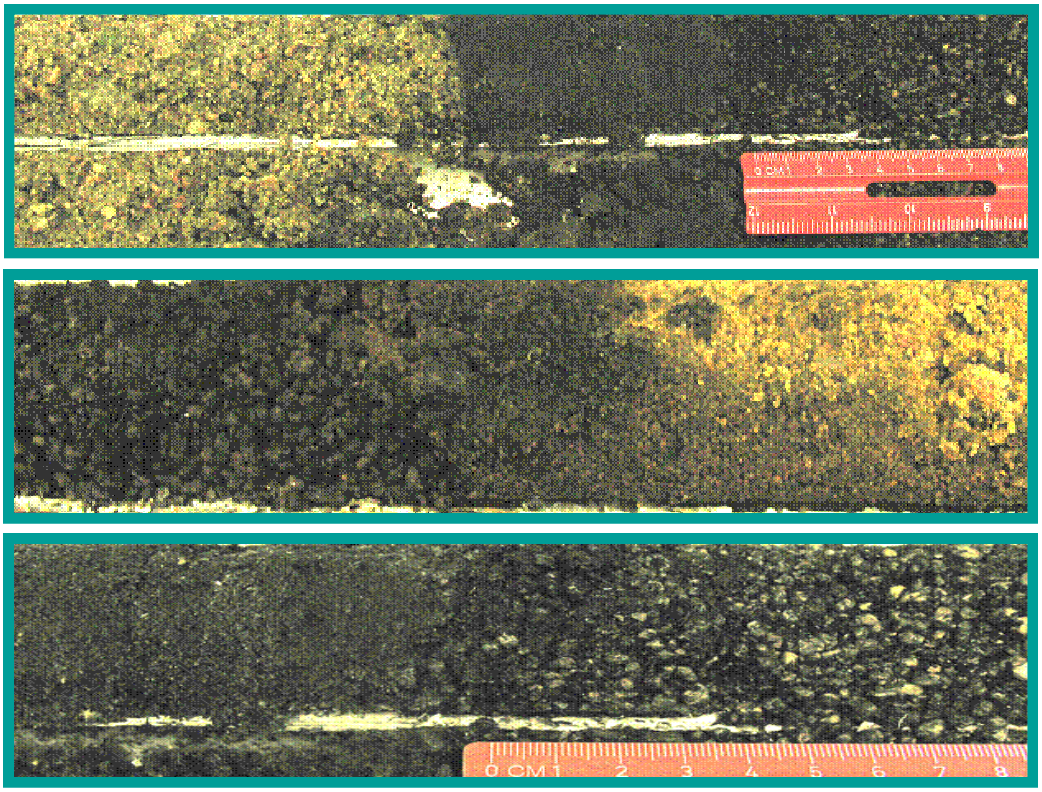
ESTCP
Cost and Performance Report

(ER-0223)



Remediation of TNT and RDX in Groundwater Using Zero-Valent Iron Permeable Reactive Barriers

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ACRONYMS AND ABBREVIATIONS

ADNT	aminodinitrotoluene
AVS	acid-volatile sulfides
bgs	below ground surface
CAAP	Cornhusker Army Ammunition Plant
DoD	Department of Defense
DO	dissolved oxygen
ESTCP	Environmental Security Technology Certification Program
Fe	iron
fgs	from ground surface
FWHM	full width at half maximum
GC/MS	gas chromatograph/mass spectrometry
HCI	hydrochloric acid
HDPE	high-density polyethylene
HMX	cyclotetramethylenetetranitramine
HPLC	high performance liquid chromatography
MCL	maximum contaminant level
MSL	mean sea level
NaOH	sodium hydroxide
NAVFAC-ESC	Naval Facilities Engineering Service Center
O&M	operation and maintenance
OHSU	Oregon Health and Science University
OD	outside diameter
ORP	oxidation reduction potential
P&T	pumping and treatment
PRB	permeable reactive barrier
PTA	Pilot Test Area
PV	present value
PVC	polyvinyl chloride
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine & cyclonite
SERDP	Strategic Environmental Research and Development Program
TAT	2,4,6-triaminotoluene

ACRONYMS AND ABBREVIATIONS (continued)

TCE	trichloroethylene
TNT	2,4,6-trinitrotroluene
U.S. EPA	United States Environmental Protection Agency
UHU	ultra high vacuum
UV	ultraviolet
XPS	x-ray photoelectron spectroscopy
ZVI	zero-valent iron

DISCLAIMER

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The project team also gratefully acknowledges the on-site support provided by Cornhusker Army Ammunition Plant (CAAP) personnel, especially Mary Wellensiek, Edward Richards, Gary Carson, and Alvin Kam.

Technical material contained in this report has been approved for public release.

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1.0 EXECUTIVE SUMMARY

This Cost and Performance Report documents the demonstration of a zero-valent iron (ZVI) permeable reactive barriers (PRB) for the removal of explosives from groundwater. The demonstration was conducted at the Cornhusker Army Ammunition Plant (CAAP) near Grand Island, Nebraska.

Performance of the PRB was evaluated by monitoring groundwater concentrations of explosives downgradient of the PRB. Data obtained during the demonstration were used to demonstrate the cost-effectiveness of this approach for long-term removal of explosives from groundwater.

The primary advantages of ZVI PRB for groundwater remediation are:

- No aboveground remediation equipment required
- Rapid conversion of groundwater to reducing conditions in which explosives are degraded
- Low operation and maintenance costs
- Long-lasting (>20 years) in situ treatment
- Cost-effective.

The cost-effective use of ZVI PRB may be limited by the depth to groundwater and the ability to install the PRB in some geologic media. However, at sites without these physical constraints, the approach can be highly effective.

1.1 DEMONSTRATION DESIGN

The demonstration was conducted at the CAAP near Grand Island, Nebraska. Groundwater at the site is at 15-20 ft below ground surface (bgs). The shallow aquifer at the site consists of medium sands with some silty material. Groundwater velocity at the site is approximately 1 to 2 ft/day.

The demonstration activities included a field study that involved installation of a mixed iron/sand PRB (30% by weight iron). The PRB was approximately 50 ft long by 15 ft deep by 3 ft thick. Monitoring activities were conducted over a 20-month period to evaluate performance of the PRB. The PRB was located within a large groundwater plume from a diffuse source resulting from production of munitions.

1.2 SUMMARY OF RESULTS

The ZVI PRB reduced concentrations of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine & cyclonite (RDX) to below detection limits throughout the duration of the project. In addition to removal of the explosives, significant changes in groundwater chemistry occurred due to the PRB. Dissolved sulfate concentrations decreased substantially as groundwater flowed through the PRB. Detailed groundwater concentration data and measured hydraulic conductivity data suggest that a portion of the water upgradient of the PRB was diverted beneath the PRB. The reason for this is not entirely known, however, we believe that it is not due to the nature of the contaminants being remediated (i.e., explosives) and that it is almost certainly related to the use of guar during installation of the PRB. We believe that guar entered the formation upgradient of the PRB and was not fully removed at the completion of the installation. This may be the primary reason for flow reduction; however, it is also possible that the guar led to strongly reducing conditions just upgradient of the PRB and the removal of sulfate as sulfide precipitates in the natural aquifer materials just upgradient of the PRB, as observed in core samples.

1.3 COMPARISON OF RESULTS WITH PRIMARY OBJECTIVES

All the primary performance criteria for this project were met. TNT and RDX values were consistently reduced to below detection limits in the aquifer downgradient of the PRB. Barrier hydraulics were successfully characterized, and we were able to identify design and operational factors that influence successful implementation and continued operation of the ZVI PRB.

1.4 COST ANALYSIS

A detailed cost comparison is provided in this Cost and Performance Report. The installation costs for the pilot scale barrier were \$138,000. The barrier was 50 ft long by 15 ft thick (i.e., ~750 ft^2), so the cost per sq ft is ~\$180. This is consistent with other demonstration-scale ZVI PRB installations.

The greatest uncertainty in cost relates to the longevity of the PRB. If the PRB had been installed without guar, we believe that a 20-year lifetime could have been expected based on the observed hydraulic conductivity and reactivity of the PRB.

2.0 INTRODUCTION

This Cost and Performance Report documents the demonstration of a ZVI PRB to remove explosives from groundwater. The general purpose of the demonstration was to evaluate the efficacy of ZVI PRB for treating explosives-contaminated groundwater.

2.1 BACKGROUND

Groundwater contamination related to the explosives TNT and RDX represents a significant and widespread problem at Department of Defense (DoD) facilities. Current remediation approaches for TNT- and RDX-impacted groundwater typically involve groundwater extraction and treatment (pump-and-treat) with treatment by carbon adsorption or ultraviolet (UV) oxidation systems, both of which are costly to install and have short life cycles (e.g., 15-year recapitalization periods). Furthermore, because of the chemical characteristics of RDX and in particular the sorptive properties of TNT, many of these pump-and-treat systems are projected to operate for decades, representing significant operation and maintenance (O&M) expenses. As an example, annual O&M costs associated with pump-and-treat remediation of groundwater impacted by TNT, related nitroaromatics, and RDX at the Milan Army Ammunition Plant in Tennessee were estimated to be in the range of $1.4 million per year (U.S. Environmental Protection Agency [U.S. EPA], 1992) and at the CAAP (U.S. EPA, 1994) approximately $1.2 million per year (U.S. Army, 2001).

Recent research has shown that TNT and RDX can be rapidly degraded using ZVI and that the use of in situ PRB has very good potential for reducing the costs associated with groundwater cleanup at TNT- and RDX-impacted sites (Tratnyek et al., 2001; Oh et al. 2001). As an added benefit, PRB can also treat a variety of contaminants (e.g., chlorinated solvents, chromate) that may co-occur in groundwater at RDX- and TNT-impacted sites. The use of ZVI PRB to treat TNT- and RDX-impacted groundwater therefore represents a significant opportunity to reduce environmental remediation costs that may jeopardize major DoD programs and initiatives.

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3.0 TECHNOLOGY DESCRIPTION

ZVI PRB are conceptually simple in situ remediation systems that involve emplacement of iron filings/shavings in a trench or similar structure oriented perpendicular to groundwater flow to form a PRB or "wall." As groundwater flows through the PRB, interactions between the water and the iron produce highly reducing conditions (i.e., a highly negative oxidation reduction potential [ORP]). Contaminants entering this highly reducing zone are chemically altered to have a significantly reduced toxicity or mobility, or are otherwise sequestered. ZVI PRB have been shown to be essentially passive, robust, and long-lived in the environment. These systems have been successfully used for some time for the control of chlorinated solvent plumes such as trichloroethylene (TCE), and are projected to have useful lifetimes of 30 years or more (O'Hannesin et al., 1998).The technologies for the installation of PRB have advanced in recent years, and lower cost installation methods have been demonstrated for a variety of site conditions. The capital equipment costs associated with PRB installation are small when compared to the cost of decades-long pump-and-treat operations. In addition, because groundwater is not removed from the subsurface (unlike pump-and-treat systems), the PRB do not negatively impact groundwater levels or supplies.

Recent laboratory studies funded by the Strategic Environmental Research and Development Program (SERDP) have demonstrated that ZVI can rapidly degrade TNT and RDX. For TNT, Tratnyek et al (2001) showed that essentially all of the degradation products become completely sequestered on the iron, a process that can be sustained for thousands of pore volumes, even at very high flow rates and contaminant loadings. Similar performance is expected in the field, although site-specific geochemical conditions may have some impact on both performance and longevity. While laboratory data indicate that reduction of RDX by iron is rapid, the fate of the degradation products is not as well understood and may not be as effective as for TNT. The RDX research (Oh et al., 2001) does however indicate that the performance of the ZVI is significantly enhanced when iron-reducing bacteria are present, and therefore a combined ZVI-bioremediation approach may be most suitable to treat RDX.

Based on the available laboratory TNT and RDX degradation data, the successful history of ZVI PRB use for chlorinated solvents, and the need for cost-effective remediation technologies to address the remediation of TNT- and RDX-impacted groundwater, we believe ZVI PRB represent a cost-effective approach for remediation of explosives in groundwater.

3.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

ZVI PRB are now an accepted remediation technology for treatment of chlorinated solvents, selected metals (e.g., chromium, arsenic), and a number of other groundwater contaminants. The technologies for PRB installation are reasonably well understood and include conventional methodologies such as sheet pile cofferdam, continuous trenching, overlapping caissons and biopolymer trench technologies (Day and O'Hannesin, 1999). Emplacement using some construction methods is limited to shallow groundwater systems (e.g., less than ~70 ft) in unconsolidated porous media. New construction methods such as soil mixing or slurry injection are currently being demonstrated for deeper systems. Site selection for the field demonstration favored sites that allow straightforward installation minimizes risks associated with the PRB design and installation process.

The main technical risks associated with this project relate to the potential influence of site-specific geochemical conditions on 1) RDX and TNT reactivity in the PRB, 2) completeness of removal of the primary contaminants and degradation products, and 3) long-term PRB performance. Several recent SERDP projects evaluated the fate of TNT and RDX degradation with ZVI in laboratory and ex situ columns under different geochemical conditions (ER-1231 and ER-1232). The site-specific, pre-design optimization studies discussed below (including ex situ ZVI columns and detailed geochemical analyses) also address this uncertainty.

3.2 THEORY OF OPERATION AND LIMITATIONS

ZVI PRB create strongly reducing conditions in water-saturated media. Those conditions lead to the abiotic reduction of a broad range of contaminants. In this case, explosives (e.g., TNT, RDX) are reduced to the corresponding amino compounds within the PRB. In the case of TNT, the triaminotoluene produced is rapidly removed from groundwater by a variety of mechanisms.

3.3 TECHNOLOGY SPECIFICATIONS

The technology performance specifications for the PRB technology usually involve the following (ESTCP, 1999):

- Treating the contaminants in the captured groundwater to below their respective maximum contaminant levels (MCL), drinking water standards, or to a risk-based alternative level
- Ensuring that the interaction between the barrier materials and the groundwater constituents does not cause environmentally deleterious materials to be released in the downgradient aquifer
- Achieving the desired hydraulic capture efficiency
- Ensuring that the barrier retains its reactivity and hydraulic capture efficiency in the long term
- Ensuring that the barrier represents a cost-effective option for the treatment of the targeted contamination at the site.

PRB are a passive technology and, as a result, once the barrier is installed, operator involvement is limited to the relatively infrequent monitoring required to ensure that the barrier is performing as designed.

3.4 FACTORS AFFECTING COST AND PERFORMANCE

A number of factors affect the cost and performance of the technology in field applications. The key factors are:

- The concentration and distribution of explosives in the groundwater to be treated will impact the costs and performance. Higher concentrations of explosives may require longer residence times in the PRB. This is not expected to be a major issue at most sites.

- The chemistry of the aquifer to be treated will impact the cost and performance. The primary issues of concern will be the presence of dissolved oxygen (DO), carbonate, nitrate, sulfate, or other species that may passivate the surface of the iron or plug the PRB.
- The depth to groundwater will impact the cost of barrier installation.
- The hydraulic conductivity of the aquifer will impact the design of the PRB (e.g., barrier thickness, iron content).
- The hydraulic gradient in the aquifer will impact the design of the PRB (e.g., barrier thickness, iron content).
- Geological heterogeneities in the aquifer.
- Seasonal variation in groundwater flow direction will impact the design of the PRB, primarily by requiring increased barrier length to ensure capture of the plume.

3.5 KEY DESIGN STEPS

Figure 1 shows the steps in the design of a PRB. These steps involve the determination of the following (ESTCP, 1999):

- Site characteristics affecting barrier design
- Reaction rates or half-lives
- Location, configuration, and dimensions of the barrier
- Emplacement options
- Cost.

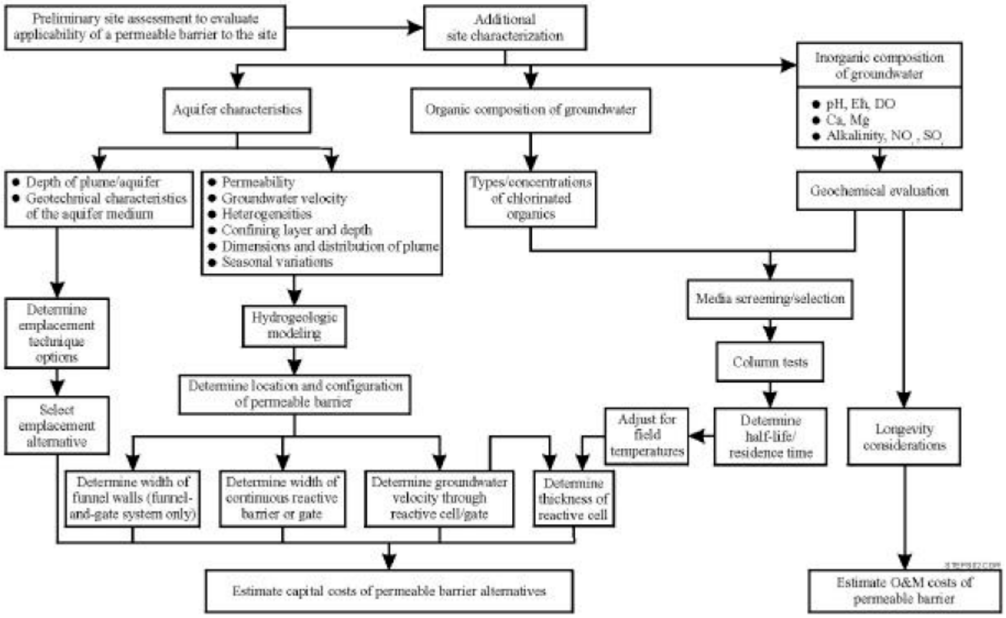

Figure 1. Steps in the Design of a PRB (ESTCP, 1999).

In the context of explosives degradation, reaction rates with ZVI are sufficiently fast that it will probably not be a major design criterion (i.e., other factors, including installation method, will probably control the width and iron content of the PRB). The width of the PRB will depend on the dimensions of the contaminant plume, as well as seasonal variations in groundwater flow direction. The depth of the barrier is determined by the depth of the contaminant plume and/or the underlying aquitard (i.e., in most cases, the barrier may be keyed into the aquitard).

3.6 MOBILIZATION, CONSTRUCTION, AND OPERATION

The procedures for installation of ZVI PRB in continuous trenches are by now relatively routine. In the context of this demonstration plan, the relatively small scope of the project necessitated using conventional excavation techniques (rather than, for example, equipment specifically designed for continuous trenching, which has high mobilization costs). For full-scale installations, it should be possible to choose the optimum approach for PRB installation.

Since ZVI PRB are passive, there are no day-to-day operational issues involving the technology. However, demonstration of longer-term performance is an important component of any PRB installation, and planning for that demonstration is important. It should, at a minimum, include a monitoring network that not only demonstrates PRB performance but can also provide indicators of PRB failure. This issue is discussed below in the context of performance at the CAAP site.

3.7 ADVANTAGES AND LIMITATIONS

Prominent alternative technologies to in situ ZVI PRB for explosives-impacted groundwater are 1) groundwater pump-and-treat followed by ex situ degradation and 2) groundwater pump-and-treat followed by adsorption on carbon.

Current approaches for the remediation of explosives-impacted groundwater typically involve long-term pump-and-treat solutions involving capital-intensive ex situ treatment components (ex situ bioreactors or ion exchange systems) and long-term O&M costs. As an example, annual O&M costs associated with pump-and-treat remediation of groundwater impacted by TNT, related nitroaromatics, and RDX at the Milan Army Ammunition Plant in Tennessee were estimated to be in the range of $1.4 million per year (U.S. EPA, 1992) and at the CAAP (U.S. EPA, 1994) approximately $1.2 million per year. At many sites, the initial capital costs for a PRB are expected to be similar to those for pump-and-treat with carbon sorption. However, the O&M costs for the PRB are expected to be far lower.

The main advantages of the remediation technology are:

- Lower capital and O&M costs than alternative technologies that involve groundwater pump-and-treat with high O&M costs
- Contaminants are destroyed, not simply transferred to another medium
- Ability to treat possible co-contaminants such as nitrate, TCE, or chromium.

The main limitations of the technology are:

- Insufficient longevity of the PRB due to loss of reactivity and/or hydraulic performance
- Installation depth limitation
- Initial capital costs.

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4.0 DEMONSTRATION DESIGN

This section describes the strategy and planning leading to the construction of the pilot barrier at CAAP and the subsequent performance evaluation.

4.1 DEMONSTRATION SITE BACKGROUND

CAAP is located near Grand Island, Nebraska. Information on the test site history and characteristics is presented in the June 1998 Annual Sampling Event for the Long-Term Monitoring Program (Woodward-Clyde, 1999). The following sections of this Demonstration Plan present a summary of this information, with significant sections of text taken directly from that report.

4.2 PHYSICAL SETUP AND OPERATION

Table 1 shows the schedule of events leading to the completion of the demonstration. The PRB was constructed at CAAP in November 2003. Preliminary monitoring of groundwater conditions in and around the PRB was conducted in December 2003, about 4 weeks after installation. The results of this preliminary monitoring event showed that groundwater was flowing through the PRB and that the explosives were being removed to below detection limits. Groundwater at the site was then sampled at 2.5, 4, 6, 12, 17, and 20 months following installation.

During the course of the project the following activities were examined:

- Changes in groundwater chemistry downgradient of the PRB
- Long-term performance of the PRB
- Groundwater flow through the PRB using tracer tests
- Characterization of hydraulic conductivity using slug tests
- Collection and analysis of core samples
- Microbiological characterization upgradient and downgradient of the PRB.

Table 1. Site Activities.

Activity	Date Completed
Site characterization	September 2003
Laboratory tests	October 2003
Performance monitoring plan	August 2003
PRB installation	November 2003
Sampling event #1	December 2003
Sampling event #2	February 2004
Sampling event #3	March 2004
Sampling event #4	August 2004
Sampling event #5	November 2004
Sampling event #6	April 2005
Sampling event #7	July 2005

Table 1. Site Activities (continued).

Activity	Date Completed
Flow tracer test	December 2004
Hydraulic conductivity tests	October 2005
Core sampling	July 2005
Microbiological sampling	July 2005

Table 2 shows participants involved in the project and their respective roles.

Table 2. Project Participants.

Project Participant	Activity
Oregon Health and Science University (OHSU)	Site characterization Monitoring network installation
GeoSyntec	PRB engineering design PRB installation management
Rice University	Microbial characterization
Pacific Northwest National Lab	XPS* analysis of soil cores
Subcontract Laboratory (Columbia Analytical Labs)	Total sulfur analyses of cores Anion and cation analyses

*XPS = X-ray photoelectron spectroscopy

4.3 DEMONSTRATION SITE CHARACTERISTICS

4.3.1 Test Site History

CAAP is located in central Nebraska near Grand Island and occupies nearly 12,000 acres, as shown in Figure 2. Figure 3 shows a map of the Load Line 2 area at CAAP. The locations of the former ponds used for the demonstration are shown on the map.

CAAP was constructed and became fully operational in 1942 as a U.S. government-owned, contractor-operated facility. CAAP was responsible for the production of artillery shells, mines, bombs, and rockets for World War II and the Korean and Vietnam conflicts. The plant was operated intermittently for 30 years with the most recent operations ending in 1973. From 1942-1945, various bombs, shells, boosters and supplementary charges were produced at CAAP using primarily TNT. From 1950-1955, artillery shells and rockets were produced using a mixture of TNT, cyclonite (RDX), and cyclotetramethylenetetranitramine (HMX).

CAAP was activated again from 1965-1973 to produce bombs, projectiles, and gravel mini-mines. Explosive wastes and residues associated with munitions loading, assembly, and packing operations have resulted in a groundwater contamination plume that originates at waste leach pits and cesspools of the CAAP load lines and extends east-northeastward into the city of Grand Island, Nebraska.

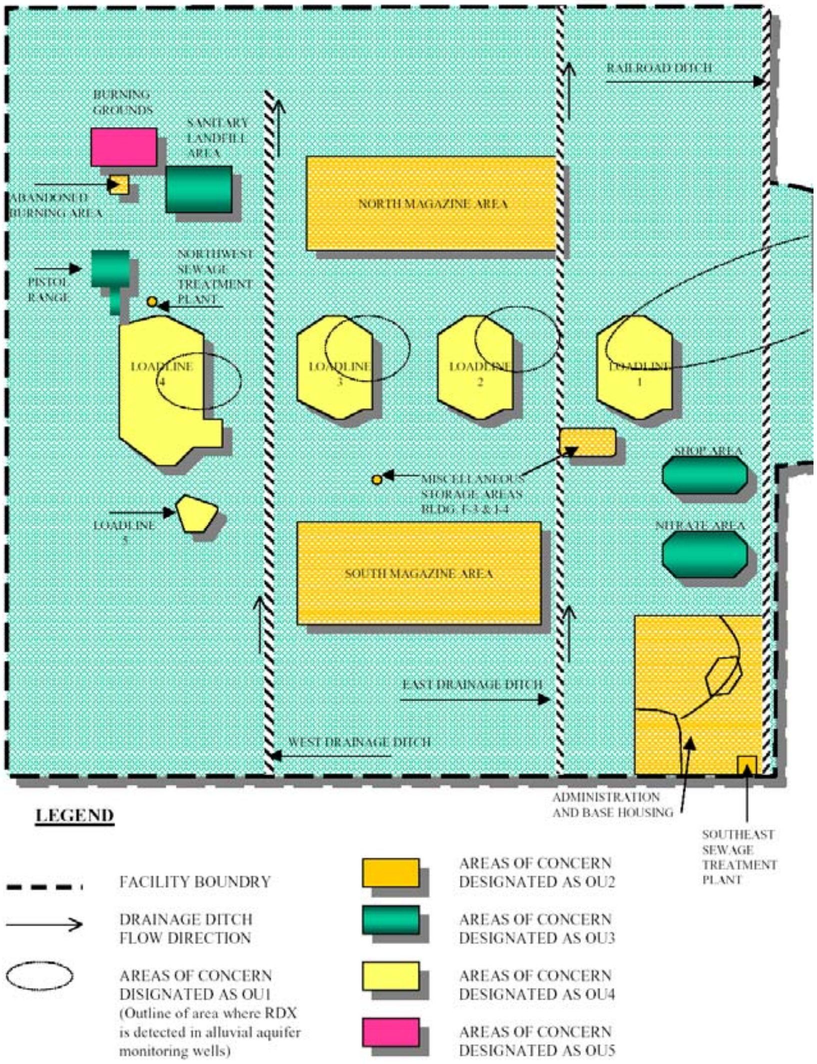

Figure 2. Map of Cornhusker Army Ammunition Plant.

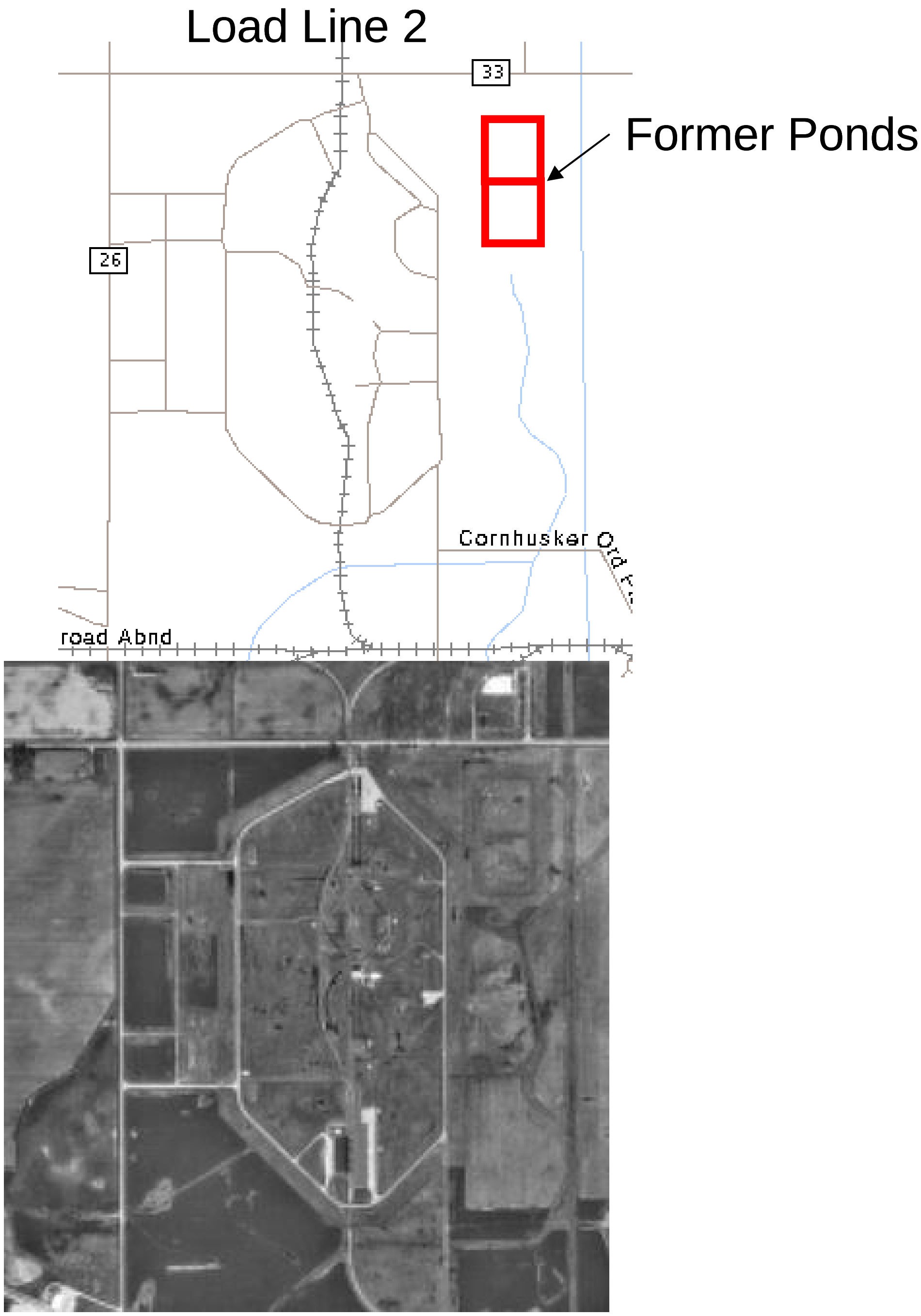

Figure 3. Map of Load Line 2, CAAP.

4.3.2 Environmental Setting, Geology, and Hydrology

The general geologic description summarized here was interpreted from soil boring logs completed during the installation of on- and off-post monitoring wells (WJE, 1993), as well as regional data from the Soil Survey for Hall County (USDA, 1962). In general, the geologic units underlying the CAAP study area are shown in Figure 4 and include (in descending order from the surface) the following:

- Alluvial silty clay and topsoil near the surface (from about 0 to 5 ft in depth)
- Alluvial sands and gravels of the Grand Island Formation (about 50 to 60 ft in thickness)
- A low-permeability, alluvial silty clay unit of the Fullerton Formation (about 5 to 15 ft in thickness), also referred to as the blue clay unit in previous reports (WJE, 1993)
- Alluvial sands and gravels of the Holdrege Formation (reported to be up to 200 ft in thickness).

These geologic units are laterally extensive across the CAAP facility and the northwestern part of the city of Grand Island. The deepest monitoring well borings (off post) extend 10 to 20 ft below the Fullerton clay unit into the Holdrege Formation.

Shallow groundwater underlying the facility occurs as an unconfined water table aquifer within the alluvial sands and gravels of the Grand Island Formation. The water table surface is generally less than 10 ft below the ground surface. Total thickness of the water table aquifer ranges from about 50 to 60 ft within the study area. Hydraulic conductivity values range up to 670 ft per day. The predominant groundwater flow direction within the water table aquifer near the CAAP facility is to the northeast towards the city of Grand Island. Regional horizontal gradients of about 0.001 have been measured in the area.

The Grand Island Formation aquifer is used regionally as a water supply source for irrigation and potable water. Locally, there are a number of irrigation wells in use east of the facility; however, all private domestic water is being supplied by the City of Grand Island. The city’s municipal well field is located southeast of the city near the Platte River (about 10 miles southeast of CAAP).

The underlying Fullerton clay is a relatively low-permeability unit that appears to act as a barrier to groundwater flow (i.e., aquitard) in the CAAP study area. Justification for this interpretation includes:

- The presence of head differences across the Fullerton clay unit as measured between the Grand Island Formation aquifer and the underlying Holdrege Formation aquifer
- The absence of contamination below the Fullerton clay unit at locations where contamination is present at the base of the Grand Island Formation aquifer.

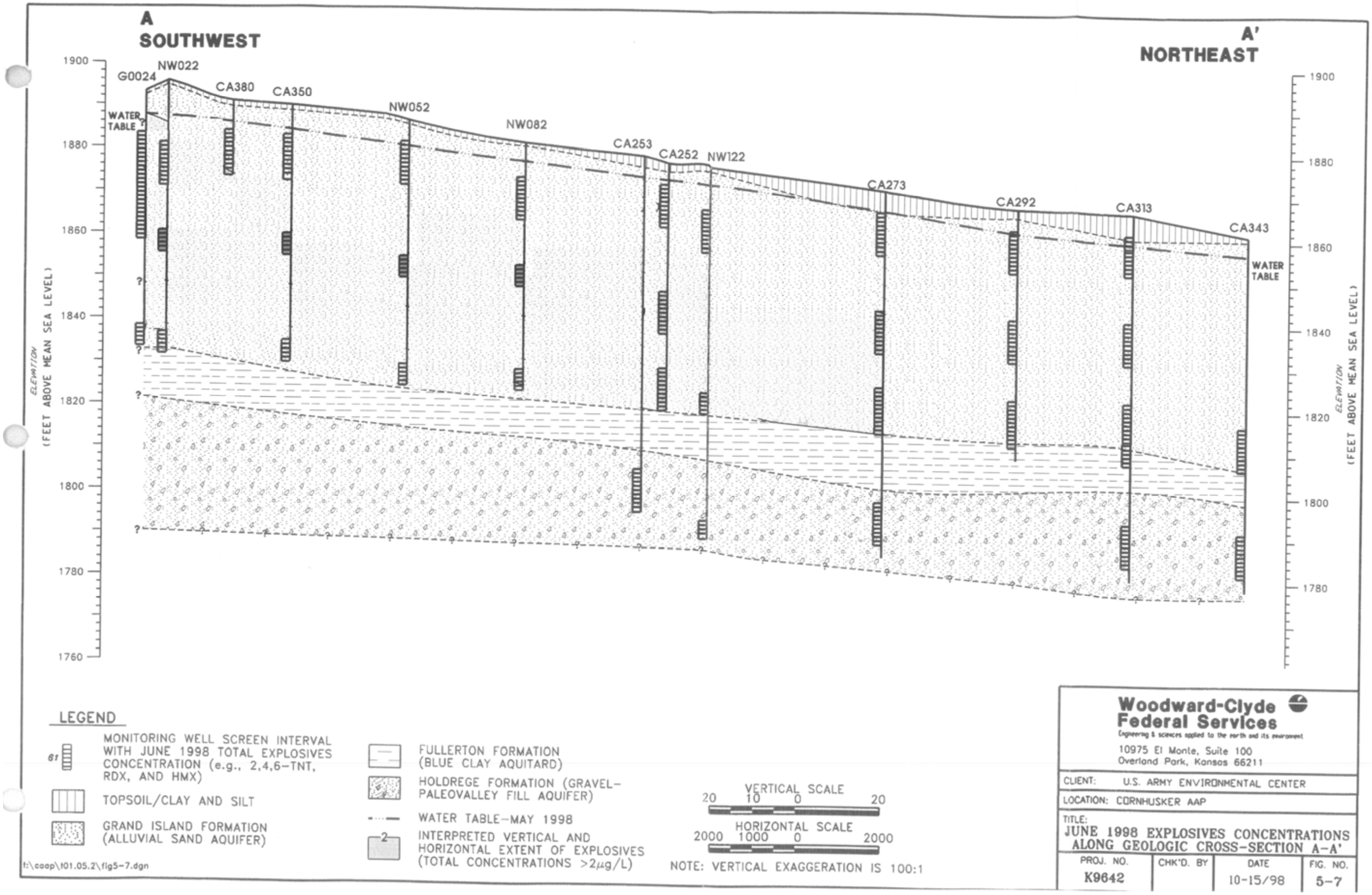

Figure 4. Geologic Cross Section.

The sands and gravels of the Holdrege Formation act as a confined aquifer unit (confined by the overlying Fullerton clay unit) in the CAAP study area. Based on water level data from the deep monitoring wells, the general groundwater flow direction in the Holdrege Formation appears to have a northeasterly component (similar to the overlying Grand Island Formation aquifer).

4.3.3 Contaminant Distribution Within the Pilot Test Area

The off-post explosives plume originates on the northeast edge of the CAAP facility (near Load Line 1) and extends more than 21,000 ft northeast into the surrounding rural and urban areas.

The axis of the off-post explosives plume trends from southwest to northeast (Figure 5). The highest explosives concentrations were located near the facility boundary. Explosives concentrations declined to the northeast. The plume was detected at depths of 6 to 57 ft bgs and approximately 5 to 33 ft below the water table. There appears to be a clean zone near the water table in the distal edges of the plume. Explosives were not detected in the deep aquifer (Holdrege Formation). The Fullerton Formation appears to act as a natural barrier, retarding the vertical migration of explosives to the underlying Holdrege Formation (gravel-paleovalley fill aquifer).

4.4 PERFORMANCE EVALUATION OBJECTIVES AND THE ASSOCIATED MONITORING STRATEGY

The performance objectives for the project are listed in Table 3. To accomplish these objectives, a network of groundwater sampling points was installed around the PRB and was sampled periodically over a 20-month period.

Table 3. Performance Objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance
Qualitative	1) "Simple to operate"	Minimal effort to operate (i.e., passive operation after installation)	Performance objective met
	2) Reduction in co-contaminants (RDX, TNT) downgradient of treatment zone	Reduce concentration of contaminants (RDX,TNT)	Performance objective met
Quantitative	1) Reduce TNT and RDX concentration downgradient of treatment zone	> 90% reduction in concentration (or less than 1 µg/L)	Performance objective met

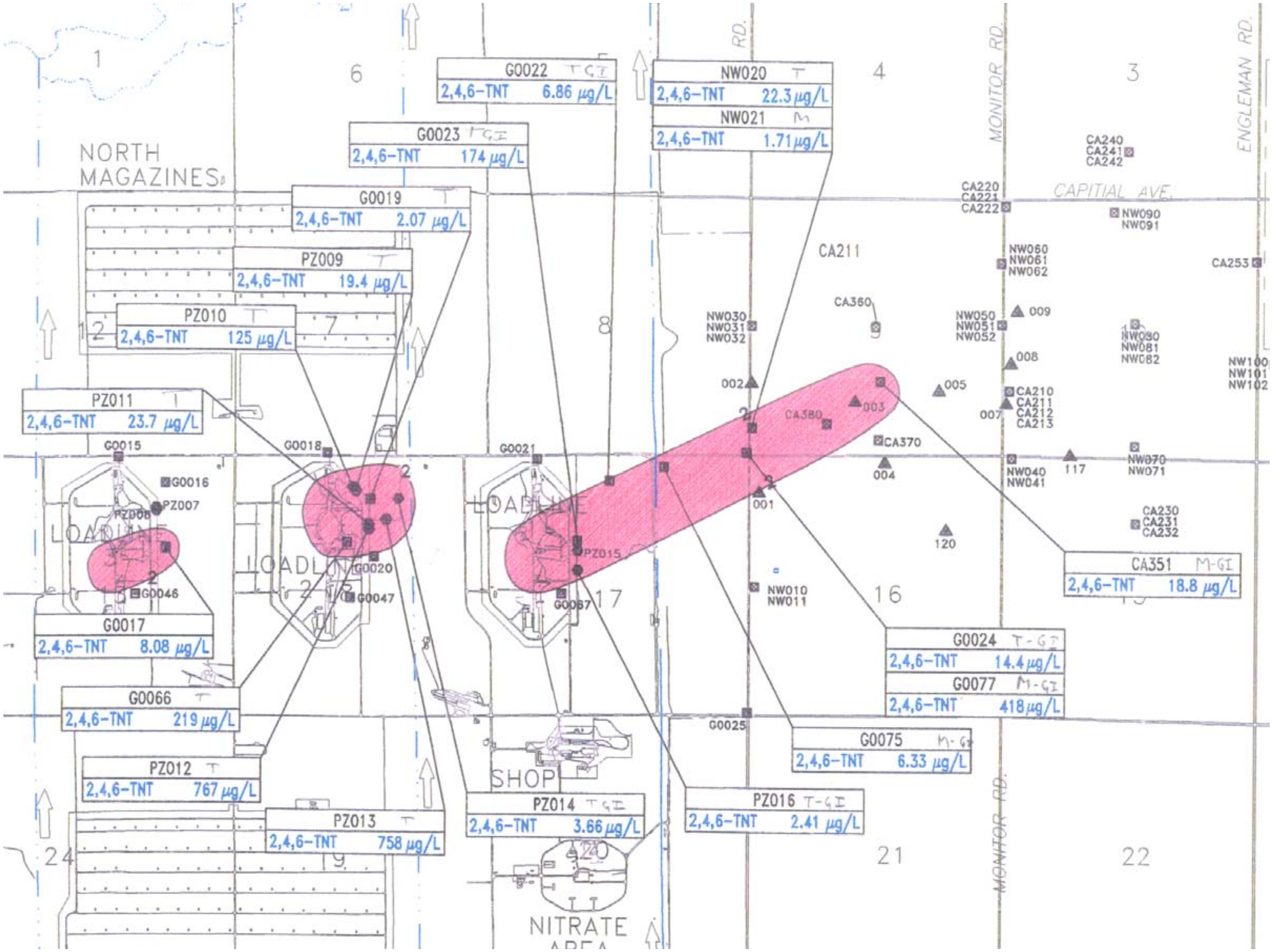

Figure 5. Site Plan View Showing the TNT Plumes from Load Lines 1, 2, and 3 at CAAP.

4.5 SAMPLING AND ANALYSIS PROCEDURES

The performance monitoring plan was designed such that sampling activities would accomplish the study's objectives. The following sections summarize the sampling and analysis activities.

4.5.1 Monitoring Frequency

In order to characterize changes following installation of the PRB and maximize the duration of the demonstration, we adopted a progressive scale in which the interval between sampling events increased over time. Seven synoptic sampling events were conducted in which the analytes listed in Table 4 were measured. Analyses were usually performed within 1 week of sample collection so that the various kinds of measurements could be gathered within a short period of time.

Table 4. Analytical Parameters.

Parameter	Sample Collection Volume	Field Preservation	Analysis Location	Sample Holding Time
TNT/RDX	1 L	Sep-Pak	OHSU	2 weeks
Anions	40 mL	none	OHSU	2 weeks
Cations	40 mL	none	OHSU	2 weeks
Dissolved oxygen	In line meter	none	Field	none
Field parameters (pH, temp, conductance, Eh)	In line meter	none	Field	none
Ferrous iron	10 mL	none	Field	none
Alkalinity	25 mL	none	field	none

4.5.2 Groundwater Sampling Procedures

The design of the multilevel samplers used at CAAP resulted in little, if any, impact on groundwater flow. Each sampling interval consisted of a direct-pushed 1-inch polyvinyl chloride (PVC) well screen that was 0.6 m in length. The screened interval was connected to the surface by 1/4-inch outside diameter (OD) high-density polyethylene (HDPE) tubing. As a result, the total volume of the "well" was approximately 300 mL and only about 1,500 mL of groundwater needed to be purged prior to sampling. Because the water table was only ~5 m bgs, a peristaltic pump could be used for sampling. Each sampling location had a dedicated section of Viton pump tubing, and the sampling rate was sufficiently slow to prevent bubble formation. Water quality parameters (DO, Eh, Ph, specific conductance) were measured in a flow-through cell immediately after the pump. Groundwater samples were collected into containers immediately following the pump.

4.5.3 Groundwater Chemical Analysis

Groundwater samples were collected and analyzed to determine explosives concentrations and the general characteristics of the groundwater. Analyses included:

- Field parameters (DO, ORP, pH, conductivity, alkalinity, and temperature)
- TNT, RDX
- Selected anions (nitrate and sulfate)
- Cations (sodium, potassium, magnesium, calcium).

Samples were collected by OHSU personnel following standard sampling protocols. Field parameters were analyzed on site. TNT and RDX samples were extracted on site using Waters "Sep-Paks" and were analyzed at OHSU. Anions and cations were analyzed at OHSU and Columbia Analytical Laboratory, Inc. by ion chromatography and wet chemical methods. Table 4 summarizes the parameters that were analyzed as part of the pre-demonstration characterization and provides details of analytical methods, container size and type, preservation method, and sample holding times.

4.5.4 Soil Core Collection

Soil (core) sampling activities were conducted on three occasions in 2005. The objective was to collect angled cores through the PRB in order to assess long-term performance. At the time of PRB installation, a number of 2-inch PVC "guide pipes" were installed at an angle towards the PRB from the upgradient direction. A Geoprobe "macrocore" was used to collect these samples. Unfortunately, because the PRB material was less cohesive than the native materials, the native materials in the core barrel prior to its arrival at the PRB prevented the PRB material from entering the core barrel. As a result, a second approach was used in which a 1-inch capped steel pipe was driven at an angle into the PRB from the surface and liquid nitrogen was used to freeze aquifer and PRB materials onto the pipe. Once again, sample collection was ineffective because retrieval of the pipe through the aquifer stripped off all the frozen material. In a third and final attempt to collect cores through the PRB, we moved to the downgradient side of the PRB and collected cores sampling upgradient. Prior to sampling, we used an excavator to remove overlying soils. We then used continuous aluminum tubes to pass all the way through the PRB and into the upgradient aquifer materials. A combination of vibration and gentle pushing was used in an attempt to facilitate collection of the PRB material. This approach was largely successful in that we were consistently able to recover samples from the interface between the upgradient aquifer materials and the PRB (although the recovery efficiency of the PRB as a whole was low).

4.5.5 Microbiological Sample Collection

Samples for molecular tools analyses (e.g., genomics) were collected in July 2005. Samples were collected into 800-mL stainless steel canisters, which were packed in dry ice and shipped overnight to Rice University.

5.0 PERFORMANCE ASSESSMENT

5.1 PERFORMANCE CRITERIA

Performance of the demonstration has been evaluated using the general performance criteria provided in Table 5. Qualitative and quantitative criteria are classed as either primary or secondary performance assessment criteria, respectively.

Table 5. Project Performance Criteria.

	Performance Criteria	Performance Metric	Confirmation Method	Location	Sample Matrix	Measurement
Primary	Qualitative					
	Extent of degradation	Decreased TNT and RDX concentrations downgradient of the PRB	TNT/RDX concentration	PTA[1]	Groundwater	TNT/RDX
	Quantitative					
	Mass flux from PRB	Decreased mass flux of TNT and RDX coming from the PRB	TNT/RDX concentration	PTA	Groundwater	TNT/RDX
Secondary	Qualitative					
	Barrier hydraulics	Tracer test	Bromide analyses	PTA	Groundwater	Anion analysis, bromide specific ion electrode
	Barrier hydraulics	Small water level changes will occur if barrier hydraulics change	Water level measurements	PTA	Groundwater	Water level tape
	Changes in microbial population	Microbial ecology will change due to the presence of the ZVI PRB	Various microbiological measurements	PTA	Groundwater, soil, ZVI	Various microbiological measurements
	Changes in downgradient groundwater geochemistry	ZVI PRB chemistry will change downgradient water chemistry	Field water parameters (DO, Eh, pH)	PTA	Groundwater	

The primary criteria constitute the performance objectives of the technology demonstration. As stated in Section 1.2, the general objective of the demonstration is to evaluate the performance of the ZVI PRB to degrade explosives in groundwater. In general, the performance criteria are used to evaluate this objective by:

- Determining the ability of the ZVI PRB to degrade explosives over the period of demonstration (20 months in this case)

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[1] Pilot Test Area

- Determining the role played by microbiological populations associated with the ZVI PRB
- Quantifying the effect of the technology on TNT and RDX degradation in groundwater
- Evaluating the difficulty in implementing this technology at the field scale.

5.2 PERFORMANCE CONFIRMATION METHODS

The success of the technology demonstration has been evaluated using the performance expectations and confirmation methods presented in Table 5. Successful implementation of the technology demonstrated that the technology results in significant reduction in TNT and RDX concentrations over the duration of the demonstration.

Performance monitoring and assessment were conducted for approximately 20 months. Groundwater samples were collected from the various monitoring wells for analysis of the parameters listed in Table 4.

The data obtained from the pilot test were used to estimate the rate and extent of degradation of TNT and RDX. Factors affecting remediation performance were identified and optimized through the pilot test.

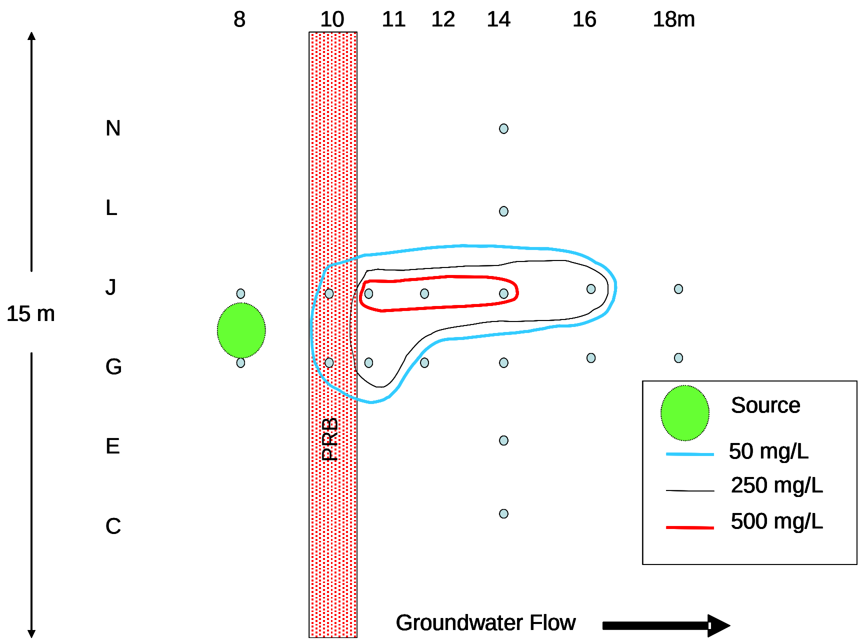
5.3 GROUNDWATER FLOW DATA

5.3.1 Flow Tracer Test

Beginning in August 2004 (i.e., 9 months after installation), a bromide tracer test was conducted to evaluate flow through the PRB. A total of approximately 1,000 L of groundwater containing 1,000 mg/L bromide was injected at a location directly between multilevel samplers G8 and J8 (Figure 6). Approximately-equal volumes of tracer were injected over three 1.5-m intervals from -5.4 to -9.9-m from ground surface (fgs) (i.e., 333 L/interval). Groundwater samples were collected periodically from the multilevel monitoring wells over a 4-month period.

Figure 6 shows the maximum bromide tracer concentrations observed at each plan-view location 44 days after the start of the bromide tracer test. The green circle represents the approximate initial aerial extent of the injected bromide source. The data confirm the general flow direction and velocity of groundwater at the site, although the average velocity of the bromide plume appears somewhat slower than the overall groundwater velocity for the site (0.1 versus 0.2 m/d) Time series bromide data from Row J (Figure 7) indicate a generally well-behaved tracer plume. Two interesting aspects of that are: 1) No tracer was observed at 6.3 m (not shown in Figure 7), even though the tracer was injected over the entire 5.4- to 9.9-m fgs depth interval. 2) For the 8.7-m fgs sampling depth, significant concentrations of tracer appear at the furthest downgradient sampling location (16, -8.7) before they appear at the two locations just upgradient (12, -8.7) and (14, -8.7). This suggests that flow may have been deflecting upwards at that point. However, to confirm that this is the case, it must be demonstrated that the K distribution within the aquifer does not contribute to the observed patterns of the geochemical data. As discussed

a) Plan View



b) Section View

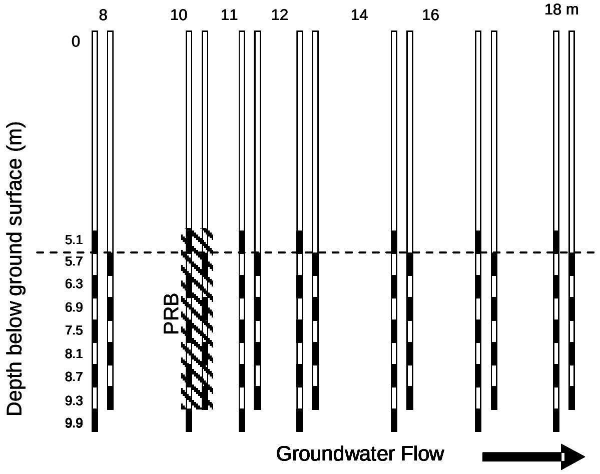


Figure 6. Site Plan View Showing Maximum Bromide Tracer Concentrations Observed at Each Plan-View Location 44 Days After the Start of the Bromide Tracer Test (a) and Cross-Section View Showing the Depths of the Multilevel Samplers (b).

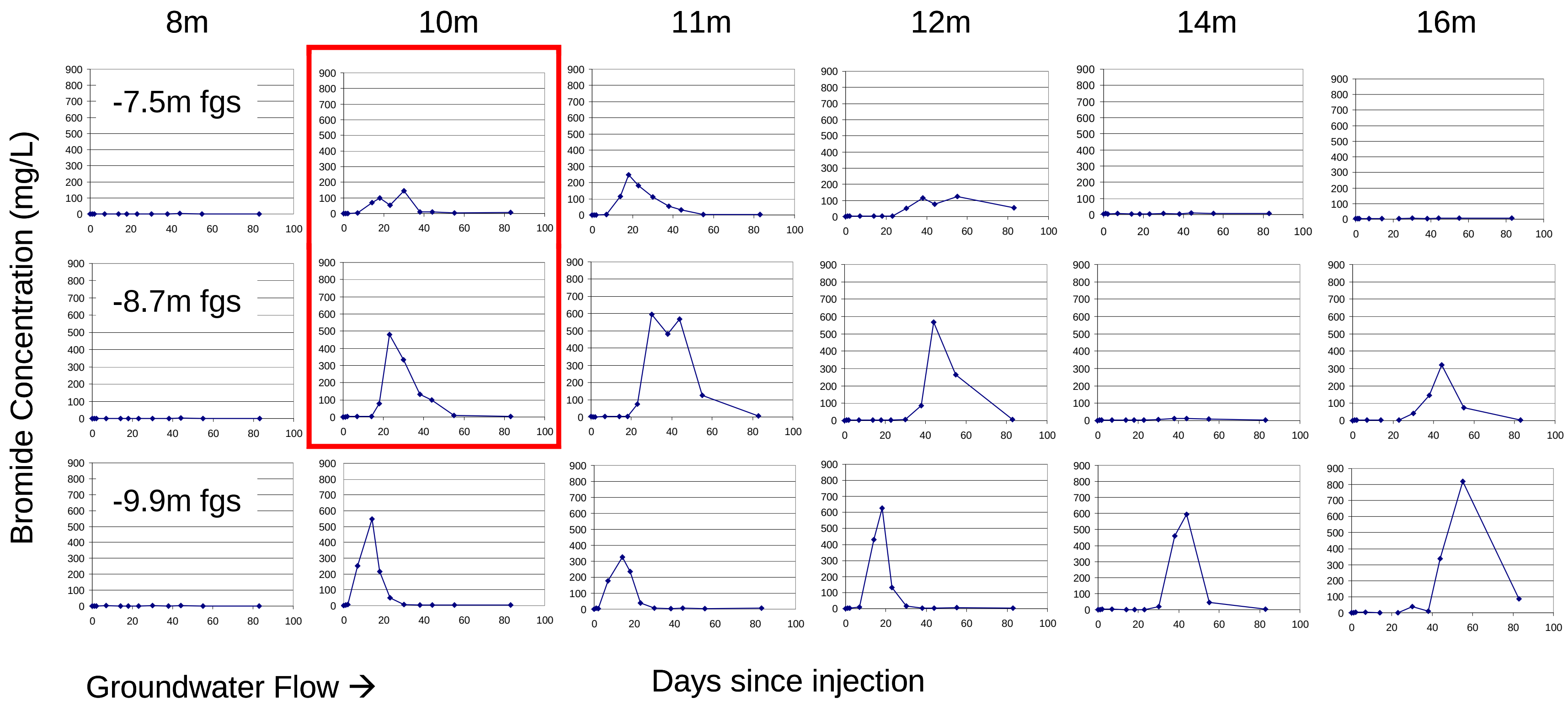


Figure 7. Time-Series Concentration Data for Bromide (mg/L) in the "J-Series" Wells. (The -6.3 fgs wells did not show any bromide concentrations at any point during the test.)

above, to accomplish this a transect of mini-slug tests were conducted between sampling rows G and J (Figure 6). Data from the slug tests are discussed in Section 5.3.2.2 and indicate that the aquifer consists of spatially-extensive strata of modest heterogeneity.

5.3.2 Groundwater Flow Direction and Velocity

Groundwater flow direction and velocity were determined seasonally using a combination of hydraulic gradient data (i.e., water table elevations measured in wells) and hydraulic conductivity data determined either by laboratory permeameter tests or in situ slug tests.

5.3.2.1 Hydraulic Gradient Data

Four wells were used to determine hydraulic gradient throughout the project. Figure 8 shows their location relative to the PRB.

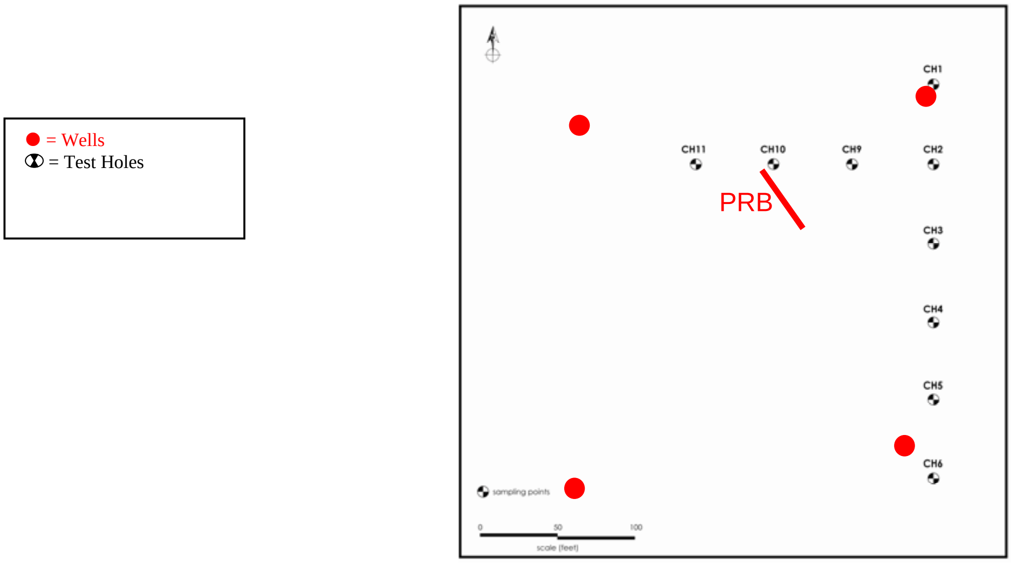


Figure 8. Site Plan View Showing the PRB (50 ft long for scale), Pre-Installation Monitoring Locations, and Locations of the Water Table Wells Used for Hydraulic Gradient Determination.

Depth to water table measurements were taken during synoptic sampling events, and water table contours for those events are shown in Figure 9. The data indicate that water generally flows to the northeast through the PRB. This is consistent with the shapes of the large groundwater contamination plumes coming from the site (e.g., Figure 4). The hydraulic gradient ranges from 0.0007 to 0.002, with a typical value of 0.001. The data suggest that hydraulic gradients tend to by higher in the spring and early summer (April-July) and lowest in the fall.

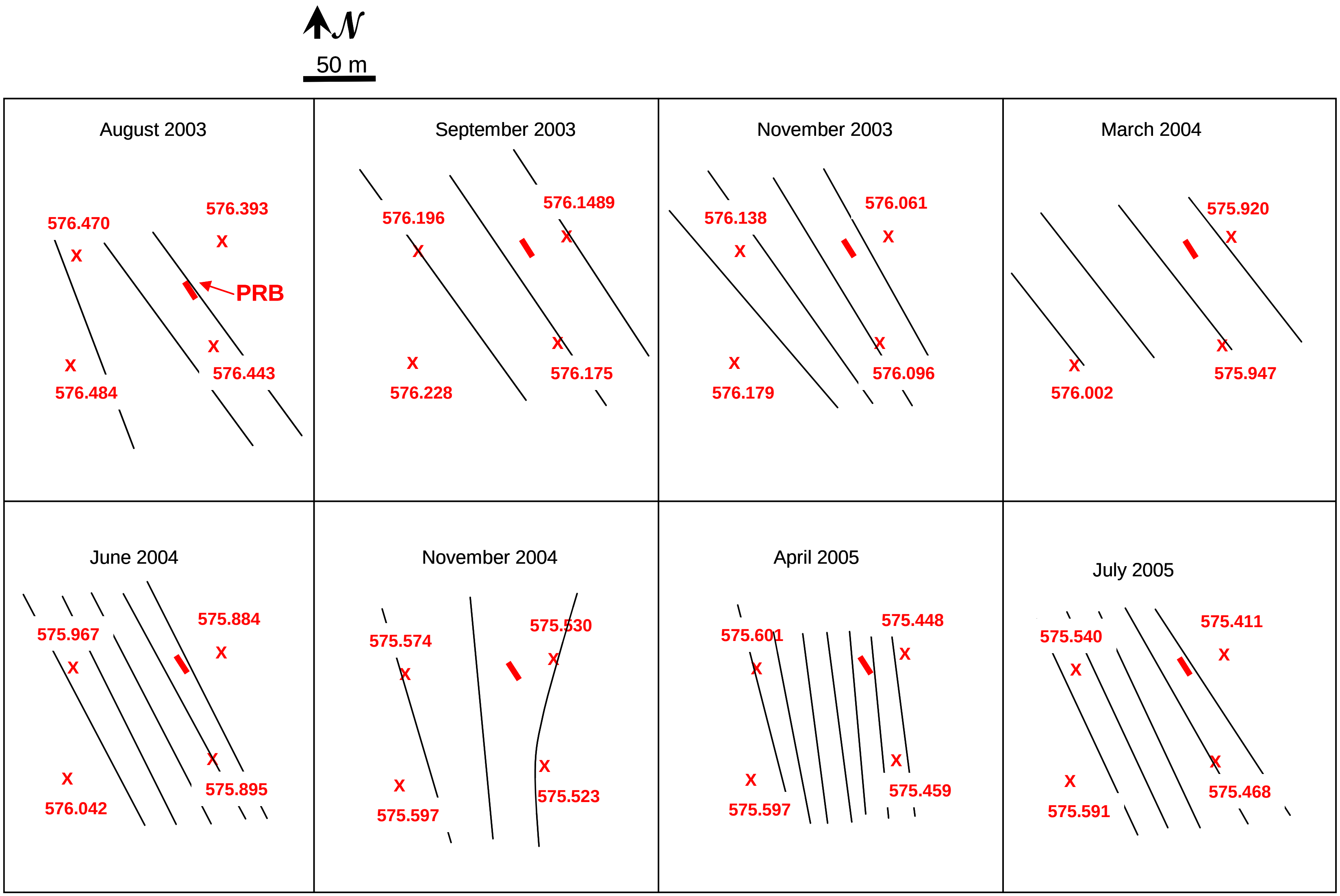


Figure 9. Water Table Contour Data (meters above mean sea level [MSL]; all contour intervals are 0.025 meters).

Data in Figure 10 show that over the course of the project the water table dropped about 1 m.

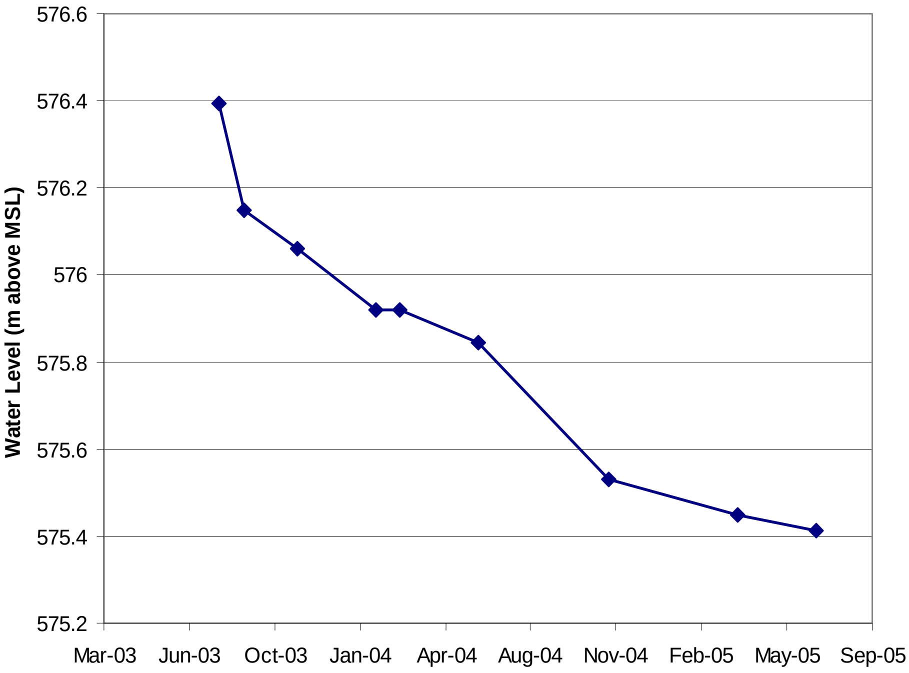


Figure 10. Water Table Elevation Data for Water Table Well CHWT1 as a Function of Time.

5.3.2.2 Hydraulic Conductivity Data

Prior to installation of the PRB, core samples collected at some of the test holes shown in Figure 8 (CH10, CH2, and CH4) were analyzed by laboratory permeameter. One-ft sections of the core were subsampled, dried, mixed, and packed into a falling-head permeameter cell. Data from these analyses are shown in Figure 11. For the depth of interest, hydraulic conductivities were generally in the 0.012 cm/s range, with a lower permeability layer present in the vicinity of 8 m bgs (K=0.0001 to 0.0005 cm/s).

To facilitate numerical modeling of geochemical and tracer flow patterns, a series of depth-specific slug tests was conducted using a 2.5-cm diameter by 30-cm long screened interval in a manner similar to Butler et al. (2002). The screened interval was placed at successive depths using direct-push equipment and a pressure transducer (Druck Incorporated, New Fairfield, Connecticut) was lowered to the screen. A partial vacuum was then applied to the drill rod, and water was drawn in through the screen to raise the water level in the rod by ~1 m. The pressure reading of the transducer was allowed to stabilize under those conditions before releasing the vacuum and tracking the decrease in water level measured by the transducer. Three tests were conducted at each 1-ft interval between 6 and 12 m fgs (Figure 12). The tests were conducted in a transect parallel to and between sampling rows G and J. The longitudinal spacing between the sets of vertical measurements was 1 m. Slug tests were also conducted within the PRB. Those data indicate that the K of the PRB was generally higher than the surrounding formation, and it was consistent with laboratory permeameter measurements of the ZBI/sand mixture (0.02 cm/s).

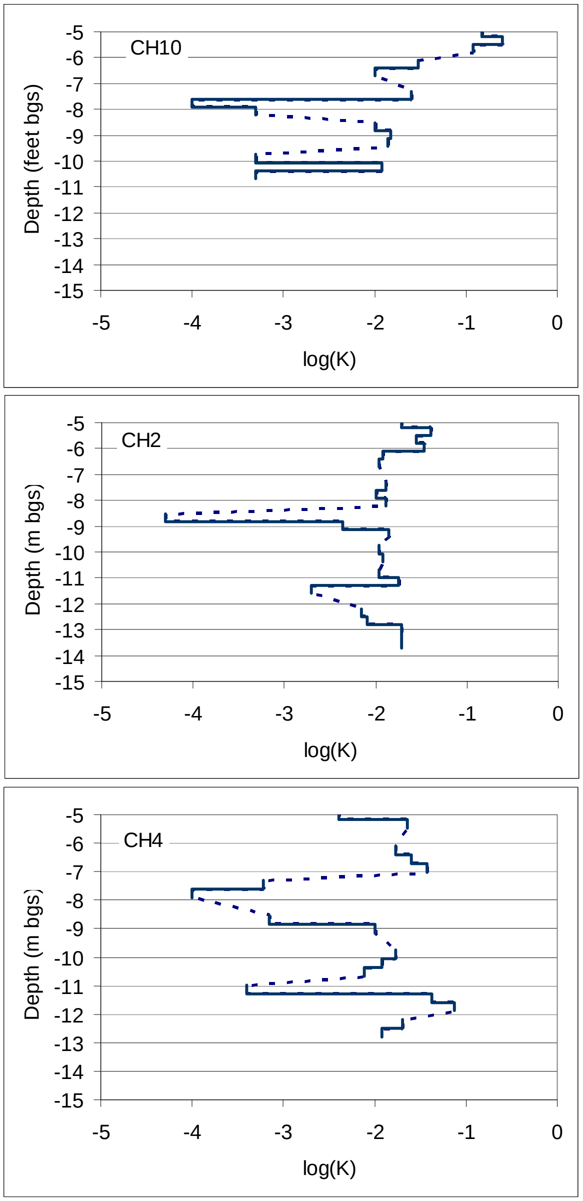


Figure 11. Hydraulic Conductivity Profiles from Test Holes CH10, CH2, and CH4 (see Figure 5) **Measured by Laboratory Permeameter.**

Depth Below Ground Surface (m)	7	8	9	10	11	12	14	16	18
6	.000	.000	.001	.008	.000	.004	.002	.003	.002
6.3	.000	.013	.004	.008	.001	.003	.005	.002	.008
6.6	.007	.003	.011	.008	.007	.008	.007	.004	.019
6.9	.008	.006	.009	.019	.008	.008	.003	.013	.019
7.2	.004	.000	.015	.019	.007	.008	.009	.025	.019
7.5	.005	.002	.000	.015	.011	.008	.015	.015	.009
7.8	.011	.002	.000	.019	.001	.006	.008	.002	.003
8.1	.019	.001	.004	.019	.001	.002	.002	.025	.015
8.4	.001	.006	.001	.019	.008	.003	.002	.015	.025
8.7	.004	.000	.015	.019	.007	.008	.009	.025	.019
9	.013	.008	.015	.019	.007	.025	.025	.019	.038
9.3	.009	.008	.013	.019	.008	.025	.025	.025	.025
9.6	.008	.025	.019	.019	.015	.019	.025	.025	.025
9.9	.003	.019	.019	.019	.019	.019	.004	.015	.019
10.2	.004	.025	.025	.019	.002	.019	.001	.019	.019
11.5	.008	.015	.025	.019	.019	.015	.019	.019	.019
10.8	.009	.004	.019	.019	.019	.013	.019	.019	.025
11.1	.015	.011	.025	.015	.019	.019	.013	.009	.019
11.4	.007	.025	.015	.013	.011	.025	.019	.019	.015
11.7	.019	.009	.025	.009	.019	.019	.019	.019	.075
12	.023	.075	.054	.009	.080	.054	.040		

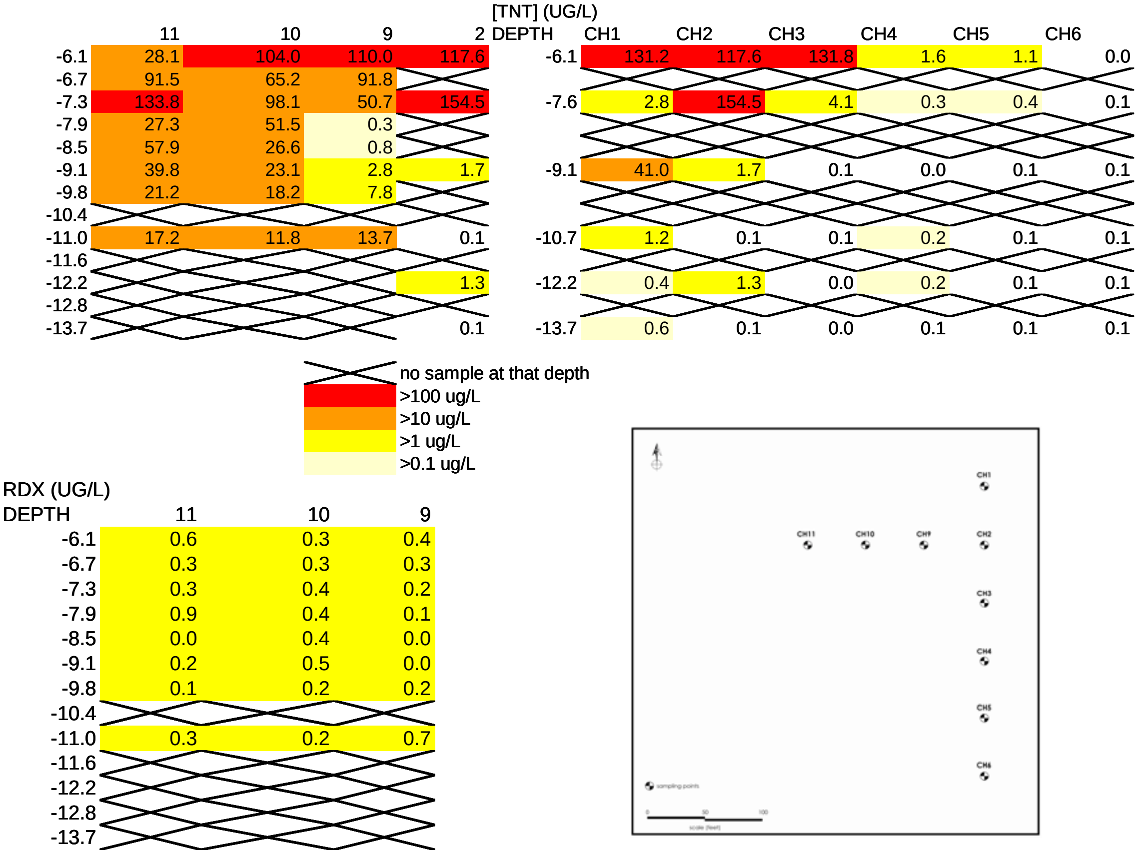
▒ =PRB

Figure 12. Measured Hydraulic Conductivity (slug test) **Data Measured in a Transect Parallel to Groundwater Flow Between Sampler Rows G and J.**

5.4 DEGRADATION OF CONTAMINANTS

5.4.1 Explosives Concentration Changes Over Time

Explosives concentrations in groundwater measured prior to installation of the PRB are shown in Figure 13. Based on those data, the PRB was located between locations CH10 and CH11 in the figure.



[TNT] (UG/L)

	11	10	9	2
-6.1	28.1	104.0	110.0	117.6
-6.7	91.5	65.2	91.8	✕
-7.3	133.8	98.1	50.7	154.5
-7.9	27.3	51.5	0.3	✕
-8.5	57.9	26.6	0.8	✕
-9.1	39.8	23.1	2.8	1.7
-9.8	21.2	18.2	7.8	✕
-10.4	✕	✕	✕	✕
-11.0	17.2	11.8	13.7	0.1
-11.6	✕	✕	✕	✕
-12.2	✕	✕	✕	1.3
-12.8	✕	✕	✕	✕
-13.7	✕	✕	✕	0.1

DEPTH	CH1	CH2	CH3	CH4	CH5	CH6
-6.1	131.2	117.6	131.8	1.6	1.1	0.0
-7.6	2.8	154.5	4.1	0.3	0.4	0.1
-9.1	41.0	1.7	0.1	0.0	0.1	0.1
-10.7	1.2	0.1	0.1	0.2	0.1	0.1
-12.2	0.4	1.3	0.0	0.2	0.1	0.1
-13.7	0.6	0.1	0.0	0.1	0.1	0.1

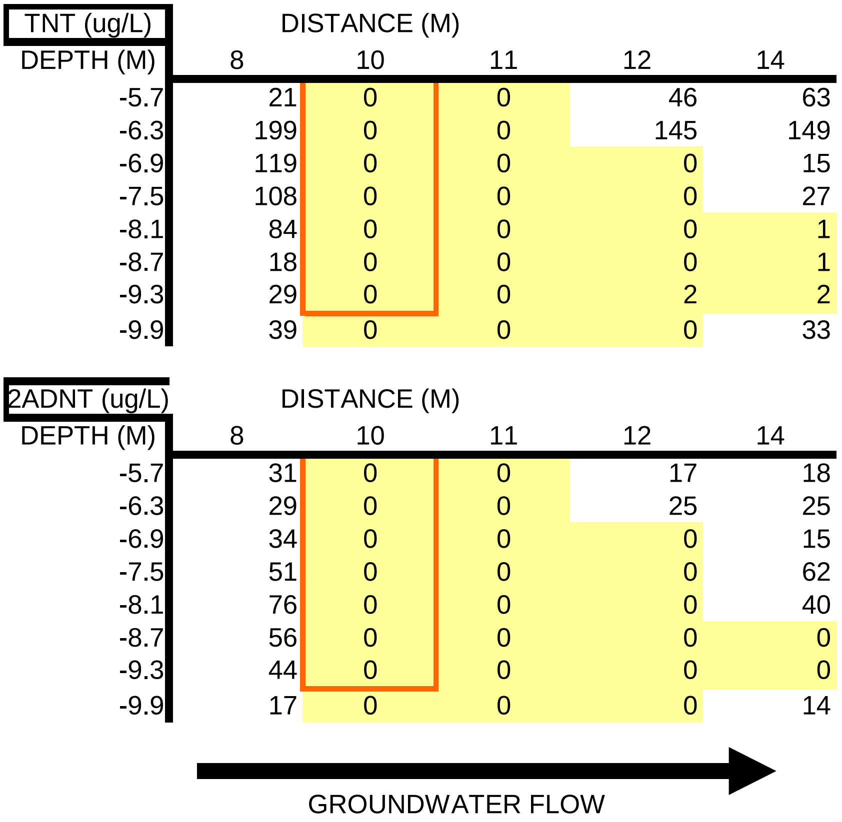
✕ no sample at that depth
🟥 >100 ug/L
🟧 >10 ug/L
🟨 >1 ug/L
▢ >0.1 ug/L

RDX (UG/L)

DEPTH	11	10	9
-6.1	0.6	0.3	0.4
-6.7	0.3	0.3	0.3
-7.3	0.3	0.4	0.2
-7.9	0.9	0.4	0.1
-8.5	0.0	0.4	0.0
-9.1	0.2	0.5	0.0
-9.8	0.1	0.2	0.2
-10.4	✕	✕	✕
-11.0	0.3	0.2	0.7
-11.6	✕	✕	✕
-12.2	✕	✕	✕
-12.8	✕	✕	✕
-13.7	✕	✕	✕

Figure 13. TNT and RDX Concentrations at the Pre-Installation Monitoring Locations and a Plan View Map Showing the Relative Positions of Those Sampling Locations.

Figures 14 through 19 show explosives concentrations in a vertical transect along the direction of groundwater flow during the period between December 2003 and July 2005. The data indicate that contaminant removal remained effective throughout that period.

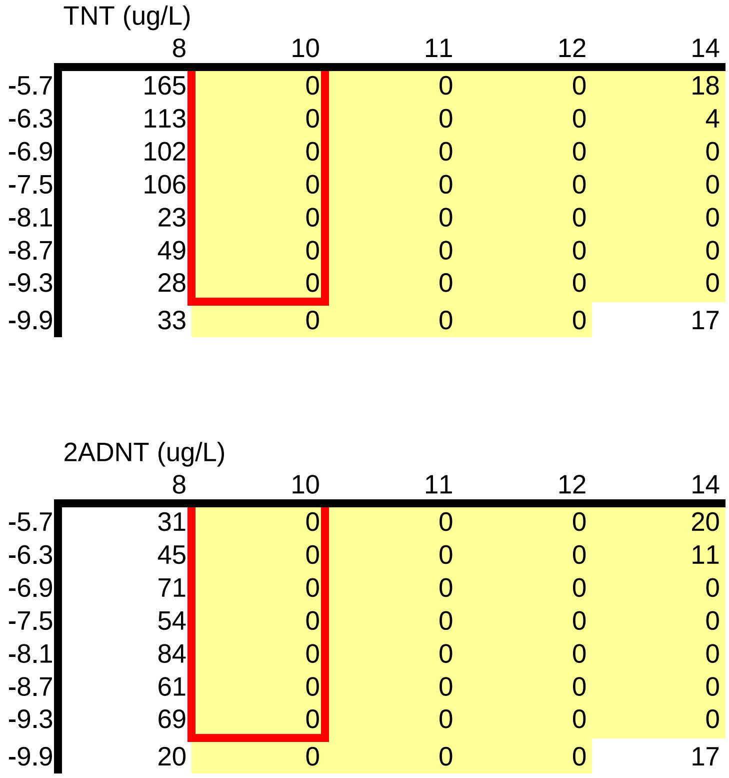


TNT (ug/L)	DISTANCE (M)				
DEPTH (M)	8	10	11	12	14
-5.7	21	0	0	46	63
-6.3	199	0	0	145	149
-6.9	119	0	0	0	15
-7.5	108	0	0	0	27
-8.1	84	0	0	0	1
-8.7	18	0	0	0	1
-9.3	29	0	0	2	2
-9.9	39	0	0	0	33

2ADNT (ug/L)	DISTANCE (M)				
DEPTH (M)	8	10	11	12	14
-5.7	31	0	0	17	18
-6.3	29	0	0	25	25
-6.9	34	0	0	0	15
-7.5	51	0	0	0	62
-8.1	76	0	0	0	40
-8.7	56	0	0	0	0
-9.3	44	0	0	0	0
-9.9	17	0	0	0	14

*ADNT = aminodinitrotoluene

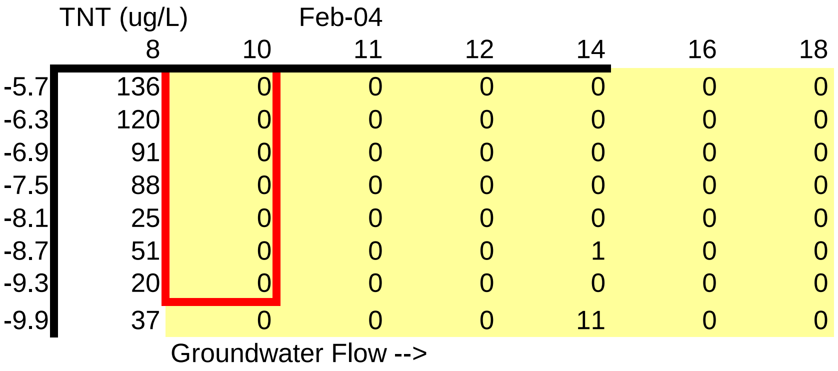
Figure 14. TNT and 2-ADNT Concentration Data from December 2003.



TNT (ug/L)	8	10	11	12	14
-5.7	165	0	0	0	18
-6.3	113	0	0	0	4
-6.9	102	0	0	0	0
-7.5	106	0	0	0	0
-8.1	23	0	0	0	0
-8.7	49	0	0	0	0
-9.3	28	0	0	0	0
-9.9	33	0	0	0	17

2ADNT (ug/L)	8	10	11	12	14
-5.7	31	0	0	0	20
-6.3	45	0	0	0	11
-6.9	71	0	0	0	0
-7.5	54	0	0	0	0
-8.1	84	0	0	0	0
-8.7	61	0	0	0	0
-9.3	69	0	0	0	0
-9.9	20	0	0	0	17

Figure 15. TNT and 2-ADNT Concentration Data from February 2004.

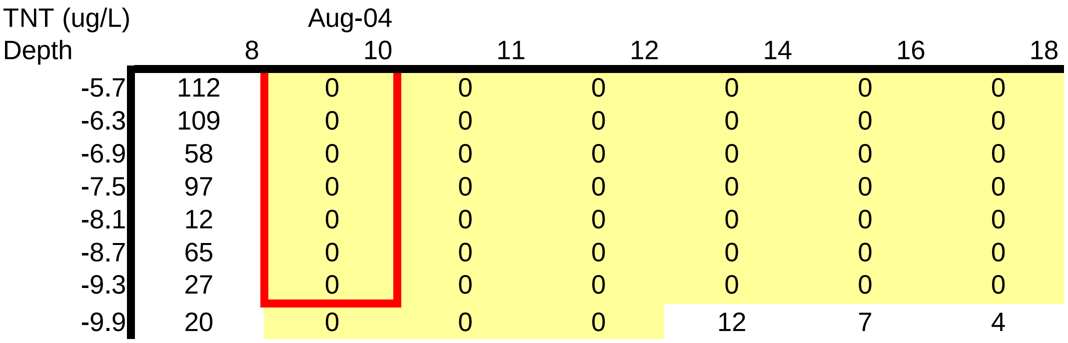


TNT (ug/L) Feb-04

	8	10	11	12	14	16	18
-5.7	136	0	0	0	0	0	0
-6.3	120	0	0	0	0	0	0
-6.9	91	0	0	0	0	0	0
-7.5	88	0	0	0	0	0	0
-8.1	25	0	0	0	0	0	0
-8.7	51	0	0	0	1	0	0
-9.3	20	0	0	0	0	0	0
-9.9	37	0	0	0	11	0	0

Groundwater Flow -->

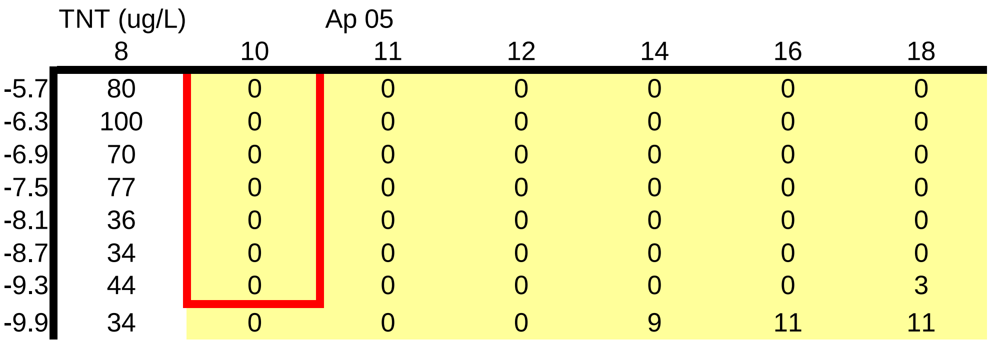
Figure 16. TNT Concentration Data from March 2004.



TNT (ug/L) Aug-04

Depth	8	10	11	12	14	16	18
-5.7	112	0	0	0	0	0	0
-6.3	109	0	0	0	0	0	0
-6.9	58	0	0	0	0	0	0
-7.5	97	0	0	0	0	0	0
-8.1	12	0	0	0	0	0	0
-8.7	65	0	0	0	0	0	0
-9.3	27	0	0	0	0	0	0
-9.9	20	0	0	0	12	7	4

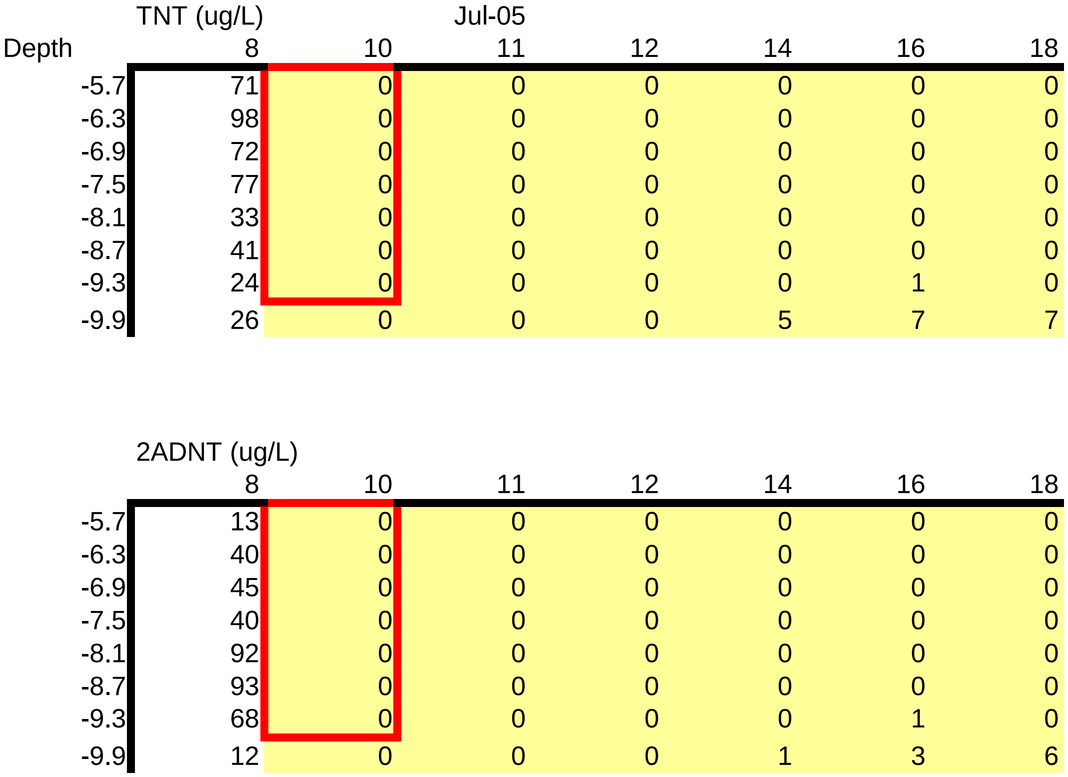
Figure 17. TNT Concentration Data from November 2004.



TNT (ug/L) Ap 05

	8	10	11	12	14	16	18
-5.7	80	0	0	0	0	0	0
-6.3	100	0	0	0	0	0	0
-6.9	70	0	0	0	0	0	0
-7.5	77	0	0	0	0	0	0
-8.1	36	0	0	0	0	0	0
-8.7	34	0	0	0	0	0	0
-9.3	44	0	0	0	0	0	3
-9.9	34	0	0	0	9	11	11

Figure 18. TNT Concentration Data from April 2005.



TNT (ug/L) Jul-05

Depth	8	10	11	12	14	16	18
-5.7	71	0	0	0	0	0	0
-6.3	98	0	0	0	0	0	0
-6.9	72	0	0	0	0	0	0
-7.5	77	0	0	0	0	0	0
-8.1	33	0	0	0	0	0	0
-8.7	41	0	0	0	0	0	0
-9.3	24	0	0	0	0	1	0
-9.9	26	0	0	0	5	7	7

2ADNT (ug/L)

	8	10	11	12	14	16	18
-5.7	13	0	0	0	0	0	0
-6.3	40	0	0	0	0	0	0
-6.9	45	0	0	0	0	0	0
-7.5	40	0	0	0	0	0	0
-8.1	92	0	0	0	0	0	0
-8.7	93	0	0	0	0	0	0
-9.3	68	0	0	0	0	1	0
-9.9	12	0	0	0	1	3	6

Figure 19. TNT and 2-ADNT Concentration Data from July 2005.

5.4.2 Push-Pull Degradation Test

Since RDX concentrations were lower in the groundwater than expected, a push-pull tracer test was conducted to examine the in situ rate of RDX (and TNT) degradation after approximately 18 months of PRB operation (May 2005). The push-pull tracer test format was chosen because it eliminates complications associated with sorption (i.e., the extent to which movement into the formation is retarded by [linear] sorption is balanced by the retardation coming back out of the formation). As a result, all of the tracers should act in a similar manner.

To conduct the test, 10 L of groundwater from upgradient of the PRB (G8Y) was pumped into a 10-L Tedlar bag, and ~1 mg of RDX and 1 mL of fluorescein dye solution was added to the groundwater. The spiked groundwater was then injected into a PVC monitoring (G10Y) well installed in the middle of the PRB (screen length ~1 m). The spiked groundwater was then followed by 1 L of water that came from G19Y to flush the sampling line. The system was allowed to sit for 30 min, and then water was removed from the well at ~1 L/min. The first liter removed contained water from within the well and was essentially free of any of the tracers. The next 20 L removed (i.e., samples 1-20) were analyzed for fluorescein, RDX, and TNT. The measured injection concentration of TNT was 71 µg/L and for RDX was 114 µg/L. Figure 20 shows normalized concentrations for each of the tracers in the successive samples. (Sample 0 represents the injection solution concentration). Detection limits for these analyses were 0.1 µg/L for TNT and 0.2 µg/L for RDX. As the data indicate, explosives concentrations were reduced to less than 1% of their initial values in ~30 min. That corresponds to a minimum of seven half lives for RDX and nine half lives for TNT (i.e., half lives of ~4 and ~3 min, respectively). Given that the residence time in the PRB is on the order of 3,000-5,000 minutes, it was expected that reactivity would not limit the lifetime of the PRB.

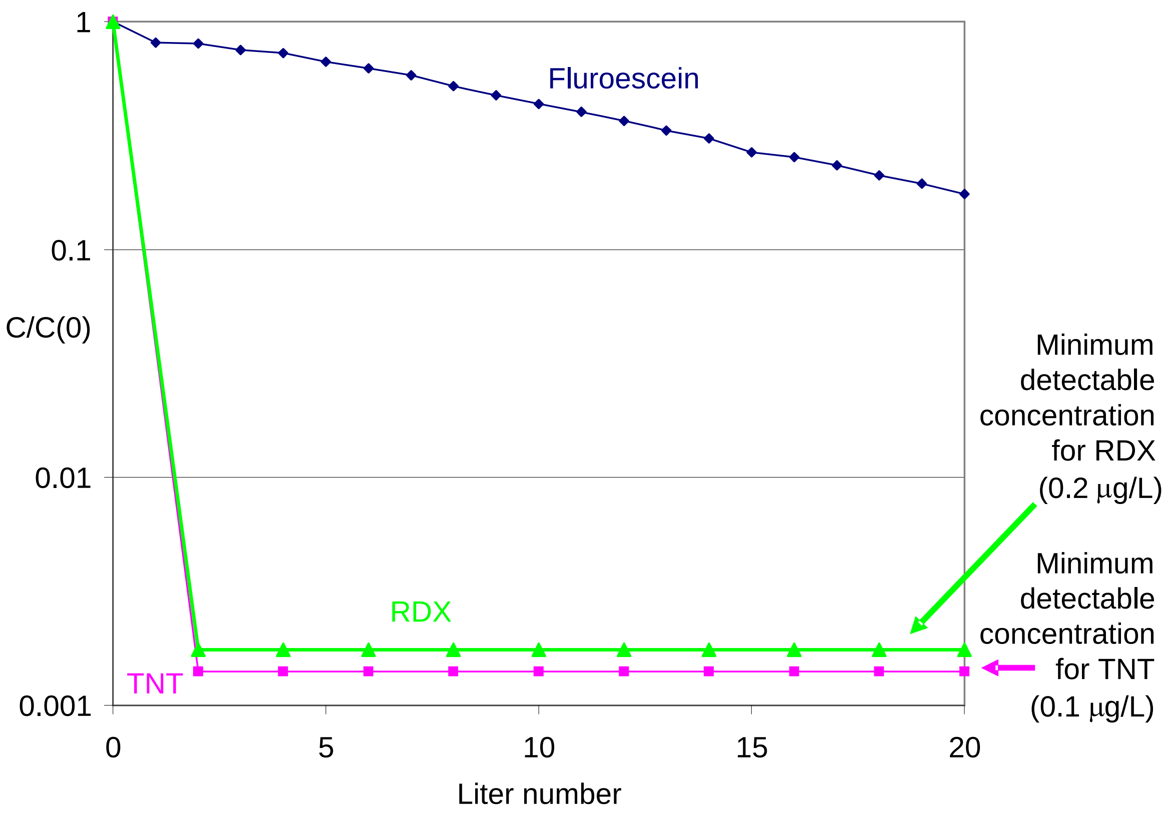


Figure 20. Tracer Recovery Data for the PRB Push-Pull Test.

5.5 GEOCHEMICAL CHANGES AND EVALUATION OF LONGEVITY

While the performance of the PRB with respect to explosives is quite straightforward, geochemical changes observed in the groundwater tell a much more complicated story and suggest that flow through the PRB may be lower than anticipated. (A complete list of inorganic water chemistry data can be found in Appendix C.)

The presence of the ZVI in the subsurface has a significant impact on both the target contaminants and the inorganic geochemistry of the groundwater. Table 6 shows typical background groundwater concentration ranges for a number of geochemical parameters. The groundwater at the site was anoxic, fairly reducing, but with a neutral pH. The most noteworthy feature was that the sulfate concentrations were relatively high.

Table 6. Typical Background Groundwater Concentration Ranges for Geochemical Parameters.

Parameter	Value	Analytical Method
Sulfate	180-410 mg/L	Hach colorometric, Ion chromatog.
Nitrate	0-12 mg/L	Hach colorometric, Ion chromatog.
pH	7-7.2	Electrode
Eh	-40 - -130 mV	Electrode
DO	0.0 – 0.2 mg/L	Electrode
Alkalinity	300-800 mg/L	Hach titration
Specific conductance	600-1200 uS-cm	Electrode
Ferrous iron	0.0-0.3 mg/L	Hach colorometric
TNT	30-200 ug/L	Waters Sep-Pak and GC/MS*
2-ADT	10-50 ug/L	Waters Sep-Pak and GC/MS
RDX	1-2 ug/L	Waters Sep-Pak and GC/MS

*GC/MS = gas chromatograph/mass spectrometry

Groundwater geochemistry data from within and downgradient from the PRB at the CAAP site one year after installation are shown in Figure 21. Ferrous iron concentrations (not shown), which were elevated following installation of the PRB, became very low downgradient of the PRB, and sulfate concentrations were significantly reduced. As has been shown the case at other sites, it is likely that much of the sulfate precipitated as sulfides (e.g., Phillips et al., 2000). Calcium concentrations were reduced from 150-200 mg/L to less than 1 mg/L in the PRB. Carbonate (alkalinity) concentrations were also reduced, probably due to the precipitation of calcite/aragonite ($CaCO_3$), and possibly mackinawite ($FeCO_3$) (Wilkin and Puls, 2003; Blowes and Mayer 1999; Mayer et al., 2001). The specific conductance of the groundwater decreased as a result of passage through the PRB, due in large part to the loss of calcium, sulfate, and carbonate alkalinity.

The vertical cross-section data in Figure 21 suggest three possible flow conditions at the PRB, either 1) flow through the bottom half of the PRB is slower than in the upper half as the result of differences in the K of the aquifer at different depths; 2) dissolved-phase concentrations in the deeper samples rebounded as the result of dissolution from aquifer materials downgradient of the PRB; or 3) the effective K of the PRB was reduced, causing some of the groundwater to divert around the PRB. Data in Figure 22 from three depths 4 m downgradient of the PRB (i.e., locations G14 and J14 in Figure 6) show that sulfate concentrations downgradient of the PRB initially dropped significantly between the first and second sampling events (either as the result of sulfate reduction or water added during PRB installation). This suggests that, at least initially, flow from the PRB to all sampling depths 4 m downgradient was both fairly rapid and uniform.

Sulfate (mg/L)	8	10	11	12	14	16	18
-5.7	264	38	1	0	10	0	1
-6.3	264	0	3	1	1	1	0
-6.9	206	0	0	5	3	2	1
-7.5	206	0	1	0	10	0	52
-8.1	308	0	3	77	155	60	130
-8.7	308	0	4	22	254	283	346
-9.3	409	169	305	325	359	325	351
-9.9	403	315	353	386	346	365	356

Ca++ (mg/L)	8	10	11	12	14	16	18
-5.7	172	1	1	1	8	55	79
-6.3	163	1	1	2	2	18	65
-6.9	162	1	1	2	9	59	178
-7.5	145	1	1	40	171	152	173
-8.1	163	1	1	63	171	185	128
-8.7	164	2	1	90	138	133	184
-9.3	165	39	172	174	183	168	164
-9.9	150	184	176	143	184	125	159

Alkalinity (mg/L)	8	10	11	12	14	16	18
-5.7	310	105	145	135	235	115	135
-6.3	285	140	155	105	160	165	100
-6.9	320	185	170	170	135	525	360
-7.5	295	170	190	135	540	135	435
-8.1	305	165	140	175	325	340	225
-8.7	315	150	165	325	340	255	365
-9.3	355	220	320	365	330	340	380
-9.9	310	345	390	290	335	300	355

Cond .(uS /cm)	8	10	11	12	14	16	18
-5.7	808	318	360	ns	446	356	434
-6.3	851	345	336	260	266	268	270
-6.9	851	390	425	346	328	305	321
-7.5	871	405	368	332	972	805	813
-8.1	882	405	399	528	726	540	723
-8.7	927	417	420	901	914	972	1022
-9.3	1091	758	1140	1144	1157	1186	1192
-9.9	1192	1125	1161	1162	1184	1161	1148

Figure 21. Groundwater Geochemistry Data from the G and J Transects in November 2004.

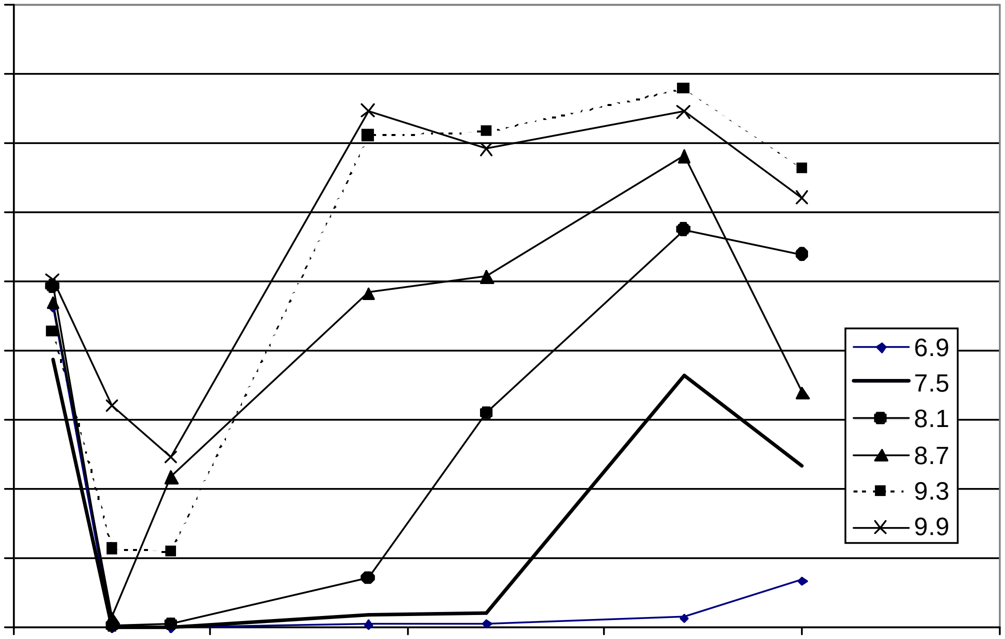


Figure 22. Time Series Sulfate Data from Three Depths at 4 m Downgradient of the PRB.

The data in Figure 22 provide two indications that dissolution from aquifer materials was not the source for rebounding concentrations. First, the fact that low concentrations of sulfate appeared 4 m downgradient of the PRB at 2-4 months after PRB installation suggests that there was not a reservoir of sulfate available on the aquifer materials. Second, if there were a source of sulfate in the aquifer, it would have been expected that the rebound would have occurred relatively rapidly, rather than gradually increasing over the course of a year. One possible reason for a gradual increase is that the pH increased from ~7 to ~9 during that year. To examine the effect of pH change on availability of sulfate, core samples collected prior to PRB installation were sequentially extracted using pH=9 deionized water.

To accomplish this, 20-gram aquifer samples were taken from 0.6-m-long core sections collected from 5.5 to 10.7 m bgs. Acidified water (20 mL) was added to each sample in a 40-mL vial, and the samples were continuously mixed for ~96 hours. The water was then separated from the core samples by centrifugation followed by filtration through a 0.45 µm filter. Sulfate and calcium were then analyzed in the extracted water. Following the initial extraction, samples were again suspended in 20 mL of acidified water and extracted a second time using the same procedure as the first extraction, followed by sulfate and calcium analyses.
The data in Table 7 indicate that extracted concentrations of both calcium and sulfate are too low to produce the groundwater concentrations observed at depths corresponding to the lower portion of the PRB.[2]

Table 7. Sulfate and Calcium in Core Extracts from CH10.

Depth (fgs, m)	Sulfate in First Extraction (mg/L)	Selfate in Second Extraction (mg/L*)	Calcium in first Extraction (mg/L)	Calcium in Second Extraction (mg/L*)
5.5 – 5.8	15	1	0.1	0.3
6.1 – 6.4	9	0	2.3	-1.2
6.6 – 6.7	13	-1	0.4	0.2
7.3 – 7.6	50	1	4	-1.8
7.6 – 7.9	47	4	1.5	-0.3
7.9 – 8.2	73	17	3.9	-1.4
8.5 – 8.8	70	11	1.8	-0.7
8.8 – 9.1	43	6	0.1	0.2
9.8 – 10.1	51	8	0.5	0.1
10.4 – 10.7	38	4	0.1	0.1

*Calculated after subtracting dissolved sulfate or calcium remaining in the sample after removing part of the water from the first extract

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[2] The ratio of water to soil for the extraction is ~4 times the ratio in the aquifer. Thus, the concentrations from the first extraction can be thought of as approximating the average concentration from the first four pore volume. Similarly, the second extract would represent the average concentration of the second four pore volumes. Based on the regional groundwater flow, and the bromide tracer test discussed below, the average groundwater velocity is on the order of 0.2 m/d. Thus, over a 20-month period one would have expected perhaps 20 pore volumes to have flowed through the 6 m downgradient of the PRB. Based on the concentrations of sulfate and calcium observed in the extracts, we conclude that the aquifer materials could not represent a source for the observed calcium and sulfate concentrations downgradient of the PRB.

To assess the ability of the PRB to reduce sulfate, time series data from within the PRB are plotted in Figure 23. The data indicate that the effectiveness of the PRB for removing sulfate substantially increased over the first 10 months of operation. (In contrast, carbonate concentrations are reduced within the PRB [Figure 23b] but do not show similar changes over time). There are two possible hypotheses for this behavior. The first is that the rate of sulfate reduction increased over time, perhaps as a result of an increased population of sulfate-reducing bacteria (sulfate-reducing bacteria have been measured downgradient of the PRB). The second is that residence time in the PRB increased during that period. Our field data do not allow us address changes in microbial population; however, based on hydraulic conductivity and tracer data discussed below, we believe that changes in residence time within the PRB did occur over the first year of PRB operation.

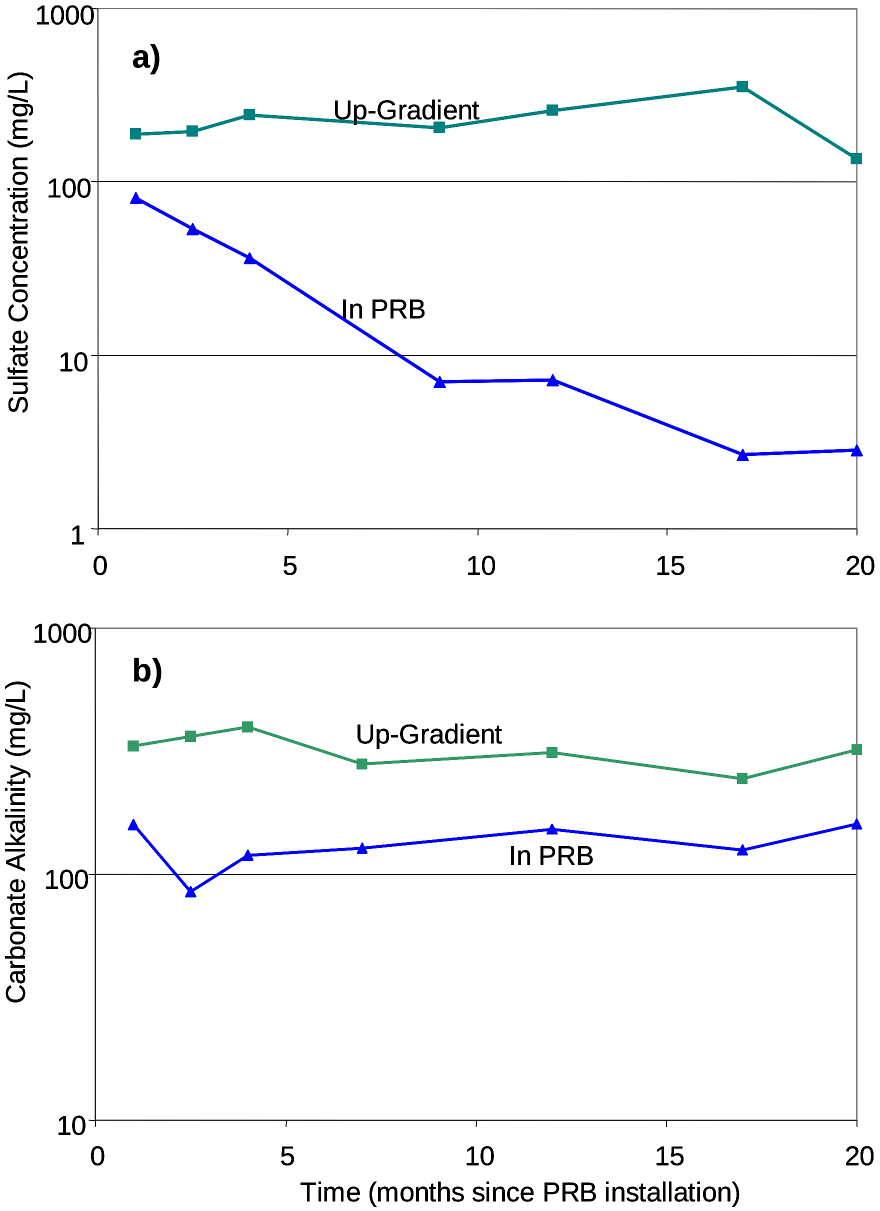

Figure 23. Time Series Plots of Sulfate (a) and Carbonate Concentrations Within and Upgradient of the PRB (b).

5.5.1 Characterization of Core Samples

In order to understand how changes in PRB hydraulic conductivity might have occurred, angled core samples (ca 30° from vertical) were collected through the PRB sampling in a downgradient to upgradient direction using a Geoprobe direct-push system with 3-m-long, 5-cm-diameter aluminum core barrels. Prior to core sample collection, the overlying soils were removed down to near the water table. Once the cores were retrieved from the subsurface, the intact cores were frozen with dry ice and transported to our laboratory. At the lab the aluminum core barrels were opened by splitting them along their lengths.

5.5.1.1 Core Sample Analytical Methods

Sulfur Analyses

Total sulfur concentrations for core sample materials were determined by first reducing the pH of sample/water slurries to basic conditions and then oxidizing all the sulfur to sulfate by sequential digestion of the slurries using hydrogen peroxide. The sulfate concentration was then determined using ion chromatography.

Acid-volatile sulfides (AVS) were determined using a modification of the approach presented by Allen et al., (1993). One gram of core sample was placed in a 40-mL septum-capped vial. The vial was connected to a second 40-mL vial via a 1/16-inch diameter stainless steel tube, which went to the bottom of the second vial. A syringe needle was inserted through the septum of the second vial to provide a vent. The second vial contained 10 mL of 0.5 M sodium hydroxide (NaOH). To collect the AVS, 10 mL of 1 M hydrochloric acid (HCI) were added to the first vial, resulting in the volatilization of all AVS, as well as carbonates. The AVS were then trapped in the NaOH and analyzed by the Hach colorometric sulfide method.

XPS

X-ray photoelectron spectroscopy (XPS) analysis was performed at the Pacific Northwest National Lab. The four samples were mounted and analyzed three or more times. A small portion of each sample was placed into separate sealed sample vials inside a recirculated N_2 purged glove box at <1 ppm O_2 and H_2O. The subdivided samples were moved to an N_2 purged glove bag (~20-30 ppm O_2 for < 5 minutes) attached to the XPS system sample introduction port for mounting and introduction into the ultra high vacuum (UHV) chamber. Samples were secured to the sample holder using a thin Mo mask. XPS measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. This system uses a focused monochromatic Al Kα x-ray (1486.7 eV) source and a spherical section analyzer. The instrument has a 16-element multichannel detector. The x-ray beam used was a 99-W, 100-mm diameter beam that was rastered over a 1.4-mm by 0.2-mm rectangle on the sample. The x-ray beam was incident normal to the sample and the photoelectron detector was at 45° off-normal. Wide scan data was collected using a pass energy of 117.4 eV. For the Ag3d5/2 line, these conditions produce full width at half maximum (FWHM) of better than 1.6 eV. Narrow scan data was collected using a pass energy of 46.95 eV. For the Ag3d5/2 line, these conditions produced FWHM of better than 0.98 eV. The binding energy (BE) scale was calibrated using the Cu2p3/2 feature at 932.62 ± 0.05 eV and Au4f at 83.96 ± 0.05 eV for known standards.

Batch Reaction Tests
Batch experiments were conducted using 60 mL Amber vial with 1.0 g/L core material added to an initial concentration of 20 mg/L TNT/RDX in deoxygenated site water. TNT, RDX, and 2,4,6-triaminotoluene (TAT) were analyzed using high performance liquid chromatography (HPLC) at pH = 7.0 in 20 mM phosphate buffer and methanol at a rotation of 40:60. The flowrate was 1.2 mL/min and the UV-vis was set at 230 nm. A Shiseido Capcell C18 column was used for the HPLC analyses.

5.5.1.2 Core Sample Results

Each soil core from the CAAP site was divided into five sections based on visual observation:

- Upgradient, unimpacted
- Upgradient, impacted
- PRB
- Downgradient, impacted
- Downgradient, unimpacted

The impacted portions were identified by a distinctly darker color (Figure 24). Collection efficiency of the PRB material was generally low because it was less densely packed than the native material. However, by sampling from the downgradient towards the upgradient face, we were able to capture the upgradient interface in four cores. All of the cores were visually similar to Figure 24, and one was selected for detailed chemical analyses by XPS, total sulfur analysis by hydrogen peroxide digestion, and AVS analysis.

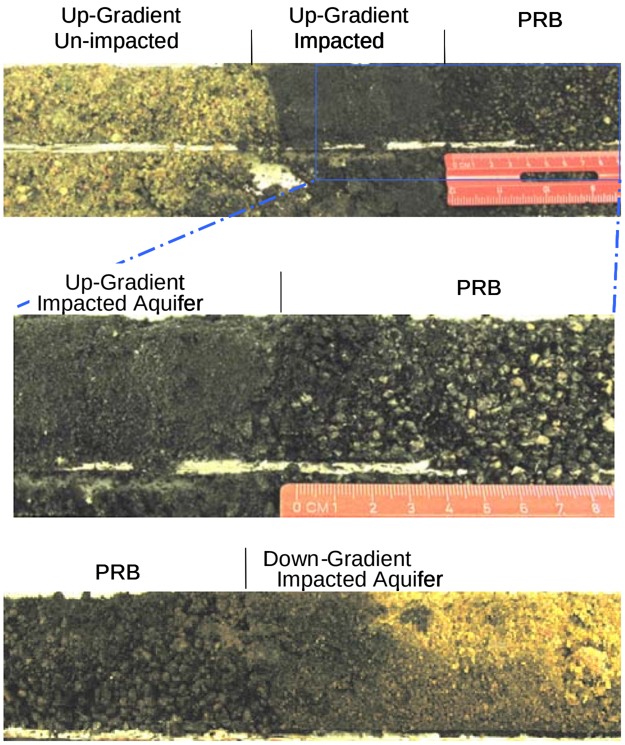

Figure 24. Photographs of the Upgradient Sand/PRB Interface from CAAP Core 4.

Total sulfur analyses of the core sections indicate that most of the precipitated sulfur occurs in the upgradient impacted zone (Table 8). This result is supported by the XPS analyses (Table 10). The distribution of sulfide is further supported by the AVS analyses (Table 8). However, the total sulfur analyses show about a factor of 5 greater sulfide concentration than the AVS analyses. Two additional cores showed similar results.

Table 8. Sulfur Analyses of CAAP Core 4.

Sample	Upgradient Unimpacted	Upgradient Impacted	ZVI PRB	Downgradient Impacted	Downgradient Unimpacted	Original Iron/Sand Mix
	4-1	**4-2**	**4-3**	**4-4**	**4-5**	**T7**
Analysis						
Total Sulfur (mg/kg)	39	554	148	0	0	0
Acid-Volatile Sulfides (mg/kg)	0.1	35	22	0	0.1	0
Zero-Valent Iron (% by weight)	0	0	28	0	0	30

Based on the sulfide concentrations on the aquifer and PRB materials, and the difference in groundwater sulfate concentrations upgradient and downgradient of the PRB, and using an approach similar to Morrison (2003), it is possible to estimate the flux through the PRB using an equation of the form:

$$q_w = \frac{M * \rho * L}{t * \Delta C} \tag{1}$$

where:

q_w=specific water flux (l/t)

M = mass per mass of core material (m/m)

ρ = density of the core material (m/l^3)

L = length of the deposition zone along the flow path (l)

t = duration over which precipitation has occurred (t)

ΔC= change in concentration upgradient and downgradient of the deposition interval (m/l^3)

Based on Darcy's Law calculation of regional groundwater flow, the specific flux into the PRB was expected to be ~0.07 m/d (groundwater velocity of 0.2 m/d assuming porosity =0.35). Based on the observed ~300-mg/L change in sulfate concentration (Table 8) and the assumption that there is a 10-cm thick precipitation zone upgradient and a 50-cm thick precipitation zone in the PRB, the calculated flux would be 0.33 cm/d (Table 9). If the porosity is 0.35, this would correspond to an average groundwater velocity over the lifetime of the PRB of ~1 cm/d, which is only 5% of the expected value. This result is consistent with the groundwater tracer data and numerical modeling presented in Johnson et al., 2007a.

Table 9. Estimated Flux into the PRB Based on Darcy's Law and Measured Sulfide Concentrations.

Parameter	Upgradient Groundwater	Upgradient Aquifer	PRB	Groundwater in PRB
Dissolved sulfur concentration (mg/mL)	0.064			0.001
Mass of sulfur per mass of core (mg/g)		0.554	0.148	
Bulk density (g/mL)		1.6	1.8	
Length of deposition zone (cm)		10	10	
Duration (days)	600			
Water flux (cm/day)	0.30			
Porosity	0.35			
Calculated linear groundwater velocity (cm/day)	0.9			

XPS analysis of the core samples also showed significant increases in the surficial concentrations of iron precipitates in the upgradient impacted zone, as well as in the PRB. The source of that iron could be the upgradient groundwater; however, background Fe2+ concentrations are generally quite low (<0.005 mg/L). The PRB represents a potentially-more-likely source of the iron. Similarly, groundwater data from the CAAP site indicate that H2 concentrations reach 35% of saturation values (i.e., 0.35 mM) within the PRB but are very low upgradient of the PRB. As discussed above, sulfate reduction is widely believed to be microbially mediated, and to involve molecular hydrogen in the reduction process, i.e., equation (1). Thus, it is also possible that the PRB is the source of hydrogen for sulfate reduction. However, for iron and hydrogen to impact aquifer materials upgradient of the PRB, they would have to "back-diffuse" against the groundwater flux entering the PRB. To examine the behavior of iron and hydrogen in this context, a simple 1-D advection-diffusion model was developed and is discussed below.

It has not been possible to experimentally confirm the sequence of events that led to permeability reduction that allowed iron precipitation and sulfate reduction upgradient of the PRB. Almost certainly, the guar played a role in that process by providing the initial K reduction and/or the carbon source for microbial growth. We have conducted some qualitative experiments with guar to examine the potential for plugging of the upgradient aquifer material by the guar. We believe that two factors could have contributed to more-than-expected movement of the guar into the native materials. First, conditions during emplacement of the guar were quite cold, and while the viscosity specifications of the guar were met, subsurface temperatures were ~15°C warmer than the ambient temperature, and this likely led to a two-fold reduction in the viscosity of the guar. Second, a large hydraulic head difference (~2-3 m) was present at the trench interface. Given its likely-reduced viscosity, it is possible that guar moved a significant distance into the native materials. Since the hydraulic conductivity of the native materials varies spatially by more than a factor of 20 (<1 to >20 m/d), it is also likely that penetration of the guar would have varied correspondingly and preferentially entered the higher-K zones. Calculations based on a guar viscosity of 100 centipoise (i.e., approximately the field-determined value for the guar) suggest that 12 hours of contact between the guar and the native materials, with a hydraulic head difference across the guar of 200 cm, could have resulted in penetration distances of 25 cm or more. This could significantly complicate flow into the PRB, and/or provide a significant upgradient carbon source for microbiological activity.

XPS Analysis

Table 10 shows the XPS data for Core 4 and the dry Peerless iron/sand mixture. XPS showed that the surfaces of all the samples consisted mainly of O, Fe, Si, C, and Al with small amounts of N, Na, Mg, P, K, and Ca. Note that the Si concentrations decrease as you go from the upgradient unimpacted zone (16.6%) into the PRB (3.7%). Table 10 also shows that the S concentration on the surface of the particles was below detection limits in the Peerless iron/sand mixture and in the upgradient unimpacted samples. Larger concentrations were observed on the surface of the upgradient impacted and PRB particles. In particular, the XPS data gave a strong signal for pyrite (FeS_2) in the upgradient impacted sample.

The Fe/O ratios for the various samples are of interest because this ratio typically reflects the amount of iron oxide on the surface of the particles. It appears that as you move into the PRB, the Fe concentration increases on the surface. Note that Fe/O ratio for the upgradient impacted and PRB particles is higher than the dry Peerless/sand mixture. This is probably due to the fact that when the iron particles are exposed to solution, active corrosion processes start in which dissolution/precipitation of the Fe particles occurs. The fact that there is a higher Fe/O ration in the upgradient impacted samples may indicate that Fe^{2+} or Fe^{3+} is back diffusing into this region.

Table 10. Elemental Atomic Percentages of Three Sub-Samples of Core 4 and of the Peerless Iron/Sand Mixture Obtained by XPS.

Element (Atomic %)	Peerless Iron/Sand Blank	Upgradient Unimpacted	Upgradient Impacted	PRB
C	7.6	7	6.1	6.5
N	0.22	0.64	0.75	0.69
O	57.4	63	54.6	51.3
Na	0.5	0.6	0.6	0.2
Mg	1	1.5	0.8	1
Al	3.4	4.6	1.7	0.8
Si	10.9	16.6	6.6	3.7
P	0.5	0.3	0.3	0.8
S	0	0	0.34*	0.24
K	0.6	0.4	0.3	0.1
Ca	0.9	1.5	0.6	0.6
Fe	17.9	3.9	27.4	34
Fe/O	0.311	0.062	0.502	0.663

TNT and RDX Degradation Kinetics

One of the most prescient questions regarding the use of PRB concerns how long the PRB would continue to function properly. There are a few ways in which a PRB can fail: (1) the PRB becomes plugged with oxides, biofilms, or other groundwater constituents, in which case the groundwater flow goes around the PRB; and (2) the iron particles become passivated and the reactivity of the particles decreases. Johnson et al. (2007a) that flow through the CAAP PRB may be reduced due to plugging. We show here that the reactivity of the particles in the PRB is still reactive and that particles in the upgradient impacted zone are also reactive toward TNT and RDX.

Table 11 shows the results for three cores and their subsamples compared to the dry Peerless iron/sand mixture. As expected, the samples from the upgradient unimpacted zone showed no reactivity toward TNT or RDX. With Core 3 and 5, the upgradient impacted samples showed reduction of TNT and RDX. The upgradient impacted sample from Core 4 was ambiguous, showing slow if any reduction of TNT/RDX. All the samples from inside the PRB demonstrated reduction of TNT and RDX. All of the rates of the core samples are approximately an order of magnitude slower than the dry Peerless iron/sand mixture, probably due to the formation of iron oxide films. The rates observed are still within the range that will be effective for removing explosives from the groundwater. The reason that an observed rate constant value is missing for the PRB sample of Core 5 is because the data is not first order and difficult to fit, although after 2 hours, all of the TNT was degraded.

Table 11. Rate Constants for TNT and RDX for Three Core Samples and a Peerless Iron/Sand Mixture (T7).

TNT/RDX K_{obs} (min^{-1})	Upgradient Unimpacted	Upgradient Impacted	PRB
T7 (sample collected during installation of the PRB)			0.1240/0.0032
Core 3	No degradation	0.0121/0.0061	0.0139/0.0058
Core 4	No degradation	No degradation	0.0140/0.0094
Core 5	No degradation	0.0230/0.0100	*

* K_{obs} was not able to be determined due to lack of “first orderness” of the data. TNT degraded to below detection limits in 2 hours.

5.6 OVERALL CONCLUSIONS

Data from the demonstration site indicate that the PRB performed more or less as expected. Groundwater flowed through the PRB, and explosives were removed below detection limits. The geochemistry of the groundwater was significantly affected by the PRB for a distance of at least 8 m downgradient. However, in the context of the contaminated groundwater plume at the site, the geochemical affects are likely to be of minor importance to overall groundwater quality.

The PRB also affected the microbial community within the subsurface. Most notably, the PRB significantly increased the reduction of sulfate to sulfide. This was probably the result of a combination of factors, the two primary ones being the reducing conditions produced by the PRB and the presence of guar remaining in the subsurface following PRB installation.

Data suggest that flow reduction resulted from loss of K in the native materials just upgradient of the PRB. Most likely this could be avoided in the future if additional care were taken in removing the guar from the system.

The net effect is that there appears to be some diversion of flow around the barrier. This was evidenced by a combination of downgradient plume data and hydrogeologic measurements (i.e., slug tests). In this demonstration, no attempt was made to completely cut off the groundwater explosives plume, but for a full-scale installation, the depth of the PRB would likely need to be sufficiently greater that a loss of permeability within the PRB would not result in under-flow. In conjunction, more care in the removal of guar, or the utilization of emplacement techniques that did not require guar (e.g., a continuous trencher), is recommended.

In situ reactivity testing suggests that the PRB will continue to degrade explosives for an extended period. Reactivity data collected using batch tests with material removed from the PRB after 20 months of operation suggest that the PRB has the capacity to perform for decades. The hydraulics of the PRB are more likely to limit long-term performance at this site.

Finally, given the groundwater conditions at the site, it is likely that less expensive techniques (e.g., edible oils) would be sufficient to remove explosives from the groundwater at CAAP. Nevertheless, in our opinion the ZVI PRB approach represents a much cheaper alternative to groundwater plume containment than does long-term pump and treat. This is discussed in Section 6.

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6.0 COST ASSESSMENT

This section discusses cost considerations involved in the application of PRB to remediate explosives in groundwater. As with most ZVI PRB, the primary cost driver is that there are fewer O&M costs associated with their use than is the case for the typical remediation alternative—pumping and treatment (P&T) of groundwater. The PRB approach also means that groundwater monitoring can occur on a time frame that is consistent with most regulatory requirements (e.g., quarterly, annually) rather than on a more frequent basis if P&T system shutdowns were likely.

6.1 SUMMARY OF TREATMENT COSTS FOR THE DEMONSTRATION

Groundwater treatment and monitoring costs incurred during the CAAP demonstration are shown in Table 12. Only costs associated with the treatment of groundwater are included. Costs associated with validation of the technology are not included. The cost of purchasing the iron ($17,600) and the construction cost ($121,000) were based on actual subcontractor invoices. The other costs are best available estimates.

Table 12. Summary of Treatment Costs.

Item	Subtotal ($)	Total Cost ($)
Pre-installation		
Site characterization	$100,000	
Bench-scale tests	$50,000	
Engineering design	$45,000	
Materials		
Iron	$17,600	
Barrier Construction		
Site preparation and barrier emplacement	$121,000	
Monitoring network	$30,000	
Disposal of trench spoils	$0	
Total Barrier Construction Costs		$363,600
Maintenance costs (20 months)	$0	
Groundwater monitoring	$210,000	
PRB core collection and analysis	$30,000	
Total Operation and Maintenance Costs		$240,000
Total Demonstration Cost		$603,600

6.2 SUMMARY OF VALIDATION COSTS FOR THE DEMONSTRATION

In addition to the costs described in Section 6.1, there were a number of additional costs that fall in the area of validation rather than demonstration. (We believe this is the case because they do not directly involve the project performance criteria.) These activities were deemed necessary in order to meet peer-reviewed science standards.

Table 13. Validation Costs for the Demonstration.

Item	Sub-Total ($)	Total Cost ($)
Hydraulic conductivity characterization	$60,000	
In situ reactivity testing	$30,000	
Other validation costs	$60,000	
Microbial characterization	$15,000	
Total Validation Costs		$165,000

6.3 SCALE-UP RECOMMENDATIONS

6.3.1 Options for Design of Full-Scale Barriers for Explosives

ZVI is extremely effective at degrading explosives in groundwater. In that context, the design of the PRB was more than required to meet the needs of the site. Alternate installation approaches (e.g., continuous trenching) could be more cost effective. Mobilization costs for a continuous trencher were too high for this demonstration but might be appropriate for full-scale implementation.

Construction of the PRB with lower iron content could also have been appropriate, given the reactivity of the explosives to the iron. However, the cost of the iron was relatively small and there may be installation issues that would argue against this approach.

Finally, in the context of this particular site, groundwater chemistry was almost naturally-reducing enough to degrade the contaminants. It is likely that other approaches (e.g., edible oils) could also have been effective at a lower cost.

6.3.2 Cost of Full-Scale Barriers for Explosives at CAAP

The full widths of the groundwater plumes at their sources at CAAP are on the order of 1,000 feet (300 m). The bulk of the contaminants near the sources at the load lines are found at depths from 15-35 ft (20 ft or 6 m vertical thickness[3]). Thus, it is likely that approximately 20,000 sq ft (1,800 m^2) of PRB would be required to capture an entire plume. The cost of a full-scale PRB could likely be reduced to \$150/ft^2 (\$1,670/m^2)[4]. Thus, it is likely that the capital costs associated with a full-scale PRB would be on the order of $3,000,000. There are four primary sources at the site (Load Lines 1-4) so, if all of those plumes are to be addressed, the capital costs would be $12,000,000.

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[3] Based on the hydraulic performance observed at the site, it may be prudent to install a wall with somewhat greater vertical thickness. However, since the degradation in PRB performance is likely to be avoidable if proper care is taken in removal of the guar, this may not be necessary.

[4] This cost analysis is based on a 3-ft longitudinal thickness. This thickness was chosen because it is consistent with the bucket widths of most large, conventional excavators. For the case of large PRB, such as the one described here, it may be appropriate to mobilize specialty equipment, which might include a narrower bucket. This could result in some cost savings, particularly for iron. However, given the current relatively low cost of iron, this is not a major consideration. It may, however, prove advantageous from a hydraulic perspective to maintain the 3-ft width but reduce the iron content of the PRB, if the reaction conditions are appropriate.

6.3.3 Life-Cycle Analysis

Because PRB are long-term technology applications, the capital investment and annual O&M costs cannot simply be added up to obtain a total cost. This is because the capital investment is a cost that is incurred immediately, whereas O&M costs for a long-term PRB (just as with a pump-and-treat system) are spread over several years or decades. Therefore, a present value (PV) calculation is used to obtain the overall or life-cycle cost of the PRB. In Table 14 a real rate of return of 2.9%, as was recommended by the Office of Management and Budget (OMB) in 2000 for long-term (30-year) projects was used to estimate PV. The PV of the PRB at CAAP is estimated at $~24 million over 30 years, assuming that iron replacement will be required after 15 years.

Table 14. Cost Comparison of Full-Scale PRB to the Current P&T Operation.

	PRB			**P&T**			
Years of Operation	**Annual Cost***	**PV of Annual Cost**	**Cumulative PV of Annual Cost**	**Annual Cost****	**PV of Annual Cost**	**Cumulative PV of Annual Cost**	**Cost Savings for PRB**
0	12,200,000	12,200,000	12,200,000	10,200,000	10,200,000	10,200,000	-2,000,000
1	200,000	194,363	12,394,363	1,200,000	1,166,181	11,366,181	-1,028,183
2	200,000	188,886	12,583,249	1,200,000	1,133,315	12,499,495	-83,754
3	200,000	183,562	12,766,812	1,200,000	1,101,375	13,600,870	834,058
4	200,000	178,389	12,945,201	1,200,000	1,070,335	14,671,205	1,726,004
5	200,000	173,362	13,118,563	1,200,000	1,040,170	15,711,375	2,592,813
6	200,000	168,476	13,287,038	1,200,000	1,010,855	16,722,231	3,435,192
7	200,000	163,728	13,450,766	1,200,000	982,367	17,704,597	4,253,831
8	200,000	159,113	13,609,880	1,200,000	954,681	18,659,278	5,049,399
9	200,000	154,629	13,764,509	1,200,000	927,775	19,587,054	5,822,545
10	200,000	150,271	13,914,780	1,200,000	901,628	20,488,682	6,573,902
11	200,000	146,036	14,060,817	1,200,000	876,218	21,364,900	7,304,083
12	200,000	141,921	14,202,737	1,200,000	851,524	22,216,424	8,013,686
13	200,000	137,921	14,340,658	1,200,000	827,525	23,043,949	8,703,291
14	200,000	134,034	14,474,692	1,200,000	804,204	23,848,153	9,373,460
15	12,200,000	7,945,646	22,420,338	1,200,000	781,539	24,629,692	2,209,353
16	200,000	126,586	22,546,924	1,200,000	759,513	25,389,205	2,842,281
17	200,000	123,018	22,669,942	1,200,000	738,108	26,127,313	3,457,371
18	200,000	119,551	22,789,493	1,200,000	717,306	26,844,619	4,055,126
19	200,000	116,182	22,905,674	1,200,000	697,090	27,541,709	4,636,035
20	200,000	112,907	23,018,582	1,200,000	677,445	28,219,154	5,200,572
21	200,000	109,725	23,128,307	1,200,000	658,352	28,877,506	5,749,199
22	200,000	106,633	23,234,940	1,200,000	639,798	29,517,304	6,282,364
23	200,000	103,628	23,338,568	1,200,000	621,767	30,139,071	6,800,503
24	200,000	100,707	23,439,275	1,200,000	604,244	30,743,315	7,304,040
25	200,000	97,869	23,537,144	1,200,000	587,215	31,330,530	7,793,385
26	200,000	95,111	23,632,255	1,200,000	570,665	31,901,195	8,268,940
27	200,000	92,430	23,724,686	1,200,000	554,582	32,455,777	8,731,092
28	200,000	89,825	23,814,511	1,200,000	538,953	32,994,730	9,180,219
29	200,000	87,294	23,901,805	1,200,000	523,764	33,518,494	9,616,689
30	200,000	84,834	23,986,639	1,200,000	509,003	34,027,496	10,040,858

*Annual PRB O&M costs (including groundwater monitoring) = $200,000

**Annual P&T O&M costs (including groundwater monitoring [U.S. Army, 2001]) = $1,200,000

P&T capital costs = $9,000,000

6.4 COST COMPARISON

Table 14 summarizes the costs of this full-scale barrier illustration and compares it to the existing alternate technology (pump and treat with carbon filtration). Capital costs for the CAAP P&T facility (not including wells and associated plumbing) was $9 million. The annual O&M cost of the pump-and-treat system was estimated by the U.S. Army (2001) to be 1.2 million/year. The pump-and-treat system is expected to continue in an open-ended manner into the future. Table 14 summarizes the comparison of permeable barrier and pump-and-treat options based on the PV of the estimated costs (that is, the estimated costs in today's dollars). As mentioned above, a real rate of return of 2.9% was used in the calculations as the discount rate. As seen in Table 14, the permeable barrier requires a higher initial capital investment. However, over time, the O&M savings keep accruing and the permeable barrier breaks even in approximately the second year, based on these calculations. O&M costs (including monitoring and barrier maintenance costs) are factored in annually. Calculations of cost savings (or additional costs) for the permeable barrier are shown in the last column. In the second year, the PV cost of the pump-and-treat system exceeds that of the permeable barrier, indicating that the permeable barrier is more cost-effective over the long term.

7.0 IMPLEMENTATION ISSUES

7.1 COST OBSERVATIONS

The costs associated with this ZVI PRB demonstration are consistent with other ZVI PRB sites. The calculated installation cost per square foot was ~$180. Monitoring costs were considerably higher than would be the case at a full-scale installation because of the detailed multilevel samplers installed at the demonstration site.

7.2 PERFORMANCE OBSERVATIONS

As with previous PRB projects, actual flow through the PRB was difficult to determine with certainty. A variety of tools was utilized, including mass balance analysis, detailed hydraulic conductivity determinations, numerical modeling, geochemical changes, and tracer tests. All of these presented a consistent picture that flow through the PRB was less than expected based on the regional hydraulic gradient and hydraulic conductivity. It is our conclusion that reduced flow was not due to degradation of the explosives but was likely due to the guar used during PRB emplacement. This could have resulted from the movement of guar into the formation prior to and during emplacement, or to microbiological changes resulting from an influx of carbon from the guar.

7.3 REGULATORY ISSUES

Regulatory issues did not pose any problems for this demonstration. However, our ability to use direct-push wells was contingent on the fact that we were located on a federal facility and thus did not have to comply with current state regulations about the construction of wells. State of Nebraska regulators were very helpful in this context; however, this may not be the case in other states where current regulations do not reflect changing understanding of the role of direct-push wells.

7.4 RESEARCH NEEDS

The two primary research needs that were evidenced in this project relate to 1) measurement of flux through PRB and 2) assessment of the role of guar in limiting flow through the PRB. Neither of these is specific to the treatment of explosives, and both have been previously identified. Nevertheless, they both remain important issues in the context of assessing field performance of PRB.

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APPENDIX A

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