/8/2001.
C_{125} is the concentration for samples collected on 6/13/2001.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Project Costs

Project cost data was not available.

Data Gaps

A brief explanation on the rationale for injecting a molasses:water solution into the A-zone while a 3:1 cheese whey:water solution into the B-zone would be useful. It is unclear why two different solutions were used in this pilot.

To aid in the assessment of the magnitude and effect of the substrate addition, data from downgradient wells such as RW-14A , RP-15B, and RW-1A should be also be collected and reviewed.

Additional samples for dissolved gases are needed to assess if VC is being broken down to ethene and ethane. To date only two samples have been analyzed at each well for dissolved gases. This is not sufficient data to establish a trend for dissolved gases.

Background concentrations for chloride should also be provided due to the proximity of the saltwater evaporation ponds. The difference of the chloride concentrations in the B-zone versus A-zone is higher by two orders of magnitude. When compared to the COC concentrations, the B-zone concentrations suggest that saltwater intrusion or brackish water may be the source of the high chloride content and not biodegradation of PCE and its daughter products.

Summary Observation and Lessons Learned

As part of the pilot study, the reductive dechlorination conditions in Pilot Test Areas A and B were evaluated. For Pilot Test Area A, the data does not indicate that PCE is biodegrading to its daughter products. However, data for Pilot Test Area B does indicate that PCE is degrading to its daughter products TCE and cis-1,2-DCE but then stalls at cis-1,2-DCE. Ethene is also detected in low concentrations in some of the samples from the Pilot Test Area B wells. Methane is also detected at the site and may be a by-product of other degradation processes.

Pilot test results indicate that cis-1,2-DCE is accumulating and may not be biodegrading. If in-situ bioremediation is considered for this site, bench-top studies should be conducted to verify that the native bacteria are capable of breaking down cis-1,2-DCE and VC to ethene. This information would assist in determining additional measures required to enhance the bioremediation process at the site including addition of other microbes.

<u>References</u>

Arcadis, Pilot Test Status Report, Romic Environmental Technologies Corporation, 2081 Bay Road, East Palo Alto, California, August 21, 2001.

Department of Toxic Substances Control (DTSC), Calsites Site Mitigation Program Properties Database (SMPPD) Profile Report, No date.

U.S. EPA, RCRA Showcase Pilot Region 9 (Romic Environmental Technologies Corporation), No date.

4.3 Teledyne Singer

Summary

A pilot study was conducted at the former Teledyne Singer site where groundwater is encountered 28-41 feet bgs. Thirteen (13) injection points were installed in a line upgradient of most monitoring wells. In August 2001, a total of 1,238 gallons of a 1:10 molassess:water solution was injected into the subsurface. Five monitoring wells were sampled over a 5-month period and monitored for PCE, TCE, cis-1,2-DCE, VC and select geochemical parameters.

Biodegradation was observed to be occurring in MW-6R located between two injections points. The biodegradation process appears to have stalled at cis-1,2-DCE which increased from 30 µg/L to 2,000 µg/L. Although decreases in PCE and TCE were observed in the other wells located downgradient, no production of cis-1,2-DCE or VC was observed which would be expected to be observed in a robust system. Molasses injections would not be expected to have traveled the distance to these four monitoring wells based on the low permeability of the aquifer and low groundwater gradient encountered at this site.

Site Background

The former Teledyne-Singer site is a 2.6 acre parcel located at 3176 Porter Drive in the City of Palo Alto, California near the intersection of Foothills Expressway and Page Mill Road. The site is within the Stanford Research Park which is part of the Hillview-Porter regional site.

From 1961 to1987, the facility was used for the manufacturing and/or assembly of electronic parts such as sweep oscillators, traveling wave tubes, and amplifiers. The site was occupied by Alfred Electronics from 1961 to 1969, and Teledyne MEC from 1975 to 1987.

Remedial investigations at the site identified two potential sources at the site. The primary source was thought to be a sump located near the east side of the property near monitoring well MW-6R. The sump and surrounding soil were removed from a 25-foot by 28-foot excavation to approximately 21.5 ft bgs. The second source was thought to be an underground storage tank (UST) and its associated drain pipe located along the south wall of the site building. The UST and surrounding soil were also removed. Two chlorinated solvent plumes in groundwater were also identified. PCE was the primary contaminant in the shallow zone and TCE the primary contaminant in the deeper zone.

In the early 1990s, groundwater extraction was initiated at the site. In March 1993, additional extraction wells were added to the Groundwater Extraction and Treatment

System (GETS) until 14 extraction wells were installed; 10 wells in the shallow zone and 4 wells in the deep zone. In 2001, only 12 extraction wells were operated; 9 wells in the shallow zone and 3 wells in the deep zone.

Site Geology/Hydrogeology

The site's subsurface geology consists of silt to gravelly sands to a depth of approximately 13-25 feet bgs. A crudely, bedded clayey silt to sandy gravel underlies the alluvium at the site and extends to at least 170 feet bgs.

Groundwater at the site is generally found within the coarser grained horizons separated to varying degrees by lower permeability horizons. The shallow groundwater zone (referred to as the shallow zone) is generally an unconfined aquifer consisting of clayey sands, silty sands, and thin gravel lenses which extend to a depth of approximately 65 feet bgs. The deep groundwater zone (referred to as the deep zone) is generally a confined aquifer consisting of interbedded clays, silts, sands, and gravels between 65 and 125 feet bgs.

Past aquifer tests for the shallow aquifer have estimated the transmissivity between 4.33-6.4 ft^2/day. Drawdown tests at MW-6R, MW-11A, MW-12, MW-16 and EW-1 noted pumping almost immediately caused the water level to draw down to the pump screen levels due to very slow recharge rates. Prior to pumping activities, the hydraulic gradient was to the east at approximately 0.015 ft/ft. Based on the November 1998 groundwater elevation data, the hydraulic gradient was still to the east at approximately 0.03-0.4 ft/ft (see Figure 4-17 and 4-18). Based on the GETS operation data, the average groundwater extraction rates for EW-1, EW-2, and MW-6R from 1993 to 1998 were 0.68 gpm, 0.75 gpm, and 0.002 gpm, respectively.

MW-18 was the only well where aquifer testing was completed. Based on aquifer testing data for MW-18, a specific capacity of 0.8 gpm/ft drawdown was observed at a pumping rate of 4.5 to 5 gpm. The average groundwater extraction rate for MW-18 from 1993 to 1998 was 1.93 gpm.

Project Description

Pilot

The pilot study conducted at the Teledyne-Singer site was to evaluate the effectiveness of using in-situ bioremediation to remediate chlorinated groundwater contamination in the shallow aquifer zone. Thirteen ¾-inch diameter injection wells were installed using direct push methods. Injection wells IW-1, IW-3, IW-5, IW-7, IW-9, IW-11, and IW-13 extended into the shallow zone aquifer and were screened 28-33 feet bgs. The remaining injection wells extended deeper into the shallow zone aquifer and were screened from 36-41 feet bgs. According to the start-up report, the screened intervals for the injection wells were staggered to impact a larger aquifer thickness. Two monitoring wells, MW-21 and MW-22, were installed in July 2001 using an 8-inch hollow stem auger. Both wells were completed to a depth of 40 feet bgs and screened from 20-40 feet bgs. Existing wells, MW-6R, EW-1, and EW-2 were screened from 20-30 feet bgs, 13-33 ft bgs, and 13-33 ft bgs, respectively. It is not clear from the pilot study report whether EW-1 and EW-2 were operating as extraction wells. Figure 4-16 shows the monitoring well and injection well locations.

Prior to the injection event, baseline groundwater samples were collected from MW-6R, MW-21, MW-22, EW-1, and EW-2 on July 17, 2001 and analyzed for VOCs, TOC, metals, nitrate, nitrite, sulfate, phosphate, and various field parameters. Table 4-5 summarizes the groundwater analyses performed on the baseline and pilot study groundwater samples.

Table 4-5. Groundwater Analyses by Well at the Teledyne-Singer Facility

Well No.	Field Parameters	U.S. EPA Analytical Methods					
		8260	300.0[a,g]	415.2[b]	365.2[c]	6010[d]	RSK175[e,f]
MW-6R	x	x	x	x	x	x	
MW-21	x	x	x	x	x	x	
MW-22	x	x	x	x	x	x	
EW-1	x	x	x	x	x	x	
EW-2	x	x	x	x	x	x	

Field parameters consist of pH, temperature, specific conductivity, D.O., ORP, ferrous iron, and turbidity.

[a] Analysis for nitrate, nitrite, sulfate, chloride, and fluoride

[b] Analysis for total organic carbon

[c] Analysis for phosphate

[d] Analysis for total and dissolved iron, antimony, arsenic, beryllium, cadmium, chromium, copper, hexavalent chromium, lead, mercury, nickel, selenium, silver, thallium, and zinc

[e] Analysis for dissolved gases (methane, ethane, and ethene)

[f] No samples were analyzed by this method.

[g] Two samples from this well were analyzed by this method.

In August 2001, a 1:10 molasses to water solution was injected using a specifically fabricated mixing/injection trailer. The injection system consisted of a double-diaphragm pneumatic pump connected to the GETS air supply. The pump was used to provide continuous pressure in the injection well manifold, ranging from 58-70 psi at the injection well head manifolds. The amount of molasses to water solution injected at each well is listed in Table 4-6 below.

After the solution was injected, groundwater samples were collected from each well for the first three days. Groundwater samples were then collected once a week for 4 weeks after the injection event. Approximately two months after the initial injection event, little difference in the TOC concentrations was observed in samples collected from the observation wells indicating that the solution was not dispersing readily into the aquifer. After approximately 5 months, the project was put on hold and no additional injections were made.

Figure 4-16. Monitoring and Injection Well Locations at the Teledyne-Singer Facility

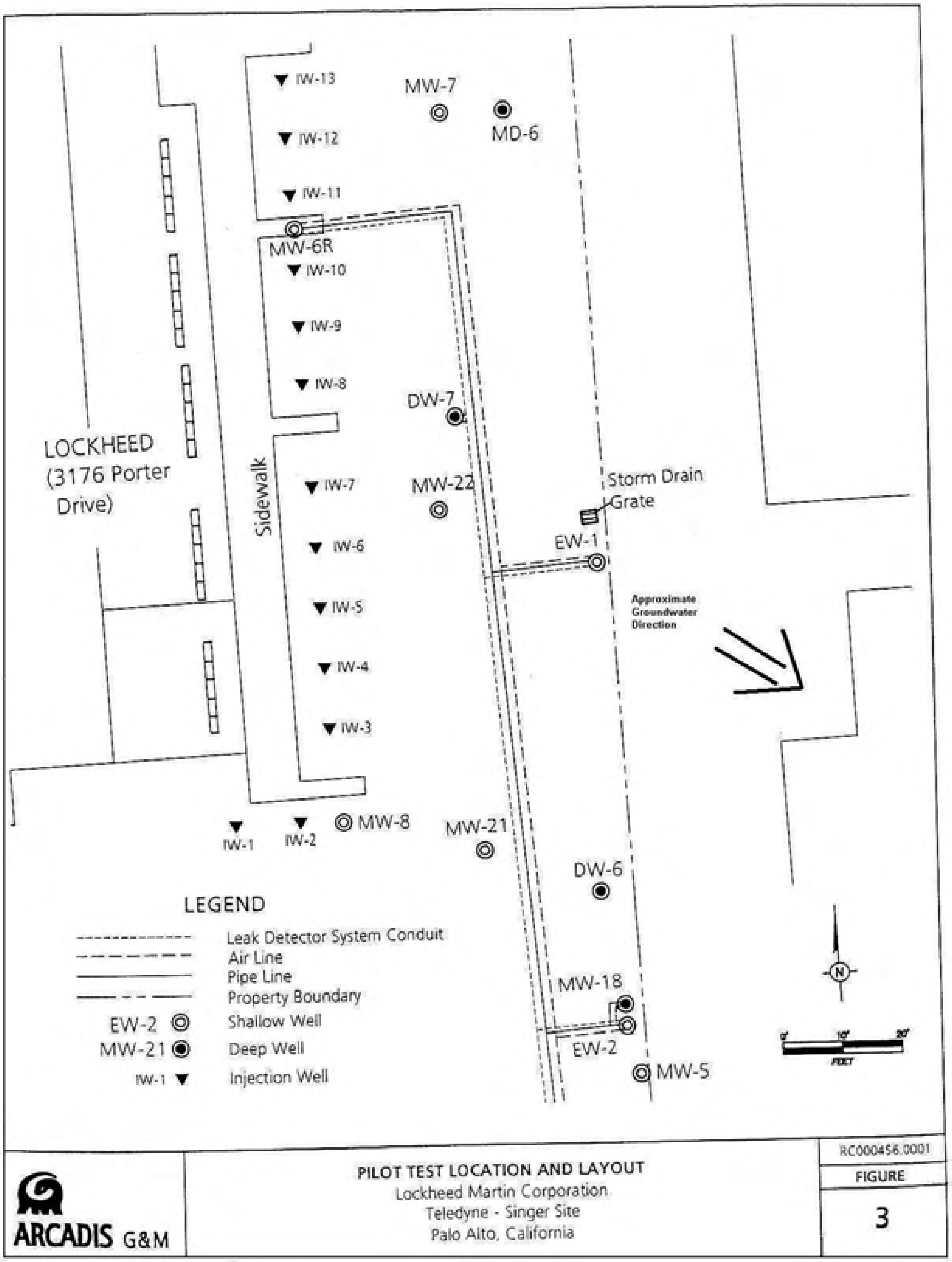


Figure 4-17. November 1998 Groundwater Elevations for Shallow Zone at the Teledyne-Singer Facility

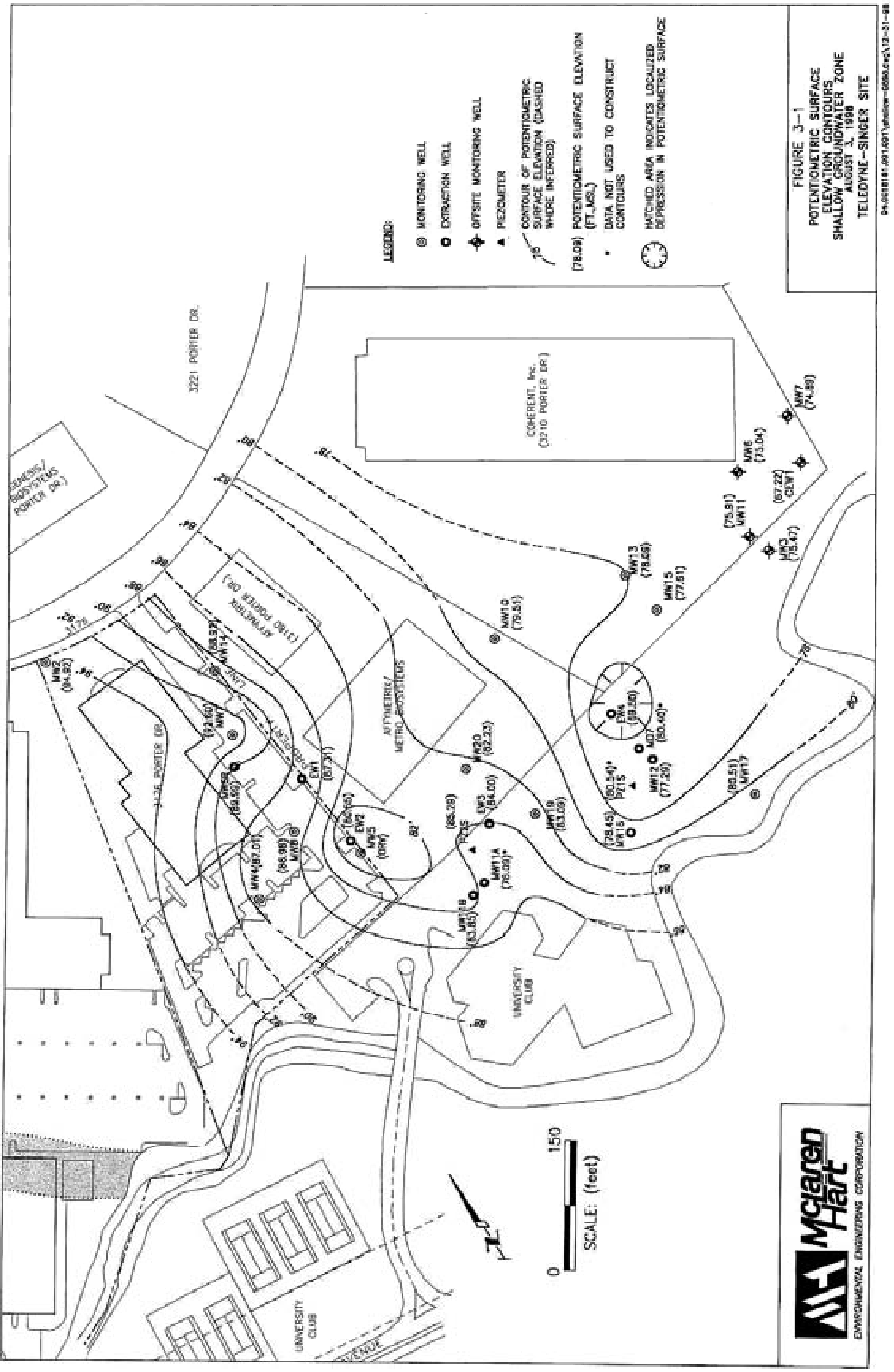


Figure 4-18. November 1998 Groundwater Elevations for the Deep Zone at the Teledyne-Singer Facility

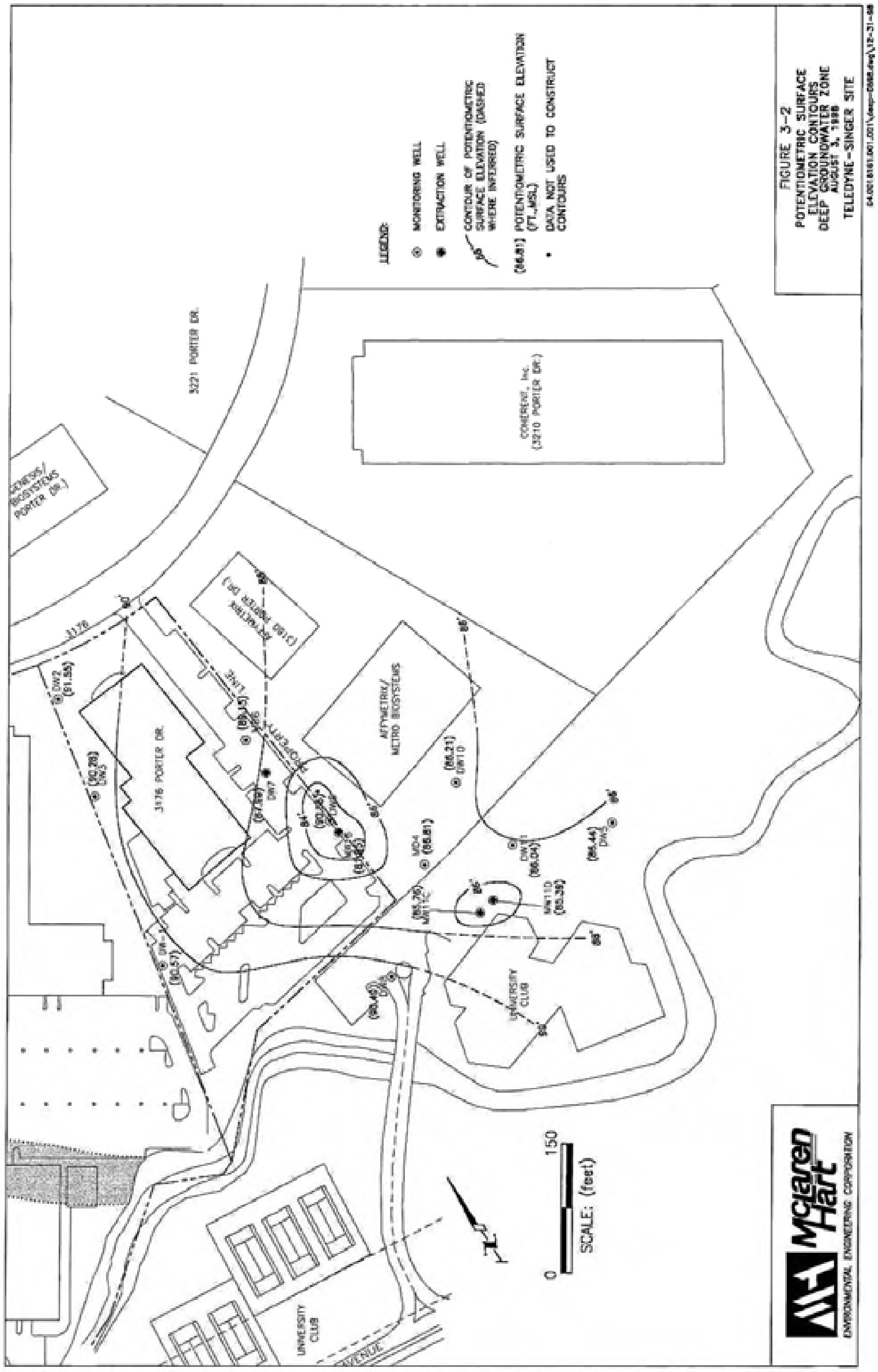


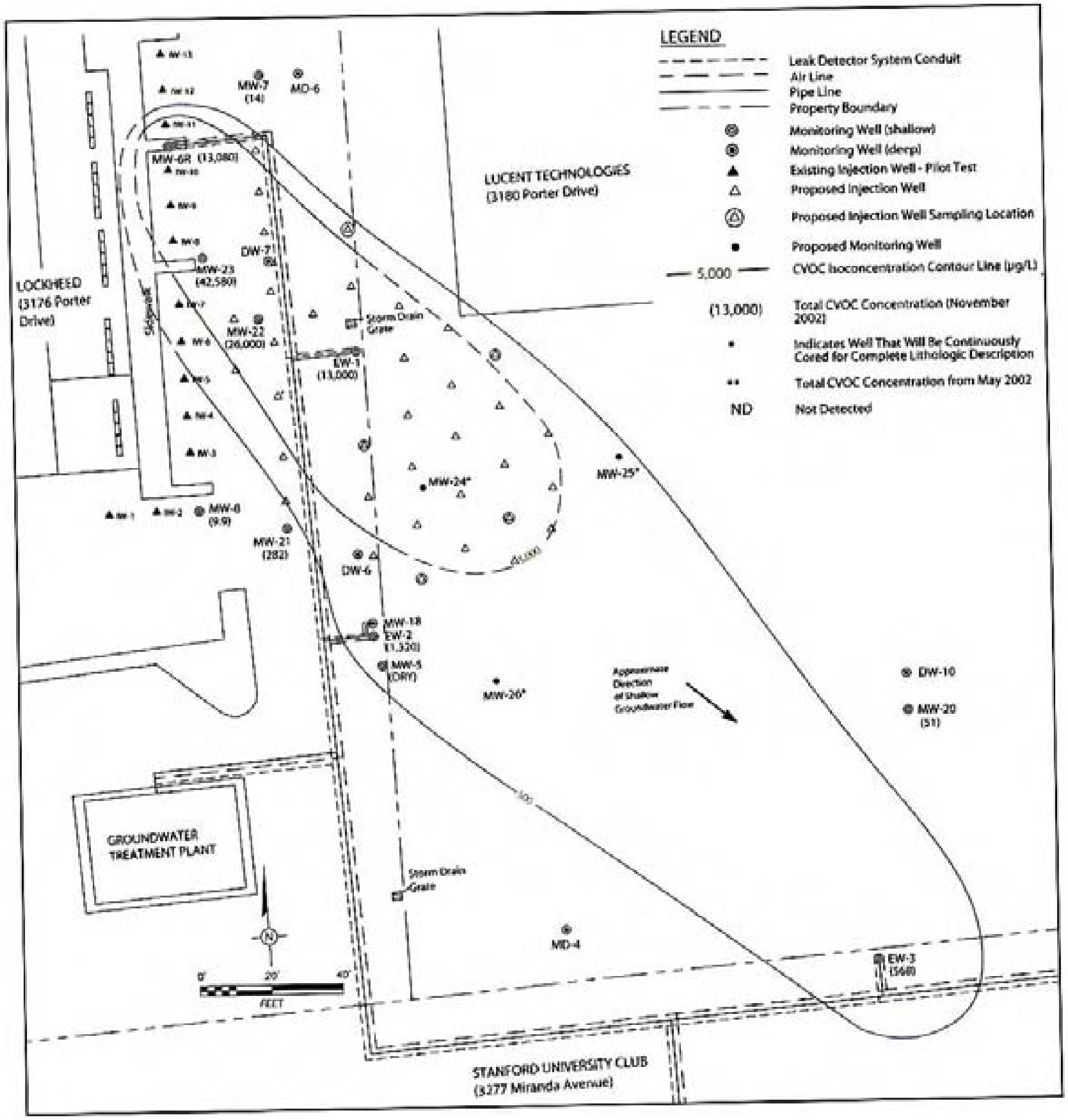
Table 4-6. Injection Events and Amounts at the Teledyne-Singer Facility

Injection Well No.	Approximate Volume Injected[1] (gallons)	Pressure (psi)	Average Flow Rate (gpm)
IW-1	100	70	0.4
IW-2	100	70	0.2
IW-3	75	70	0.2
IW-4	100	70	0.1
IW-5	100	70	0.4
IW-6	23	70	0.05
IW-7	100	70	0.3
IW-8	100	70	0.2
IW-9	130	60	5.9
IW-10	100	60	4.5
IW-11	100	70	0.2
IW-12	110	70	0.4
IW-13	100	58	0.25
Total	**1238**		

[1] The volumes listed were injected on 8/6/2001 at a ratio of 1:10 molasses to water.

In May 2003, the responsible parties submitted a workplan to expand the in-situ bioremediation system as the primary remedial action on the site. The expanded system would consist of 35 permanent injection wells installed by hollow stem auger instead of direct push. The direct push method is suspected to have smeared the boring walls preventing the molasses solution from diffusing into the aquifer. Three new monitoring wells MW-24, MW-25, and MW-26 were also installed. Figure 4-19 shows the locations of the proposed injection and monitoring wells. Injection of a 20:1 water/molasses mixture was scheduled to start in January 2004. The existing GETS will continue to operate to ensure control of the groundwater plume is maintained. If the in-situ bioremediation is found to interfere with the operation of the GETS, it would be modified as needed.

Figure 4-19. Proposed Expanded In-Situ Bioremediation System at Teledyne-Singer



Project Performance

Appendix E contains the groundwater monitoring results for the five wells monitored as part of the pilot study. Contaminant concentrations including the baseline concentrations for all wells were graphed and included in Appendix E. Figures 4-20 through 4-24 present graphs with concentration and select geochemical parameter trends. These figures also present tables with qualitative and quantitative indications of biodegradation conditions at each well.

Over the seven month monitoring period for the pilot project, PCE concentrations decreased in all five of the monitoring wells. Except for MW-6R, however, the decreases appear to be independent of the molasses injections. Because BOD and TOC concentrations did not increase at monitoring wells MW-21, MW-22, EW-1 and EW-2, it is apparent that the molasses amendment solution did not reach these downgradient well locations. Molasses injections would not be expected to have traveled the distance to these four monitoring wells based on the low permeability of the aquifer and low groundwater gradient encountered at this site. Other indicators that the amendment injections were not effective at these locations are the higher ORP levels, high dissolved oxygen levels and the lack of elevated concentrations of cis-1,2-DCE or vinyl chloride, the expected daughter products of PCE or TCE. ORP levels decreased in these wells, but always remained above +100 mV, indicative of aerobic conditions. Low concentrations of cis-1,2-DCE and vinyl chloride were detected in EW- 1 and cis-1,2-DCE was detected in MW-22. Additionally, the TCE concentration trend for these four wells remained unchanged throughout the pilot test compared to the PCE concentration trend (see Figures 4-20 thru 4-24). PCE concentrations remained constant during the last two months of the pilot test.

MW-6R is the only well where conditions appear to have been enhanced via the molasses amendment injections. This well is located about five feet from two injection points, midway between the injection points, where molasses injections would likely have reached. ORP levels dropped from over 400 mV to around -100 mV, indicative of reducing conditions. PCE biodegraded to its daughter products, TCE and cis-1,2-DCE. As no vinyl chloride was detected, the process appears stalled with cis-1,2-DCE not biodegrading (see Figure 4-24).

For all of the wells, only two data points were available for total iron, ferrous iron, nitrate and sulfate. These data indicate large decreases in total iron with no corresponding increases in ferrous iron. Nitrate concentrations did not change in any of the monitoring wells. Sulfate concentrations decreased most at MW-6R and to a lesser extent at MW-22 and EW-1. There was little or no decrease in sulfate concentration at MW-21 and EW-2. Additional data would be needed to establish any trend. No data were available for methane, ethene or ethane as samples were not analyzed for these parameters. (Refer to Figure E-6a thru E-15 in Appendix E).

Figure 4-20. Data Analyses for Monitoring Well MW-21 at the Teledyne Singer Site

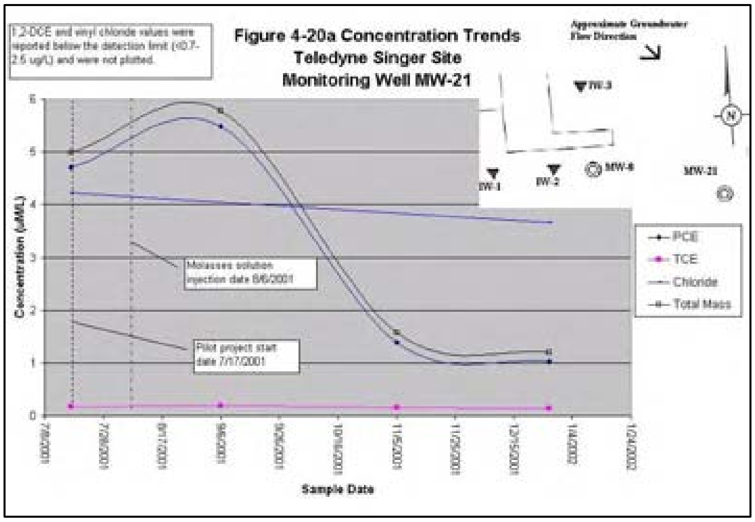


Figure 4-20a Concentration Trends
Teledyne Singer Site
Monitoring Well MW-21

1,2-DCE and vinyl chloride values were reported below the detection limit (<0.7-2.5 ug/L) and were not plotted.

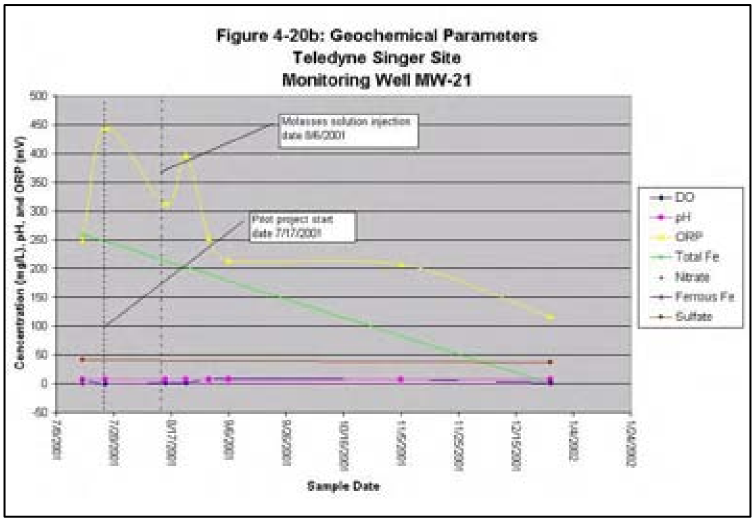


Figure 4-20b: Geochemical Parameters
Teledyne Singer Site
Monitoring Well MW-21

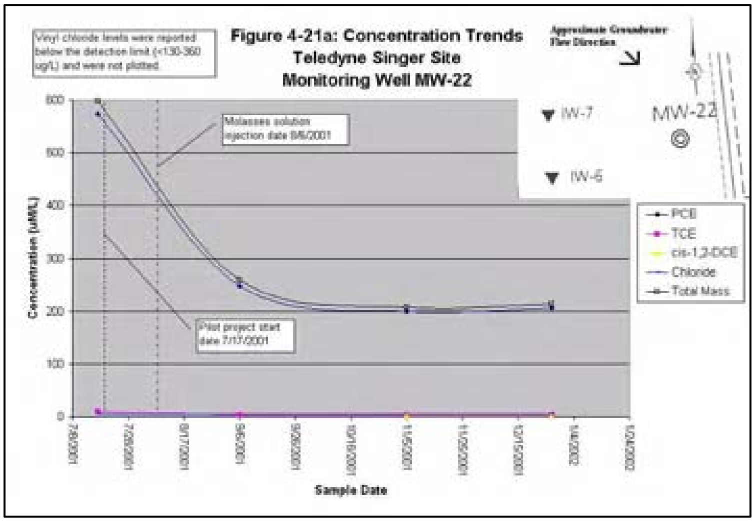
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-21	+	0			-		SE

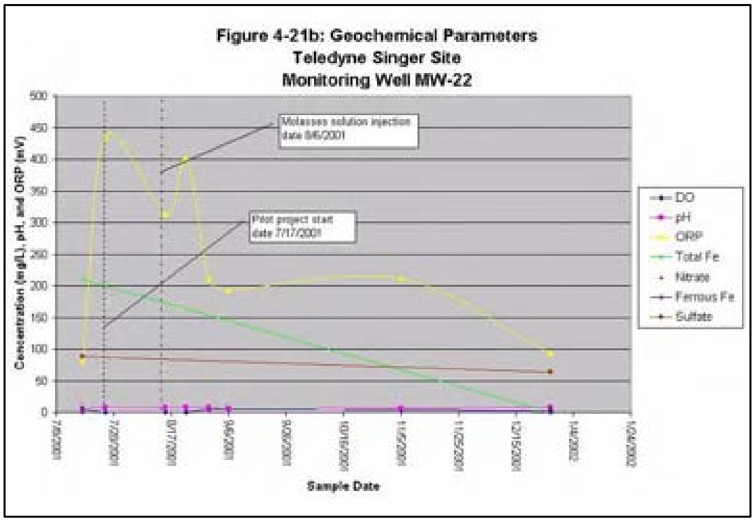
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{163} (µg/L)	% reduced	C_o (µg/L)	C_{163} (µg/L)	% reduced	C_o (µg/L)	C_{163} (µg/L)	% reduced	C_o (µg/L)	C_{163} (µg/L)	% reduced
MW-21	780	170	78%	23	19	17%	<2.5	<0.7	--[a]	<2.5	<0.7	--[a]

Note: C_o is the baseline concentration for samples collected on 7/17/2001.
C_{163} is the concentration for samples collected on 12/27/2001.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".
[a] The percent reduction was not calculated because the baseline or final sample concentration was below the detection limit.

Figure 4-21. Data Analyses for Monitoring Well MW-22 at the Teledyne Singer Site





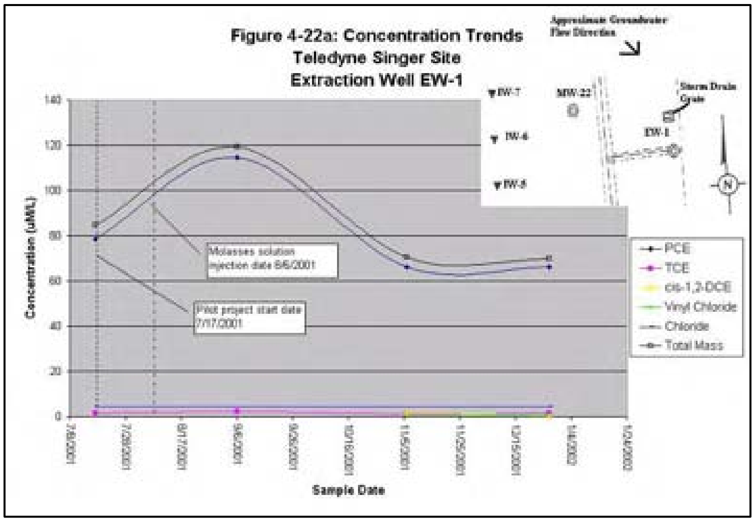
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-22	+	0	0		+		SE

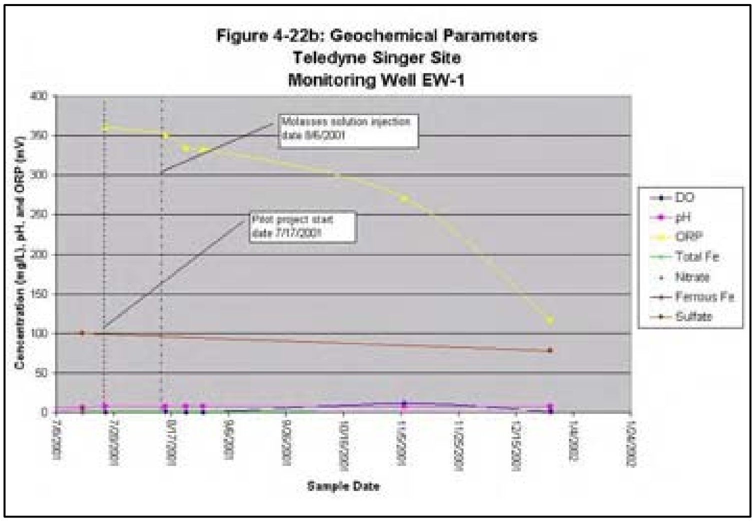
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o	C_{163}	% reduced	C_o	C_{163}	% reduced	C_o	C_{163}	% reduced	C_o	C_{163}	% reduced
	(µg/L)			(µg/L)			(µg/L)			(µg/L)		
MW-22	95000	34000	64%	1200	430	64%	<360	<130	--[a]	<360	<130	--[a]

Note: C_o is the baseline concentration for samples collected on 7/17/2001.
C_{163} is the concentration for samples collected on 12/27/2001.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".
[a] The percent reduction was not calculated because the baseline or final sample concentration was below the detection limit.

Figure 4-22. Data Analyses for Monitoring Well EW-1 at the Teledyne Singer Site





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
EW-1	+	0	-	+	-		SE

Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_{163} (µg/L)	% reduced	C_o (µg/L)	C_{163} (µg/L)	% reduced	C_o (µg/L)	C_{163} (µg/L)	% reduced	C_o (µg/L)	C_{163} (µg/L)	% reduced
EW-1	13000	11000	15%	180	180	0%	<360	<50	--[a]	<36	50	-38%

Note: C_o is the baseline concentration for samples collected on 7/17/2001.
C_{163} is the concentration for samples collected on 12/27/2001.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".
[a] The percent reduction was not calculated because the baseline or final sample concentration was below the detection limit.

Figure 4-23. Data Analyses for Monitoring Well EW-2 at the Teledyne Singer Site

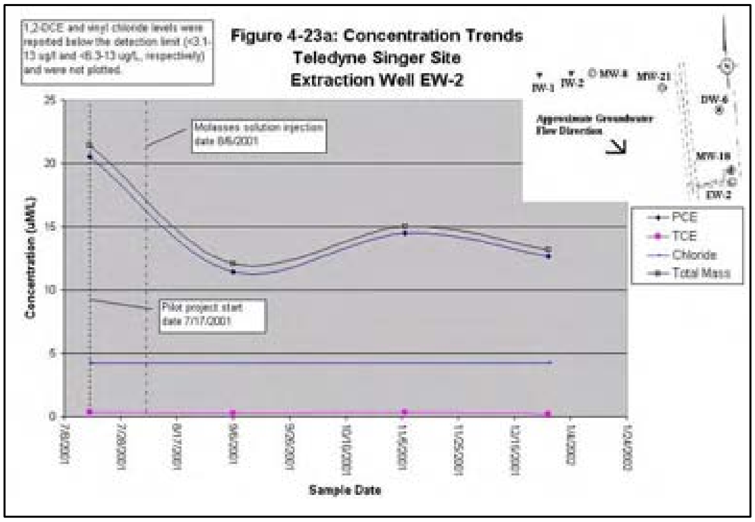


Figure 4-23a: Concentration Trends
Teledyne Singer Site
Extraction Well EW-2

1,2-DCE and vinyl chloride levels were reported below the detection limit (<3.1-13 ug/l and <6.3-13 ug/L, respectively) and were not plotted.

Molasses solution injection date 8/6/2001

Pilot project start date 7/17/2001

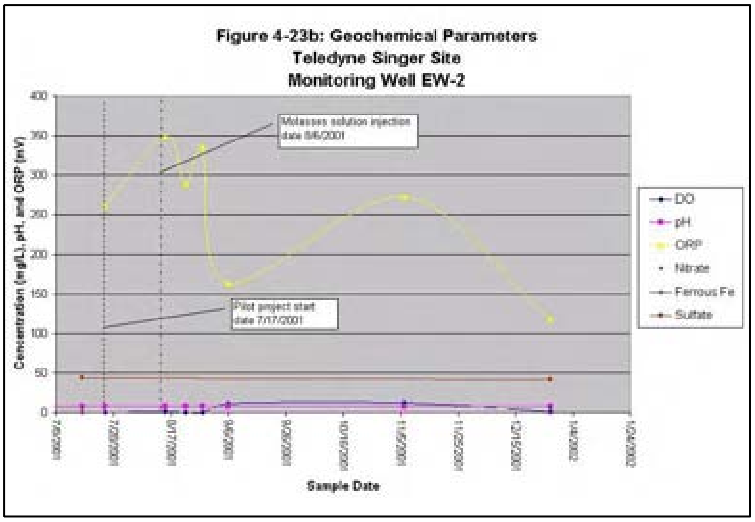


Figure 4-23b: Geochemical Parameters
Teledyne Singer Site
Monitoring Well EW-2

Molasses solution injection date 8/6/2001

Pilot project start date 7/17/2001

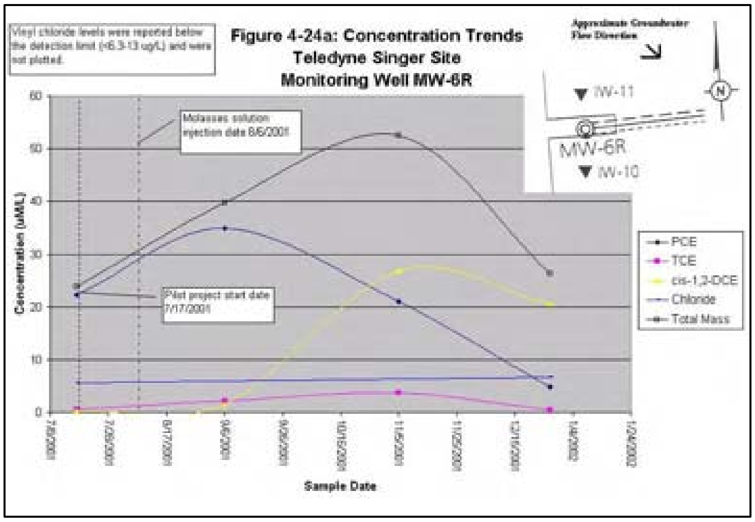
Well Number	**Contaminant Mass Loss**				**Enhanced Geochemical Conditions**	**Increased Dissolved Gases**	**Evaluation Rating**
	PCE	**TCE**	**DCE**	**VC**			
EW-2	+	0			-		SE

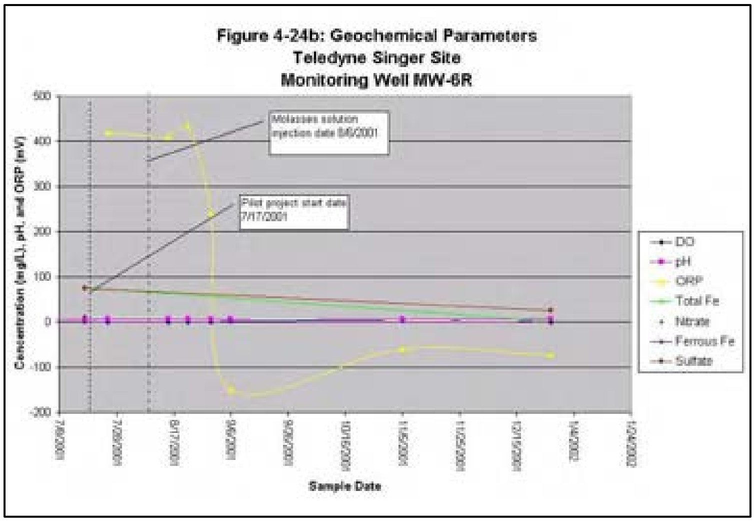
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	**PCE**			**TCE**			**cis-1,2-DCE**			**Vinyl Chloride**		
	C_o (µg/L)	**C_{163}**	**% reduced**	**C_o (µg/L)**	**C_{163}**	**% reduced**	**C_o (µg/L)**	**C_{163}**	**% reduced**	**C_o (µg/L)**	**C_{163}**	**% reduced**
EW-2	3400	2100	38%	43	28	35%	<13	<7.1	--[a]	<13	<7.1	--[a]

Note: C_o is the baseline concentration for samples collected on 7/17/2001.
C_{163} is the concentration for samples collected on 12/27/2001.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".
[a] The percent reduction was not calculated because the baseline or final sample concentration was below the detection limit.

Figure 4-24. Data Analyses for Monitoring Well MW-6R at the Teledyne Singer Site





Well Number	**Contaminant Mass Loss**				**Enhanced Geochemical Conditions**	**Increased Dissolved Gases**	**Evaluation Rating**
	PCE	**TCE**	**DCE**	**VC**			
MW-6R	+	0	+		+		ME

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	**PCE**			**TCE**			**cis-1,2-DCE**			**Vinyl Chloride**		
	C_o	**C_{163}**	**% reduced**	**C_o**	**C_{163}**	**% reduced**	**C_o**	**C_{163}**	**% reduced**	**C_o**	**C_{163}**	**% reduced**
	(µg/L)			**(µg/L)**			**(µg/L)**			**(µg/L)**		
MW-6R	3700	810	78%	89	56	37%	30	2000	-6567%	<13	<6.3	--[a]

Note: C_o is the baseline concentration for samples collected on 7/17/2001.
C_{163} is the concentration for samples collected on 12/27/2001.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".
[a] The percent reduction was not calculated because the baseline or final sample concentration was below the detection limit.

PCE, TCE, cis-1,2-DCE and vinyl chloride concentrations for the December 2001 groundwater sampling event were compared to the July 17, 2001 baseline concentrations to provide an estimate of the percentage of contaminant removed.

PCE and TCE concentrations at MW-6R were reduced by 78% and 37%, respectively, while cis-1,2-DCE concentrations increased greatly. The percent reduction of vinyl chloride at MW-6R was not calculated since values were below the detection limit.

At the other four monitoring wells, PCE concentrations were reduced between 15% and 78%. TCE concentrations were reduced between 17% and 64% at MW-21, MW-22, and EW-2 while no change was observed at EW-1. For cis-1,2-DCE and vinyl chloride, the percent reduction was not calculated since the baseline and final concentrations were below the detection limit. An exception is EW-1 where the vinyl chloride concentration increased by 38%.

Project Costs

The cost associated with the pilot study was not available.

Data Gaps

Sampling and analyses for dissolved gases methane, ethene, and ethane were included in the pilot project plan but were not performed. Future work should include analyses for these parameters which would provide a positive indication that biodegradation processes are being carried out to the desired end products.

Only the baseline sampling and final sampling event included analyses for the electron acceptor parameters (total iron, ferrous iron, nitrate, and sulfate). Additional data points are necessary to establish a trend with any certainty. Total iron appears to greatly decrease, but the ferrous ion concentration does not show a corresponding increase. The large decrease in total iron in some of the wells (200,000 mg/l to 0 mg/l in MW-22, 250,000 mg/l to 0 mg/l in MW -21, and 75,000 mg/l to 0 mg/l in MW-6R) appears suspect and should be reviewed for sampling and analytical errors.

Groundwater data for MW-7 and MW-8 should be assessed for enhanced reducing conditions since they are located downgradient of the injection points. Data for MW-8 should be reviewed since it is located approximately 8 feet downgradient from IW-2 and 18 ft from IW-1. Historical data for MW-21 and MW-22 should also be reviewed to determine if a trend can be established.

Summary Observation and Lessons Learned

Enhanced biodegradation was not observed in the wells downgradient of the injection wells. This was clearly due to the aquifer's low permeability and the low groundwater gradient encountered at this site. Resulting low groundwater flow velocities were not sufficient to transport the injected molasses solution over the distance to the downgradient monitoring wells during the course of the pilot project.

Limited PCE biodegradation was observed in MW-6R located between two injection wells where conditions were enhanced by the molasses injections. At MW-6R, PCE biodegraded to its daughter products, TCE and 1,2-DCE but then stalled at cis-1,2-DCE. Decreases in PCE concentrations at MW-21, MW-22, EW-1, and EW-2 appear to be occurring independently of in-situ bioremediation since TCE concentrations remained constant, little 1,2-DCE was generated, and vinyl chloride was not detected. Ethene was not analyzed in samples collected after start of pilot test. Future in-situ bioremediation efforts should include a microcosm study to evaluate if dechlorinating microbes are present, and sampling and analysis for ethene.

Due to the aquifer's low permeability, a rough estimate of the hydraulic velocity would have helped in placing downgradient monitoring wells. Using November 1998 groundwater contours, the hydraulic gradient was estimated to be 0.035 ft/ft in the shallow aquifer zone. Assuming a hydraulic conductivity of 6.4 ft^2/day and aquifer thickness of 25 feet, the groundwater velocity was estimated to be 0.03 ft/day. Assuming a plug of water travels 65 feet (the distance from the nearest injection well to EW-2) the estimated travel time is 2176 days.

Due to the high pressures observed during the amendment injections, injection wells installed during the pilot study should be checked to determine if the bentonite seals are still intact. Bentonite seals in direct push injection wells at another Palo Alto site had failed when injection pressures were observed around 20 psi. If the bentonite seals failed, the amendments may have dispersed in more permeable sections of the aquifer which did not coincide with the depth interval of the well screens.

Reference

Arcadis G&M Inc., In-situ Reactive Zone (IRZ) Pilot Test Start-up Report, Lockheed Martin Corporation, Teledyne-Singer Site, 3176 Porter Drive, Palo Alto, California, October 2001.

Arcadis G&M Inc., IRZ Pilot Test Status Report Teledyne-Singer Site, 3176 Porter Drive, Palo Alto, California, January 2002.

Department of Toxic Substances Control (DTSC), Calsites Site Mitigation Program Properties Database (SMPPD) Profile Report, No date.

DTSC, Fact Sheet: Teledyne-Singer Site Enhancement to the Remedial Action Plan, October 2003.

4.4 Electro-Coatings

Summary

A total of one-hundred and twenty-nine (129) temporary injection points have been installed at the former Electro-Coatings site as part of the full-scale bioremediation system. A molasses:water mixture was injected into the groundwater on 4 separate injection events at the site; one in April 1997, one in February 1998, one in March 1999, and one in October 2000. The total amount of this mixture injected was not available. Ten monitoring wells were sampled over approximately 6 years. Groundwater samples were analyzed for PCE and its daughter compounds, ORP, pH and DO.

Prior to system startup most wells in and immediately downgradient of the injection grid had PCE concentrations below the detection limit. PCE decreased in MW-4 and MW-5 by 43% and 95%, respectively, but these wells also had low initial PCE concentrations of 63µg/l and 10µg/l, respectively. TCE decreased in all wells between 71% and 99.9%. cis-1,2-DCE decreased within the injection grid area except at MW-4 where it increased by 1,827%. Vinyl chloride increased in MW-4 by 530% and was detected at lower concentrations in MW-5, MW-14, MW-16, MW-17, and MW-18. Ethane and ethene were detected at low concentrations in MW-10, MW-13, MW-14, MW-16 and MW-17

Site Background

From 1952 until 1995, Electro-Coatings performed metal plating operations, including nickel plating, at the 1401 and 1421 Park Avenue facility located in Emeryville, California. A vapor degreaser located inside the southwest corner of the 1421 Park Avenue building was gravity fed by an outside aboveground storage tank. TCE was originally used in degreasing operations until 1973 when it was replaced with TCA. In 1992, vapor degreasing operations were discontinued and replaced with a liquid-alkaline soak process. In 1995, plating operations were discontinued, and the associated plating equipment was removed from the site. Operations at the site resulted in the groundwater becoming contaminated with chlorinated solvents and metals.

Between 1977 and 1985, 24 groundwater monitoring wells were installed at the site and on adjacent properties. Elevated levels of chromium and TCE were detected in groundwater in the late 1970s and early 1980s. In 1995, the site owner initiated a pilot study to evaluate anaerobic reductive dechlorination and metals precipitation via an in-situ reactive zone as an alternative to a conventional pump and treat system.

In April 1997, in-situ bioremediation was implemented as the remediation alternative. Site cleanup is being completed under a state voluntary cleanup program overseen by the RWQCB Region 2 (Oakland office). In December 2002, the 1401 Park Avenue property clean-up was considered complete by the RWQCB and was approved for development of 43 condominiums and 10 live-work units. The 1421 Park Avenue property is still under remediation which is being overseen by the RWQCB. Figure 4-25 shows the locations of monitoring wells and injection points located at the 1401 and 1421 Park Avenue property.

Site Geology/Hydrogeology

The former Electro-Coatings facility is located in the San Francisco Bay Area, at an elevation of approximately 15 feet below sea level, on a low-lying plain bordering the San Francisco Bay. The site and surrounding area are underlain by interfingering tideland and alluvial deposits which occur along the eastern margin of the San Francisco Bay. The alluvial deposits consist of clay, silt, sand, and gravel, while the tideland deposits consist primarily of clay. Past investigations have encountered permeable units of sand and gravel between 5 to 25 feet bgs within the shallow water-bearing zone. A blue clay zone is present throughout the site and underlies the shallow water-bearing zone at a depth of approximately 25 feet bgs. Based on the 1994 report “Summary of Site Conditions”, three monitoring wells constructed below the shallow water-bearing zone were installed and screened as follows: MW-3A between 57-61 ft, MW-18A between 35-50 ft, and MW-20 between 31-51 ft. A slight vertically downward hydraulic head was observed in deep monitoring wells MW-3A and MW-18A while a 3-foot vertically upward hydraulic head was observed at deep monitoring well MW-20. According to the 1994 report “Summary of Site Conditions”, the upward hydraulic head at MW-20 was thought to indicate that contaminants were not likely to migrate below the shallow aquifer under natural conditions.

Groundwater is found at depths of 3.5 to 8 feet bgs. Groundwater velocity is estimated to be 60 feet per year. TCE and chromium are the primary contaminants in the groundwater at the site. TCE concentrations from April 1995 (prior to initiation of the pilot study) were as high as 17,000 µg/L at monitoring well MW-14. Historical groundwater data from on-site wells indicated that, over the past 10 years, TCE concentrations have been slowly decreasing. For example, TCE concentrations in groundwater samples collected in June 1985 at MW-10 were 12,000 µg/L while samples collected in August 1995 had TCE concentrations at 10,000 µg/L. Figure 4-26 shows the historical groundwater flow direction and groundwater elevations from the last available monitoring report for 2002.

Project Description

Pilot Study

A pilot study was conducted between August 1995 and February 1996 to determine if TCE degradation and metals precipitation could be enhanced by an anaerobic in-situ reactive zone. The pilot study mainly focused on whether in-situ bioremediation could effectively treat hexavalent chromium in groundwater. Since TCE was also detected in groundwater, the pilot study also tried to determine if concurrent TCE biodegradation could be achieved. This review only focuses on TCE degradation results.

As part of the pilot study, two observation wells (OW-1 and OW-2) were installed 15 feet apart from each other and approximately 25 feet and 10 feet downgradient of MW-11, respectively. A drive point (DP-1) was also installed approximately 7.5 feet upgradient of MW-10. The two observation wells were completed to a total depth of 20 feet and screened from 5 to 20 feet bgs. The drive point was completed to a total depth of 20.5 feet and screened from 13.5 to 19.5 feet bgs.

Baseline groundwater samples were collected on August 22, 1995 from monitoring wells MW-10, MW-11, MW-12, MW-3B, OW-1, and OW-2 and analyzed for halogenated volatile organic compounds (HVOCs), nitrate, nitrite, and sulfate. During the pilot study, groundwater samples were collected from 14 monitoring wells and analyzed for HVOCs using U.S. EPA Method 5030/8010, and periodically analyzed for nitrate, nitrite, and sulfate using U.S. EPA Method 300.0. Samples from select wells were also analyzed for biological oxygen demand (BOD), chemical oxygen demand (COD), and heterotrophic plate count (HPC). Field measurements for temperature, pH, DO, and the ORP were also collected. Table 4-7 lists the analyses performed on samples collected from wells that were monitored as part of the pilot study.

Table4-7. Groundwater Analyses By Well For the Pilot Study at the Former Electro-Coatings Facility

U.S. EPA Method	MW-3A	MW-3B	MW-3C	MW-4	MW-5	MW-10	MW-11	MW-12	MW-13	MW-14	MW-20	OW-1	OW-2	DP-1
8010[a]	x	x	x	x	x	x	x	x	x	x	x	x	x	x
300.0[b]		x	x			x	x	x	x	x		x	x	x
200.7[c]	x	x	x	x	x	x	x	x	x	x	x	x	x	x
7196[d]	x	x	x	x	x	x	x	x	x	x	x	x	x	x
BOD						x	x						x	x
HPC		x	x			x	x	x		x			x	x

[a] U.S. EPA Method 8010 used to analyze samples for HVOCs. Concentrations reported in pilot study report included PCE, TCE, cis- and trans-1,2-DCE, vinyl chloride, 1,1-DCE, 1,1,1-TCA, 1,1-DCA, and 1,2-DCA.
[b] U.S. EPA method 300.0 used to analyze samples for nitrate, nitrite, and sulfate.
[c] U.S. EPA method 200.7 used to analyze samples for total chromium.
[d] U.S. EPA method 7196 used to analyze samples for hexavalent chromium.

Solutions of "blackstrap" molasses and tap water were injected primarily into MW-11 with the exception of one injection at OW-1 and three injections at DP-1. Table 4-8 lists the injection dates, quantities and solution ratio for each injection event. The molasses solution at MW-11 was injected using a gravity-feed system on a biweekly basis. At DP-1, the solution was injected using an air-operated, double-diaphragm pump but details on the amount of pressure used were not available. In December 1995, supernatant from a local wastewater treatment system was added to the molasses solution. Supernatant was added to the solution due to low plate counts (53 CFU/mL) observed in the October 1995 sample from MW-14, located 160 feet downgradient of MW-11. After injections, no additional samples were analyzed to confirm an increase in the plate count at MW-14. However, plate count results for MW-10, MW-11, and OW-2 showed bacteria counts dropped after four months. Plate counts at MW-12 were inconclusive since the initial plate count results were 13,000 CFU/ml but after two months were reported at >5,700 CFU/ml.

Table 4-8. Molasses Injection Quantities and Concentrations

Well No.	Date	Quantity (gallons)	Water:Molasses Ratio	Solution Inoculated?
OW-1	12-22-95	330	10:1	Yes
DP-1	8-22-95	25	4:1	
	12-22-95	115	4:1	Yes
	3-14-96[a]	100	4:1	Yes
MW-11	8-22-95	50	100:1	
	9-5-95	50	100:1	
	9-19-95	50	100:1	
	10-3-95	50	100:1	
	10-17-95	50	100:1	
	10-31-95	50	100:1	
	11-14-95	50	100:1	
	11-28-95	50	100:1	
	12-4-95	50	100:1	
	12-22-95	158	20:1	Yes
	1-4-96	150	20:1	Yes
	1-19-96	150	20:1	Yes
	2-1-96	150	20:1	Yes

[a] 150 mg of B-12 was also added to the solution

Full-Scale System

A total of one-hundred and twenty-nine (129) temporary injection points have been installed at the former Electro-Coatings site as part of the full-scale bioremediation system. In April 1997, forty-six (46) temporary injection points were installed at the 1401 Park Avenue property along with fifty-two (52) injection points on the 1421 Park Avenue property. The depth of the injection points ranged between 20-24 feet bgs with a few points with depths ranging from 6-17 feet bgs.

As part of the October 2000 injection event, thirty-one (31) additional wells were installed on the southern portion of the 1401 Park Avenue property with depths ranging from 6 to 20 feet bgs. Each injection point was screened over a 5-foot interval located above the bottom of the well. Figure 4-25 shows all the injection points installed on both the 1401 and 1421 Park Avenue properties as of October 2000 while Figure 4-27 shows only the injection points installed at the 1401 Park Avenue property.

Four molasses injection events have been performed at the site; one in April 1997, one in February 1998, one in March 1999, and one in October 2000. According to the “Closure Report” dated March 2001, the 4th injection event concentrated on the 1401 property while the other 3 injection events were performed at the 1401 and 1421 properties. For the first three injection events, a 5:1 solution of tap water/molasses and a small amount of supernatant (to provide additional bacteria capable of degrading TCE according to the

Figure 4-25 Monitoring and Injection Wells for the Former Electro-Coatings Facility at the 1401 and 1421 Park Avenue Property

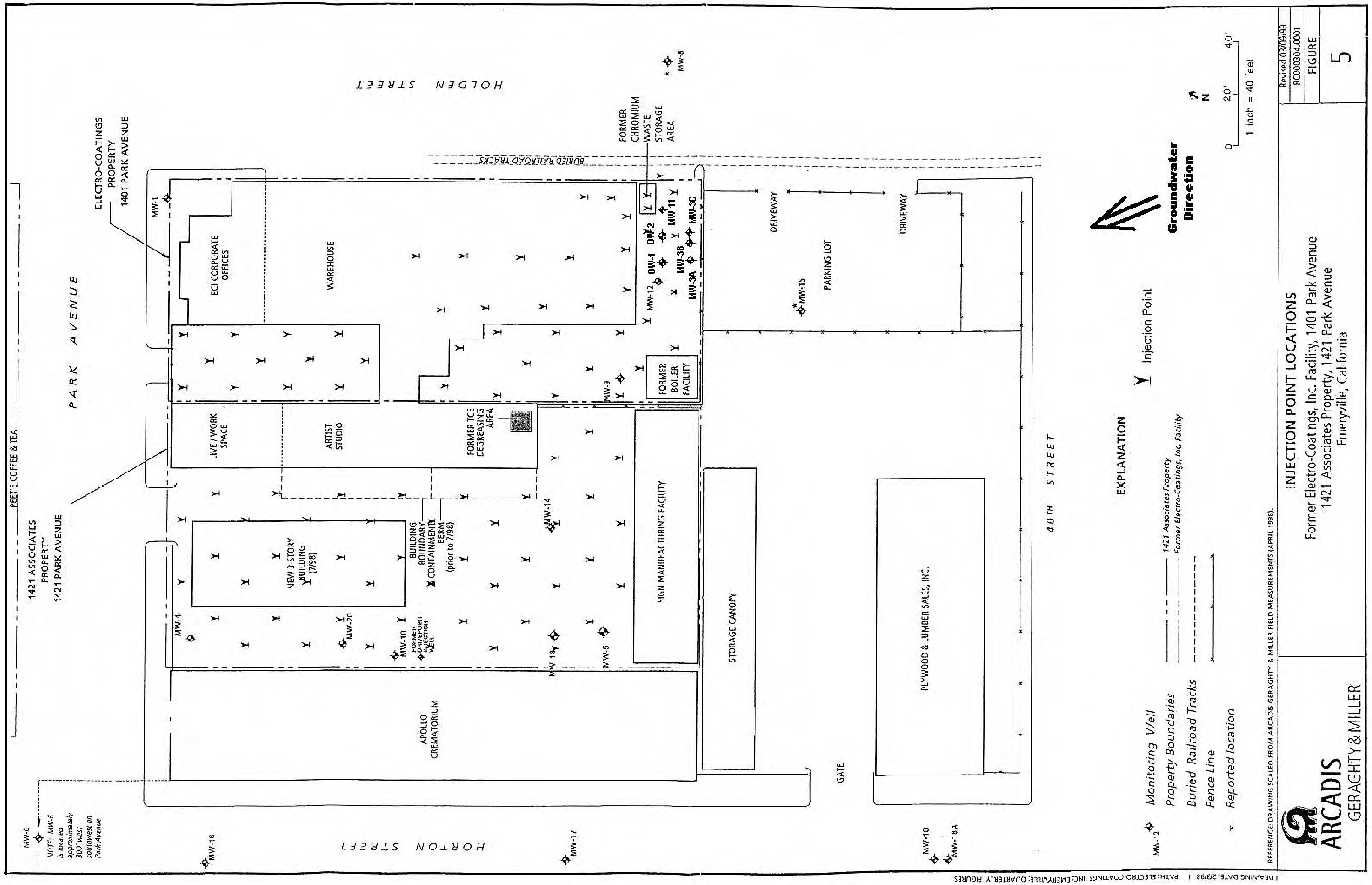
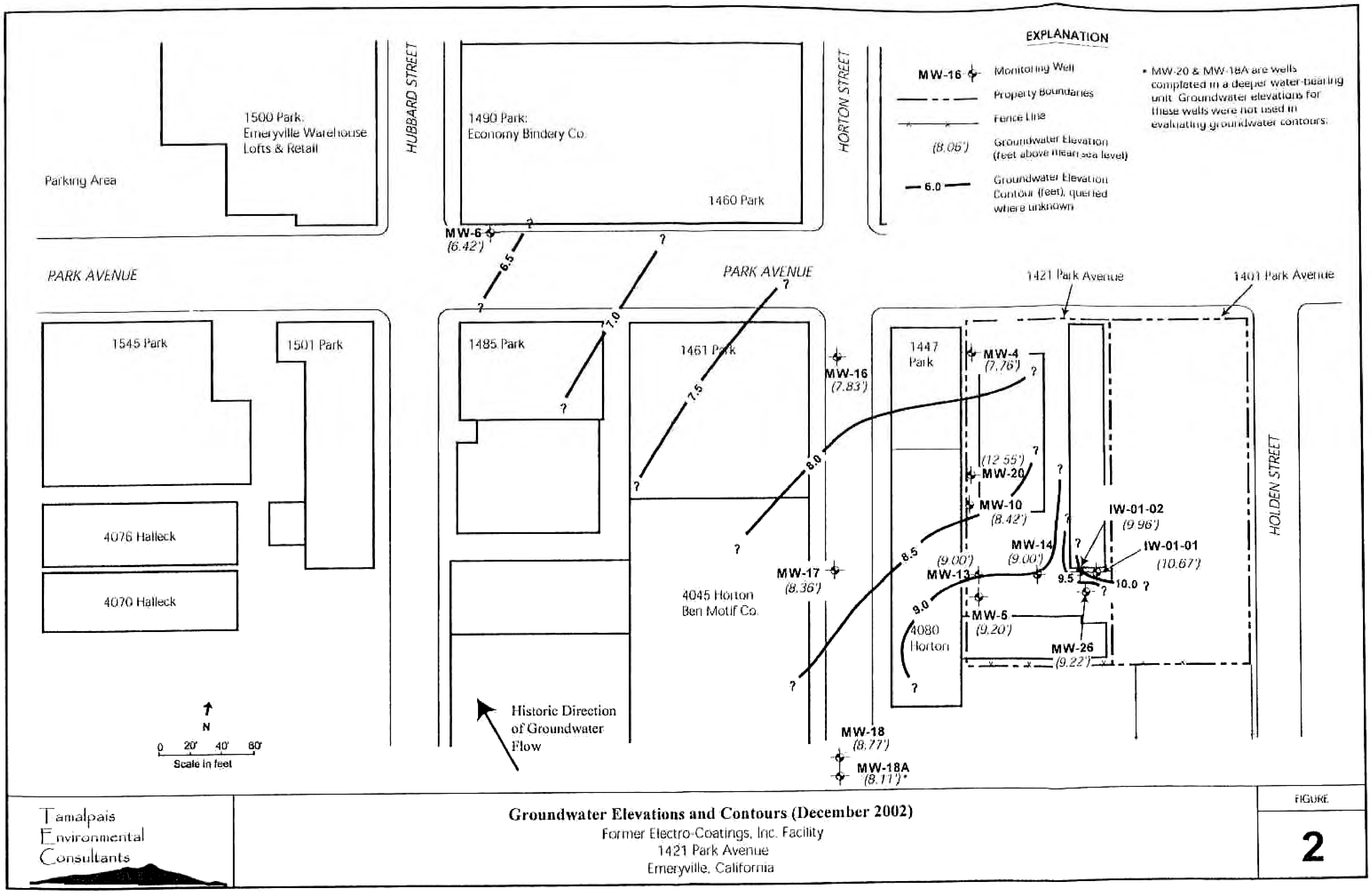


Figure 4-26   2002 Groundwater Elevations at the Former Electro-Coatings Facility



consultant) were used. The reagent was mixed on-site and manually injected into the subsurface at pressures between 35 to 40 pounds per square inch (psi) using a centrifugal pump. During the first injection event, each injection point received 25 gallons of molasses, 1 gallon of supernatant, and 125 gallons of water. No data was available on the volume and composition of the solution used for the second and third events. For the fourth injection in October 2000, approximately 175 gallons of the 20:1 tap water/molasses solution was injected into each of the new 31 injection points.

After the October 2000 injection event, all on-site and upgradient monitoring wells and injection wells on the 1401 Park Avenue property were abandoned including MW-1, MW-3A, MW-3B, MW-3C, MW-8, MW-9, MW-11, MW-12, MW-15, OW-1, and OW-2. Final concentrations in these wells were not available for this report.

In March 2002, a workplan was submitted for additional molasses injections to be conducted on and adjacent to the 1421 Park Avenue property. The proposed plan included installing 29 injection wells on and around the 1421 Park Avenue property (see Figure 4-28). Direct push technology is to be used to install the injection wells, screened between 7-12 feet bgs and spaced approximately 30 feet apart. The plan calls for approximately 250 gallons of molasses solution to be injected at each injection point at pressures up to 40 psi. The molasses solution is also to be injected into IW-01-01 and IW-01-02. According to the consultant, the molasses solution will be replaced with cheese whey. As of July 2003, these additional wells have not been installed due to right-of-way issues with the City of Emeryville.

Project Performance

Appendix B contains the groundwater monitoring results for all wells monitored as part of the pilot study and the full-scale system. Tables listing the qualitative and quantitative results for all wells are also provided in Appendix B. Figures 4-29 through 4-39 present graphs with concentration and select geochemical parameter trends. These figures also present tables with qualitative and quantitative indications of biodegradation conditions at each well.

Pilot Study

Concentration and select geochemical parameter trends for OW-1, OW-2, MW-10, MW-14, MW-13 and MW-4 are presented in Figures 4-29 thru 4-34. Results for MW-4, MW-10, MW-13, and MW-14 are presented since these wells are sampled in the full-scale system while OW-1 and OW-2 were installed specifically for the pilot study.

Reviewing the pilot study results between 8/22/95 and 9/13/96, PCE and TCE do not appear to biodegrade faster due to the molasses injections around MW-11. Initial PCE and TCE concentrations in wells around MW-11 were low (<0.5 – 10µg/L and 4.7-290µg/l, respectively). Although cis-1,2-DCE, a daughter product of TCE, was also detected in these wells, the fluctuating concentrations appear to be independent of the molasses injections. Vinyl chloride concentrations in OW-1 and MW-3C increased slightly while decreasing in MW-12. Vinyl chloride trends could not be established for the other wells because either no results were available or it was detected in only one sample. No results were available for methane, ethane, and ethene for all wells.

Based on DO, ORP and nitrate results, enhanced geochemical conditions were present in OW-1, OW-2, MW-3B, MW-11, and MW-12. ORP concentrations in these wells decreased greatly when the molasses/supernatant solution was injected. However, sulfate concentrations increased in MW-11, OW-1, and OW-2 after these injections even though ORP readings indicated sulfate reducing conditions were present.

A PCE concentration spike was observed in MW-12 and MW-3A around the beginning of March 1996 approximately one month after the last injection. The cause of the spike is not known.

For MW-10 near DP-1, TCE concentrations decreased when the molasses solution was injected and cis-1,2-DCE was generated after injecting the molasses/supernatant solution. However, the process appears to have stalled at cis-1,2,-DCE. No results were available for methane, ethane, and ethene concentrations. DO, ORP, nitrate, and sulfate concentrations indicated enhanced geochemical conditions were present. ORP and sulfate concentrations decreased when molasses/supernatant solution was injected.

For the downgradient wells MW-5, MW-13, and MW-14, little geochemical data was collected to determine if enhanced conditions were present. Molasses injections at MW-11 did not appear to have an effect on PCE, TCE, and cis-1,2-DCE concentrations at these wells. (Refer to Appendix B, Figures B-15 thru Figure B-34 for trend plots of the geochemical, electron acceptor and biological parameters).

At the end of the pilot test, PCE concentrations decreased in wells near MW-11 except at MW-3C where concentrations increased by 1240%. It should be noted that initial concentrations in all wells around MW-11 were low (1-10µg/L). TCE and cis-1,2-DCE concentrations increased in half the wells while it decreased in the other wells. Vinyl chloride was only detected in MW-3C at the end of the pilot study. At MW-10, TCE, initially detected at 11,000µg/L decreased by 60% while cis-1,2-DCE increased by 911%. At MW-14, located approximately 130 feet downgradient from MW-11, TCE decreased by 42% but a percent change in cis-1,2-DCE and vinyl chloride couldn’t be calculated since the detection limit value was higher than the initial value.

Since amendment injections for the pilot study were only performed mainly at MW-11 and a few at DP-1and OW-1, the distance between the monitoring well locations and injection point was taken into consideration. At MW-13, located 175 feet downgradient of MW-11, TCE and cis-1,2-DCE concentrations increased by 19% and 20%, respectively. MW-4 (located 280 feet and 180 feet downgradient of MW-11 and DP-1, respectively) had PCE concentrations that increased by 63% but TCE and cis-1,2-DCE concentrations that decreased by 59% and 5%, respectively.

Figure 4-27. Injection Wells at the 1401 Park Avenue Property for the Former Electro-Coatings Facility

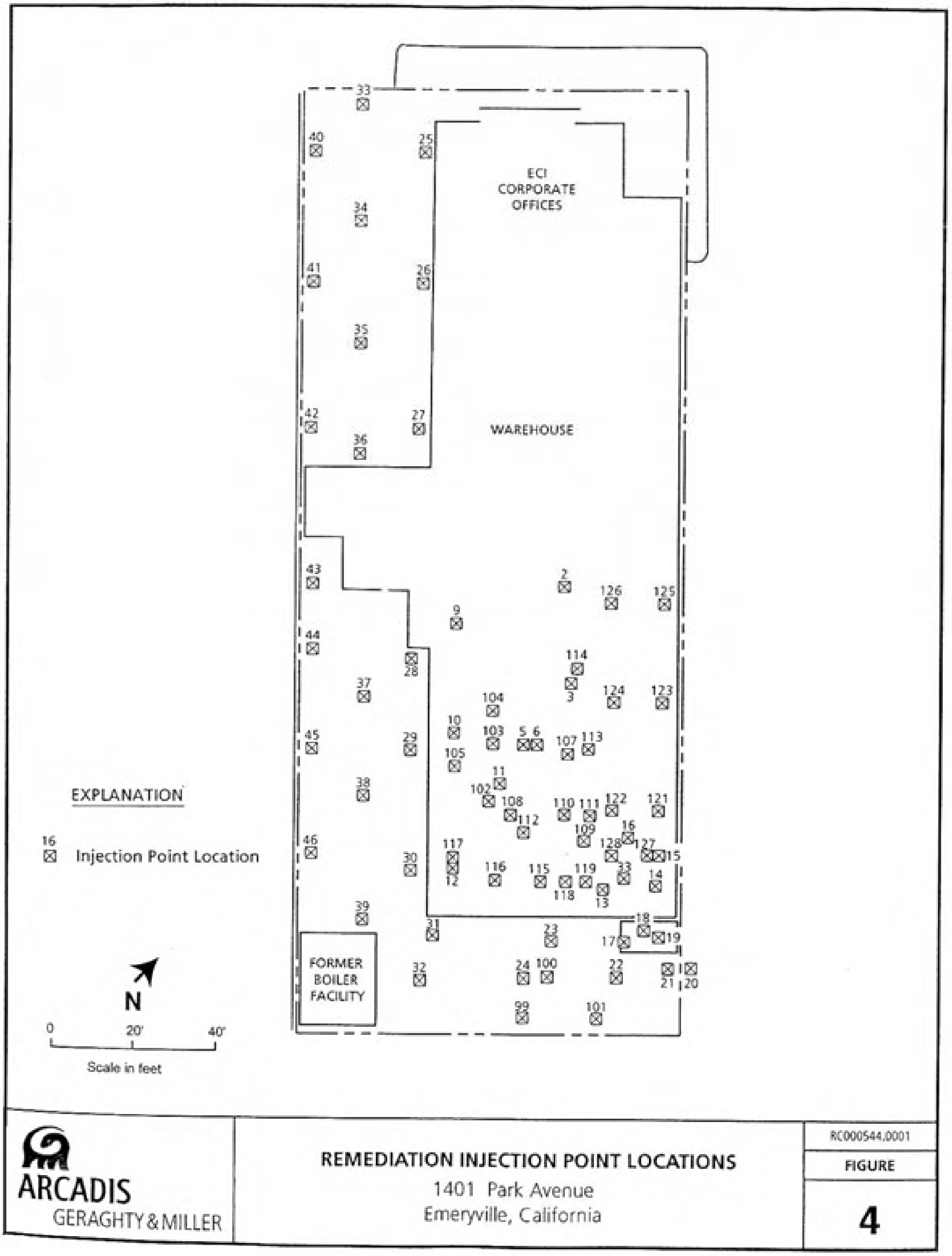


Figure 4-28. Proposed 2002 Injection Well Locations for 1421 Park Avenue Property at the Former Electro-Coatings Facility

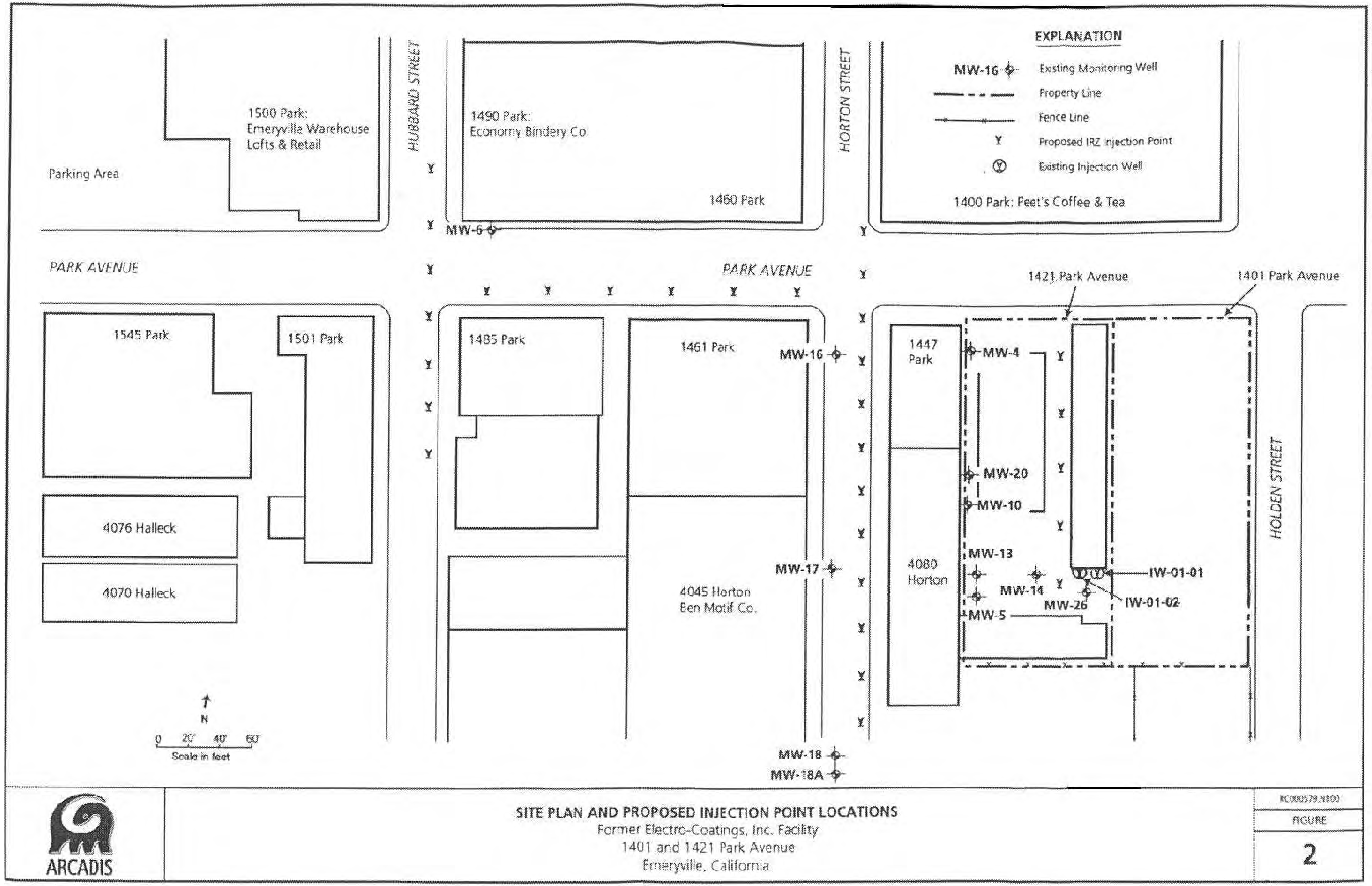
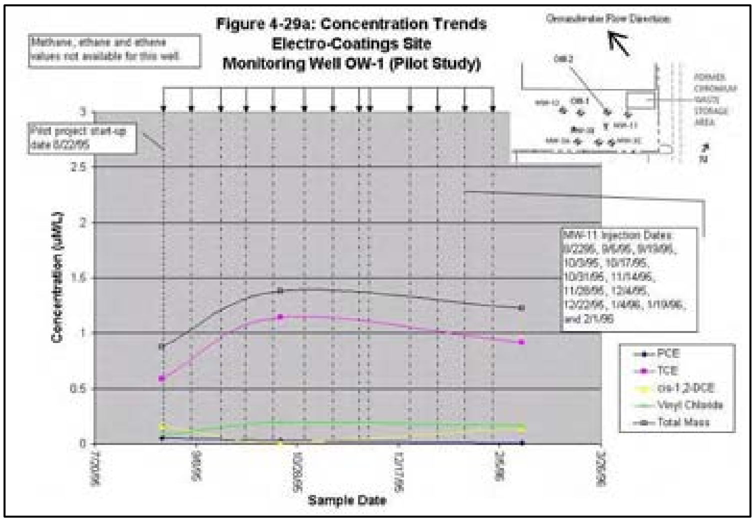
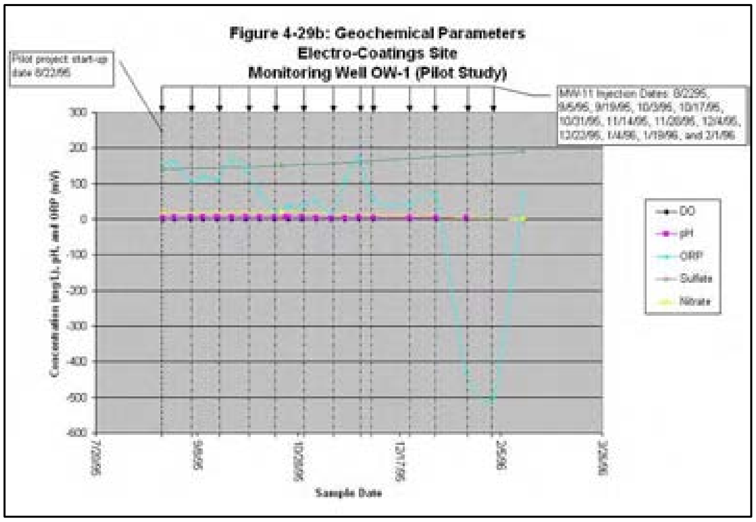


Figure 4-29. Data Analyses for Pilot Study:OW-1 at the Electro-Coatings Facility





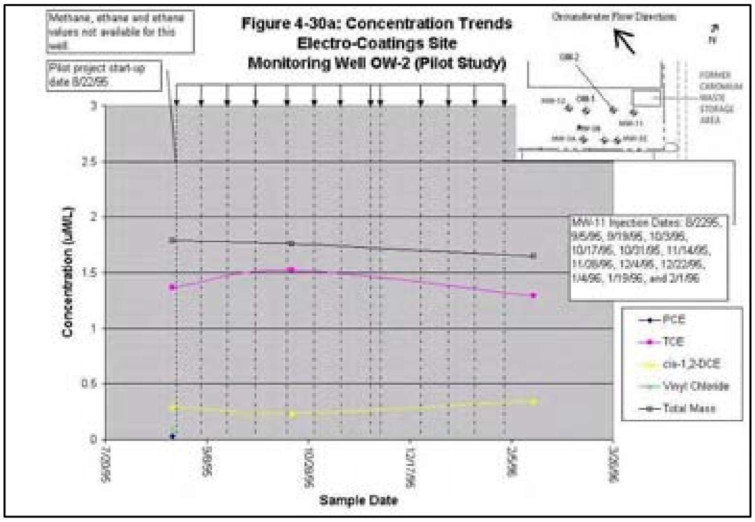
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
OW-1	0	0	0	0	+		SE

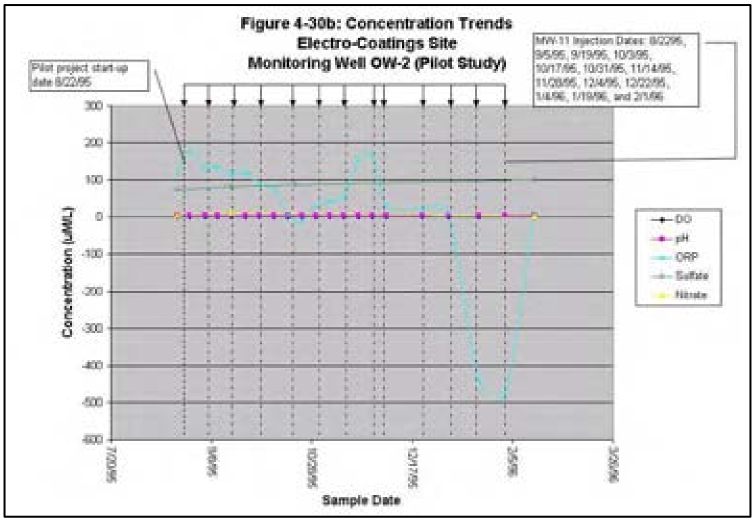
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced
OW-1	8.9	1.7	81%	77	120	-56%	16	14	13%	4.5	<10	--

Note: C_o is the baseline concentration for samples collected on 8/21/1995 and 8/22/95.
C_i is the concentration for samples collected on the last recorded sample date which was 2/16/96.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-30. Data Analyses for Pilot Study:OW-2 at the Electro-Coatings Facility





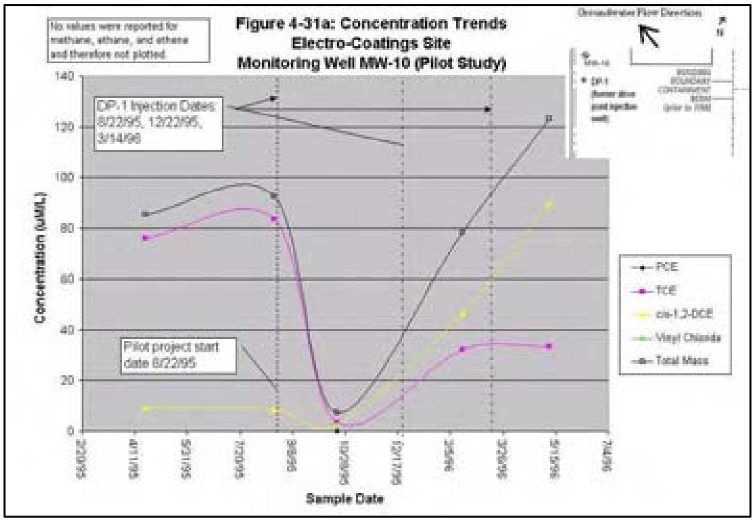
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
OW-2		0	0		+		SE

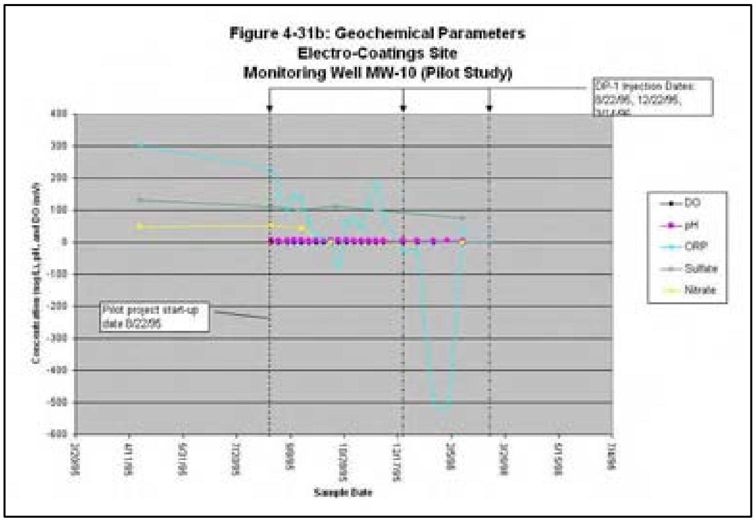
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced
OW-2	4.9	<5	--	180	170	6%	29	34	-17%	5.6	<10	--

Note: C_o is the baseline concentration for samples collected on 8/21/1995 and 8/22/95.
C_i is the concentration for samples collected on the last recorded sample date which was 2/16/96.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-31. Data Analyses for Pilot Study: MW-10 at the Electro-Coatings Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-10		+	+		+		ME

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced
MW-10	<250	<250	--	11000	4400	60%	860	8700	-911%	<500	<500	--

Note: C_o is the baseline concentration for samples collected on 8/21/1995 and 8/22/95.
C_i is the concentration for samples collected on the last recorded sample date which was 5/9/96.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-32. Data Analyses for Pilot Study: MW-14 at the Electro-Coatings Facility

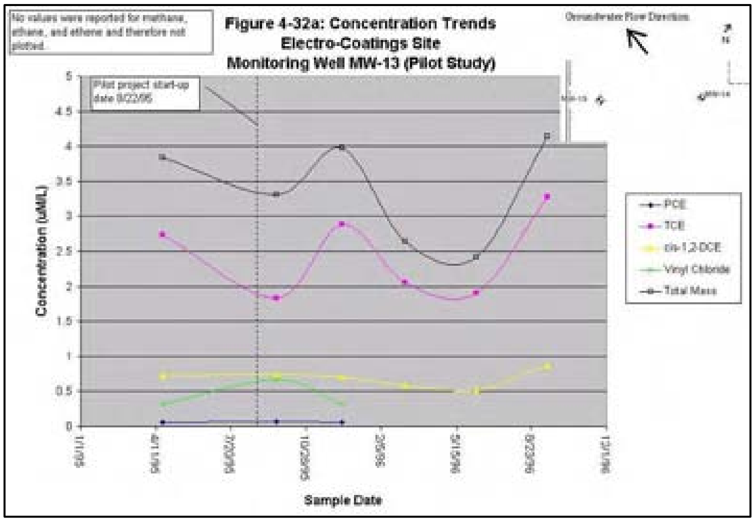


Figure 4-32a: Concentration Trends
Electro-Coatings Site
Monitoring Well MW-13 (Pilot Study)

No values were reported for methane, ethane, and ethene and therefore not plotted.

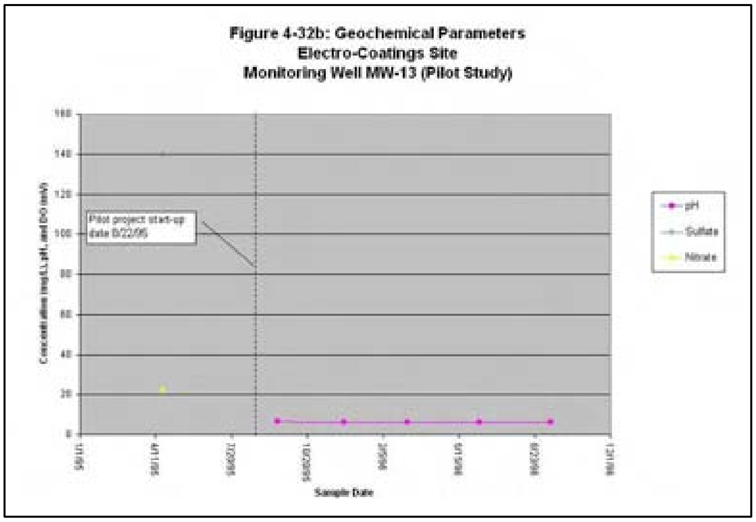


Figure 4-32b: Geochemical Parameters
Electro-Coatings Site
Monitoring Well MW-13 (Pilot Study)

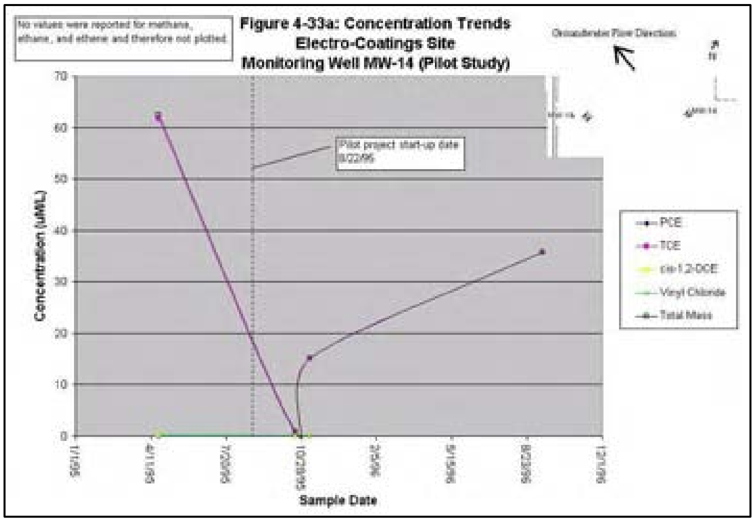
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-14		-	0	0	+		SE

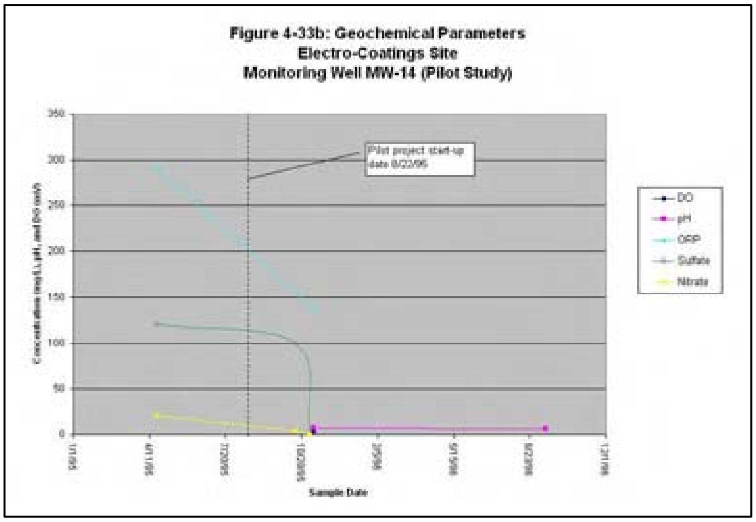
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced
MW-14	<10	<1000	--	8100	4700	42%	36	<1000	--	<20	<2000	--

Note: C_o is the baseline concentration for samples collected on 8/21/1995 and 8/22/95.
C_i is the concentration for samples collected on the last recorded sample date which was 9/13/96.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-33. Data Analyses for Pilot Study: MW-13 at the Electro-Coatings Facility





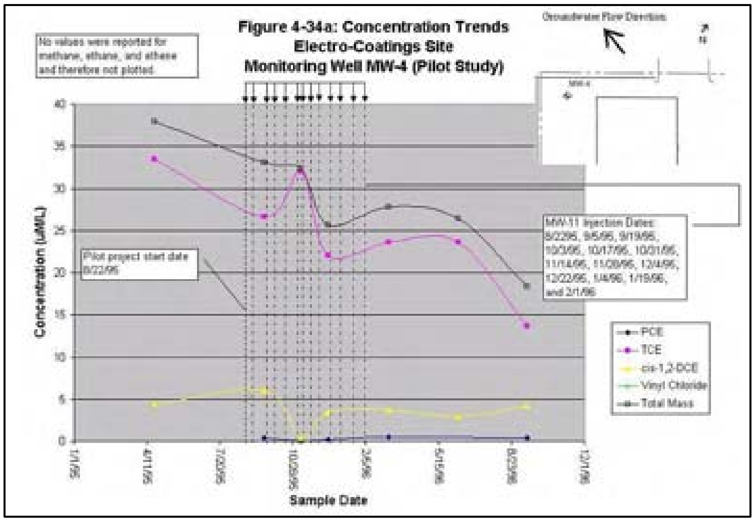
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-13	0	-	+	0			SE

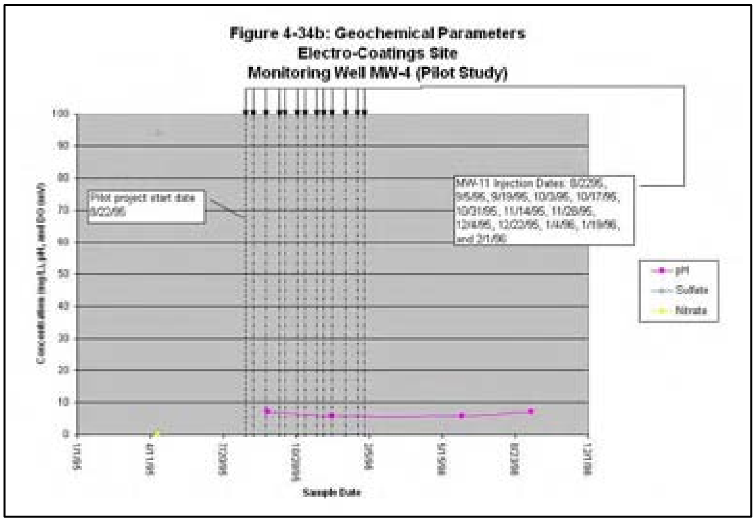
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced
MW-13	8.9	<50	--	360	430	-19%	70	84	-20%	20	<100	--

Note: C_o is the baseline concentration for samples collected on 8/21/1995 and 8/22/95.
C_i is the concentration for samples collected on the last recorded sample date which was 9/13/96.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-34. Data Analyses for Pilot Study: MW-4 at the Electro-Coatings Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-4	0	+	+				SE

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced
MW-4	<50	63	-26%	4400	1800	59%	430	410	5%	<100	<100	--

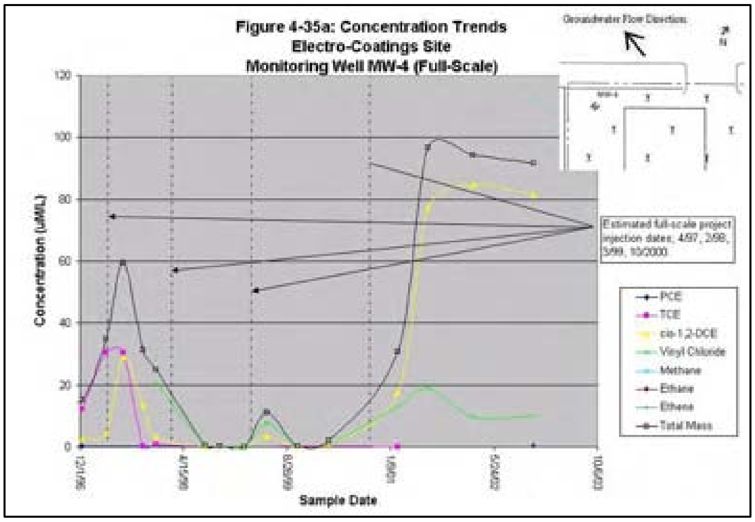
Note: C_o is the baseline concentration for samples collected on 8/21/1995 and 8/22/95.
C_i is the concentration for samples collected on the last recorded sample date which was 9/13/96.
% reduced is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

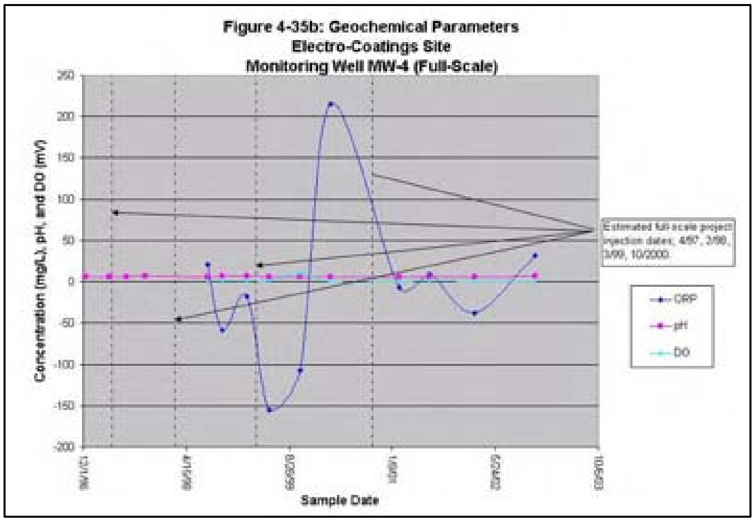
Full-Scale System

For the full-scale project, the molasses injections appeared to enhance PCE, TCE, cis-1,2-DCE and vinyl chloride biodegradation at select wells within the injection grid. PCE concentrations were generally low at the start of the full-scale project for all of the monitoring wells and were either reported below the detection limit or between 10 and 63 µg/L. MW-5 and MW-13 had decreasing PCE concentrations while MW-4 and MW-10 exhibited no change. TCE, cis-1,2-DCE, and vinyl chloride concentrations decreased at most wells except MW-4 where it appears that the process may have stalled at cis-1,2-DCE. Downgradient wells, MW-16 and MW-17, showed decreases in TCE and its daughter compounds concentrations. At MW-18, a gradual decreasing trend is observed except for two anomalous readings. These anomalies might be due to sampling or reporting errors since results remained fairly consistent prior to and after these readings. Methane, ethane, and ethene were detected in MW-13 while only methane and ethane were detected in MW-10. For the remaining wells, these gases were either not detected or no data was available. DO, ORP and pH were the only geochemical parameters available for the full-scale samples which indicate potential enhanced conditions. (Refer to Figure B-47 thru Figure B-60 in Appendix B). Results for MW-4, MW-10, MW-13, MW-14, and MW-16 are presented in Figures 4-35 thru 4-39 since these wells were located either within or downgradient of the injection points.

Most wells in and immediately downgradient of the injection grid had PCE concentrations below the detection limit. PCE decreased in MW-4 and MW-5 by 43% and 95%, respectively, but these wells also had low initial PCE concentrations of 63µg/l and 10µg/l, respectively. TCE decreased in all wells between 71% and 99.9%. cis-1,2-DCE decreased within the injection grid area except at MW-4 where it increased by 1,827%. Vinyl chloride increased in MW-4 by 530% and was detected at lower concentrations in MW-5, MW-14, MW-16, MW-17, and MW-18. Ethane and ethene were detected at low concentrations in MW-10, MW-13, MW-14, MW-16 and MW-17. Increasing methane concentrations were detected in injection grid wells MW-10, MW-13, and MW-14 in three 1998 samples but no additional results were available to indicate that this trend continued. Methane concentrations detected in MW-10, MW-13, and MW-14 were several orders of magnitude higher than the other contaminant concentrations and do not appear in Figures 4-35 thru 4-39. Decreasing methane concentrations were observed in downgradient wells MW-16 and MW-17. At the other wells, methane, ethane, and ethene were either not detected or had only one datum available.

Figure 4-35. **Data Analyses for Full-Scale System: MW-4 at the Electro-Coatings Facility**





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-4	0	+	+	+		-	SE

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o	C_i	% reduced	C_o	C_i	% reduced	C_o	C_i	% reduced	C_o	C_i	% reduced
	(µg/L)			(µg/L)			(µg/L)			(µg/L)		
MW-4	63	<36	43%	1800	<36	98%	410	7900	-1827%	<100	630	-530%

Note: C_o is the baseline concentration for samples collected on 9/13/96.
C_i is the concentration for samples collected on the last recorded sample date which was 12/12/02.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-36. Data Analyses for Full-Scale System: MW-10 at the Electro-Coatings Facility

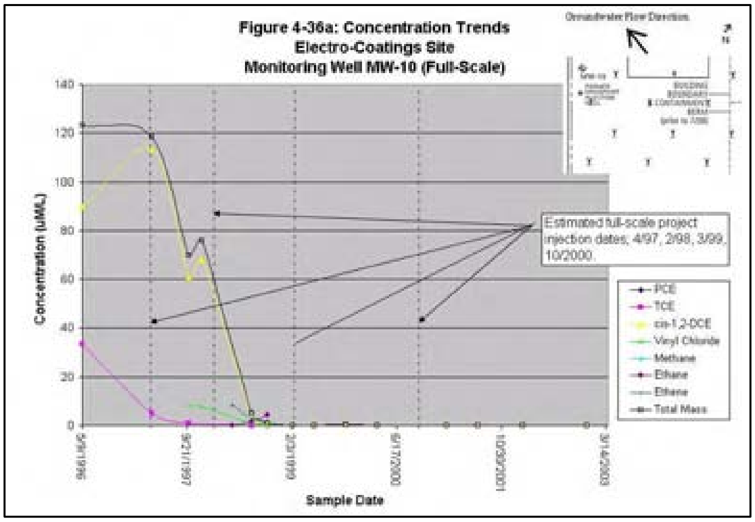


Figure 4-36a: Concentration Trends
Electro-Coatings Site
Monitoring Well MW-10 (Full-Scale)

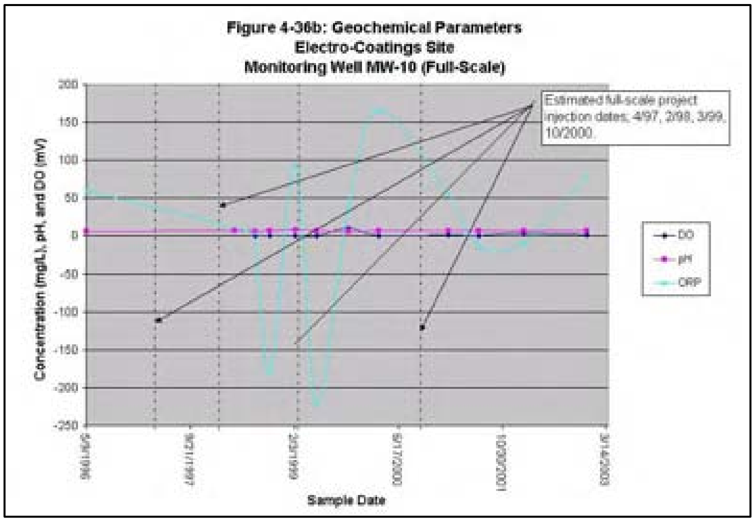


Figure 4-36b: Geochemical Parameters
Electro-Coatings Site
Monitoring Well MW-10 (Full-Scale)

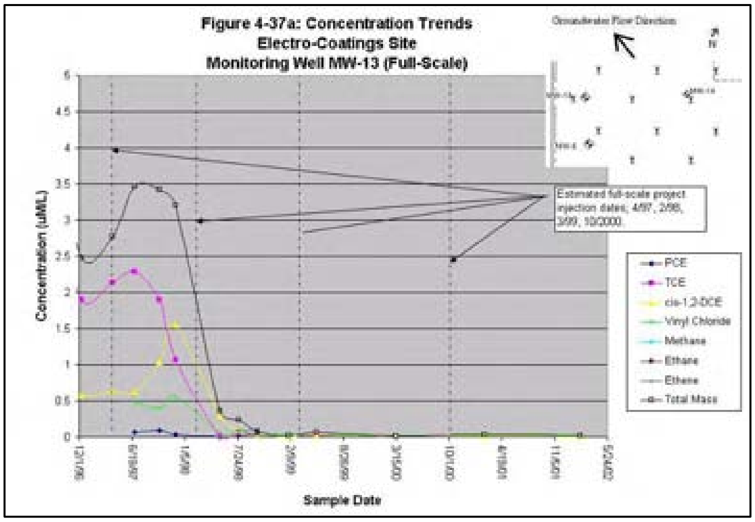
Well Number	**Contaminant Mass Loss**				**Enhanced Geochemical Conditions**	**Increased Dissolved Gases**	**Evaluation Rating**
	PCE	**TCE**	**DCE**	**VC**			
MW-10	0	+	+	+		+	ME

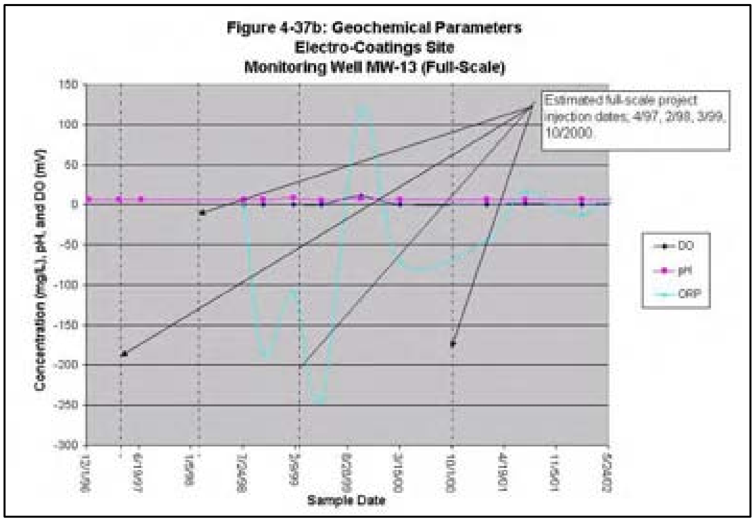
Note: “+” = Positive evidence “-” = No evidence “Blank” = Not available “0” = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	**PCE**			**TCE**			**cis-1,2-DCE**			**Vinyl Chloride**		
	C_o	**C_i**	**% reduced**	**C_o**	**C_i**	**% reduced**	**C_o**	**C_i**	**% reduced**	**C_o**	**C_i**	**% reduced**
	(μg/L)			**(μg/L)**			**(μg/L)**			**(μg/L)**		
MW-10	<250	<0.5	--	4400	10	99.8%	8700	2.3	99.97%	<500	<0.5	--

Note: C_o is the baseline concentration for samples collected on 5/9/1996.
C_i is the concentration for samples collected on the last recorded sample date which was 12/11/02.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-37. Data Analyses for Full-Scale System: MW-13 at the Electro-Coatings Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-13	+	+	+	+		+	ME
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced							

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced	C_o (µg/L)	C_i	% reduced
MW-13	<50	<0.5	--	430	<0.5	99.9%	84	<0.5	99.4%	<100	<0.5	--

Note: C_o is the baseline concentration for samples collected on 9/13/96.
C_i is the concentration for samples collected on the last recorded sample date which was 12/11/02.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-38. Data Analyses for Full-Scale System: MW-14 at the Electro-Coatings Facility

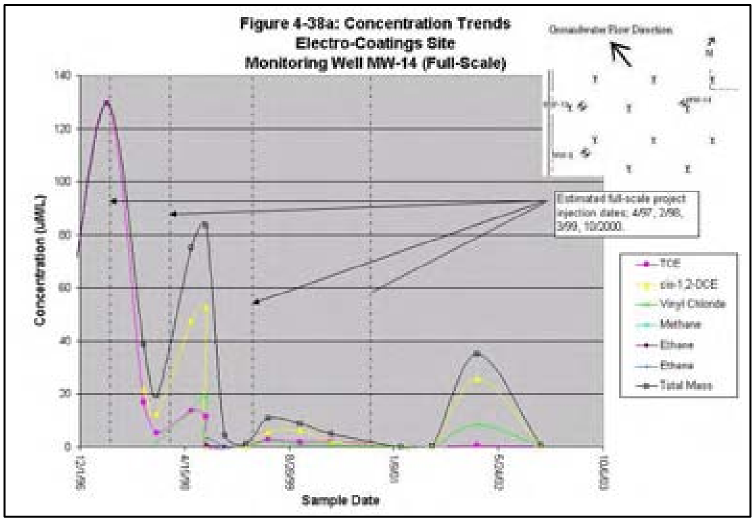


Figure 4-38a: Concentration Trends
Electro-Coatings Site
Monitoring Well MW-14 (Full-Scale)

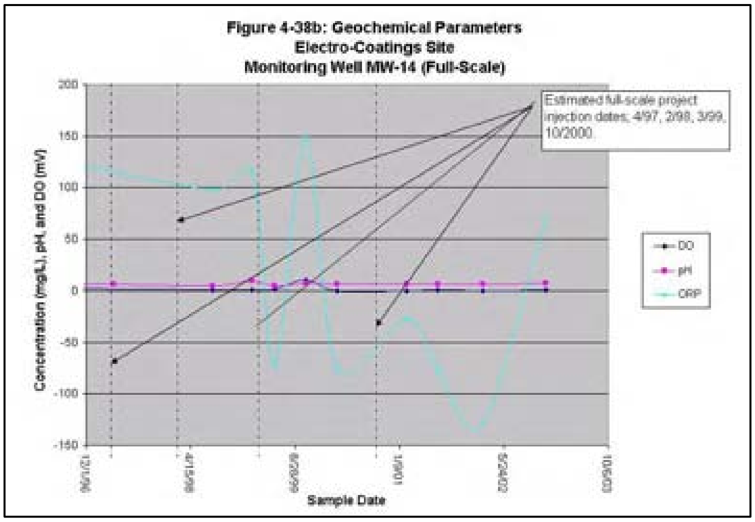


Figure 4-38b: Geochemical Parameters
Electro-Coatings Site
Monitoring Well MW-14 (Full-Scale)

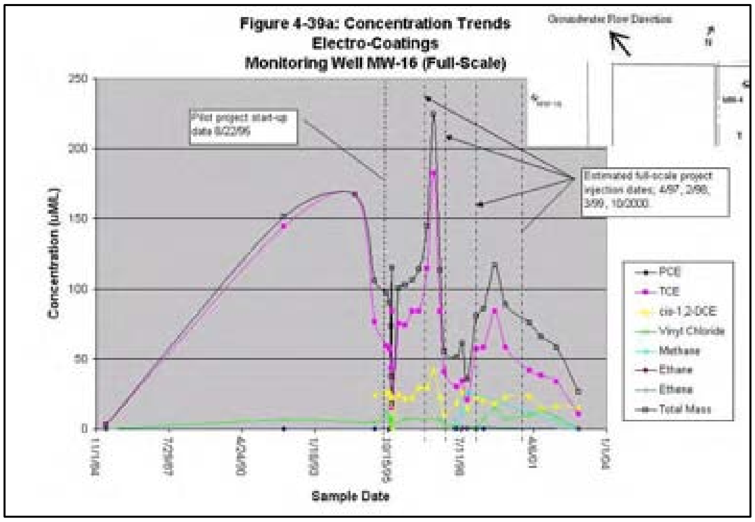
Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-14		+	+	+		-	SE

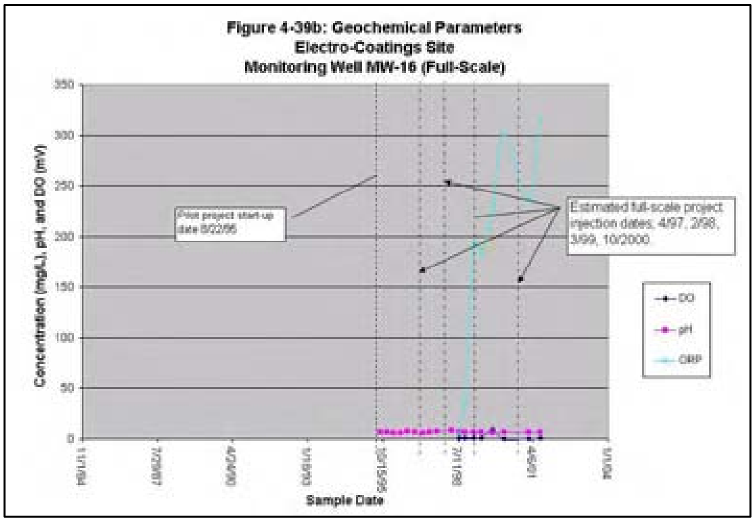
Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o	C_i	% reduced	C_o	C_i	% reduced	C_o	C_i	% reduced	C_o	C_i	% reduced
	(µg/L)			(µg/L)			(µg/L)			(µg/L)		
MW-14	<1000	<0.5	--	4700	6.6	99.9%	<1000	34	--	<2000	11	--

Note: C_o is the baseline concentration for samples collected on 9/13/96).
C_i is the concentration for samples collected on the last recorded sample date which was 12/12/02.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Figure 4-39. Data Analyses for Full-Scale System: MW-16 at the Electro-Coatings Facility





Well Number	Contaminant Mass Loss				Enhanced Geochemical Conditions	Increased Dissolved Gases	Evaluation Rating
	PCE	TCE	DCE	VC			
MW-16	0	+	+	+		-	SE

Note: "+" = Positive evidence "-" = No evidence "Blank" = Not available "0" = No change
HE = highly enhanced ME = moderately enhanced NE = Not enhanced SE = Slightly enhanced

Well Number	PCE			TCE			cis-1,2-DCE			Vinyl Chloride		
	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced	C_o (µg/L)	C_i (µg/L)	% reduced
MW-16	<1000	<5	--	11000	1400	87%	2200	1500	32%	<200	11	--

Note: C_o is the baseline concentration for samples collected on 9/13/96.
C_i is the concentration for samples collected on the last recorded sample date which was 12/12/02.
% removed is the percent difference of the baseline concentration and the concentration for samples collected on day "i".

Project Costs

The overall project cost and detailed breakdown of capital, and operations and maintenance (O&M) costs were not available.

Data Gaps

Currently, monitoring wells are located along the downgradient side of the 1421 Park Avenue property. Additional monitoring wells should be installed east of MW-14 and north of MW-10 and MW-4 to confirm PCE, TCE and their daughter products are being degraded and not accumulating. Injection points have been pushed in this area but no monitoring wells are available to evaluate the effectiveness of these injections.

The organic fatty acids or total organic concentration was not monitored as part of the pilot study or full-scale treatment study. Monitoring of this parameter would help determine the amount of time the amendment remains in the aquifer, the rate of dispersion, and the need for additional injection events.

Plate count data and microbial speciation would be useful to determine if adequate populations of the appropriate microbes are present. This data could be used to determine the type and amount of supernatant or other augmentation needed to enhance breakdown of TCE to its final daughter products, ethene and ethane.

For the pilot and full-scale study, methane, ethane, and ethene concentrations were not measured at most wells. These measurements are used as an indication for biodegradation of chlorinated solvents to their appropriate end products.

Summary Observation and Lessons Learned

Historical groundwater monitoring data for TCE and its daughter products suggested that limited reductive dechlorination was occurring. During the pilot study, cis-1,2-DCE and vinyl chloride (VC), the degradation products of TCE, were either not detected or were sporadically detected in many of the wells in the study area. It should be noted that the pilot study focused on whether enhanced bioremediation could effectively reduce hexavalent chromium detected in groundwater on the 1401 Park Avenue property. The locations of the pilot study wells reflect this since a majority of them were installed near the former waste chromium storage area.

For the full-scale system, PCE and TCE concentrations appear to have been reduced in monitoring wells on the 1421 Park Avenue property and downgradient wells. Degradation products of TCE were detected in most wells with the highest recorded concentrations reported at MW-4. cis-1,2-DCE and vinyl chloride concentrations at MW-4 were about two orders of magnitude higher than the values reported at the other monitoring wells in the injection grid. It is unclear why these contaminants are present in

MW-4 at these higher concentrations compared to other downgradient monitoring wells in the injection grid. Low concentrations of ethane and ethene were detected in MW-10, MW-13, MW-14, MW-16 and MW-17 but there was not sufficient data available to establish a trend.

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4.5 Dow Chemical Company, Pittsburg Facility

Summary

Dow Chemical installed an enhanced in-situ bioremediation system (EISB) at their Pittsburg facility to treat groundwater contaminated with PCE, carbon tetrachloride and their daughter products. The current EISB system consists of thirty-nine circulation wells that circulate groundwater and amendments between screened intervals in the middle and deep aquifer zones. These 39 circulating wells have been installed to create 3 biozones which consists of several segments Each segment is comprised of 3 circulation wells and one monitoring well located directly downgradient of the circulation wells. The current EISB system has injected approximately 100,000 gal/yr of a mixture of propylene glycol and ammonium polyphosphate. Groundwater from more biologically active areas at the site are blended with this solution and injected into the circulation wells to enhance biodegradation as needed.

Of the 3 biozones, the western biozone appeared to show the best signs of biodegradation with PCE, carbon tetrachloride, and some of their daughter products decreasing in 2 of 3 wells monitored. Decreases in MW-004C and MW-100C for PCE, TCE, cis-1,2-DCE and VC were 96-99.5%, 93 -99.7%, 63 -99.6%,and 66-99%, respectively. However, the results for the other biozones show that the biodegradation process appears to be stalling at cis-1,2-DCE and vinyl chloride.

Site Background

The Dow Chemical Company (Dow) owns and operates a chemical manufacturing facility that occupies approximately 993 acres in Pittsburg, California (Figure 4-40). The site is bounded by the New York Slough on the north, the Pittsburg-Antioch Highway on the south, Loveridge Road on the west, and parklands and commercial areas on the east. Residential areas exist further to the south beyond the Antioch-Pittsburg Highway.

From 1969 to 1991, this chemical manufacturing facility produced chlorinated solvents, including carbon tetrachloride and tetrachloroethene. From 1939 to 1991, Dow also operated a chlor-alkali plant that used elemental mercury as the electrical conductor in a mercury cell manufacturing process to produce chlorine, sodium hydroxide, and hydrogen. Current operations are focused on manufacturing latex, agricultural chemicals, fumigants, fungicides, and hydrochloric acid. In addition to chemical manufacturing activities, Dow conducts chemical development research at its Pittsburg facility. The Calpine Corporation operates a power plant on site, producing electricity and steam. The Cynera Company and M.G. Generon fabricate reverse osmosis membranes on the Dow property. The site also contains an active Class II (designated) solid waste landfill and a number of closed solid waste disposal units.

Previous site investigations detected VOCs and SVOCs at elevated concentrations in groundwater underlying the Dow facility. Significant contamination plumes were identified in the interior of the site and near the perimeter adjacent to New York Slough and Bundesen Bay. Table 4-9 summarizes the principal organic contaminants identified in groundwater beneath the site. Table 4-10 summarizes the maximum reported 2000-2001 concentrations of several VOCs for each groundwater zone in the interior and near the perimeter of the site.

Table 4-9. Contaminants Detected in Groundwater at the Dow Facility

Organic Contaminants in Groundwater	
tetrachloroethene (PCE)	methylene chloride ($MeCl_2$)
trichloroethene (TCE)	chloromethane (CM)
1,2-dichlorethene (1,2-DCE)	1,2-dichloropropane (1,2-DCP)
1,1-dichloroethene (1,1-DCE)	hexachlorobenzene (HCB)
1,2-dichloroethane (1,2-DCA)	hexachloroethane (HCA)
1,1-dichloroethane (1,1-DCA)	pentachlorophenol (PCP)
vinyl chloride (VC)	benzene
carbon tetrachloride (CCl_4)	toluene
chloroform (CF)	

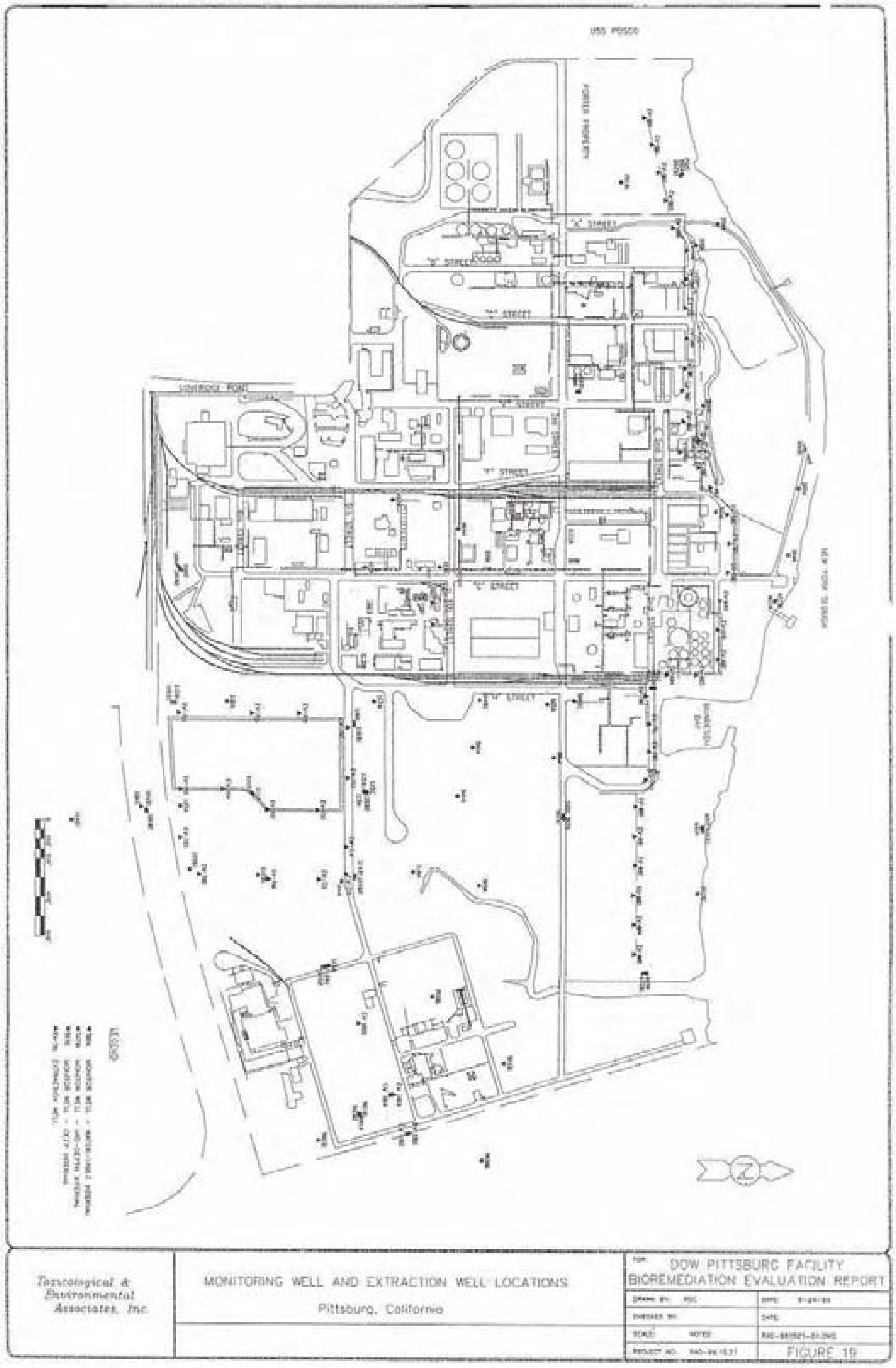
Table 4-10. Maximum Concentrations of VOCs in Each Groundwater Zone at the Dow Facility

Contaminant	2000-2001 Maximum Concentrations (µg/l)		
	Water Table	Mid-Depth	Deep
PCE	2,600	120,000	69,000
TCE	3,100	5,700	26,000
1,2-DCE	4,500	9,800	10,000
1,1-DCE	ND	310	45
1,2-DCA	ND	ND	73
1,1-DCA	150	59	210
VC	210	560	500
CCl_4	450	48,000	100
CF	850	37,000	35,000
$MeCl_2$	ND	35,000	19,000
ND = Not detected			

Site Geology/Hydrogeology

The Dow Pittsburg facility is located in the Pittsburg Plain Groundwater Basin that is bounded by the hills south of the facility, the western portion of the Sacramento-San Joaquin River Delta in the north, Bay Point in the west, and the City of Antioch in the east. The basin is filled with unconsolidated fluvial and alluvial sediments deposited in the Sacramento-San Joaquin River Delta and in alluvial fans formed by streams draining the hills south of the facility. Groundwater at the Dow facility is first encountered at depths beginning from approximately 2 to 13 feet below ground surface (bgs). Sitewide groundwater velocities and hydraulic conductivities (K) from the semi-annual self

Figure 4-40. **Site Layout with Monitoring and Extraction Well Locations at the Dow Facility**



From the Dow Bioremediation Evaluation Report monitoring report for March and September 2003 are presented in Table 4-11. Groundwater velocities determined using conservative tracer tests for the individual biozones are also listed in Table 4-11.

Table 4-11. Groundwater Velocities and Hydraulic Conductivities for Water Bearing Intervals at the Dow Facility

Water Bearing Interval	Sitewide K (ft/day)	Velocity (ft/yr)				
		Sitewide		Biozone (performed 5/01 – 5/02[a])		
		3/03	9/03	Western	Central	Northern
Water Table	0.13 to 15	0.2 to 160	0.2 to 180	--	--	--
Mid-Depth	0.34 to 342	0.4 to 4200	0.3 to 4200	--	2628	1314
Deep	0.01 to 250	0.08 to 1500	0.08 to 2100	3066 to 4745	5220	5475

[a]Based on conservative tracer results reported in the "Review of Bioremediation System, The Dow Chemical Company, Pittsburg, California, August 2004."

The subsurface lithology consists of low permeability silty clay in the upper 40 feet (designated as the water-table interval) with a saturated sand unit extending from approximately 40 to 135 feet bgs. A low permeability layer consisting mostly of clay is also present between approximately 85 to 110 feet bgs in the northern portion of the site. This lower clay layer extends southward from the northern boundary of the facility (New York Slough) and pinches out approximately 200 feet south of 2nd Street. Where present, the lower clay layer divides the saturated sand unit into two intervals designated as the mid-depth interval (40-85 feet bgs) and the deep interval (110-135 feet bgs). As the lower clay layer thickens along the northern boundary of the facility (toward the Slough), the mid-depth interval of the saturated sand unit generally becomes thinner/finer grained and apparently pinches out in various locations near the Slough bank. However, due to the past dredging activities in Bundensen Bay, this clay layer was removed creating a hydraulic pathway between the B-zone and the Bay. Regionally, a clay layer exists below the deep interval of the saturated sand unit from approximately 130 to as much as 800 feet bgs. Table 4-12 summarizes the water-bearing intervals at the Dow site.

Table 4-12. Groundwater Depths at the Dow Facility

Aquifer Zone	Typical Depths (ft bgs)	Average Thickness (ft)
Water Table Interval	2 to 40	35
Mid-Depth Interval	40 to 80	20
Deep Interval	80 to 135	35

Project Description

In July 1998, Dow Chemical started to assess the biogeochemical conditions and submitted a report to the RWQCB in November 1998. The report evaluated existing analytical groundwater data to demonstrate contaminants were biodegrading naturally at the site using the three lines of evidence developed in the U.S. EPA and AFCEE guidelines. As part of the review, groundwater samples from 16 wells were analyzed and observed to contain nitrate-reducing bacteria, sulfate-reducing bacteria, and methanogens.

Dow then conducted a series of four microcosm studies in September 1998 through January 2000. Two microcosm studies focused on identifying the best source of electron donor(s) for the pilot study. Two other studies evaluated the need to use bioaugmentation and the potential for bioremediation on a site-wide basis.

Pilot Scale and Field Testing

After the biogeochemical and microcosm results were obtained, two pilot tests were conducted; Field Test 1 around Well 201B1 located in the Porter Property area, and Field Test 2 around EW-684 adjacent to Bundesen Bay. Field Test 1 consisted of two injection wells and three monitoring points while Field Test 2 had five injection points and two monitoring points.

For Field Test 1, two 2-inch diameter injection points were installed 5.3 feet from each other and screened between 32-37 feet bgs. Both injection wells were installed upgradient of three monitoring wells. A solution of consisting of 100 pounds (lbs) of sodium formate, 140 lbs of 60% sodium lactate syrup, 50 lbs of ammonium phosphate, 50 lbs of ammonium chloride, and 1,400 gallons of extracted groundwater was injected via gravity into both injection points. The solution was split evenly between the injection points and injected at a rate of 1 to 2 gallons per minute. Amendments were then carried past the monitoring points by natural groundwater movement.

At the Field Test 2 area, five 2-inch diameter injection points were installed along with one 2-inch diameter monitoring well. An existing monitoring well was also used. The injection points were installed in a circle (diameter of 20 ft) around the two monitoring wells and were screened at the same interval as the existing monitoring well. The screened interval for the existing monitoring well was not available in the report. A solution of consisting of 150 lbs of sodium formate, 250 lbs of sodium acetate, 440 lbs of 60% sodium lactate syrup, 50 lbs of ammonium phosphate, 75 lbs of ammonium chloride, and 3,500 gallons of extracted groundwater was injected via gravity into the injection points. The solution was split evenly between the injection points and injected at a rate of 35 to 40 gallons per minute. The amendments were then drawn to the monitoring points by pumping 7,240 gallons from the existing well which is little more than one pore volume (6,500 gallons).

For both field tests, groundwater samples were collected just prior to the first injection and analyzed for COCs, dissolved gases, ammonia, phosphate and electron donors. After the initial injection, the points were sampled every two weeks. These samples were analyzed for VOCs, O_2, CO_2, methane, ethane, ethane, ammonia, phosphate, and electron donors. Other data collected in the field included pH, temperature, ORP, alkalinity, specific conductivity, and dissolved oxygen. Based on the electron donor results in the third round of samples, a second injection event was performed in the second week of December 1998. In the pilot study report, only one sample had CO_2 values reported but no discussion was provided on how the results compared to historical values.

The report concluded that sulfate-reducing and dechlorinating bacteria existed at the site which could be stimulated in-situ by adding amendments to enhance biodegradation.

Based on modeling results, 25 circulation wells spaced on 100-foot centers would be effective in distributing amendments. These wells were proposed in the Bundesen Bay Area and in the western portion of the site. Modeling results also indicated that groundwater discharges exceeding 5μg/l would be eliminated within 2-5 years after system start-up with amendments distributed as far north as the Slough Bank within 2 years. The model results indicated that within 20 years groundwater contaminant concentrations under the entire site would be successfully remediated to levels determined to be acceptable.

Full Scale

The full-scale enhanced in-situ bioremediation (EISB) system was designed to function much like a bioreactor, with hydraulic control over groundwater discharge (i.e., effluent). Eleven effluent monitoring wells were installed in locations considered optimal by Dow Chemical for measuring the EISB system performance. According to Dow and the RWQCB, the circulation well operations are based on data generated by tracer tests, slug tests, and pumping tests. The circulation wells are operated to:

- Establish hydraulic control and function like a bioreactor with very specific discharge locations (approximately 20 feet up-gradient from the effluent monitoring wells),
- Capture influent from the source area and circulate it several times (~14 circulation cycles or an average of 70 days retention time) through the mid- and deep-zones while amendments, occasionally including microbes present in groundwater collected from an area of high biological activity, are added, and
- Biodegrade most contaminants close to the injection well, since that's where most of the biomass forms.

The full-scale operation of the EISB system began in March 2000 with 31 circulation wells. Twenty-eight (28) existing monitoring wells installed as part of the chlorinated volatile organic compound (CVOC) monitoring program were used to monitor groundwater for enhanced biological activity. After 8 months of continuous operation, the operation of the EISB system was temporarily interrupted between November 2000 and June 2001 due to scheduled maintenance and bioremediation optimization (TEA, November 2001). As part of the optimization, five additional circulation wells (BWs) were installed and brought online along with eleven (11) effluent monitoring wells, located downgradient from select circulation wells to evaluate the EISB system performance (see Table 4-13). In August 2002, three additional BWs were added to the Western Bioremediation Zone.

The current EISB system consists of thirty-nine circulation wells. Thirteen wells are located in a linear pattern on the western side of the facility, downgradient of suspected contaminant source areas. These wells are intended to intercept contaminants in groundwater flowing in a northwesterly direction and form the "western bioremediation zone" or western biozone. Fifteen wells are located in a linear pattern along 2nd, G, and 3rd Streets in the central area of the facility and form the central biozone. The remaining eleven wells for the northern biozone are located in the western edge of Bundesen Bay and the northern perimeter of the facility. Table 4-13 lists the circulation and monitoring wells that have been monitored as part of the EISB system.

The 39 circulation wells, approximately130 feet deep, were installed with two screened intervals separated by a blank casing section. The typical well design consisted of a 30-foot long upper screen interval and a 20-foot long lower screen interval separated by a 50-foot well seal. The upper well screen straddled the mid-depth interval which is located from about 35 to 85 feet bgs. The lower well screen interval was set near the bottom of the deep interval about 100 to 130 feet bgs.

Using a pump string with inflatable packers inside each well, groundwater was extracted through one of the two well screens, mixed with liquid amendments, then forced (under pressure) back into the formation through the other well screen. Wells in which groundwater was extracted from the deep interval and circulated back into the mid-depth interval were termed "*up-pumping wells.*" Conversely, wells where the groundwater was extracted from the mid-depth interval and circulated back into the deep interval were termed "*down-pumping wells.*" Within each bioremediation zone the order of up-pumping and down-pumping wells alternates linearly. The linear circulation well pattern was intended to form extended zones of enhanced bioremediation by creating contiguous cells of circulating amended groundwater. Figure 4-41 illustrates the circulation pattern for the bioremediation zone cross section.

From March 2000 to July 2001, the initial 31 circulation wells were all up-pumping and were sampled from the deep interval. As part of the system optimization, additional tests were conducted to characterize subsurface conditions. These tests were conducted in the 3 biozones and included hydrologic circulation tests, conservative tracer tests, electromagnetic borehole flowmeter tests, in-situ electron donor tests, and microcosm tests on 21 sediment samples. Additional geotechnical testing and chemical analysis were also conducted along with recording lithologic logs for 67 new boreholes. Based on these results, the pumping direction in 18 circulation wells were reversed to down-pumping and sampled from the mid-depth interval while the other 18 circulation wells remained up-pumping.

In July 2001, amendment injections were resumed on a bi-weekly batch-injection basis. In December 2002, the system optimization activities were completed. The EISB system was down for 8 months between July 2003 and February 2004 to perform bi-annual cleaning at 28 circulation wells. The conversion of in-well pump strings to surface skid-mounted pumping units was also started at 33 circulation wells in October 2003 and is expected to be completed by August 2004 (TEA, August 2004).

Table 4-13. Wells Used to Monitor the Full-Scale Dow EISB System

Bioremediation Zone					
Western		**Central**		**Northern**	
BW-000	**MW-004C**	BW-500	MW-422B	***BW-606***	EW-684-2
BW-001	**MW-100C**	***BW-501***	MW-422C	***BW-607***	EW-780
BW-002	**MW-101B**	BW-502	MW-423B	***BW-608***	EW-781-2
BW-003	MW-201B1	BW-503	MW-423C	***BW-609***	MW-406B1
BW-004	MW-201C	***BW-503-2*****	MW-424B	***BW-610***	MW-406C
BW-100	MW-202B1	BW-504	MW-424C	BW-611	MW-407B1
BW-101	MW-202C	***BW-505***	MW-425B	BW-612	**MW-600C**
BW-102*	MW-210B	BW-506	MW-425C	BW-613	**MW-603B**
BW-103*	MW-210C	***BW-507***	**MW-502C**	BW-614	MW-610B
BW-104*		BW-508	**MW-511C**	BW-615	MW-610C
BW-200		***BW-600***	**MW-623C**	***BW-616***	**MW-629B**
BW-201		BW-601			**MW-631B**
BW-202		***BW-602***			**MW-633B**
		BW-603			TP-413B1
		BW-604			TP-413C
		BW-605			

Note: * - Circulation wells installed in 2002.
** - Replaced BW-503.
BW-### = Circulation well
EW- #### = Extraction well
TP-#### = Piezometer

Well numbers ending with an “A” indicate the well screen is in the shallow zone, “B” in the mid-depth zone, and “C” in the deep zone.

- Wells in **bold** indicate effluent monitoring wells installed to evaluate performance of EISB system.
- Monitoring wells (MW) not in bold are associated with the sitewide CVOC groundwater monitoring program. These wells were initially used to monitor the full-scale EISB system.
- Circulation wells in ***bold italics*** indicate wells where the pumping direction was changed from up-pumping to down-pumping.

Initially, liquid amendments consisted of a 30% solution of sodium formate mixed with a 60% solution of sodium lactate and a 56% solution of ammonium polyphosphate. Table 4-14 lists the amendment dosage reported in the draft 2001 construction and operation report. In July 2001, amendment injections resumed with a bi-weekly batch-injection of a sodium lactate/ammonium polyphosphate amendment solution.

In October 2002, these injections were changed to a bi-weekly batch-injection of propylene glycol/ammonium polyphosphate (TEA, August 2004). Sodium formate was discontinued due to well fouling problems and only sodium lactate was added as an electron donor during the first half of 2002. During the 2nd half of 2002, propylene glycol replaced sodium lactate as the electron donor material based on microbiological testing results that demonstrated it had a similar capacity to enhance biodegradation but at a much lower cost (TEA, February 2003). The percentage of propylene glycol and ammonium polyphosphate was not available but approximately 100,000 gal/yr was used by the EISB system.

Figure 4-41. Groundwater Circulation Pattern Induced by Circulation Wells at the Dow Facility

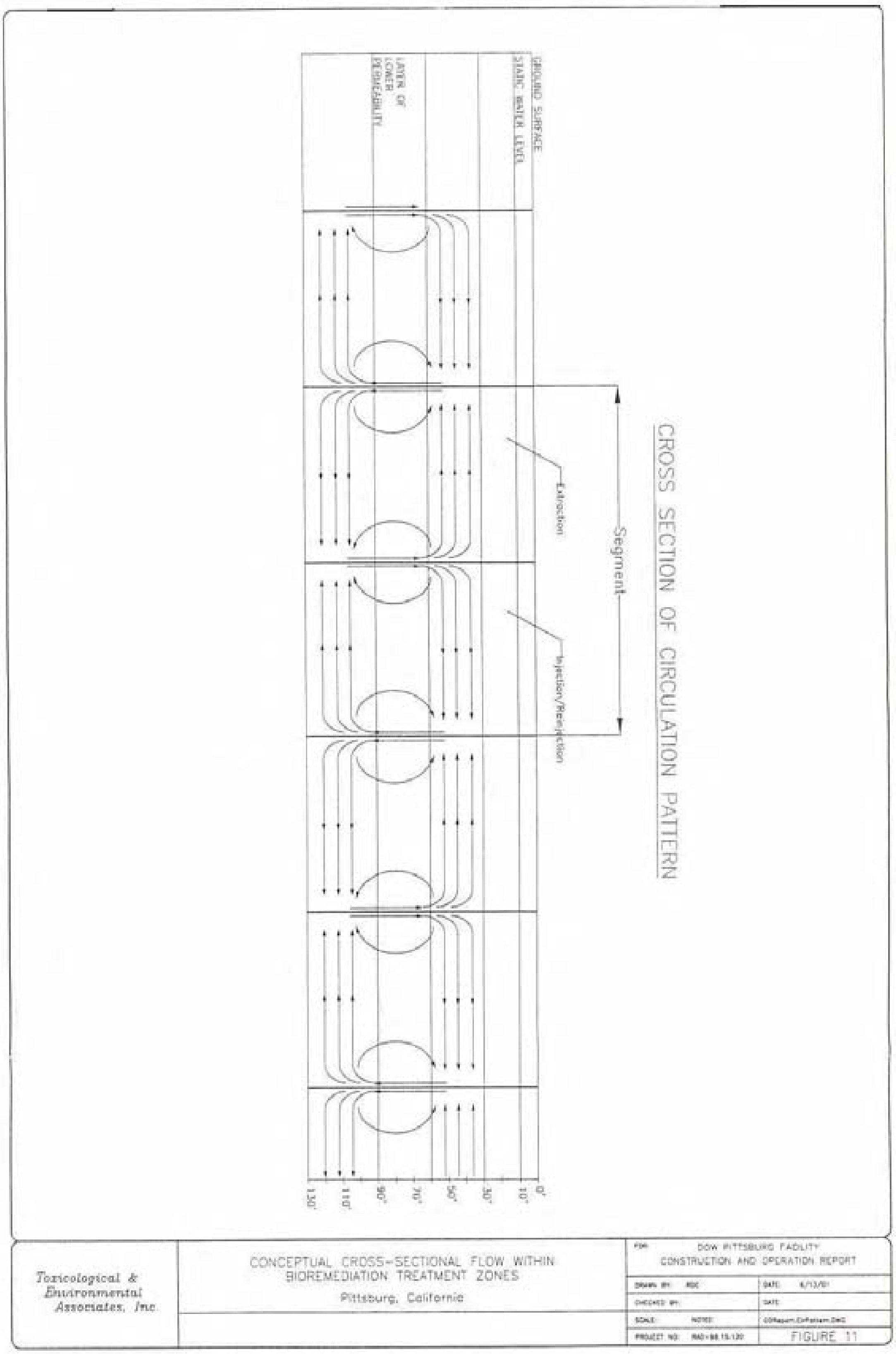


Table 4-14. Amendment Dosage for the Dow EISB System

Amendment	Bioremediation Zones (gallons/day/well)					
	Central and Northern			Western		
	Mid-depth	Deep	Total	Mid-depth	Deep	Total
Sodium lactate	2	1	3	1	4	5
Sodium formate	6	2	8	2	9	11
Ammonium polyphosphate	1	1	2	1	1	2
Total	**9**	**4**	**13**	**4**	**14**	**18**

Initially, extracted groundwater used with the amendments was stored in four 10,000-gallon tanks where small amounts of organic substrate and nutrients were added to stimulate bacteria. Added as needed were ferrous chloride to precipitate hydrogen sulfide, sugar to deplete oxygen, and a buffering agent to neutralize pH. Facility-supplied nitrogen was also added periodically to minimize the oxygen content within the storage tanks.

Liquid amendments were then mixed with groundwater from these tanks in a nitrogen-purged, truck-mounted tank using a centrifugal pump and delivered to each circulation well via truck. At each circulation well, the mixture was injected by connecting a hose to the well head using a no-drip quick-connect fitting. A metered amount of mixture was injected into the well at a rate of approximately 15-25 gpm. Groundwater to amendment ratios and exact quantities added to each well were not available. According to the third quarter 2001 progress report for the EISB system, the amendment mixture was injected into both up-pumping and down-pumping wells on a daily basis (Monday through Friday).

Once the mixture was injected, groundwater was circulated using the circulations wells continuously for 24 hours per day, 7 days per week at a pumping rate ranging from 2-12 gpm. Additional liquid amendment injections were then added to each circulation well as appropriate (method not determined). Pumping rates were determined for each well based on aquifer capacity at individual well locations. Groundwater was circulated at the minimum pumping rate to maintain groundwater flow across the bioremediation zones from upgradient contamination areas.

During the second half of 2004, surface skid-mounted pumping units were installed for groundwater circulation and amendment addition. Valves at the well head allow reversing the circulation flow direction and injection zones. Amendments are added from a 250-gallon storage tank located at the well head. Groundwater is circulated continuously with an estimated average retention time of 70 days or 14 circulation cycles. System operation is checked daily by trained on-site personnel (excluding weekends and holidays).

EISB Monitoring Program

During the first 8 months of operation, 28 existing monitoring wells installed as part of the CVOC monitoring program were sampled and analyzed for the following analytes: VOCs, sulfates, sulfides, ferrous and ferric iron, nitrate, nitrite, phosphate, ammonia, manganese, acetate, formate, lactate/propionate, hydrogen, acetylene, carbon dioxide, methane, ethane, ethene, and propene. As part of the system optimization, these wells were replaced by the 11 effluent wells located approximately 20 feet downgradient of the circulation well segments. Table 4-15 lists the bioremediation treatment segment along with the associated effluent and circulation wells currently used to evaluate EISB performance. Figures 4-42 thru 4-44 show the location of each segment. From October 2000 to September 2002, as many as 13 circulation well sampling events were also conducted to assess the system's biological activity. Circulation wells are currently sampled and analyzed by Dow on a semi-annually basis. In 2002, EISB monitoring program began reporting destruction rate efficiencies (DREs) for the 11 effluent monitoring wells downgradient of 11 bioremediation treatment "segments". Since results were reported as DREs, circulation and monitoring well data that were provided in past progress reports were not reported for 2003 and 2004.

To calculate DREs, an average influent flux concentration was calculated for each segment based on stochastic model results using 1996 groundwater monitoring data. Of the 260 data points from the 1996 data set, only 10 groundwater monitoring data points were updated with 1999-2003 data. The average flux concentration was calculated based on a cross-sectional area upgradient of the bioremediation segment and was not calculated for individual contaminants. The total contaminant concentration detected in each effluent well sample was used as the effluent flux concentration. The DRE is calculated by subtracting the effluent flux concentration from the average influent flux concentration and dividing this result by the average influent flux concentration.

Figure 4-42. Modified 2002 Full-Scale EISB System at the Dow Facility

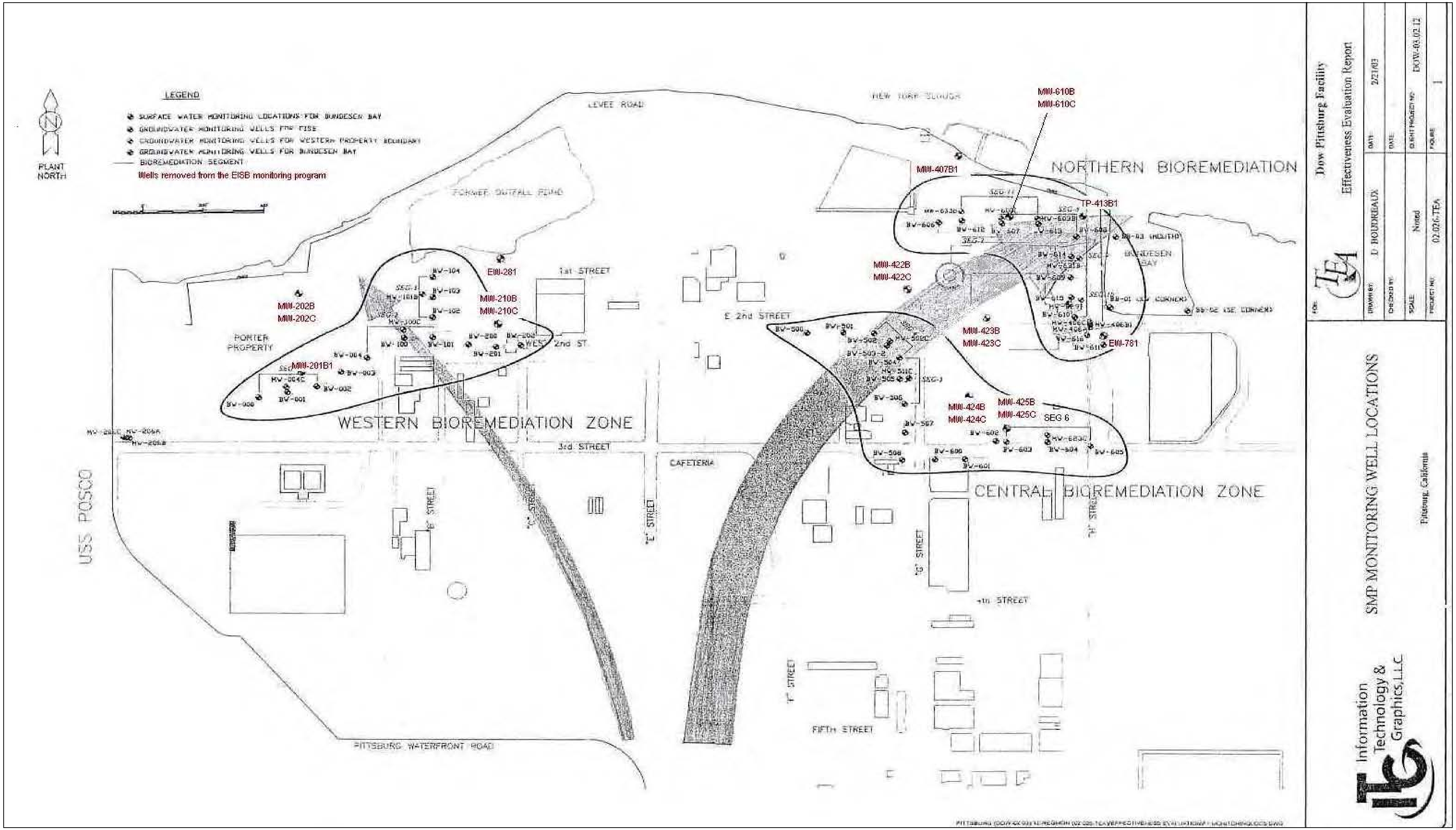


Figure 4-43. Circulation and Monitoring Well Locations in Central and Northern Bioremediation Zone at Dow Facility

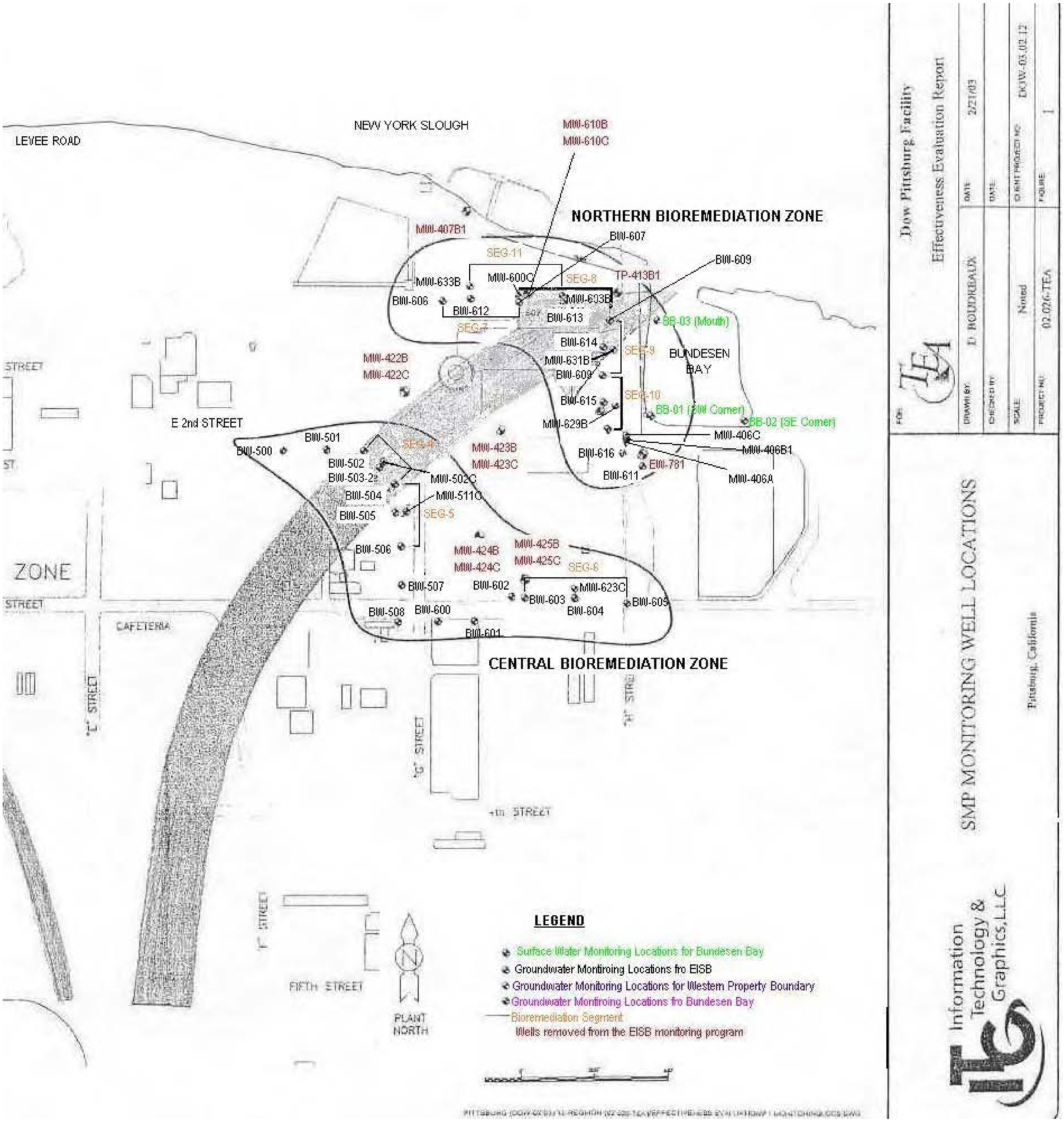


Figure 4-44. Circulation and Monitoring Well Locations in Western Bioremediation Zone at Dow Facility

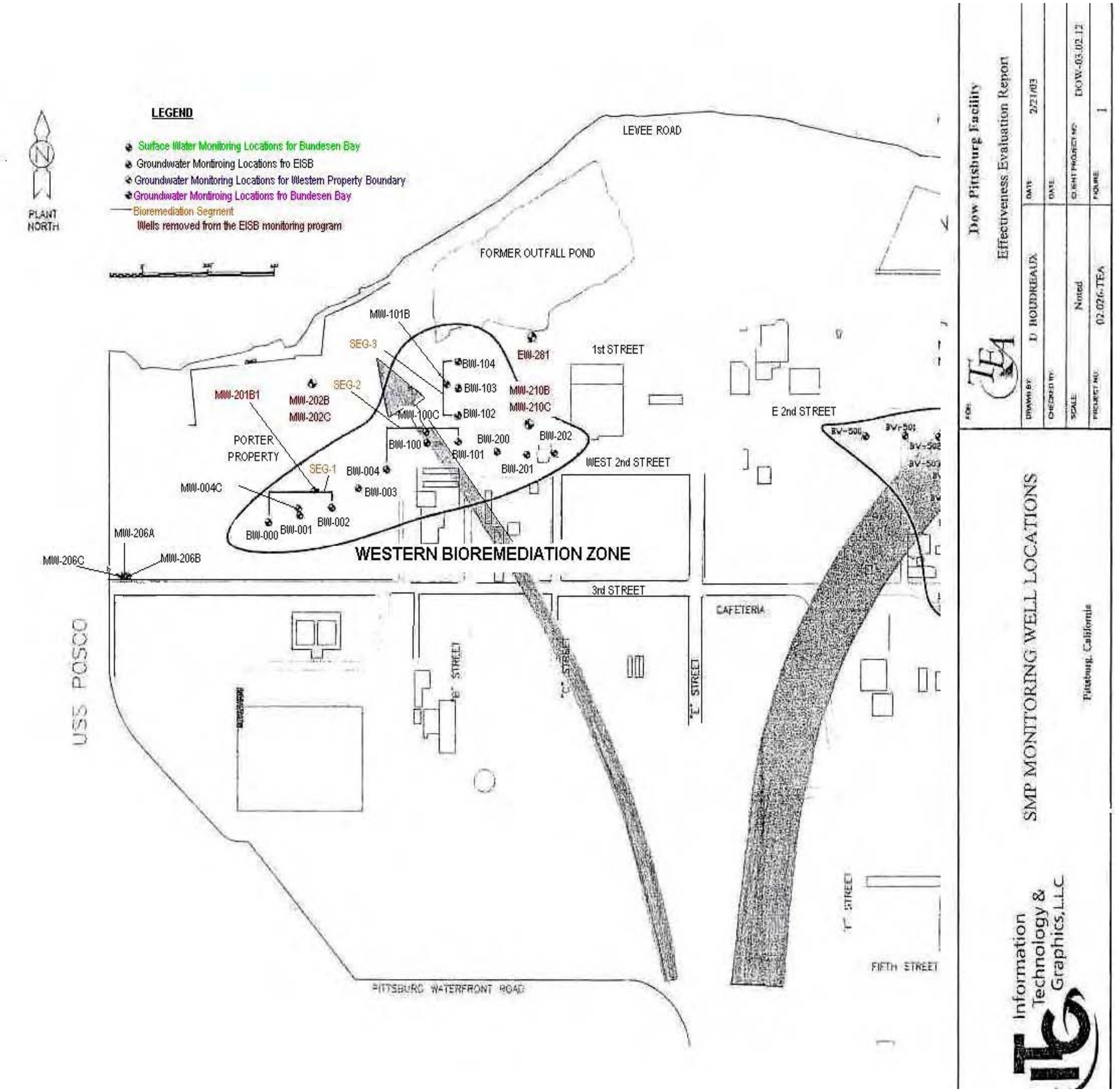


Table 4-15. Bioremediation Treatment Segments and Associated Circulation and Monitoring Wells at the Dow Facility

Biozone	Segment No.	Associated Wells		
		Monitoring	Circulation	Comments
Western	1	MW-004C	BW-000, BW-001, BW-002	D/C(~20ft from BW-001)
	2	MW-100C*	BW-004, BW-100, BW-101	D/C (~30 ft from BW-100)
	3**	MW-101B	BW-102, BW-103, BW-104	D/C (~30 ft from BW-103)
Central	4	MW-502C	BW-502, BW-503-2, BW-504	U/C:D[a](~20 ft from BW-503-2)
	5	MW-511C*	BW-504, BW-505, BW-506	D (~20 ft from BW-505)
	6	MW-623C	BW-603, BW-604, BW-605	D (~20 ft from BW-604)
North	7	MW-633B*	BW-606, BW-612, BW-607	D (~30 ft from BW-612)
	8	MW-603B	BW-607, BW-613, BW-608	D/C(~20 ft from BW-613)
	9	MW-631B*	BW-608, BW-614, BW-609	D (~30 ft from BW-614)
	10	MW-629B*	BW-609, BW-615, BW-610	D (~40 ft from BW-615)
	11	MW-600C	BW-612, BW-607, BW-613	D/C (~20 ft from BW-607)

*Wells installed after the fourth quarter of 2001.
**This segment did not start operation until after the second quarter in 2002.
[a] Until the third quarter of 2001, BW-503 was downgradient of MW-502C. A new circulation well was installed in after the 3rd quarter of 2001 where it was upgradient of MW-502C which is labeled BW-503-2.
C = Crossgradient D = Downgradient D/C = Downgradient/crossgradient U/C = Upgradient/crossgradient

Project Performance

This review focused on the current monitoring well system which provides the latest available data on how the system has performed after several years of operation. These wells are all located downgradient and in close proximity to the bioreactor circulation wells in each of the three bioremediation zones. Their location is considered optimal to demonstrate that enhanced biodegradation has occurred, versus locations midway between circulation wells and farther downgradient. Based on the groundwater flow direction and velocity, wells located farther downgradient of the circulation wells would exhibit little biological activity. Data were reviewed but not presented for the discontinued monitoring wells.

These discontinued wells provide data on baseline conditions and performance for a period (three-quarters to one and a half years) after initial startup at greater distances away from the injection points (circulation wells). It should also be noted that this review does not include analysis of the circulation well results. As pumping direction in the circulation wells was changed and records of these changes were unavailable, review of these results was considered problematic. The 2003 and first quarter of 2004 groundwater data for circulation wells were also not reported since DRE values were reported for each bioreactor segment instead.

Figures 4-45 through 4-61 present graphs with concentration and select geochemical parameter trends. These figures also present tables with qualitative and quantitative indications of biodegradation conditions at each well. Data from the current EISB system were used to assess performance of the three in-situ biological treatment systems (biozones) installed at the Dow Pittsburg Facility. Concentration graphs for each well over time along with plots of geochemical and biological parameters were prepared for analysis by DTSC. Data collected after startup of the EISB system were used to determine contaminant trends and to assess effectiveness of the EISB treatment system.

Concentration trends for contaminants and their breakdown products are plotted for each of the monitoring wells in units of micromoles per liter. The COCs are PCE, TCE, 1,2-DCE, vinyl chloride, carbon tetrachloride, chloroform, methylene chloride, and chloromethane. The ultimate biodegradation products are the dissolved gases, methane, ethane and ethene.

Discussion of the performance monitoring results is grouped by biozones and presented below. For each of the biozones, the estimated percentage of contaminant removed based on samples collected immediately after the March 17, 2001 full-scale system start-up date are presented in a table for select wells in Figures 4-45 thru 4-61. Negative percentages represent an increase in contaminant concentrations compared to the baseline. If the detection limit reported for C_i (initial concentration) was greater than the value reported for C_f (final concentration), or if both C_i and C_f were reported below the detection limit, a percentage was not calculated.

Western Biozone:

Contaminant concentrations in Western Biozone area are relatively low compared to concentrations observed in Central and Northern Biozone areas. In terms of overall contaminant mass, only MW-004C which had low initial contaminant levels shows a clear reduction. Some reduction in parent compound concentration and formation of daughter products is evident in MW-100C and MW-101B. Complicating analysis is a large unexplained concentration spike that appears in two monitoring wells (MW-004C and MW-101C) corresponding to the 2/13/02 sampling event. This spike was not evident in MW-101B screened at a different interval, the mid-depth aquifer zone. An unexplained spike in concentration was observed at MW-101B a few months later that corresponds to the 9/25/02 sampling event. Anaerobic reducing conditions were generally maintained in all three monitoring well locations based on the dissolved oxygen and ORP measurements. ORP measurements did fluctuate between 350 and -350 mV, but dissolved oxygen was maintained at consistently low concentrations in all three MWs.

Consistent patterns among the three MWs for other geochemical or dissolved gas parameters were not apparent. The data points for sulfate in the two deep interval MWs indicates a 200 to 800 mg/l drop in sulfate concentration around the 2/13/02 sampling event and then a 500-600 mg/L increase over the next year. Sulfate reduction is generally accompanied by increased sulfides, which were not detected at significant levels. Results for each well are further discussed below:

MW-004C (located adjacent BW-001). Data for a 35 month period is available. All contaminant concentrations were generally low during the period monitored except for the unexplained spike in concentrations on 2/21/02 (see Figure 4-45). PCE & TCE concentrations were initially low (189 µg/L and 341 µg/L, respectively) and were reported below detection limits (50 µg/L and 20 µg/L, respectively) for the three sampling events during the period June 2002 to March 2003. 1,2-DCE, chloroform, VC, and methylene chloride concentrations decreased, while ethene concentrations were observed to increase with the highest concentration reported on 2/23/04 at 415 µg/L. By the last sampling event, PCE, TCE, 1,2-DCE and VC concentrations dropped to <5 µg/L on 3/23/04. The groundwater pH and dissolved oxygen content are within the range expected for an anaerobic environment (6< pH<8.5, DO<2 mg/L). Consistent patterns for alkalinity and sulfate concentrations over the monitoring timeline are not apparent. A major drop in sulfate and alkalinity occurred during the 2/13/02 sampling event but concentrations were observed to rebound close to previously observed levels approximately one year later. Additional data are needed to confirm whether this is real or due to a sampling or analytical problem. The decrease in sulfate concentrations appears to coincide with an increase in ORP well above the -210 mV level which sulfate reduction is expected to occur. Refer to Figure A-127 thru Figure A-130 in Appendix A for trends in ORP, sulfate, and alkalinity.

Figure 4-45. Data Analyses for MW-004C in the Western Biozone

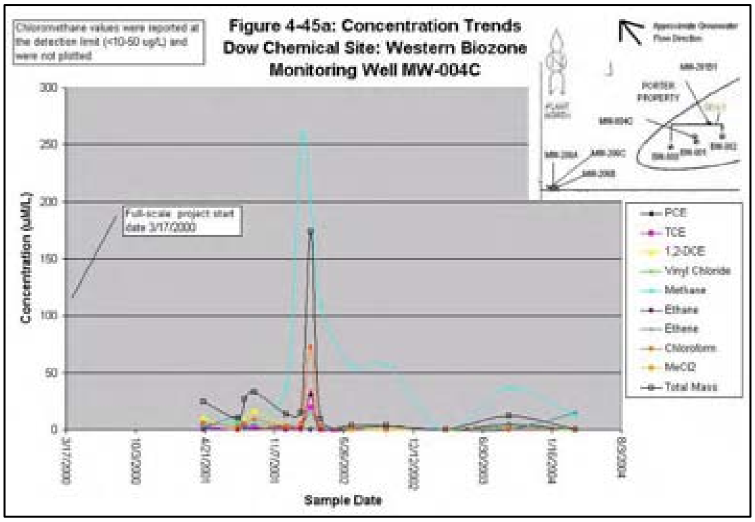


Figure 4-45a: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-004C

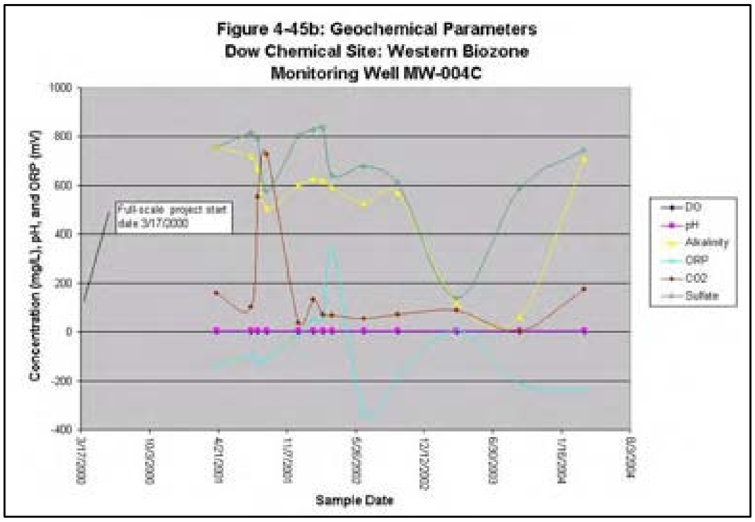


Figure 4-45b: Geochemical Parameters
Dow Chemical Site: Western Biozone
Monitoring Well MW-004C

Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-004C		+	+	+	+				+	+	HE

Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

Monitoring Well MW-004C											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
189	<1	99.5%	341	<1	99.7%	1080	4	99.6%	204	2.3	99%
CCl_4			Chloroform			Methylene chloride			Chloromethane		
<50	<1	--[a]	720	6.8	99%	<100	<1	--[a]	<50	<1	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value.

MW-100C (located adjacent to BW-100). The overall contaminant concentration appears to be decreasing (see Figure 4-46). An overall reduction in carbon tetrachloride concentration was observed along with an increase in chloroform and methylene chloride concentrations. Similar to MW-004C, a large concentration spike was observed on 3/20/02. 1,2-DCE concentrations decreased overall while vinyl chloride concentrations remained constant. Ethene and methane concentrations increased while ethane remained constant. For the first 9 months, the sulfate concentration fluctuated, possibly due to upgradient conditions. The large decrease in the sulfate on 3/17/2003 appears to coincide with decreased ORP values within the range for sulfate reducing conditions (e.g. approximately -200mV). ORP values remained below -200 mV during the next sampling periods but sulfate concentrations increased by approximately 500 mg/L during this same period. Carbon dioxide concentrations appeared to generally increase, while alkalinity fluctuated but remained about the same. Upgradient monitoring well data was not available to assess whether these changes were due to changing upgradient conditions. Refer to Figure A-131 thru Figure A-134 in Appendix A for trends in ORP, sulfate, carbon dioxide, and alkalinity.

Figure 4-46. Data Analyses for MW-100C in Western Biozone

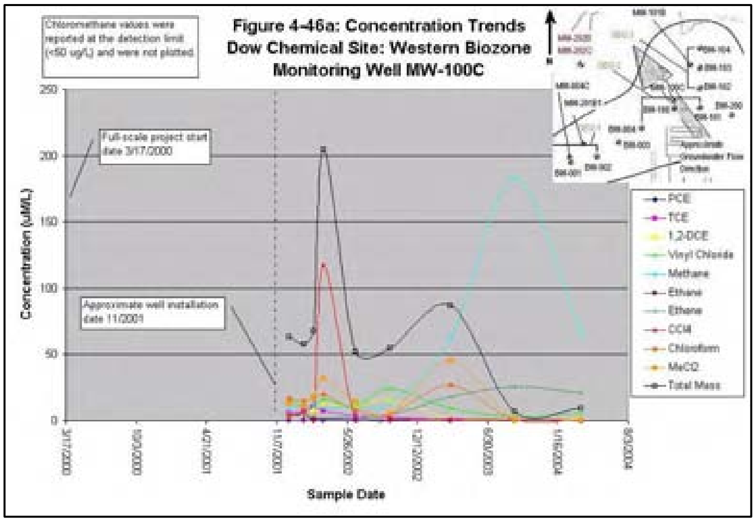


Figure 4-46a: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-100C

Chloromethane values were reported at the detection limit (<50 ug/L) and were not plotted

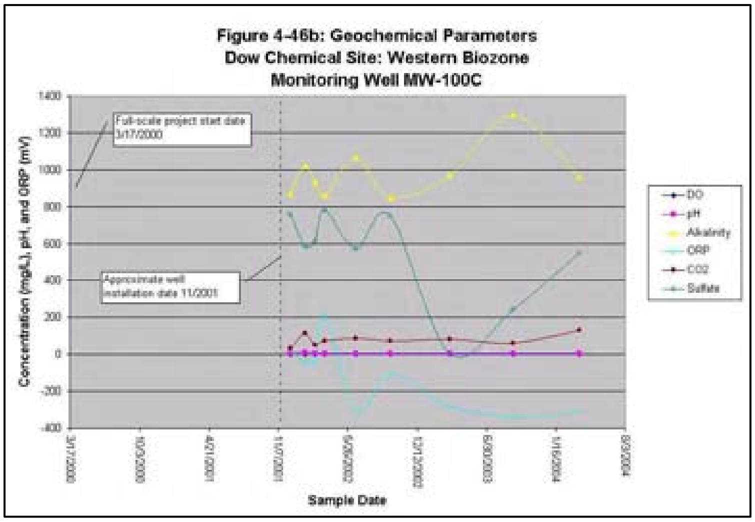


Figure 4-46b: Geochemical Parameters
Dow Chemical Site: Western Biozone
Monitoring Well MW-100C

Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-100C	+	+	+	+	+	+	+		+	-	HE

Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

Monitoring Well MW-100C											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
570	24	96%	770	55	93%	400	150	63%	1000	340	66%
CCl_4			Chloroform			Methylene chloride			Chloromethane		
580	<40	93%	2000	59	97%	660	<40	94%	<50	<40	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review.
NA = Not available. No data or one data point is available.
[a] The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW-101B (located adjacent to BW-103). Overall contaminant concentrations decreased over a 28-month period (see Figure 4-47). Over this same period, there was an overall decrease in PCE and TCE concentrations with a corresponding increase in 1,2-DCE, vinyl chloride and ethene concentrations. Chloroform concentrations decreased over this period while methylene chloride concentrations did not change. Ethane was detected. Alkalinity and sulfate concentration decreased slightly while carbon dioxide greatly increased. These trends appear independent of changes in ORP. Refer to Figure A-135 thru Figure A-138 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-47. Data Analyses for MW-101B in Western Biozone

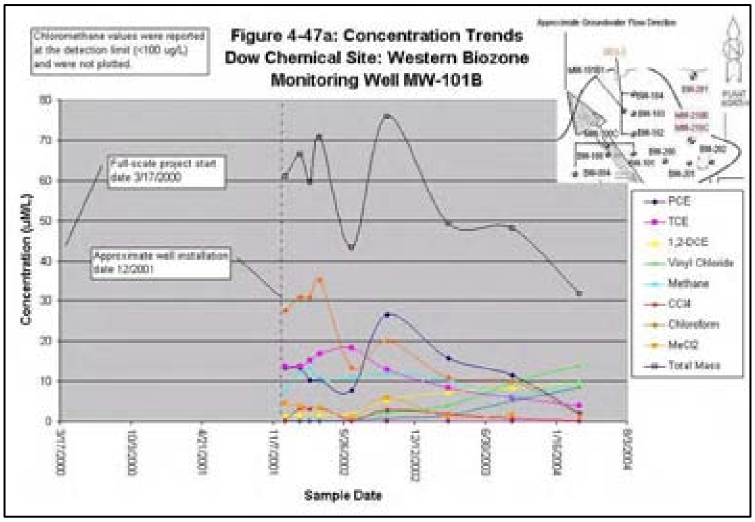


Figure 4-47a: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-101B

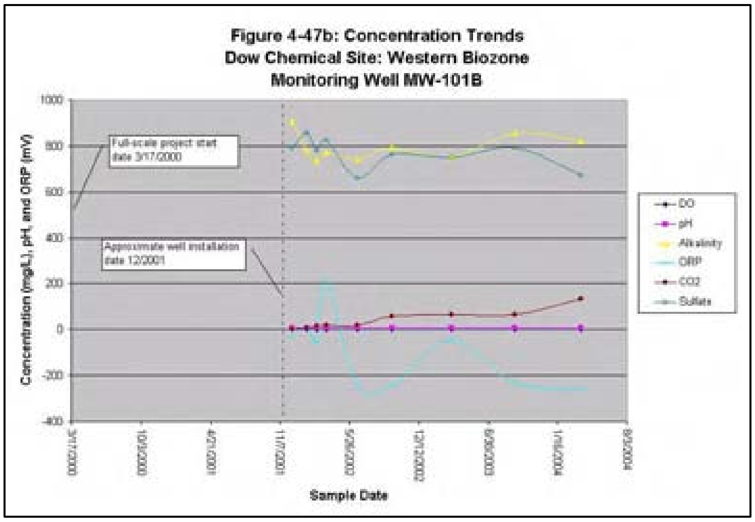


Figure 4-47b: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-101B

Monitoring Well	**Contaminant Mass Loss**								**Enhanced Geochemical Condition**	**Elevated Dissolved Gases**	**Biodegradation Rating**
	PCE	**TCE**	**DCE**	**VC**	**CCl_4**	**CF**	**$MeCl_2$**	**CM**			
MW-101B	+	+	-	-	+	+	+		+	+	HE

Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

Monitoring Well MW-101B											
C_i	**C_f**	**% reduction**	**C_i**	**C_f**	**% reduction**	**C_i**	**C_f**	**% reduction**	**C_i**	**C_f**	**% reduction**
(µg/L)			**(µg/L)**			**(µg/L)**			**(µg/L)**		
PCE			**TCE**			**1,2-DCE**			**Vinyl chloride**		
2200	350	84%	1800	510	72%	140	960	-586%	<50	870	-164%
CCl_4			**Chloroform**			**Methylene chloride**			**Chloromethane**		
65	32	51%	3300	190	94%	230	<50	78%	<100	<50	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW-206B and MW-206C (background wells, located west of the biozone). Each well only had five data points for a two-year period. No data were available on the geochemical, dissolved gas, or electron acceptor parameters at either well. An overall increase was observed at MW-206B due to an increase in CCl_4 concentration (see Figure 4-48). PCE and chloroform concentrations did not change nor were the daughter products of PCE detected. At MW-206C, overall contaminant concentrations increased slightly due to increases in 1,2-DCE and TCE while vinyl chloride concentrations did not change (refer to Figure 4-49).

Figure 4-48. Data Analyses for MW-206B in the Western Biozone

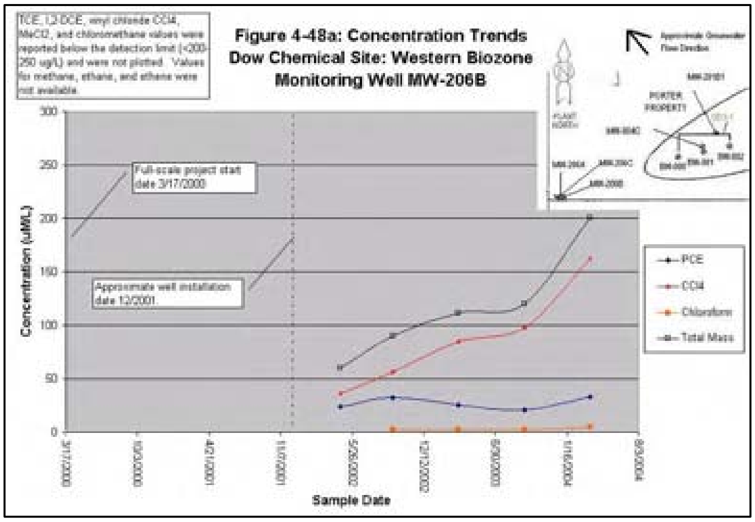


Figure 4-48a: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-206B

TCE, 1,2-DCE, vinyl chloride CCl4, MeCl2, and chloromethane values were reported below the detection limit (<200-250 ug/L) and were not plotted. Values for methane, ethane, and ethene were not available.

Full-scale project start date 3/17/2000

Approximate well installation date 12/2001.

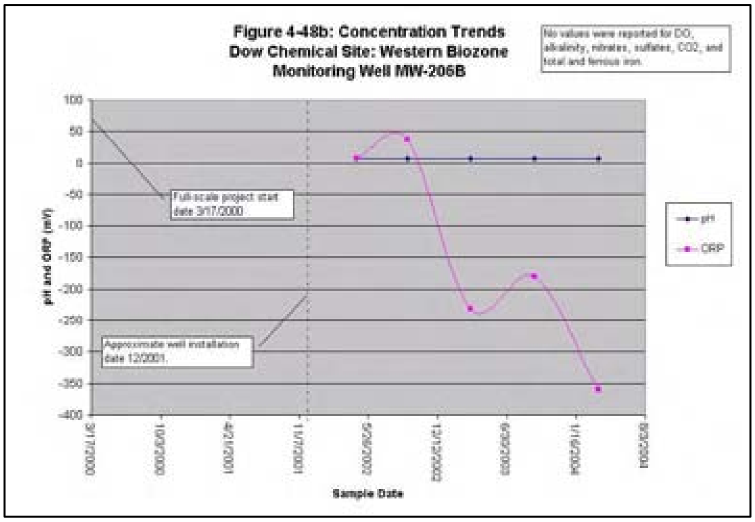


Figure 4-48b: Concentration Trends
Dow Chemical Site: Western Biozone
Monitoring Well MW-206B

No values were reported for DO, alkalinity, nitrates, sulfates, CO2, and total and ferrous iron.

Full-scale project start date 3/17/2000

Approximate well installation date 12/2001.

Figure 4-49. Data Analyses for MW-206C in the Western Biozone

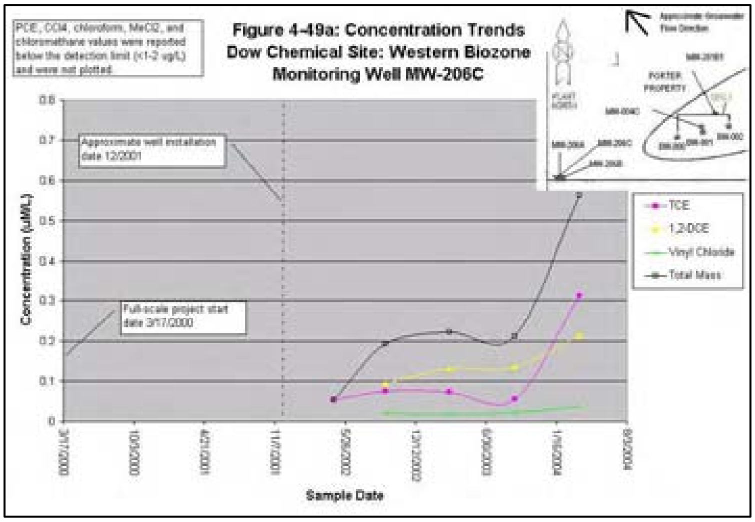


Figure 4-49a: Concentration Trends Dow Chemical Site: Western Biozone Monitoring Well MW-206C

PCE, CCl4, chloroform, MeCl2, and chloromethane values were reported below the detection limit (<1-2 ug/L) and were not plotted.

Approximate well installation date 12/2001

Full-scale project start date 3/17/2000

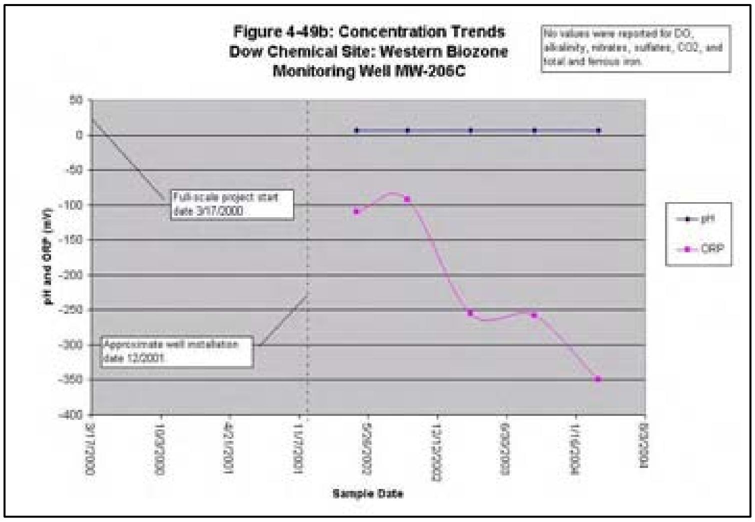


Figure 4-49b: Concentration Trends Dow Chemical Site: Western Biozone Monitoring Well MW-206C

No values were reported for DO, alkalinity, nitrates, sulfates, CO2, and total and ferrous iron.

Full-scale project start date 3/17/2000

Approximate well installation date 12/2001

Central Biozone:

Of the three biozones, the Central Biozone has the highest contaminant concentrations. Monitoring well data for MW-422C, MW-423C, MW-502C, MW-511C, and MW-623C were evaluated since these wells had the most current data. MW-422C and MW-423C are not part of the EISB system but are located 170ft and 270 ft downgradient, respectively, of the central biozone segments. There appears to be either little net change or an increase in total contaminant mass for the majority of these monitoring wells (4 out of 5) in this biozone. One monitoring well, MW-623C located in the eastern most segment of the biozone, shows little or no contamination. Decreasing PCE concentrations are observed in four of the five monitoring wells. MW-422C shows significant increase in PCE over the monitoring interval. Concentrations of TCE, either a breakdown product of PCE or a parent compound, appear somewhat constant (MW-422C), increasing (MW-423C), or decreasing (MW-502C and MW-511C) during the period monitored. Results for CCl_4 show the compound degraded in three monitoring wells (MW-422C, MW-502C and MW-511C) and was not detected in the remaining two monitoring wells. Biodegradation of parent compound contaminants has clearly occurred or is occurring as evidenced by significant concentrations of breakdown or daughter products in the monitoring wells: chloroform, methylene chloride, and 1,2-DCE. These breakdown products, however, appear to persist at significant concentrations, and increasing in some instances. Chloroform and methylene chloride are generally considered more readily biodegradable than their parent compounds. Dissolved gases ethene and ethane were detected but only at low levels. Anaerobic conditions were maintained in the biozone as indicated by consistently low dissolved oxygen (DO) levels and generally negative ORP measurements in the monitoring wells. Without current data or further understanding of the upgradient groundwater contamination plume and the consequent variation in influent flux of contaminants to the system, it is difficult to assess the degree of biodegradation due to the biozone. No explanation is given in the reports why all of the current monitoring wells are screened in the deeper C-zone interval and monitoring of the mid-depth B-zone interval was discontinued.

MW-502C (located adjacent to BW-503-2). PCE and its daughter products were detected at high concentrations ranging from 170-1600 µM/L over a 32 month period. Overall contaminant mass remained somewhat constant over the first 20 months except for a spike on 9/24/2001 followed by a large drop on 11/14/2001. The overall concentrations then decreased over the last 12 months at this well (see Figure 4-50). PCE concentrations decreased while TCE concentrations increased and then leveled. Low concentrations of 1,2-DCE increased slightly while no vinyl chloride was detected. Overall carbon tetrachloride and methylene chloride concentrations decreased while chloroform concentrations remained unchanged. Dissolved oxygen (< 1 mg/l) and ORP measurements (147 to -363 mV range) indicate anaerobic conditions were maintained. An unexplained spike and drop in ORP was measured on 3/20/2002 and 6/18/2002, respectively. Carbon dioxide concentrations decreased greatly during the first 6 months of monitoring then increased to a level higher than initially observed. Overall, alkalinity concentrations increased. Sulfate concentrations decreased over the first 26 months but then increased to a level higher than initially observed in the last 6 months. The spike and drop in ORP did not appear to have an effect on concentrations of sulfates or alkalinity, but did appear to coincide with the increase in CO_2 levels. Refer to Figure A-39 thru Figure A-42 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-50. Data Analyses for MW-502C in Central Biozone

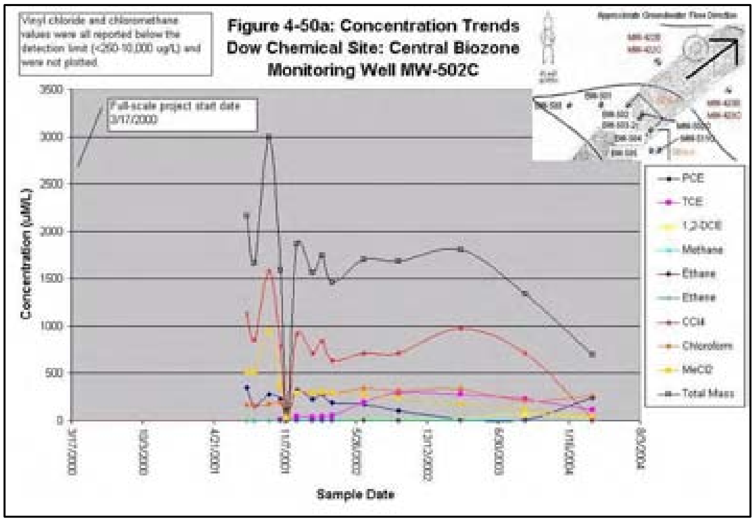


Figure 4-50a: Concentration Trends
Dow Chemical Site: Central Biozone
Monitoring Well MW-502C

Vinyl chloride and chloromethane values were all reported below the detection limit (<250-10,000 ug/L) and were not plotted.

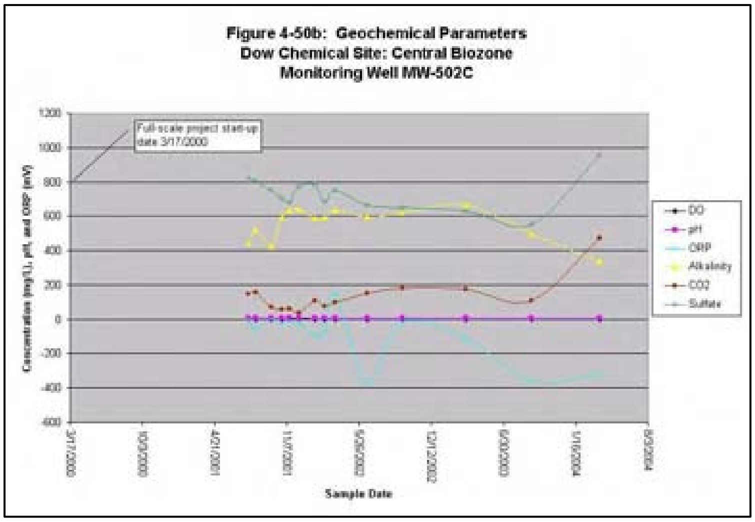


Figure 4-50b: Geochemical Parameters
Dow Chemical Site: Central Biozone
Monitoring Well MW-502C

Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-502C	-	-				+	0		+	+	HE

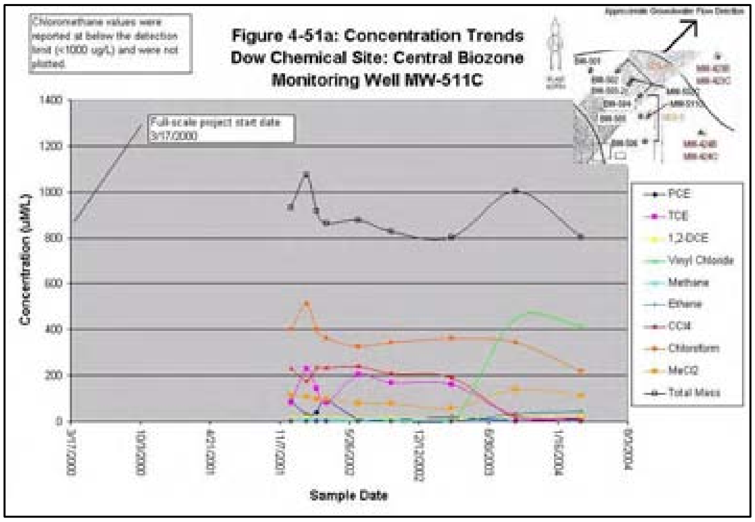
Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

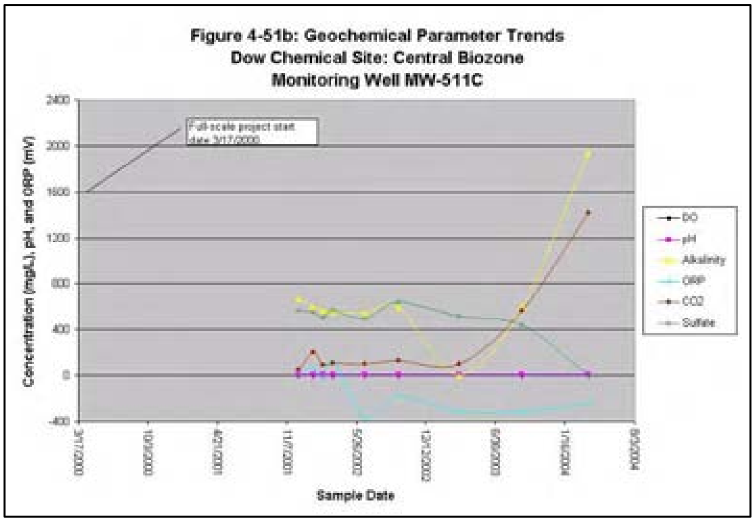
Monitoring Well MW-502C											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
58000	40000	31%	<10000	15000	-50%	<10000	2620	--	<10000	<500	--[a]
CCl_4			Chloroform			Methylene chloride			Chloromethane		
174000	2400	99%	20200	31000	-53%	43400	3500	92%	<10000	<500	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW-511C (located adjacent to BW-505). Overall contaminant mass appeared constant over the 28-month period. PCE concentrations decreased during this period while 1,2-DCE concentrations increased. Methylene chloride concentrations did not change much during this period and little ethane or ethene was generated (refer to Figure 4-51). TCE and carbon tetrachloride concentrations were observed to decrease while vinyl chloride concentrations were observed to increase between the 3/17/03 and 9/16/03 sampling events. Concentrations for both contaminants appear to level off during the last 6 months of monitoring. Overall ORP values decreased and remained in a range indicative of sulfate reduction. Overall alkalinity decreased greatly which appeared to coincide with the decrease in ORP but the last 12 months of data show the alkalinity concentration increased to a level higher than initially observed. Sulfate concentrations fluctuated, and overall showed only a major decrease in concentration over the last 12 months. These fluctuations appeared to coincide with ORP fluctuations. Overall carbon dioxide concentrations appeared to remain level over this period. Refer to Figure A-43 thru Figure A-46 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-51. Data Analyses for MW-511C in Central Biozone





Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-511C	0	+	0	-	+	+	0		+	+	HE
Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced											

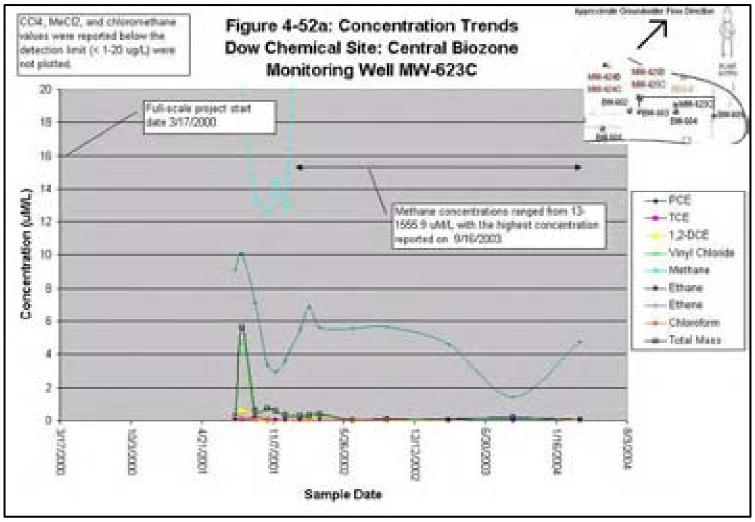
Monitoring Well MW-511C											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
15000	1500	90%	11000	1700	85%	1300	2600	-100%	<500	26000	-5100%
CCl_4			Chloroform			Methylene chloride			Chloromethane		
35000	<1000	97%	48000	26000	46%	9600	9500	10%	<1000	<1000	--[a]

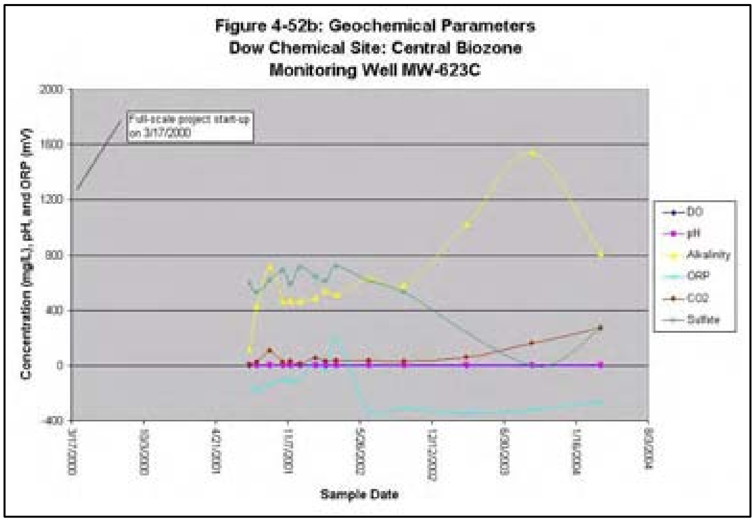
C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a] The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW-623C (located adjacent to BW-604). Only very low contaminant levels around 1 µM/L were detected. PCE and TCE concentrations were very low and less than 0.01µM/L (see Figure 4-52). 1,2-DCE and vinyl chloride levels decreased to less than 0.1µM/L. Carbon tetrachloride and methylene chloride concentrations were reported below the detection limits. Chloroform concentrations decreased to less than 0.01µM/L. Overall ethene levels decreased over the first 20 months but then increased during the last 6 months. Ethane was detected at low levels of less than 0.1µM/L. Dissolved oxygen and ORP levels indicate generally anaerobic conditions were being maintained. ORP levels during the first 8 months indicated nitrate reducing conditions, after which the ORP dropped to levels that indicated sulfate reducing conditions for the last 21-months of monitoring. This drop also appears to correspond to a large decrease in sulfate concentrations and a slight increase in sulfide concentrations. However, over the last 6 months, sulfate concentrations were observed to increase while sulfide concentrations were not detected. Alkalinity and methane concentrations also increased over the first 21 months but then appeared to decrease over the last 6 months. Carbon dioxide concentrations were low in comparison to the alkalinity and appeared to remain stable. Refer to Figure A-47 thru Figure A-50 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Some wells initially monitored at the start of the EISB system did not indicate overall contamination level reduction and were dropped from the monitoring program. For most of these wells, the contaminant levels remained relatively constant. A few wells did show a general decrease in PCE with an increase in TCE such as MW-423C. Other wells such as MW-422C showed a decrease in carbon tetrachloride but with little overall change in the other contaminants.

Figure 4-52. Data Analyses for MW-623C in Central Biozone





Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-623C	0	0	0	0		0			+	-	SE
Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced											

Monitoring Well MW-623C											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(μg/L)			(μg/L)			(μg/L)			(μg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
<5	<3	--[a]	<5	<3	--[a]	16.1	2.2	86%	<5	1.8	--[a]
CCl_4			Chloroform			Methylene chloride			Chloromethane		
<5	<3	--[a]	<5	<3	--[a]	<10	<3	--[a]	<5	<3	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW-422C (located downgradient of MW-502C). Increased concentrations of PCE, 1,2-DCE, methylene chloride ($MeCl_2$), and total COC mass were reported over a 19 month period (refer to Figure 4-53). TCE concentration does not appear to have changed. Carbon tetrachloride concentrations decreased while overall chloroform increased. Ethane and ethene were also detected in low concentrations. ORP values during this period were indicative of nitrate reducing conditions. Overall alkalinity decreased with its curve paralleling the ORP curve. Overall sulfate, ferric iron, and ferrous iron concentrations increased during this period while dissolved and total manganese concentrations remained constant. The increases in the sulfate, ferric iron, and ferrous iron concentrations may be due to fluctuations in background concentrations. Refer to Figure A-31 thru Figure A-34 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-53. Data Analyses for MW-422C in Central Biozone

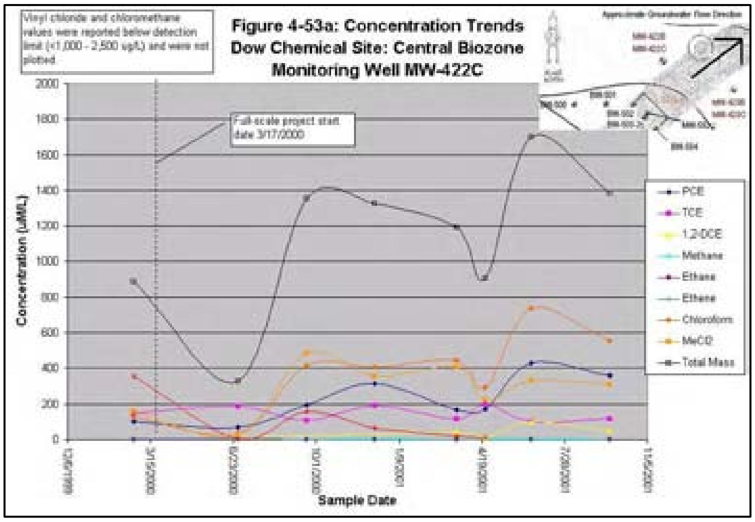


Figure 4-53a: Concentration Trends
Dow Chemical Site: Central Biozone
Monitoring Well MW-422C

Vinyl chloride and chloromethane values were reported below detection limit (<1,000 - 2,500 ug/L) and were not plotted

Full-scale project start date 3/17/2000

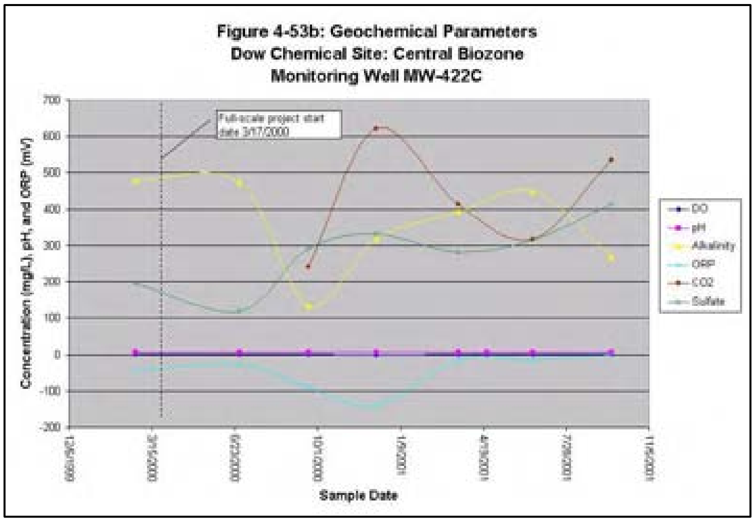
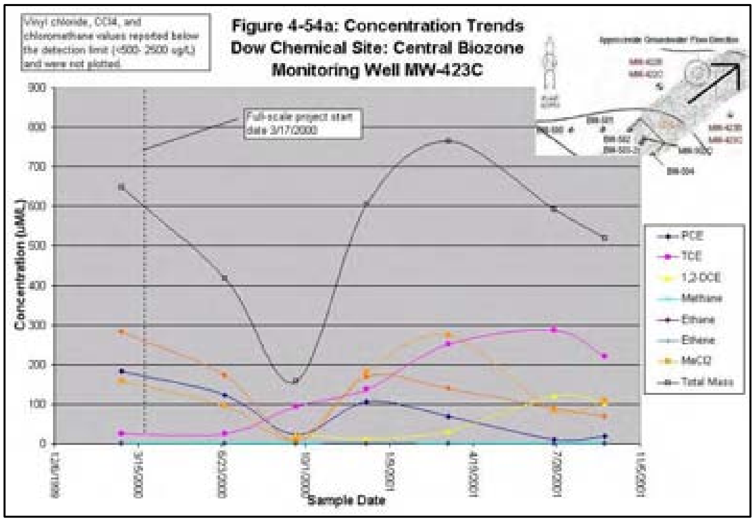


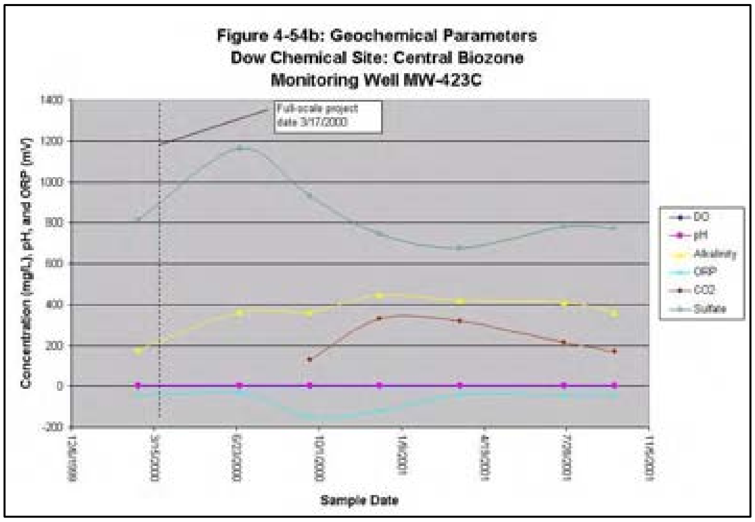
Figure 4-53b: Geochemical Parameters
Dow Chemical Site: Central Biozone
Monitoring Well MW-422C

Full-scale project start date 3/17/2000

MW-423C (located downgradient of MW-502C). After system startup, overall contaminant mass, PCE, and carbon tetrachloride concentrations decreased (see Figure 4-54) followed by increasing concentrations of TCE and 1,2-DCE. However, increased 1,2-DCE concentrations appear to be independent of the TCE concentrations. Chloroform and methylene chloride concentrations appear to be decreasing. Overall alkalinity decreased while sulfate and carbon dioxide increased. Monitoring indicated consistently anaerobic conditions were maintained. Dissolved oxygen was low and ORP values were indicative of nitrate reducing conditions during the entire monitoring period. Refer to Figure A-35 thru Figure A-38 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-54. Data Analyses for MW-423C in Central Biozone



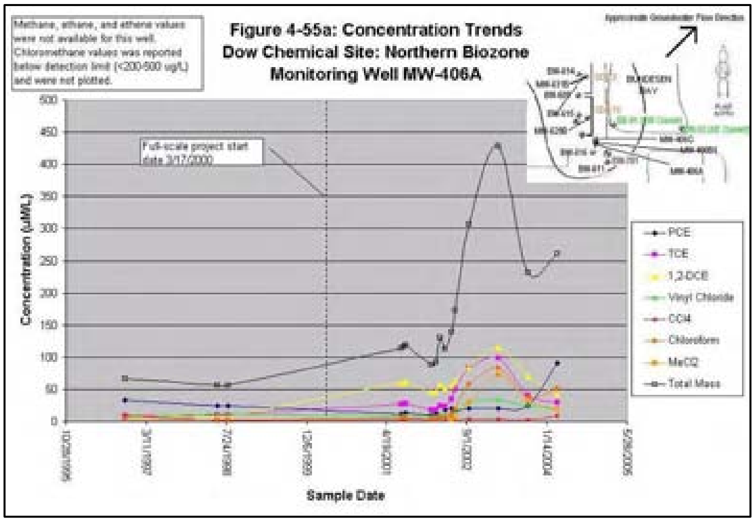


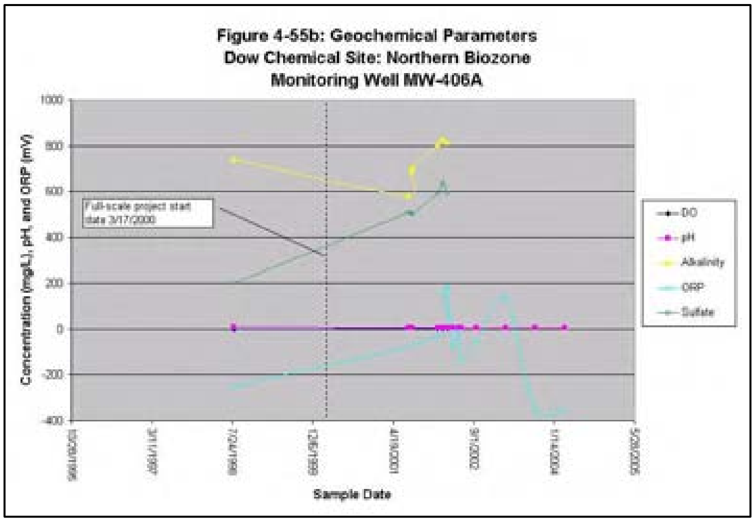
Northern Biozone:

Initially, five monitoring wells were used to assess EISB performance. This number was reduced to 4 monitoring wells after the system was optimized. MW-600C was removed from the monitoring program in the latter half of 2002 since it was thought to be located in an isolated pocket of product based on higher observed contaminant flux in the effluent compared to the influent. The other four monitoring wells were initiated approximately thirteen to twenty-three (13-23) months after system startup. MW-406A, MW-406B1 & MW-406C monitoring well cluster are also included in this review since data from the initial period immediately after system startup on 3/17/2000 until recently were available. Overall contaminant mass generally increased at each monitoring well in the 406 monitoring well cluster. At MW-603B there was some reduction in 1,2-DCE concentration with a corresponding increase in vinyl chloride concentration, and a small decrease in total contaminant mass except for the last 6 months where an increase in vinyl chloride, 1,2-DCE and total mass were observed. At MW-633B little or no contaminant was detected during the monitoring period. At the remaining two more centrally located monitoring wells, MW-629B and MW-631B, biodegradation processes are apparent with decreases in parent compounds, as well as appearance and reductions in daughter products. In MW-631B total contaminant mass appears to have greatly decreased, while in MW-629B, the total contaminant mass appeared to remain level. During the periods monitored, anaerobic conditions were generally maintained as indicated by low dissolved oxygen levels and measured ORP levels that fluctuated but were generally negative.

MW- 406A (located downgradient of BW-616, not part of EISB system). The overall contaminant mass increased greatly during this period. Concentrations of PCE, TCE 1,2-DCE, vinyl chloride, chloroform, and methylene chloride have been increasing over a 36-month period since system startup (refer to Figure 4-55). Over the last 12 months, PCE concentrations increased while TCE and 1,2-DCE concentrations decreased and vinyl chloride concentrations remained level. Carbon tetrachloride concentrations showed no change while chloroform and methylene chloride concentrations decreased over the last 12 months. DO was observed to also decrease over the last 12 months. However, no data was available for sulfate and alkalinity concentrations during this period. Data for other geochemical parameters was not available during this same period.

Figure 4-55. Data Analyses for MW-406A in Northern Biozone





MW- 406B1 (downgradient of BW-616). A large PCE concentration spike is observed around June 2000, about three months after system start-up. This spike is followed by a sharp decrease, and then followed by another gradual increase in most contaminants approximately two years after start-up (see Figure 4-56 above). A sharp increase in methylene chloride concentrations was observed during the last 6 months. During the 24-month period after start-up, carbon tetrachloride concentrations decreased while byproducts of chloroform and methylene chloride increased independently of each other. PCE, TCE, VC, and 1,2-DCE concentrations increased. The increases in PCE and its daughter products, however, seem independent of each other. A small amount of ethene was also detected. A large positive spike in the ORP (514 mV) was reported on 8/29/2000 two months after the COC concentration spike. After this spike, ORP levels dropped and fluctuated between +100mV and -351mV. The DO was generally low, reported under 2 mg/L except on 2/23/2000 at 6.3 mg/L and 6/14/2001 at >1.1 mg/L. Overall alkalinity, sulfate, and carbon dioxide concentrations increased. Propene concentrations also decreased and have remained constant at this well. Unfortunately, data was only available for 20 months after start-up for the geochemical parameters, dissolved gases, and electron acceptors. Refer to Figure A-76 thru Figure A-79 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-56. Data Analyses for MW-406B1 in Northern Biozone

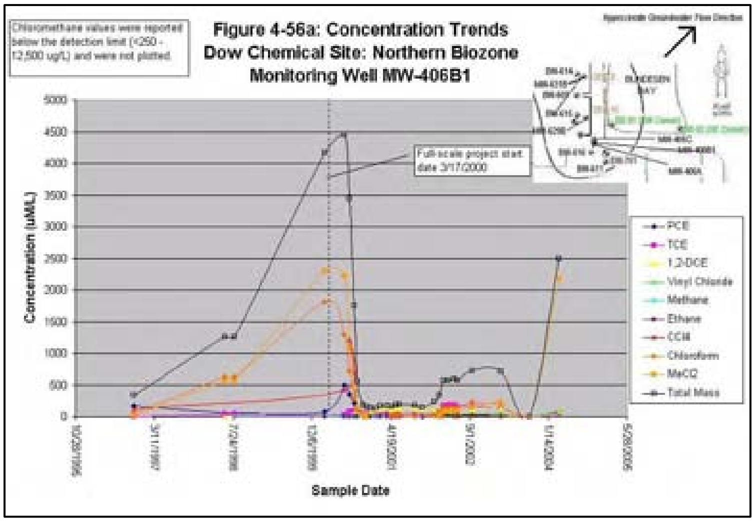


Figure 4-56a: Concentration Trends
Dow Chemical Site: Northern Biozone
Monitoring Well MW-406B1

Chloromethane values were reported below the detection limit (<250 - 12,500 ug/L) and were not plotted.

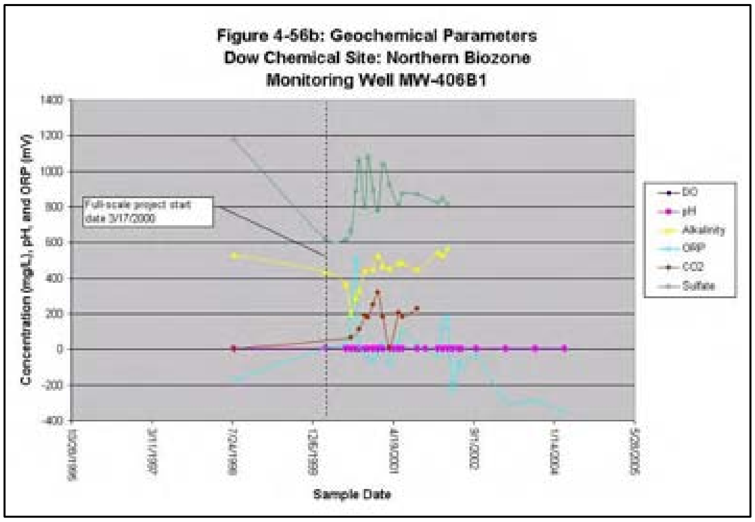


Figure 4-56b: Geochemical Parameters
Dow Chemical Site: Northern Biozone
Monitoring Well MW-406B1

MW- 406C (located downgradient of BW-616). Over the 36-month period after start-up, total contaminant mass increased, including increased concentrations of PCE, carbon tetrachloride, and their daughter products (see Figure 4-57). Only a small amount of ethene was detected. ORP and sulfate concentrations fluctuated and became constant 15 months after start-up while alkalinity and carbon dioxide concentrations increased. Refer to Figure A-80 and Figure A-83 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-57. Data Analyses for MW-406C in Northern Biozone

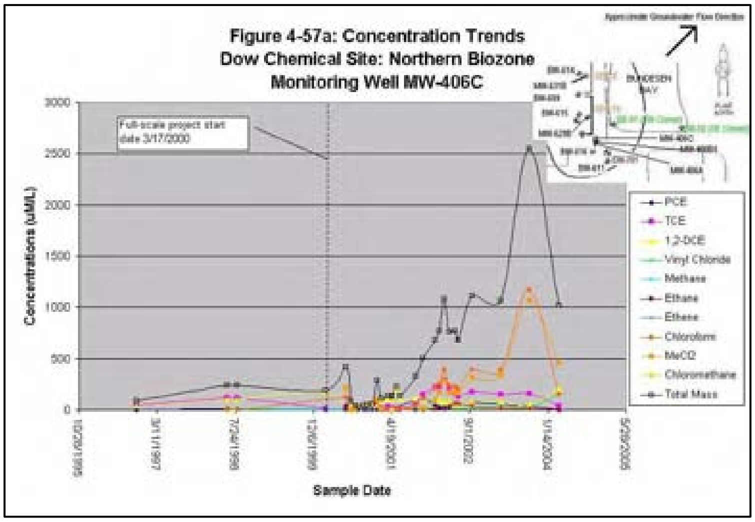


Figure 4-57a: Concentration Trends
Dow Chemical Site: Northern Biozone
Monitoring Well MW-406C

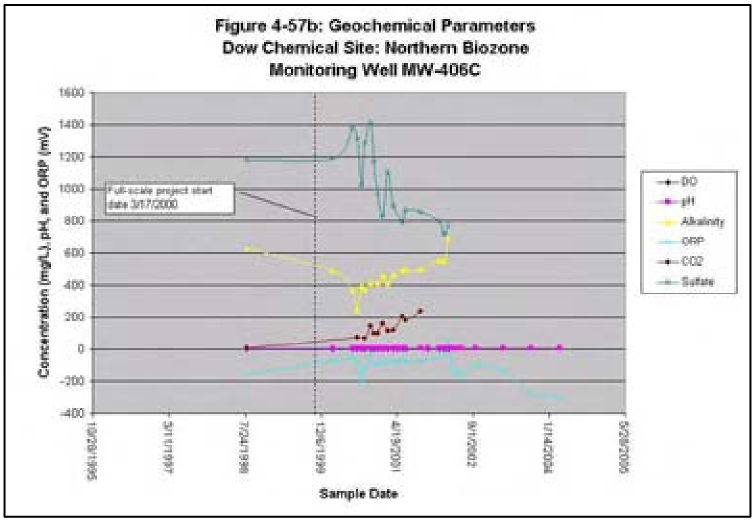


Figure 4-57b: Geochemical Parameters
Dow Chemical Site: Northern Biozone
Monitoring Well MW-406C

MW-603B (adjacent to BW-613). Overall contaminant mass decreased little over a 36-month period since start-up (see Figure 4-58). Higher levels of ethene were detected while 1,2-DCE and VC levels show an initial reduction then remained constant. PCE, TCE, and carbon tetrachloride and its daughter products are detected at very low levels. Except for one sampling event ORP levels were generally negative, ranging to as low as -325mV. Overall alkalinity appears to be decreasing. Sulfate concentrations spiked on three occasions with no apparent pattern. Ferrous iron decreased over the first 10 months, then fluctuated at levels close to those initially observed. Refer to Figure A-84 thru Figure A-87 in Appendix A for sulfate, ORP, CO2, ferrous iron and alkalinity.

Figure 4-58. Data Analyses for MW-603B in Northern Biozone

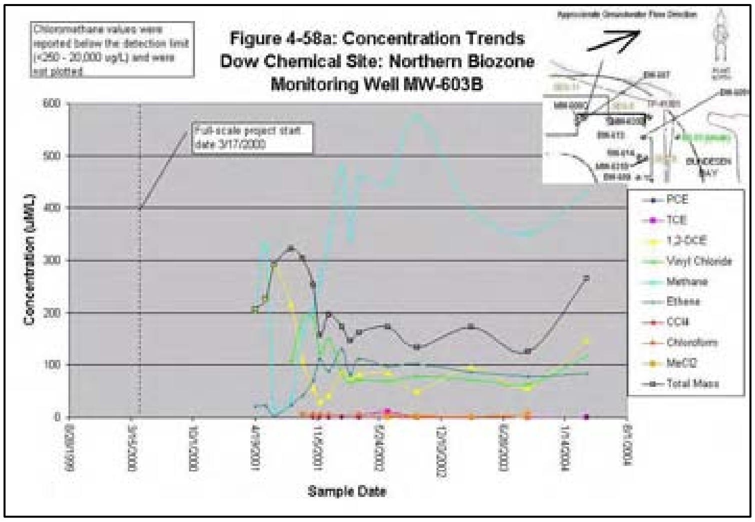


Figure 4-58a: Concentration Trends
Dow Chemical Site: Northern Biozone
Monitoring Well MW-603B

Chloromethane values were reported below the detection limit (<250 - 20,000 ug/L) and were not plotted

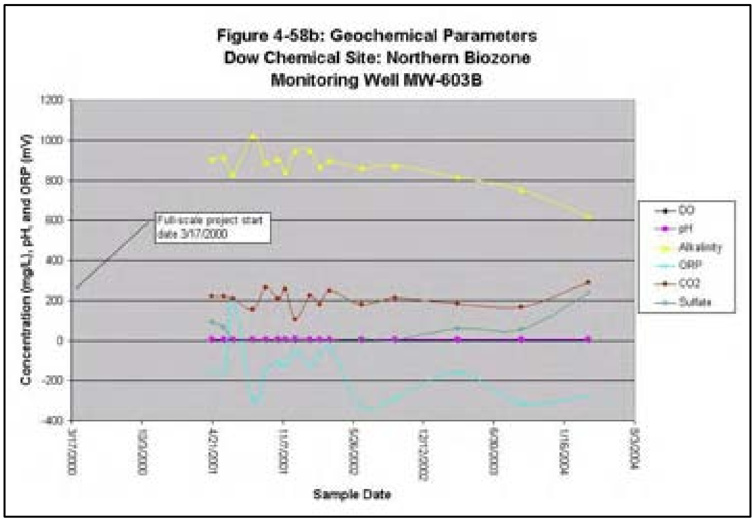


Figure 4-58b: Geochemical Parameters
Dow Chemical Site: Northern Biozone
Monitoring Well MW-603B

Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-603B	0	0	-	-	0	0	0		+	-	SE

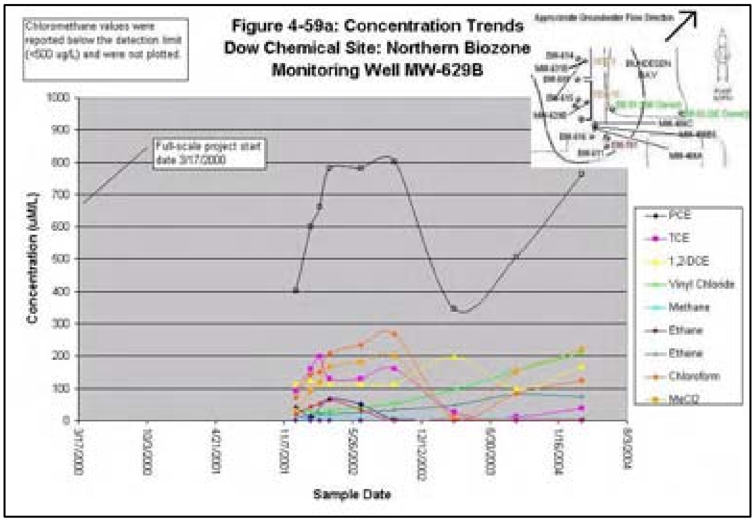
Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

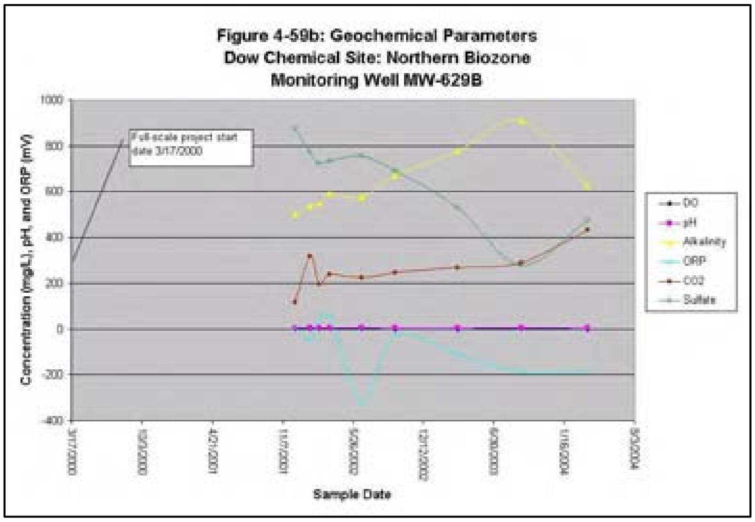
Monitoring Well MW-603B											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
<20000	<500	--[a]	<20000	<500	--	<20000	14300	--[a]	<20000	7400	--[a]
CCl_4			Chloroform			Methylene chloride			Chloromethane		
<20000	<500	--[a]	<20000	<500	--	<40000	<500	--[a]	<20000	<500	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a] The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW-629B (located adjacent to BW-615). Data was available for a 28-month monitoring period starting 20 months following the project start. Initially, contaminant levels and overall mass appear to increase for the first 10 months, decrease over the next 6 months, and then gradually increase again over the last 12 months (refer to Figure 4-59). Biodegradation processes are clearly evident at this well location. PCE appears to have been degraded to TCE. TCE concentrations then decreased while concentrations of daughter products, 1,2-DCE and vinyl chloride, increased. Carbon tetrachloride, chloroform, and methylene chloride decreased over the 16 month period. Ethene concentrations also appear to increase over this period. Overall sulfate concentrations appeared to be decreasing while alkalinity and carbon dioxide increased during the first 22 months. In the last 6 months, sulfate and carbon dioxide concentrations increased while alkalinity decreased. Ferrous iron concentrations remained constant. ORP levels fluctuated between +100mV and -180mV, except for one drop in ORP to -300mV. There appears to be a delay between the drop in ORP and the observed decrease in sulfate concentrations at this well. This pattern, however, may be due more to upgradient conditions (influent to the system) which are not available. Refer to Figure A-92 thru Figure A-95 in Appendix A for sulfate, ORP, CO2, ferrous iron and alkalinity.

Figure 4-59. Data Analyses for MW-629B in Northern Biozone





Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-629B	+	+	-	-	+				+	-	ME

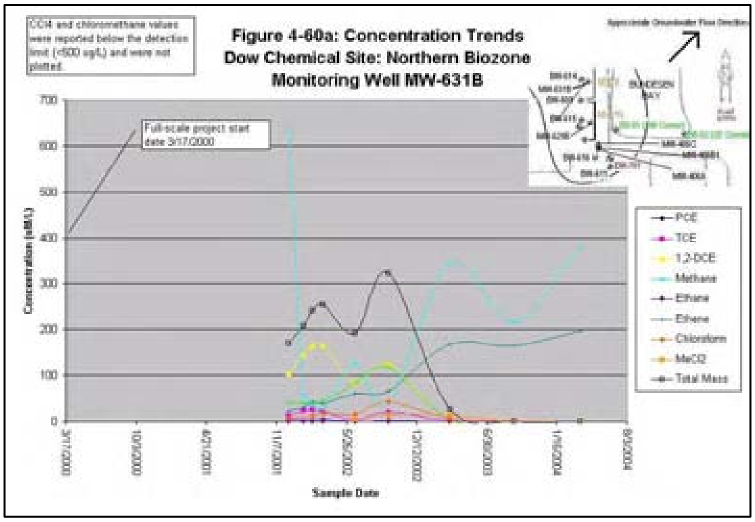
Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

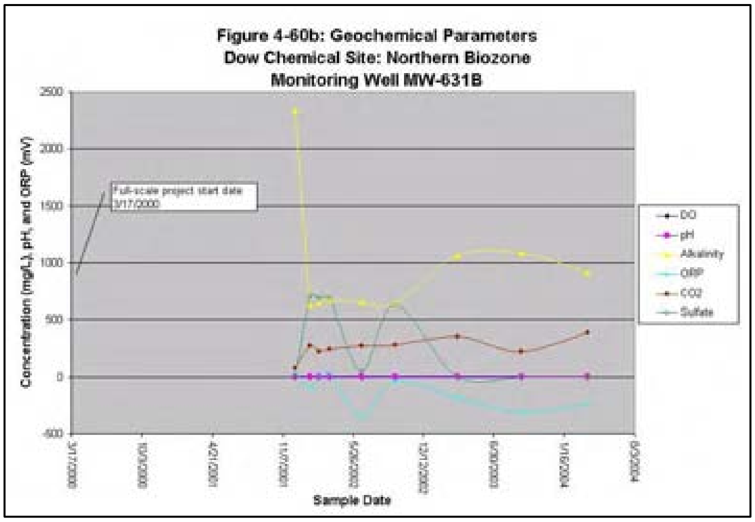
Monitoring Well MW-629B											
C_i (µg/L)	C_f (µg/L)	% reduction	C_i (µg/L)	C_f (µg/L)	% reduction	C_i (µg/L)	C_f (µg/L)	% reduction	C_i (µg/L)	C_f (µg/L)	% reduction
PCE			TCE			1,2-DCE			Vinyl chloride		
6600	450	93%	12000	5100	58%	11000	16160	-47%	2200	13000	-491%
CCl_4			Chloroform			Methylene chloride			Chloromethane		
3200	<500	84%	8600	15000	-74%	1500	11000	-633%	<500	<500	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value.

MW-631B (located adjacent to BW-614). The overall contaminant level decreased over the 28-month monitoring period with 1,2-DCE and VC appearing to be degraded while ethene increased (refer to Figure 4-60). Low concentrations of TCE, chloroform, and methylene chloride are observed. On 1/24/2002, a drop in alkalinity coincided with a sharp increase in sulfate and carbon dioxide concentrations. Reported ORP values indicated conditions for possible iron reduction but ferrous iron concentrations remained constant during this period. A sharp drop in the ORP was reported on 6/20/2002 which corresponded to a sharp drop in the sulfate concentration while carbon dioxide and alkalinity concentrations remained constant. As ORP values increased another spike in the sulfate concentrations was observed with no change in alkalinity and carbon dioxide. As ORP dropped to levels indicative to sulfate reduction, a sharp decrease in sulfate concentration was observed along with an increase in the alkalinity and carbon dioxide concentrations. Ferrous iron concentrations at this time were also observed to decrease. Refer to Figure A-96 thru Figure A-99 in Appendix A for sulfate, ORP, CO2, ferrous iron and alkalinity.

Figure 4-60. Data Analyses for MW-631B in Northern Biozone





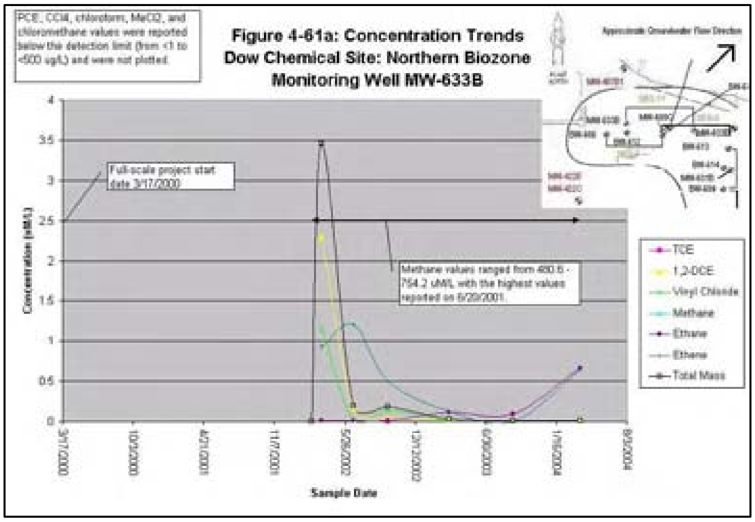
Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-631B	+	+	+	+	0	+	0		+	+	HE
Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced											

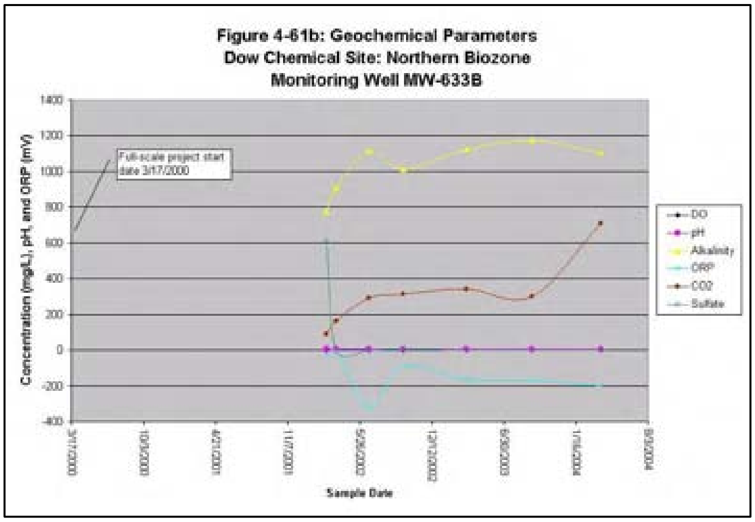
Monitoring Well MW-631B											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
740	<10	99%	1700	<10	99%	10000	3	99.9%	2600	3.6	99.9%
CCl_4			Chloroform			Methylene chloride			Chloromethane		
<250	<10	--[a]	960	9	99%	<250	<10	--[a]	<500	<10	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value .

MW- 633B (located adjacent to BW-612). This monitoring well appears relatively clean compared to the other wells in the north biozone having very low concentrations of contaminants (refer to Figure 4-61 and Appendix A). Ethane and ethene were detected at low levels. Increases in alkalinity and carbon dioxide appear to coincide with decreases in ORP values. Sulfate concentrations decreased sharply and remained at low levels for the duration while ferrous iron concentrations appear to remain constant. Refer to Figure A-100 thru Figure A-103 in Appendix A for sulfate, ORP, CO2, and alkalinity.

Figure 4-61. Data Analyses for MW-633B in Northern Biozone





Monitoring Well	Contaminant Mass Loss								Enhanced Geochemical Condition	Elevated Dissolved Gases	Biodegradation Rating
	PCE	TCE	DCE	VC	CCl_4	CF	$MeCl_2$	CM			
MW-633B		0	-	-					+	+	ME

Note: "+" = Positive evidence, "-" = Negative evidence, "blank " = Not available, "0" = No change
HE = highly enhanced, ME = moderately enhanced, NE = Not enhanced, SE = Slightly enhanced

Monitoring Well MW-633B											
C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction	C_i	C_f	% reduction
(µg/L)			(µg/L)			(µg/L)			(µg/L)		
PCE			TCE			1,2-DCE			Vinyl chloride		
<500	<1	--[a]	<500	<1	--[a]	<500	0.57	--[a]	<500	<1	--[a]
CCl_4			Chloroform			Methylene chloride			Chloromethane		
<500	<1	--[a]	<500	<1	--[a]	<500	<1	--[a]	<10	<1	--[a]

C_i = First reported result after the full-scale system start-up date 3/17/01.
C_f = Last reported result available for this review
NA = Not available. No data or one data point is available.
[a]The percent reduction was not calculated because the initial and final sample concentration was below the detection limit or the C_i detection limit was greater than the reported C_f value.

Project Costs

As part of the feasibility study (RWQCB, no date), the enhanced in-situ bioremediation system was compared to several different pump-and-treat systems. The median cost for these pump and treat systems were estimated between $29-49 million with an annual operation and maintenance (O&M) cost of $5 million. The in-situ bioremediation "Bio Barrier" had an estimated median cost of $18 million with an annual O&M cost of $2 million. The median capital costs include the development, operation, and maintenance for all alternatives.

Additional costs not included in the table above include additional subsurface characterization, cleaning of the EISB system wells, and process optimization such as modifications to the amendment pumping system.

Data Gaps

After reviewing the available data for the three biozones, three main data gaps were identified: (1) no upgradient groundwater sampling data was obtained after implementing the project in March 2000. Influent concentration flux calculations used to assess treatment efficiency are being based on 1996 groundwater data, (2) details on pumping patterns and amendment injections were not available and (3) incomplete data existed due to changes in the EISB monitoring program where sampling at some monitoring wells were discontinued and replaced with new monitoring wells installed after the EISB system had been implemented.

For the entire site, including northern, western and central plume areas, time series iso-concentration plots are needed for each of the contaminant parent compounds and their breakdown products. These should be done separately for each of the two aquifer intervals being remediated. A minimum of 3 or more time series plots are needed (for each parent compound and breakdown products, and for each zone) including the most current data, interim mid-point conditions, and initial conditions encountered at the onset of the treatment program. These plots are needed to establish an overall trend in site conditions that could not be assessed by reviewing individual well data. These plots would clearly establish what the overall effect of the in-situ bioremediation program at the site has been, whether or not there is a clear, overall reduction in parent compounds, and whether expected breakdown products are accumulating and being effectively degraded.

Sampling of key monitoring wells was discontinued in all three source areas (northern, western, and central) around November 2001, after over a year of operation. New monitoring wells were installed to replace these, fewer in number, and generally closer to injection/extraction wells within the biozone.

In general, the wells where monitoring was discontinued did not clearly indicate significant biodegradation had occurred over time. These wells also appear to have been well located to monitor biozone performance. An explanation is needed why these wells have been abandoned and new wells installed.

Operating data is needed to further understand how the system has been operated, especially with respect to sampling events and locating monitoring wells.

a. Have the flow rates changed over time? Per discussions with the RWQCB, the pumping direction of the injection and extraction wells may have been periodically reversed. It is important to know when these changes were made, especially with respect to sampling events.

b. Amendments. Were the amounts injected consistent among all injection wells and what were these amounts? Because the injection and extraction wells were reversed periodically, this history is needed to know where and when each zone was amended.

System Modeling Results.

a. How was the system expected to perform? The system should have been modeled to assess how the system would perform over time given initial concentrations of parent compounds and breakdown products. These modeled or expected results should have been compared to monitoring data collected to date. The 3 systems have been in operation over several years (since March 2000), and significant biodegradation within the biozone and immediately downgradient should be evident.

b. Based on the results of the conservative tracer tests, the amount of mixing between the B and C zone is estimated at 14 circulation cycles or a retention time of 70 days. One would expect more homogenization of the groundwater plume and more consistent results between monitor wells within and between zones.

Monitoring appears inconsistent with respect to the numbers and locations of intermediate and deeper aquifer monitor wells.

Why are new and current MWs only located adjacent to injection wells? A better location to assess overall system effectiveness would be a midpoint well, located generally downgradient on a line that bisects the line between the two wells.

Currently, the monitoring wells selected for the EISB monitoring program are comprised mainly of the deep zone (Zone C) wells, a few mid-depth (Zone B) wells in the northern and western biozones, and no shallow (Zone A) wells in any of the biozones. There are no monitoring wells located between the central and northern biozones, or downgradient of the western biozone to assess the magnitude or influence of enhanced biodegradation conditions in the groundwater.

Summary Observation, Conclusions, and Observations

The Dow Pittsburg site contamination is complex, involving several plume areas, multiple parent compounds with associated breakdown products, and several depth intervals. Dow has initiated an extensive effort to bioremediate the plumes (identified as the northern, central and western bioremediation zones), as well as to monitor bioremediation control parameters and the effectiveness of the “biozone” in reducing contaminant concentrations and preventing off-site migration.

The remediation system has been operational now for about four years, and significant biodegradation is expected to be evident. In reviewing sampling results for monitor wells, as well as biozone injection/extraction wells, it is clear that some biodegradation has occurred in many of the wells. This is evidenced by reduction in concentrations of parent compounds, appearance and reduction of breakdown products, depletion of some electron donors and maintaining anaerobic redox conditions. However, it is unclear from the available data how effective the biozone has been in reducing overall contaminant concentrations or preventing the downgradient migration of contaminants.

There are a significant number of monitoring wells where there has been little or no reduction in a parent compound or where breakdown products have accumulated but are not being reduced. It is not clear from monitoring well data that there is a trend toward reducing contaminant concentrations. There is considerable variation and no apparent consistency in contaminant concentrations trends between wells located within the same bioremediation zone or within the same aquifer depth interval of that bioremediation zone. It is not clear from reports reviewed what results were expected based on the system design, especially for monitoring locations downgradient after four years of operation of the three installed biozone systems.

For most circulation wells, contaminant concentrations fluctuated and in some instances increased over time. Concentrations in circulation wells would be expected to reach a steady state condition if the appropriate amount of amendments and conditions existed for anaerobic degradation. Increasing parent compound and daughter product concentrations were observed at a significant number of the monitoring wells. For the system to be considered effective, monitoring well concentrations should either exhibit some of the biodegradation patterns expected for PCE and carbon tetrachloride or at least show an overall decrease in total contaminant amount over time. For several monitoring wells, this was not observed. In many cases concentrations fluctuated over time. There was no clear pattern of the circulation wells cutting off and treating contaminants, preventing their downgradient migration.

The system does not appear to be effective in reducing concentrations of TCE, which may either be a parent compound or a breakdown product of PCE. TCE concentrations appear to increase or remain constant in most monitoring wells. In some monitoring wells PCE reductions are observed with increases in TCE concentrations, while in other wells PCE concentrations seem to either increase or remain the same. Single carbon chlorinated compounds typically biodegrade more readily than two or more carbon compounds. CCl_4 does appear to be biodegrading based on concentration reductions observed in most monitor wells where CCl_4 has been present. However, concentrations of $MeCl_2$, which also should be readily biodegradable, are seen to increase or remain constant in many of the monitoring wells.

Currently, the effectiveness of the EISB system is demonstrated by calculating a destruction rate efficiency (DRE) based on the total contaminant mass flux for each biozone segment. The influent concentration flux used to calculate a DRE for each of the 10 biozone segments is based on an interpolated value from a 1996 data set using a 3-dimensional modeling program. The effluent concentration flux is based on the concentration observed at the monitoring well immediately downgradient from the circulation wells. DRE calculation method appears inappropriate for a number of reasons. The average concentration flux may not represent the mass flux of contaminants into biozone since the most of the wells used for this calculation were sampled only once. Since the monitoring well contaminant concentrations vary and at times exceed the calculated influx concentration, a DRE value does not seem appropriate. A negative DRE would indicate a source of contaminants that may be entering the system due to changing subsurface conditions. The concentration trends for the monitoring wells that comprise the segments within each biozone should be shown graphically as molar concentration for each contaminant of concern over time instead of as DRE.

Methane concentrations are detected at amounts several times higher than the concentrations for CCl_4 and its daughter products at wells in close proximity of the slough. The elevated methane concentrations are observed in the western biozone at MW-202B1; in the northern biozone at MW-407B1, MW-603B, MW-631-B, MW-633B, and TP-413B1; and in central biozone at MW-425B and MW-623C. The elevated methane concentrations may be indicative of other contaminants or organics degradation occurring at the site.

To show a reduction in the COC concentrations, it is recommended that the sum of the molar mass of PCE, CCl_4, and their associated daughter products be plotted and presented. The individual molar amounts for PCE, CCl_4, and their daughter products should also be plotted using the same concentration scale to allow the reviewer to quickly assess the relative biodegradation activity at the well for each COC.

The fluctuating concentrations in the monitoring wells may be due to the grab sampling method used. Grab samples provide point in time and space data which may be affected by injection and changing pumping direction in circulation wells. The use of diffusion bag samplers to collect a composite sample instead of a grab sample would provide a time-integrated sample over a longer duration that may provide a more representative sample of the conditions in the biozones.

To allow the reviewer to independently analyze the available data, responsible parties (RPs) and their consultants should be required to provide electronic copies of all spreadsheets used and their associated data. The data for this site is collected by several different consultants and presented in several different reports. This makes review extremely difficult and burdensome and lessens the value of the reports.

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5 Findings

- In-situ biological treatment appears to be more of an emerging than a demonstrated technology. Although it has been considered as a remedial alternative at many California sites and a number of pilot-scale projects have been completed, there are but a few sites where in-situ biological treatment has been implemented full-scale for chlorinated solvents. Only 6 of the 31 in-situ biological treatment projects the survey identified in California were indicated to be full-scale implementations. Projects selected for case study were those that were full scale, and which offered the most potential to demonstrate success. Due to the limited number of full-scale applications, only three of the five projects selected for case study were actually full-scale projects.

- Field implementations of in-situ biological treatment are far more complicated than the laboratory and bench studies that have been conducted to demonstrate the efficacy of the technology. An analysis of available data for the five case study projects did not find the classic “cascading” series of curves associated with reductive dechlorination of chlorinated solvents at any of these sites.

- For all five sites studied, the data suggest that biodegradation was occurring to some degree. However, except possibly for one site, it was not clear that biodegradation was proceeding in a reliable, demonstrative manner that would be desired for a final remedy. For example, at the Dow Site, biodegradation of mono-carbon compounds (carbon tetrachloride and its less-chlorinated analogues chloroform, methylene chloride and chloromethane) and di-carbon compounds (PCE and TCE) was possibly occurring in different locations, but biodegradation was not apparent and consistent for both types of compounds in any well where they occurred together.

- For several sites and many monitoring wells, there was no apparent change in any parameter measured as a result of implementation of the bioremediation system. Such results are discouraging.

- At three of the five case study sites there was a build-up of cis-1,2-DCE, and no evident production of subsequent degradation products (e.g., vinyl chloride, ethene). These data indicate that the biodegradation process has “stalled” at these sites. As the compound cis-1,2-DCE is formed almost exclusively by biological degradation of TCE, increasing concentrations are a clear indicator that TCE is being biodegraded. However, where cis-1,2-DCE does not degrade further to vinyl chloride and eventually to ethene, the net effect is to only transform TCE into cis-1,2-DCE.

- None of these sites where “stalling” was apparent had been inoculated with the microorganisms known to effect complete degradation of TCE. Further, as site managers became aware of this problem, there was no contingency program in place to inoculate the site with bacteria capable of degrading the accumulated cis-1,2-DCE. The “stalling” effect has received much attention in the literature. One explanation for stalling is that the microorganisms that can completely dechlorinate PCE or TCE are not so widely distributed as the relatively ubiquitous microorganisms that degrade PCE and TCE to cis-1,2-DCE. This explanation is supported by experiments where sites stalled at cis-1,2-DCE were inoculated with microorganisms capable of complete dechlorination and the complete dechlorination then proceeded.

- Biodegradation of chlorinated solvents is clearly indicated when monitoring finds biodegradation products that could only result through a biodegradation pathway. The key compounds to measure for biodegradation of 2-carbon chlorinated compounds are cis-1,2-DCE, vinyl chloride and ethene. In all five case studies, cis-1,2-DCE was measured, and in four cases vinyl chloride and ethene was measured.

- Measurement of the suite of organic chemicals that document the changing molar ratios between parent and daughter compounds throughout a biodegradation pathway is important to confirm that biodegradation is effectively occurring at a site.

- Measurement of redox condition and geochemical parameters promotes an understanding of the biodegradation pathway at a site, and is necessary to assess that optimum conditions for the biodegradation process have been established. For several sites evaluated, limited or no geochemical parameters were reported for either the pilot scale or full-scale application of the bioremediation technology.

- The presence of bacteria capable of reducing the targeted chlorinated compounds is essential for bioremediation technology to be effective. Increasing the population of bacteria capable of bioremediation in the subsurface treatment zone (aquifer) is one clear objective of a bioremediation project. However, in only two of the sites reviewed were the specific bacteria thought to be responsible for biodegradation enumerated. While several sites relied on the presence of biodegradation products (vinyl chloride, in particular) as an indication that bioremediation would be successful, no site where “stalling” at cis-1,2-DCE occurred went through the effort of determining if the resident microbial community included those species that could effect complete dechlorination.

- In-situ bioremediation gives rise to patterns of chemical concentrations - both for organic compounds and inorganic compounds. These patterns are important in assessing the effectiveness of the biogradation process at a specific site. Relative increasing or decreasing trends of monitored target compounds, biodegradation intermediates, end products, geochemical parameters, donor electron concentration, etc. are best presented graphically. The units for organic compounds (targeted compounds) are most interpretable when given in units of micromoles/liter, as opposed micrograms/liter.

- For all sites, the specific goals or cleanup objectives for the site were vague or undefined, and monitoring – in terms of well placement based on travel times, degradation rates and compounds to be analyzed – and were not clearly lined to a pre-implementation analysis of expected results. Well defined and quantitative goals or benchmarks are needed to guide the development of an adequate monitoring program and serve to establish the success or failure of a project. Without such specific goals, monitoring programs suffer, project success becomes subjective and comparison of the relative success of projects is problematic or not possible.

6 Recommendations

In-situ bioremediation of chlorinated solvents has been implemented at a number of sites within California. From a review of the five sites included in this report, several trends became so apparent that the following recommendations are made:

- An overall project goal should be established to judge the success or failure for the project. For groundwater contamination plume cleanup, the goal should address the final concentrations or total mass of contaminants remaining in the plume that the remedy expects to achieve and the associated timeframe to achieve these levels. For a barrier wall, the goal should address the final contaminant concentrations to be achieved at a specified distance downgradient of the barrier. The project goal should directly relate to the overall remediation goals established for the site (e.g., approved Remedial Action Plan).

- Objectives for in-situ bioremediation projects should be clearly defined, measurable and linked to the conditions that promote or enhance biodegradation that the system was designed to achieve. Examples of specific objectives for bioremediation would include:
    - reducing the oxidation reduction potential (ORP) to a condition that encourages reductive dechlorination at targeted wells (a measurable objective),
    - assuring distribution of carbons sources, nutrients and micro-organisms throughout a targeted volume as represented by samples from specific monitoring wells (a measurable objective),
    - measuring the increases and decreases over time in targeted compounds, transient intermediate products, final end products and geochemical indicators associated with the biodegradation pathways that are expected to occur at the site.

- Groundwater sampling results should be plotted in a manner that allows comparison with the expected patterns of contaminant decrease and increase (parent compounds and degradation products) for the biodegradation pathway being enhanced. Areal groundwater contaminant concentration contour plots of the target compounds and expected degradation products are most useful for this purpose.

- Groundwater data should be presented for wells and groupings of wells in a manner that illustrates the increase (if any) in biodegradation associated with the project; this typically requires graphical presentations that compare and contrast the measured concentrations and trends observed over time; such results should be compared with predicted and expected (“textbook”) results that represent successful attainment of objectives established for the project. Plotting molar concentrations of target and degradation products versus time is the best means to visualize whether the degradation products are being produced according to the predicted biodegradation pathway stoichiometry.

- In-situ bioremediation projects should include a Contingency Plan in the event the biodegradation process appears to have "stalled" or be incomplete. The plan should address methods to correct deficiencies that become apparent after implementation, including bioaugmentation, modification of redox conditions, enhancing electron donor/carbon source distribution, etc.

- An up-front (pre-implementation) analysis of the in-situ biological treatment system and how it will perform over time and over the volume of the contamination plume is essential for developing an adequate monitoring program and assessing the on-going performance of the system. Various groundwater models have been developed for this purpose which may be applicable or modified for a specific project or application.

- Tracer Study – Due to the complex hydrogeology in California, a tracer study should be incorporated in the design of an ISB system to confirm the system operation and its capability to transport amendments.

- Bioaugmentation – Prior to project implementation, areal groundwater should be evaluated to confirm that the microorganisms present are capable of completely degrading the target compounds to desired environmentally benign end products. If this not the case, the feasibility of a bioaugmentation program should be investigated.

- Data Accessibility – One of the hurdles in reviewing these reports was difficulty in reviewing the data. In most cases, the raw data was available but not in a format easy review concerning plots and calculations. Electronic copies of datasheets used in data analysis (i.e., spreadsheets, graphs, etc.) should be provided along with the hard copy of the report for easy review.

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