Evaluation of Permeable Reactive Barrier Performance

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Evaluation of Permeable Reactive Barrier Performance

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Tri-Agency Permeable Reactive Barrier Initiative

Members:
U.S. Department of Defense
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and

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Naval Facilities Engineering Service Center (NFESC), Port Hueneme, California and Battelle, Columbus, Ohio are the coordinating partners for the DoD study. Battelle coordinated the preparation of this report for the Tri-Agency PRB Initiative, a consortium that was formed to leverage the resources, expertise, and site experience of the three agencies. The Tri-Agency PRB Initiative operates under the umbrella of the Federal Remediation Technologies Roundtable. Charles Reeter is the project officer at NFESC for this study. Arun Gavaskar (Project Manager), Bruce Sass, Neeraj Gupta, Eric Drescher, Woong-Sang Yoon, Joel Sminchak, James Hicks, and Wendy Condit from Battelle conducted the investigation of PRB performance at DoD sites.

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Matt Turner with New Jersey Department of Environmental Protection (NJDEP) coordinated the ITRC contribution and played an important role in disseminating the study results through other ITRC members and through the ITRC website.

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ABBREVIATIONS AND ACRONYMS

AFB	Air Force Base
AFRL	Air Force Research Laboratory
AFCEE	Air Force Center for Environmental Excellence
Cl^-	chloride
CVOC	chlorinated volatile organic compounds
DCE	dichloroethylene
DFC	Denver Federal Center
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
EM	Environmental Management
ESTCP	Environmental Security Technology Certification Program
Fe (II)	ferrous iron
FHWA	Federal Highway Administration
FY	Fiscal Year
GSA	General Services Administration
ICPS	inductively coupled plasma spectrometry
ITRC	Interstate Technology Regulatory Council
MCL	maximum contaminant level
NAS	Naval Air Station
NFESC	Naval Facilities Engineering Service Center
NO_3^-	nitrate
NRMRL	National Risk Management Research Laboratory
O&M	operation and maintenance
ORD	Office of Research and Development
ORP	oxidation-reduction potential
PCE	perchloroethylene
PLFA	phospholipid fatty acids
PRB	permeable reactive barriers
PV	present value
RFI	RCRA Facility Investigation
RI/FS	Remedial Investigation/Feasibility Study
RPM	remedial program manager
S^{2-}	sulfide
SO_4^{2-}	sulfate

SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethylene
TDS	total dissolved solids
U.S.	United States
U.S. EPA	United States Environmental Protection Agency
USACE	U.S. Army Corps of Engineers
USCG-SC	U.S. Coast Guard Support Center
VC	vinyl chloride
VOC	volatile organic compound

1.0 INTRODUCTION

Permeable reactive barriers (PRB) are developing into an entire new class of technologies for groundwater remediation. A permeable barrier is a porous “barrier” that is placed in the path of a groundwater plume, in various configurations. The barrier, or at least the permeable portion of the barrier, contains a reactive or adsorptive medium that helps remove the contaminants from the plume, as the groundwater flows through the barrier. The primary advantage of permeable barriers is their passive operation and the resulting potential for long-term cost savings.

The technology emerged in the mid-1990s with the use of granular zero-valent iron as a reactive medium for treatment of groundwater contaminated with chlorinated volatile organic compounds (CVOCs), such as trichloroethylene (TCE) and perchloroethylene (PCE). More recently, there is interest in developing other treatment media and methods of construction to address a broader variety of contaminants and sites.

1.1 Goal of Tri-Agency PRB Projects

In February 2000, representatives of the United States (U.S.) Department of Defense (DoD), U.S. Department of Energy (DOE), and U.S. Environmental Protection Agency formed the Tri-Agency PRB Initiative to coordinate the evaluation of this important technology. The combined expertise and experience of these three government agencies resulted in critical information sharing and strategy formulation that maximized the efficiencies of the three studies. The Interstate Technology and Regulatory Council (ITRC), a consortium of 40 state environmental agencies, partnered with DoD to support this initiative.

Under this initiative, the three agencies conducted field performance evaluations of several PRBs installed at sites under their purview. The general goal was to evaluate the longevity and hydraulic performance of several PRBs in various geologic settings. These are the two issues that the agencies identified as being the most important to address, based on the experience at several PRB sites across the country. The results of these studies are being provided to the remedial program managers (RPMs) at government owned sites to aid in decision-making at both existing PRB sites and sites where PRBs may be applicable. In addition, the results of these studies are being widely disseminated to potential government and industrial users through distribution of the project reports on government websites, as well as through more targeted distribution to interested parties.

The three agencies (and ITRC) coordinated their efforts through periodic teleconferences and meetings. At these conferences, the agencies updated each other on their ongoing field evaluation efforts, important results, and future monitoring plans. This constant flow of information allowed each agency to adjust its evaluation strategy with every new piece of information. In this fashion, lessons learned were quickly incorporated and efforts were realigned in appropriate directions. This report contains a summary of the conclusions and recommendations from the three studies.

1.2 Project Coordinators

Naval Facilities Engineering Service Center (NFESC), Port Hueneme, California and its coordinating partner Battelle, Columbus, Ohio conducted the performance evaluation of PRBs at DoD-owned sites. The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) sponsored the DoD study. Other partners in the DoD study included the following organizations:

- ☐ U.S. Army Corps of Engineers (USACE)
- ☐ Air Force Research Laboratory (AFRL)
- ☐ Air Force Center for Environmental Excellence (AFCEE), through its coordinating partner, Waste Policy Institute, Texas.

Oak Ridge National Laboratory, Oak Ridge, Tennessee, the coordinating partner for DOE's Environmental Management (EM) 50 Program, conducted the evaluation at DOE-owned sites. The U.S. EPA study was conducted by the Subsurface Protection and Remediation Division of the National Risk Management Research Laboratory, U.S. EPA, Ada, Oklahoma. The U.S. EPA study was facilitated by cooperation with the U.S. Coast Guard Support Center (USCG-SC), Federal Highway Administration (FHWA), and General Services Administration (GSA).

In addition to this summary report, the three agencies prepared detailed reports describing the methodology and results of their evaluations (Gavaskar et al., 2002; Liang et al., 2001; and Wilkin et al., 2002).

1.3 Project Objectives and Technical Approach

The two primary objectives of the three agencies' studies were:

- Assessing the longevity of PRBs made from iron, the most common reactive medium used so far. Longevity refers to the ability of a PRB to maintain its reactivity and hydraulic performance (residence time and capture zone) in the years following its field installation.

- Assessing the hydraulic performance of various PRBs in terms of their ability to capture the targeted portion of the upgradient plume and to provide the influent groundwater with the required residence time in the reactive medium.

The general technical approach followed by the three agencies consisted of one or more of the following elements:

- Reviewing existing field data from existing PRBs

- Conducting additional treatability studies, field PRB monitoring, and computerized modeling at selected PRB sites to fill in any data gaps

- Recommend suitable long-term design/monitoring strategies for existing and new permeable barriers.

Although field data from PRBs at several sites initially were examined, the study subsequently focused on those sites that afforded the necessary range of site characteristics and PRB designs. In addition, sites with a longer history of operation were selected, especially for the longevity evaluation. The DoD study focused primarily on PRBs installed at the following sites:

- Former Naval Air Station (NAS) Moffett Field, California
- Former Lowry Air Force Base (AFB), Colorado
- Seneca Army Depot, New York
- Dover AFB, Delaware.

The DOE study focused on the PRBs installed at the following sites:

- Y-12 Security Complex, Tennessee
- Uranium Mill Tailings Site, Monticello, Utah
- Rocky Flats Site, Colorado
- Kansas City Plant, Missouri
- Paducah Gaseous Diffusion Plant, Kentucky
- Portsmouth Plant, Ohio.

The objective of the research conducted in U.S. EPA's portion of the Tri-Agency Initiative is to evaluate the geochemical and microbiological processes within zero-valent iron treatment zones in permeable reactive barriers that may contribute to decreases in iron reactivity and decreases in reaction zone permeability that, in turn, may eventually lead to system plugging and failure. Using advanced surface analytical techniques together with detailed coring and water sampling programs at two geographically, hydrogeologically, and geochemically distinct iron barrier installation sites, specific research objectives were to:

1) Characterize the type and nature of surface precipitates forming over time at the upgradient aquifer/iron interface, within the iron zone, and at the downgradient/iron interface

2) Develop conceptual models that predict the type and rate of precipitate formation based on iron characteristics and water chemistry

3) Identify type and extent of microbiological activity upgradient, within and downgradient in at least one of the chosen sites to evaluate microbiological response or effects from emplaced iron into an aquifer system

4) Develop practical and cost-effective protocols for long-term performance assessments at permeable reactive barrier installations.

Two field sites were evaluated in the U.S. EPA portion of the TRI:

- U.S. Coast Guard Support Center (USCG-SC) site near Elizabeth City, North Carolina, and
- Denver Federal Center (DFC) in Lakewood, Colorado.

These sites provided a range of PRB designs and hydrogeologic characteristics that could be studied so that appropriate guidance could be provided for future applications. The sites studied also had a broad range of contaminants, such as TCE, PCE, chromium, and radionuclides.

The longevity evaluation conducted by the three agencies consisted of one or more of the following elements:

- Groundwater geochemistry monitoring
- Iron core collection and analysis
- Geochemical modeling
- Accelerated column tests

The longevity of iron barriers is potentially limited by formation of precipitates in the iron, upon long-term contact with groundwater. Common mineral precipitates found in field-installed zero-valent iron barriers and in columns designed to simulate field barrier processes include iron hydroxides and oxyhydroxides, iron sulfides, iron and calcium carbonates, and iron hydroxy carbonates and sulfates (green rusts). Mineral precipitation is not consistent from site to site, however, and some barriers contain many of these precipitates while others contain very little. Understanding the processes that control the rate and type of mineral precipitation is important in barrier planning and design as well as monitoring the performance of installed barriers.

The hydraulic performance evaluation conducted by the three agencies used one or more of the following tools:

- Water level measurements
- HydroTechnics™ in-situ flow sensors
- Colloidal borescope (down-hole instrument)
- Groundwater flow modeling

2.0 PRB EVALUATION AT DEPARTMENT OF DEFENSE SITES

Although field data from PRBs at several DoD sites initially were examined, the project subsequently focused on those sites that afforded the necessary range of site characteristics and PRB designs. The longevity evaluation focused primarily on two sites:

- Former Naval Air Station (NAS) Moffett Field
- Former Lowry AFB.

These two sites were selected because the PRBs there were installed a few months apart around the beginning of 1996 (that is, they had sufficient history of field operation) and because the groundwater at these sites was relatively high in total dissolved solids (TDS), an important factor in accelerating the determination of precipitation potential and longevity. The hydraulic performance evaluation focused primarily on four sites:

- Former NAS Moffett Field (funnel-and-gate)
- Former Lowry AFB (funnel-and-gate)
- Seneca Army Depot (continuous reactive barrier)
- Dover AFB (funnel with two gates).

These sites provided a range of PRB designs and hydrogeologic characteristics that could be studied so that appropriate guidance could be provided for future applications. In addition to these primary focus sites, PRBs at other sites, such as Cape Canaveral Air Station (Hangar K) and former NAS Alameda, initially were examined, but were de-emphasized as resources were focused on field investigations at sites that appeared to offer the most features of interest for the project. Also, a separate detailed study at former NAS Alameda (Einarson et al., 2000) provided sufficient information for this evaluation.

Tables 2-1, 2-2, and 2-3 summarize the important features of the PRBs at the two key sites, former NAS Moffett Field and former Lowry AFB.

2.1 Methods

The performance assessment objectives were achieved by using a select variety of tools that allowed the project to fill in the data gaps identified in the existing information from the PRB sites. Both performance objectives, longevity and hydraulic performance, presented significant challenges for the project. The strategy consisted of a combination of tools to address each objective and overcome the limitations of each individual tool.

2.1.1 Longevity Evaluation Strategy. From the beginning of the project, it was clear that developing predictions about the life of a granular iron barrier would be difficult, given the short history of the technology in the field, the lack of information on kinetic rates of precipitation and reactivity loss that could be used in predictive models, and the difficulty of conducting any kind of laboratory simulations that would mimic the exposure of the iron to many pore volumes (i.e., long periods) of groundwater. Tools that initially were used in the current project to evaluate longevity include the following:

☐ Analysis of inorganic constituents in groundwater influent and effluent
☐ Analysis of iron cores collected from field PRBs
☐ Geochemical modeling

Table 2-1. Design Features of PRBs at DoD Sites

PRB Site Name, City, State	Pilot/Full Scale (Installation Date)	Type of Barrier [(a)]	Reactive Medium	PTZ [(b)] and Reactive Medium Thickness	Gate/ Barrier Width (ft)	Barrier Depth (ft)	Amount of Iron (tons)	Source of Iron	Notes
Former NAS Moffett Field	April 1996	F&G	100% iron	2 ft PTZ, 6 ft iron	10	25	75	Peerless Metal Powders	
Former Lowry AFB	December 1995	F&G	100% iron	2 ft PTZ, 5 ft iron	10	17		Master Builder	

(a) F&G = Funnel and gate; CRB = Continuous reactive barrier

(b) Pretreatment zone (PTZ) is any medium used for homogenizing flow or chemically pre-treating the groundwater.

Use N/A for not available or not applicable.

Table 2-2. Site Hydrogeology and Hydraulic Parameters of the PRB at DoD Sites

PRB Site	Aquifer Conductivity (ft/day)	Groundwater Gradient (ft/ft)	Groundwater Velocity (ft/day)	Aquifer depth (ft bgs)	Water table depth (ft bgs)	Primary Contaminants and concentrations	Notes
Former NAS Moffett Field	0.1 to 633	0.005 to 0.009	0.0017 to 19.0	25	5	TCE (1,700 µg/L)	
Former Lowry AFB	1.1 to 3.1	0.035	0.013 to 0.36	17	6	TCE (71 µg/L)	

Table 2-3. Site Groundwater Geochemistry at DoD Sites

PRB Site	pH	ORP (mV)	DO (mg/L)	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Alkalinity (mg/L)	Cl (mg/L)	SO4 (mg/L)	NO3 (mg/L)	Silica (mg/L)	Other (mg/L)	Notes
Former NAS Moffett Field	7.0	134	0.6	820	180	65	390	45	360	3.1	24		
Former Lowry AFB	6.9	-13.2	0.66	2,900	290	86	530	100	1,000	4	24		

Tools that have become fairly conventional for evaluating precipitation in field PRBs include groundwater monitoring (influent and effluent) and iron core collection and analysis. By analyzing the groundwater influent and effluent (or upgradient and downgradient) to the PRB, the loss of inorganic constituents (e.g., calcium, magnesium, alkalinity, sulfate, silicate, etc.) sustained by the groundwater can be measured as it moves through the reactive cell of the PRB. The differences in or loss of groundwater constituents represents the potential precipitation that has occurred in the PRB. However, there are two challenges to using these tools:

- First, the losses in inorganic constituents measured in the groundwater often do not match the amount of precipitate observed on core samples of iron collected from the PRB. This mismatch can partly be explained by the fact that there is considerable uncertainty in the spatial extrapolation of the amount of precipitate observed on small core samples of iron to the rest of the reactive cell, as precipitates may be unevenly deposited in different parts of the iron.

- Second, even if the amount of precipitate formed could be accurately determined, it is unclear how these precipitates distribute on the iron surfaces (whether in mono-layers that use up maximum surface area or in multiple layers that conserve the available reactive sites). Also, because the mechanism through which the precipitates may be bound to the iron and the process by which electrons are transferred between the iron and the contaminants is unclear, it is difficult to correlate loss of surface area with loss of reactivity. In other words, could iron continue to react with the contaminants through a layer of precipitates on its surface?

Geochemical modeling previously has been used to elucidate the precipitation process (Battelle, 1998; Gavaskar et al., 2000; Sass et al., 2001). Two types of models are available – equilibrium models (models that assume an infinitely long contact time between the iron and the groundwater constituents) and kinetic models (models that can be can be calibrated to contact time, if the various reaction kinetics or rate constants involved are known). Because the kinetics of iron-groundwater reactions have not yet been documented, although attempts have been made by some researchers (Yabusaki et al., 2001) to do that, kinetic models have limited applicability. However, equilibrium models are useful for identifying the *types*, if not the quantity, of precipitates; these models were used in the current project to understand the kinds of precipitation reactions occurring in the iron and provide some indication of what to look for when analyzing the iron cores.

Given the limitations of the indicative tools described above, there was a need for *direct* empirical evidence of any decline in reactivity of the iron due to exposure to groundwater. Therefore, accelerated column tests were conducted to simulate the field performance of PRBs at former NAS Moffett Field and former Lowry AFB. The objective of the accelerated column tests was to examine if and to what extent the reaction rates (or half lives) of the contaminants would deteriorate when the iron was exposed to many pore volumes (i.e., long periods) of contaminated groundwater flow. Unlike tests conducted by John Hopkins University (Arnold and Roberts, 2000; Totten et al., 2001), which currently is studying the effect of individual inorganic and organic constituents in groundwater on the iron, the accelerated column tests in the current project were conducted with actual groundwater from the two sites (former NAS Moffett Field and former NAS Lowry AFB) simulated. The same iron that is in these PRBs (Peerless Metal Products, Inc., iron at for NAS Moffett Field, and Master Builder, Inc., iron at former Lowry AFB) was used to pack the two columns. A small amount of oxygen scavenger was added to the groundwater influent to the columns to restore the low dissolved oxygen (DO) levels of the native groundwater, because the groundwater is relatively anaerobic at both sites. Therefore, the interplay of factors occurring in the two field PRBs were simulated as closely as possible.

Higher groundwater flowrates were maintained in the columns than were present in the field PRBs, in order to accelerate the exposure of the iron to the groundwater. Previous studies (O'Hannesin, 1993) have shown that contaminant half-lives are independent of the flowrate; this was confirmed through half-life measurements conducted at different flowrates during the current project. Accelerating the flow through the column permits an examination of the changes in reactivity of the iron when exposed to many pore volumes (or several years) of groundwater flow. Given the short history of field PRBs (6 years maximum), this simulation provides valuable insights into the future behavior of the iron-groundwater systems at these sites.

2.1.2 Hydraulic Performance Evaluation Strategy. The permeable reactive barriers technology relies upon the use of hydraulic characteristics of the site for successful performance over the short- and long-term. Therefore, a careful consideration of the hydrogeologic issues must be incorporated at all stages of the project: site screening, characterization, design, construction, and performance assessment. Most of the reports about sub-optimum performance at some PRB sites may be attributed to hydraulic factors. The issues of concern include insufficient residence time resulting in contaminant breakthrough, inability to verify flow through the reactive cell, plume bypass around, under, or over the barrier, seasonal fluctuations in groundwater flow that result in variation in performance, and effect of nearby site features such as drains, surface water, operating pump-and-treat systems, etc. Almost all of these issues can be related to the two primary objectives involved in designing a PRB and monitoring its hydraulic performance:

- Ensuring that the PRB will capture the desired portion of the plume, and
- Ensuring that the desired residence time in the reactive cell will be met.

Thus the two primary interdependent parameters of concern when designing a PRB are hydraulic capture zone width and residence time. Capture zone width refers to the width of the zone of groundwater that will pass through the reactive cell or gate (in the case of funnel-and-gate configurations) rather than pass around the ends of the barrier or beneath it. Capture zone width can be maximized by maximizing the discharge (groundwater flow volume) through the reactive cell or gate. Residence time refers to the amount of time contaminated groundwater is in contact with the reactive medium within the gate. Residence times can be maximized either by minimizing the discharge through the reactive cell or by increasing the flowthrough thickness of the reactive cell. Thus, the design of PRBs must balance the need to maximize capture zone width (and discharge) against the desire to increase the residence time. Contamination occurring outside the capture zone will not pass through the reactive cell. On the other hand, if the residence time in the reactive cell is too short, contaminant levels may not be reduced sufficiently to meet regulatory requirements.

The basic tools and methods that can be used at various stages of a PRB project for improving the probability of successful implementation have been discussed in details in the design guidance (Gavaskar et al., 2000). The two classes of design used in the current study are:

- Site Characterization – this includes developing a detailed understanding of the site geology, hydrogeology, contaminant distribution, and seasonal fluctuations and incorporating the ranges in these aspects into the PRB design to maximize successful implementation.

- Groundwater Flow Modeling – this includes incorporating the site parameters into the computer simulation tools so that the spatial and temporal variations in these parameters can be evaluated and the appropriate safety factors can be determined for PRB design and monitoring system configuration.

The hydraulic performance evaluation strategy consisted of two major elements. One, an effort was made to conduct more detailed characterization of the flow regime around existing field barriers. Two, groundwater modeling was used to obtain a better understanding of the various factors that determine flow at these PRB sites. The objective was to get a better understanding of the groundwater capture zone and residence time at these sites. Therefore, most of the evaluation was conducted on the upgradient side of the PRBs. Groundwater flow direction and velocity ultimately are the two key parameters that need to be estimated to make this determination. The evaluation included the following tools:

- Water-level measurements
- Slug tests
- In-situ flow sensors
- Colloidal borescope
- Groundwater modeling.

Former NAS Moffett Field, Lowry AFB, Seneca Army Depot, and Dover AFB were the sites subjected to a more detailed evaluation. These sites provided a wide range of site and PRB design characteristics.

2.2 Former NAS Moffett Field (Mountain View, CA)

Both geochemistry and hydrologic issues were evaluated at this site, which has a pilot-scale funnel-and-gate system for a regional TCE plume.

2.2.1 Site Description. The funnel-and-gate PRB at the former NAS Moffett Field PRB site has been monitored and evaluated in significant details as part of a previous ESTCP project (Battelle, 1998). The surficial aquifer at this site is divided into two aquifer zones–a shallow zone (A1) and a deep zone (A2). The barrier is installed in the A1 zone of the surficial semi-confined aquifer at the site. The A1 aquifer zone is approximately 25 ft deep. Borings at the site suggest that several sand channels exist in the otherwise silty sand aquifer. The barrier was installed in a funnel-and-gate configuration through a major sand channel (Figure 2-1) within the lower conductivity silty and clayey layers. In general, the site reflects channeled groundwater flow in a multi-layered aquifer system. Peerless Metal Powders, Inc., Detroit, Michigan, supplied the granular iron used in the PRB.

2.2.2 Results and Discussion. Following are results of the field performance measurements at NAS Moffett Field and results of the long-term column test with groundwater from NAS Moffett Field.

2.2.2.1 Groundwater Chemistry Evaluation. At former NAS Moffett Field, TCE, PCE, and cis-1,2 DCE in the effluent from the reactive cell iron continues to be below their respective MCLs and below detection. Most of the treatment occurred in the upgradient half of the iron. A noticeable clean groundwater front is not clearly identifiable in the downgradient aquifer, although there are some preliminary signs that it could occur in the future. After five years of PRB operation in the sand channel enclosed by silty clay sides, it was expected that introduction of CVOC-free groundwater effluent would lead to a noticeable improvement in downgradient groundwater quality, despite some contrary site conditions. One or more of the site conditions that could be acting to delay or prevent an improvement in downgradient groundwater quality are:

- Less groundwater flowing through the more conductive reactive cell or gate than is predicted or than is flowing around or below the PRB. In some wells screened at shallower depths, a proportionate relative decline in CVOC and inorganic constituents (e.g., calcium) is noticeable over time, which would support this scenario. CVOC levels

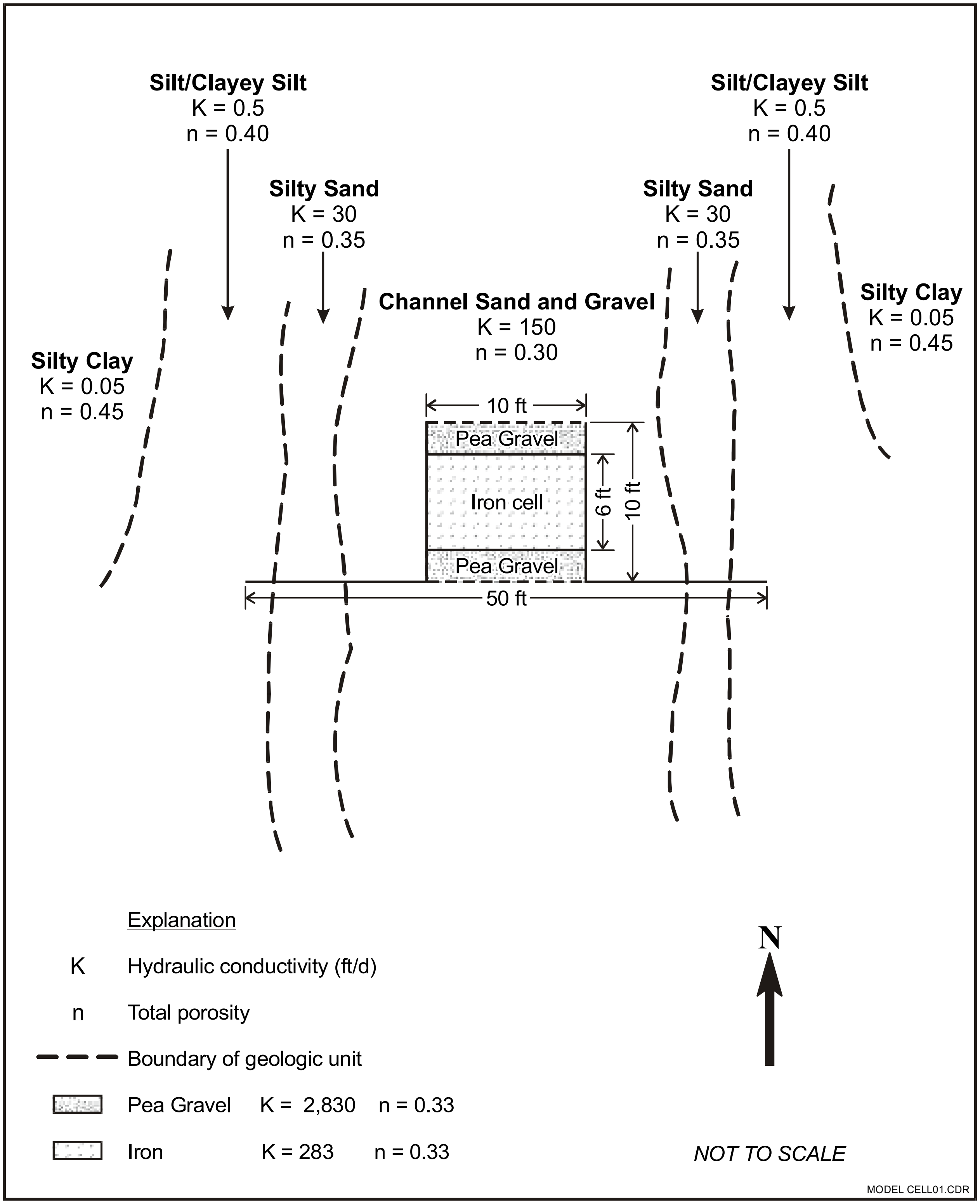


Figure 2-1. PRB at Former NAS Moffett Field Relative to Lithologic Variations in the Surrounding Aquifer

have declined somewhat over time in the upgradient aquifer too, making the determination more difficult.

- Recontamination of cleaner groundwater effluent from the PRB with contaminated groundwater flowing under the PRB (the pilot-scale PRB intentionally was not keyed into the clay layer for fearing of breaching a thin aquitard) or from the lower aquifer zone. The downgradient monitoring wells that are screened at a depth near the base of the PRB continue to be the most contaminated, indicating that there is underflow. However, vertical gradients that were upward in the vicinity of the PRB before PRB installation have consistently turned downward after the installation; this would tend to reduce the mixing of groundwater flowing under and through the PRB.
- Contaminated groundwater flowing around the funnel walls of the pilot-scale PRB that was designed to capture only a small part of a regional plume. This is less likely because the sand channel, which probably accounts for most of the groundwater flow in the local region of the PRB, directs flow mostly through the gate. The funnel walls encounter minimal additional groundwater flowing through the silty-clay deposits around the channel.
- Diffusion of CVOCs trapped in the silty clay layers surrounding the sand channel. This type of contaminant persistence has been observed at other sites, even with pump-and-treat systems. However, diffusion is a slow process and water quality improvement immediately downgradient of the PRB would still be expected.

2.2.2.2 Evaluation of Iron Cores and Silt Deposits. At former NAS Moffett Field, geochemical analysis of iron cores from the PRB showed the following:

- Calcium, silicon, and small amounts of sulfur were the elements identified on the iron particles.
- Aragonite, calcite (both forms of calcium carbonate), and iron carbonate hydroxide (similar to siderite) were the mineral species identified on the iron particles these minerals were concentrated in the iron samples collected from the upgradient edge of the reactive cell, indicating that the rest of the iron had not encountered much precipitation.

Calcite, iron oxyhydroxide (FeOOH) or goethite, ettringite (calcium-aluminum sulfate), and katoite (calcium-aluminum silicate) were the mineral species identified in the silt from the silt traps in the monitoring wells in the PRB at former NAS Moffett Field. The elements iron and magnesium were identified in the silt, but could not be associated with any particular mineral species. Some mineral species (such as feldspar, muscovite, mica and clay minerals) that probably originated from the pea gravel (granite) were also identified. The presence of minerals in the silt traps that are traceable to the groundwater indicates that not all the precipitates formed deposit on the iron medium. Finer, colloidal particles can be transported by the flow to other locations within the PRB, some of which become trapped in the monitoring wells.

2.2.2.3 Evaluation with Accelerated Column Tests. Long-term accelerated column tests were conducted with groundwater from the field PRBs at former NAS Moffett Field and former Lowry AFB. The columns were packed with fresh iron obtained from the same sources that were used at these two sites. The two columns were adjusted to a flow rate whereby pH and ORP reached a plateau (indicating that the majority of the reactions between the iron and groundwater had occurred in the column), but was fast enough that many pore volumes of groundwater could be passed through the column (or many years of PRB operation could be simulated). After some trial-and-error, a flow rate of 12.5 ft/day was eventually established as optimum for the column test. At this flow rate, all the precipitates generated stayed in the column (at higher flow rates, there was a tendency for finer precipitates to be transported out with the flow. If a representative normal flow rate of 0.5 ft/day is assumed at both sites, than the flow in the columns is accelerated 25 times. The 1,300 pore volumes of groundwater passed through each column and the 1.5 years of column testing simulate 30 years or more of operation of the field PRBs. A related test conducted with the same columns showed that the TCE half-life was independent of the flow rate over a wide range of flow rates.

The column tests show that over the 1,300 pore volumes of flow that the iron was exposed to, the half-life of TCE increased approximately by a factor of 2 in the Moffett Field column. While some effects of aging may be intrinsic to the iron, itself, or to the manufacturing process, the loss of reactivity is probably due to the inorganic content of the water and the subsequent precipitation of dissolved solids on the iron surfaces. Former NAS Moffett Field has groundwater with a moderate level (between 500 to 1,000 mg/L) of dissolved solids.

2.2.2.4 Hydrogeologic Evaluation. The purpose of hydrogeologic investigations conducted under the project was to evaluate the major issues related to capture zone and residence time based on these existing two classes of tools. These two hydraulic issues were investigated by:

- ☐ Conducting a field evaluation of PRBs at various DoD sites, and
- ☐ Conducting computer simulations to evaluate the effects of hydraulic variations and characterization uncertainties.

PRBs have been installed at DoD sites with a variety of site characteristics. Overall, the PRBs have been fairly effective over a wide range of site conditions.

Water level surveys provide information on groundwater gradients and capture zones for PRBs to demonstrate that groundwater is flowing through the barrier at a rate, which will ensure adequate destruction of the contamination. Several rounds of water level surveys were performed at the selected DoD PRB sites during the project. In general, the groundwater surveys demonstrated a positive gradient in the expected flow direction through the PRBs, that is, when gradients were measured from upgradient to downgradient aquifer. For example, positive gradients were observed in periodic monitoring of PRBs at Dover AFB, former NAS Moffett Field, Seneca Army Depot, and former Lowry AFB.

Within the PRBs themselves, hydraulic gradients were extremely flat, which is expected of highly permeable and porous media. A few transient flow reversals were reported, for example, at the Moffett Field site, but these occurrences appear to have been temporary and generally within the measurement error (Battelle, 1998). At former NAS Moffett Field, monitoring conducted during a previous project showed that some mounding appeared to be occurring at the downgradient end of the PRB, which may indicate that groundwater discharge from the highly permeable PRB media to the generally less permeable aquifer meets with some resistance. Among all the PRB sites evaluated under the current project, the PRB at former NAS Moffett Field provided the most certainty in terms of verifying a groundwater capture zone and occurrence of flow through the PRB, probably because the sand channel surrounded by silty-clay deposits constrained flow from diverging to the sides. Close examination of the water level data reveals flow divides occurring about half way across the length of each funnel wall. Based on these water levels an approximate estimate of capture zone is 30 ft. The capture zone includes the flow directly upgradient of the 10-ft-wide gate and halfway across 20-ft-wide funnel wall. Water-level surveys are a key monitoring activity for confirming gradients at PRB sites.

Based on a typical hydraulic gradient of 0.007, observed during water level mapping events, and a typical hydraulic conductivity of 30 ft/day, representative of slug test results in the sand channel, a typical groundwater velocity of 0.7 ft/day and a residence time of 9 days are estimated. This residence time estimate matches the results of a tracer test (Battelle, 1998) conducted during a previous project. The wide variability in the hydraulic conductivities measured at different locations in the aquifer and the likelihood of preferential pathways in the iron medium itself, as seen in the tracer test, create substantial uncertainty in the groundwater velocity and residence time estimates.

2.3 Former Lowry AFB (Denver, CO)

Lowry AFB has one of the first PRBs installed in the field; it was installed in December 1995 to address a TCE plume.

2.3.1 Site Description. The aquifer at former Lowry AFB is comprised of 11 ft of silty-sand to sand and gravel in an unconfined aquifer which overlies weathered claystone bedrock 23-30 ft bgs (Versar, Inc., 1997). Some degree of heterogeneity is present in the form of sand and clay lenses. The barrier was set up in a funnel-and-gate arrangement with funnel walls at an angle to the reactive cell (Figure 2-2). The iron for the barrier was supplied by Master Builders Supply, Streetsboro, Ohio.

2.3.2 Results and Discussion. The results of the field measurements and accelerated column tests for Lowry AFB are described in this section.

2.3.2.1 Groundwater Chemistry Evaluation at Former Lowry AFB. Groundwater samples were collected from the PRB at former Lowry AFB in the current project in September 1999, approximately 4 years after installation of the PRB. Groundwater samples were collected in all wells inside the reactive cell and in the upgradient and downgradient pea gravel zones that are adjacent to the reactive cell. In addition, aquifer wells were sampled immediately upgradient and downgradient of the reactive cell.

Results of groundwater sampling shows that TCE is the major contaminant in the groundwater; smaller concentrations of *cis*-DCE and *trans*-1,2-DCE also were observed in the aquifer. CVOC concentrations declined slightly in the upgradient pea gravel due to quick horizontal and vertical mixing in the porous zone. The contaminants were undetectable in most of the reactive cell wells and are entirely below detection in the downgradient portion of the cell. These results demonstrate that the reactive cell is degrading the contaminants to below their respective MCLs (<5 µg/L for PCE and TCE; <70 µg/L for DCE). TCE, *cis*-DCE, and *trans*-1,2-DCE are present in the downgradient aquifer as a result of mixing with contaminated groundwater flowing around the pilot-scale PRB. Trends such as rising pH, declining ORP, and declining DO as water moves into the reactive cell indicate that the barrier was functioning normally, after four years of operation. Lower conductivity values in the reactive cell wells compared to aquifer wells suggests some precipitation of solids inside the reactive cell.

Results of inorganic analysis shows a considerable decline in alkalinity, calcium, magnesium, silica, and sulfate as the groundwater flows through the reactive cell, which suggests mineral precipitation inside the barrier.

2.3.2.2 Iron Coring at Former Lowry AFB. Approximately 18 months after the former Lowry AFB barrier had been in operation, iron core samples were collected for analysis (Versar, 1997). The cores were sent to the University of Waterloo for mineralogical and microbiological analysis and the results were reported by EnviroMetal Technologies, Inc. (ETI, 2000). The mineralogical analysis showed that calcite and aragonite were the main carbonate minerals detected; however, siderite was found in one sample. A greater concentration of carbonates was found in the upgradient portion of the barrier than in the middle and downgradient portions. Core samples collected nearest the upgradient face contained 4 grams calcium carbonate per 100 grams of sample. Several other compounds were found throughout the reactive barrier including green rust, magnetite, and amorphous iron hydroxide. Microbiological analysis

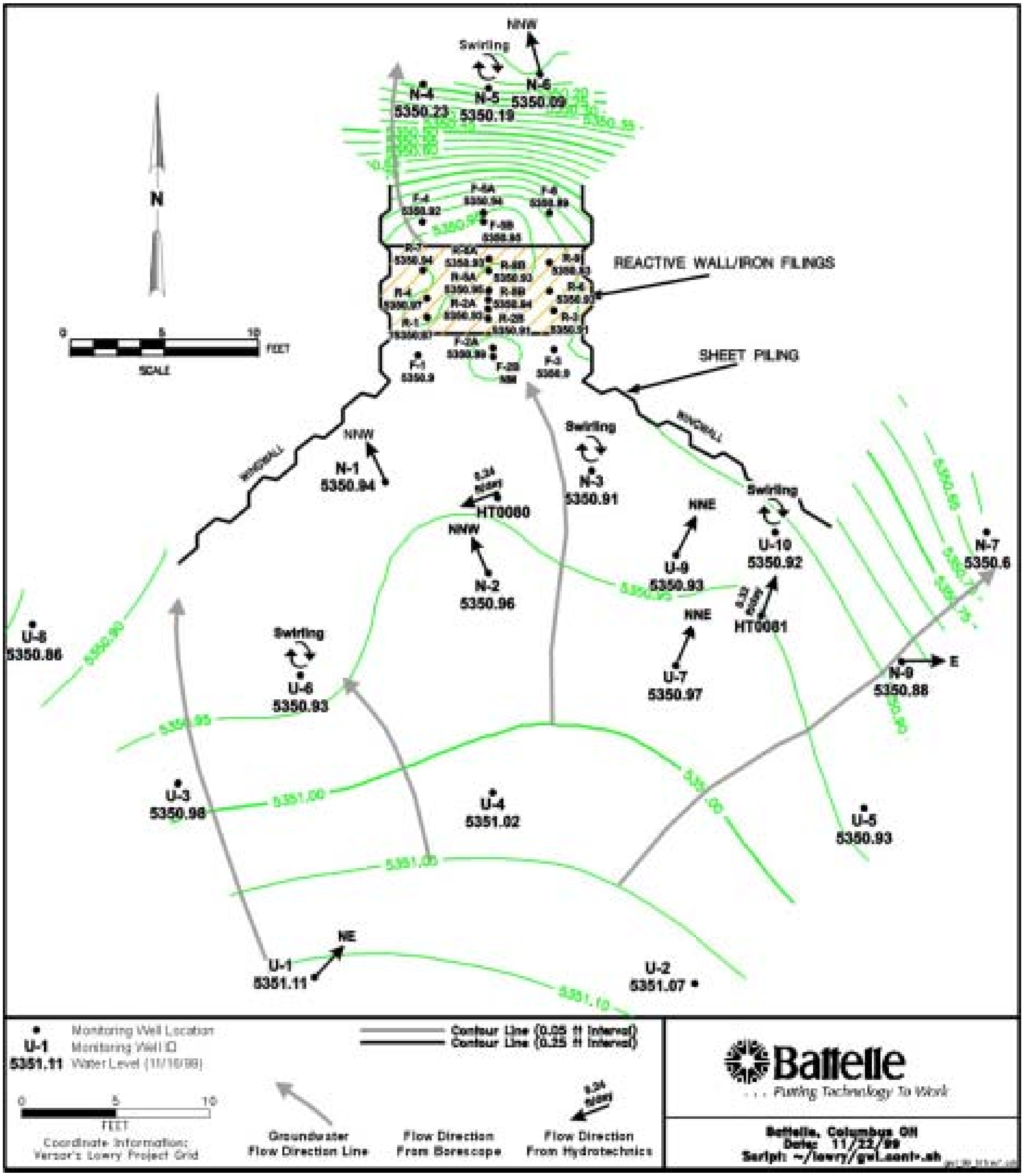


Figure 2-2. Design Hydraulic Flow Regime at Former Lowry AFB PRB

showed slightly higher microbial populations at the influent end than elsewhere within the wall. The microbial populations in the wall were thought to be of the same order of magnitude as in similar types of aquifers and soils.

Iron cores were collected at former Lowry AFB in September 1999, approximately 4 years after PRB installation. Results from the earlier study (ETI, 2000) differ in some aspects from those observed in the recent project. Most notable is the absence of calcium carbonate from the iron core samples collected in this project (in September 1999). Normally, XRD is very sensitive to calcite and aragonite, so these minerals are unlikely to have been overlooked in diffraction patterns. Also, the total carbon content was only about 2 percent and the analysis did not reveal an excess of carbon in the barrier samples compared to the control (unused) sample. Moreover, the carbon that was detected in the iron samples was attributed to the reduced (graphitic) carbon coatings. One explanation is that the recent samples were not collected sufficiently close to the upgradient interface where most of the carbonate precipitation is occurring. Another possibility is that the different analytical methods used in the two studies gave different results. The reason for the difference in carbonate detection in the two studies still is unclear.

2.3.2.3 Evaluation with Accelerated Column Tests. Long-term accelerated column tests were conducted with groundwater from the field PRBs at former NAS Moffett Field (see Section 2.2.2.3) and former Lowry AFB. The column tests show that over the 1,300 pore volumes of flow that the iron was exposed to, the half-life of TCE increased approximately by a factor of 4 in the Lowry AFB column, as compared to a factor of 2 in the Moffett Field column and. While some effects of aging may be intrinsic to the iron, itself, or to the manufacturing process, other differences may be due to the inorganic content of the water and the subsequent precipitation of dissolved solids. Former NAS Moffett Field has groundwater with a moderate level of dissolved solids (between 500 to 1,000 mg/L) and former Lowry AFB has groundwater with relatively high levels of dissolved solids (greater than 1,000 mg/L); consequently, Lowry AFB showed a greater decline in reactivity over the same period of exposure to groundwater as the Moffett Field column.

The column test results indicate the following:

- The geochemical constituents of the groundwater do affect the reactivity of the iron upon long-term exposure to groundwater.
- The rate of decline in iron reactivity over time is dependent on the native level of certain dissolved solids (e.g., alkalinity, sulfate, calcium, magnesium, and silica) in the groundwater.
- The PRB is likely to be passivated before the entire mass of zero-valent iron is used up, unless some way of regenerating or replacing the reactive medium is developed and implemented.

2.3.2.4 Hydrogeologic Evaluation. At Lowry AFB, gradients were relatively strong in the upgradient aquifer and indicated not only flow progressing in the expected direction toward the reactive cell, but also the asymmetric nature of the capture zone due to the effect of an adjacent stream on the east side. The capture zone at Lowry AFB appears to be approximately 20 ft wide, with 10 ft of capture directly upgradient of the gate and 10 ft along the western funnel wall. Most of the flow upgradient of the eastern funnel wall appears to be directed towards the flowing stream on the east. Based on the hydraulic conductivities measured during slug tests and the hydraulic gradient obtained from water level measurements, a typical groundwater velocity of 0.2 ft/day and a typical residence time of 25 days are estimated. A moderate variability in the hydraulic conductivity estimates in the sandy aquifer creates some uncertainty in these estimates.

At Lowry AFB, all the slug tests showed an exceptionally narrow conductivity range indicating a relatively homogeneous aquifer.

2.4 Other DoD Sites

Primarily hydrologic evaluations were conducted at two additional sites, Seneca Army Depot and Dover AFB, to obtain a broader perspective on hydraulic performance issues and the monitoring tools involved.

2.4.1 Seneca Army Depot (Romulus, NY).

Seneca Army Depot has a continuous reactive barrier that is one of the relatively longer PRBs that has been installed to capture a fairly wide TCE plume.

2.4.1.1 Site Description.

Groundwater flows through fractured shale and overlying glacial till at Seneca Army Depot (Parsons Engineering Services, Inc., 2000). The aquifer is unconfined. The PRB at Seneca is a 600-ft-long continuous trench, approximately 1 ft wide and keyed into competent shale bedrock 5-10 ft bgs (Figure 2-3). The barrier consists of a 50/50 mixture of sand and iron. Overall, the Seneca Army Depot site reflects a shallow glacial till aquifer with a long, thin PRB designed to treat a diffuse plume spread over a large area. During the current project, 14 new 2-inch monitoring wells were installed (two inside the PRB and 12 in the surrounding aquifer, near the northern end of the PRB) to determine the flow divide and the capture zone.

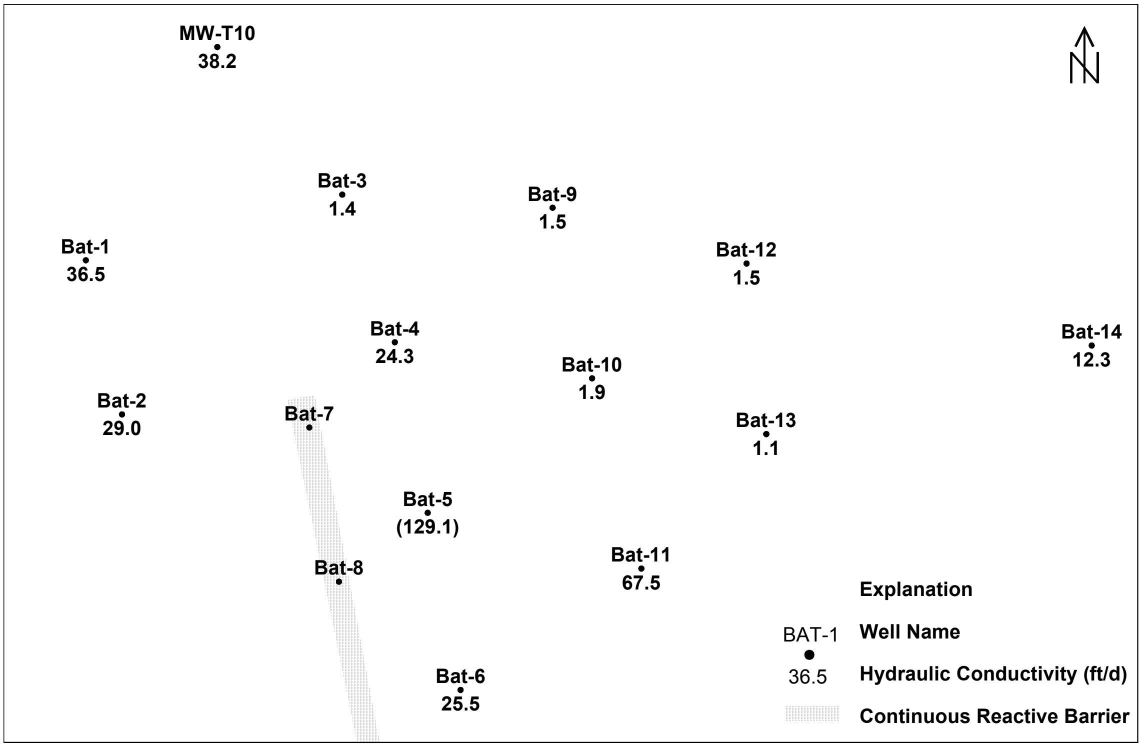


Figure 2-3. Hydraulic Conductivity Values (ft/d) from Slug Tests at the Seneca Army Depot CRB Showing Variations in Hydraulic Conductivity at the Site

2.4.1.2 Hydrogeologic Evaluation.

At Seneca Army Depot and Dover AFB, the flow divide and therefore the capture zone were difficult to determine. At Dover AFB, the native gradient itself is low. At Seneca Army Depot the difficulty was that the PRB was relatively thin (1 ft flowthrough thickness) and generated a very minor disturbance in the natural flow patterns.

At both these sites, uniformly screened monitoring wells and multiple monitoring events led to at least some events that afforded discernible groundwater flow trends. To conserve limited resources, the monitoring well network at Seneca Army Depot was limited to one end of the relatively long PRB. The water level map for this site for April 2001 shows a steep gradient immediately upgradient of the PRB and flat water levels farther away. It also shows that the flow lines are pointing towards the PRB at the northern end of the site indicating capture of the plume from that area. However, during July 2001 the water levels are flat upgradient of the PRB showing the seasonal effects on the flow patterns and residence times. In both cases there is a downward gradient from upgradient to downgradient wells indicating the flow is occurring through the PRB.

2.4.2 Dover AFB (Dover, DE).

Area 5 at Dover AFB has a funnel-and-gate type PRB that intercepts a PCE plume.

2.4.2.1 Site Description.

The funnel-and-gate PRB at Dover AFB was designed, installed, and monitored as part of a SERDP-funded project by Battelle (Battelle, 2000). The aquifer at the Dover AFB site consists of unconfined silty sand deposits overlying a thick clayey confining layer. The aquifer is approximately 20-25 ft thick and fairly homogenous, except for several silty-clay lenses in the upper portion of the aquifer. The hydraulic gradient in the area is fairly low (0.002) and variable, with noticeable seasonal fluctuations. The PRB consists of a funnel-and-gate system with two gates (Figure 2-4). Interlocking sheet piles (Waterloo Barrier™) constitute the funnel and caisson excavations filled with reactive media (iron) constitute the two gates. The Dover AFB site represents a low-flow velocity setting in a thick, homogenous aquifer. As part of the current project, water level measurements and colloidal borescope measurements were performed at this site.

2.4.2.2 Hydrogeologic Evaluation.

Seasonal fluctuations in the gradient must be accounted for in the analysis of water level data. For example, at Dover AFB, historical measurements indicated that groundwater flow direction changed by about 30° on a seasonal basis (Battelle, 2000). This had a considerable effect in determining an optimum design and orientation of the PRB so that the PRB was perpendicular to the flow during most times of the year. At least four quarters of water level data should be obtained to account for seasonal fluctuations in groundwater velocity and direction, before designing a PRB. In addition, information on long-term extremes in water levels and flow directions obtained from historical records, where available, should be considered in the designing PRBs.

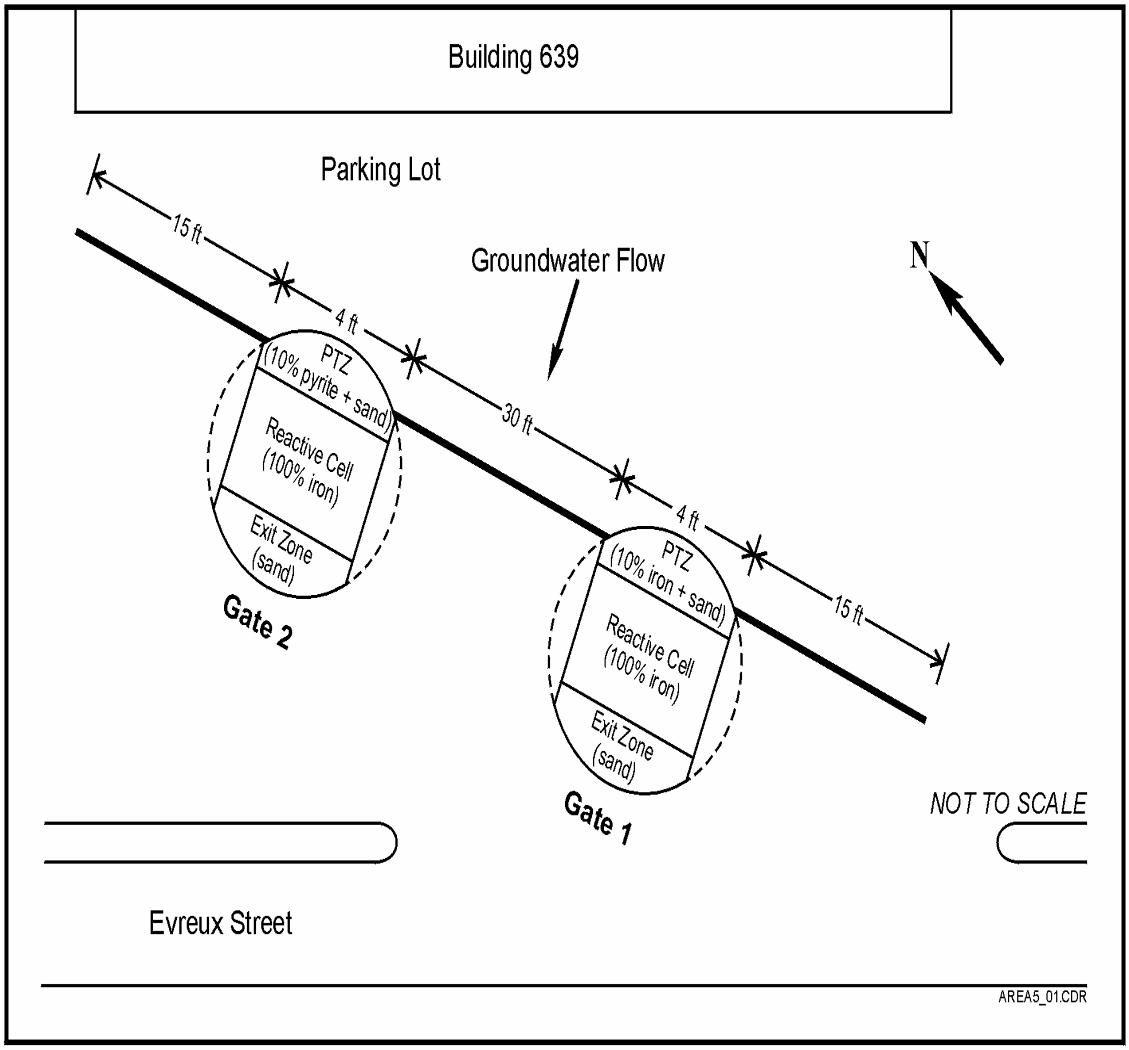


Figure 2-4. Plan View of PRB at Dover AFB

3.0 PRBs AT SITES EVALUATED BY U.S. EPA

The evaluation conducted by U.S. EPA focused on PRBs at Elizabeth City and Denver.

3.1 U.S. Coast Guard Support Center (Elizabeth City, NC)

A continuous trencher was used for the first time to install a PRB at this site.

3.1.1 Site Description. In June of 1996, a 46 m long, 7.3 m deep, and 0.6 m wide permeable reactive barrier (continuous wall configuration, Figure 3-1) of zero-valent iron was installed at the U.S. Coast Guard-Support Center site located in Elizabeth City, North Carolina (USCG-SC). The reactive wall was designed to remediate hexavalent chromium-contaminated groundwater, in addition, to treating portions of an overlapping, larger plume of trichloroethylene (TCE). A monitoring network of over 130 subsurface sampling points was installed in November of 1996 to provide detailed information on spatial and temporal changes in pore water geochemistry (Puls et al., 1999). Information about the design of this PRB and initial performance data were published in Blowes et al. (1999a,b).

3.1.2 Methods. Groundwater sampling, iron core analysis, and geochemical modeling were the methods used to evaluate the performance of this PRB.

3.1.2.1 Groundwater Sampling. Groundwater was sampled from monitoring wells using peristaltic or submersible pumps. In all cases, low-flow (150 to 250 mL/min) purging and sampling methods were used to minimize chemical and hydrological disturbances in an around the monitoring wells. Groundwater was pumped through a flow-through cell equipped with calibrated electrodes for pH, oxidation-reduction potential (ORP), specific conductance, and dissolved oxygen. Stabilization of electrode readings was tracked as a function of time (every 1 minute). Final values were recorded after 3 successive readings within ±0.10 for pH, ±10 mV for ORP, ±3% for specific conductance, and ±10% for dissolved oxygen. After stabilization of the electrode read-outs, turbidity was generally less than 5 NTUs. Filtered samples (0.45 µm) were collected for the analysis of anions and cations. Unfiltered samples were collected for the analysis of volatile organic compounds and dissolved gases.

Colorimetric methods were used in the field for determining concentrations of dissolved oxygen, Fe (II), and hydrogen sulfide. Ferrous iron and sulfide concentrations were measured using the 1,10 phenanthroline and methylene blue indicators, respectively. Dissolved oxygen was determined by using tests kits that utilize the indigo carmine indicator (DO>1 mg/L), but more typically the rhodazine D (DO<1 mg/L) colorimetric indicator was employed. Alkalinity determinations were conducted in the field by titrating samples with standardized sulfuric acid to the bromcresol green-methyl red endpoint.

Quality assurance and quality control practices for field measurements included frequent checks of electrodes against buffer solutions (pH, ORP, specific conductance). Dissolved oxygen measurements were checked by reading air-saturated water and comparing results with the temperature-dependent solubility of oxygen in water. In addition, sodium sulfite was added to water to test the performance of dissolved oxygen electrodes at low DO levels. Alkalinity measurements were checked by determinations of prepared sodium carbonate solutions and prepared ferrous ammonium sulfate solutions were used to check ferrous iron measurements. In general, the methods employed in this study were found to be suitable for the analysis of geochemical parameters at the PRB sites investigated in this study. It is worthwhile to note that ferrous iron measurements, ORP measurements, and DO measurements can be challenging at PRB sites and extra effort must be expended in order to collect high-quality data for these parameters. The high pH conditions frequently encountered at PRB sites favor rapid oxidation of Fe (II). Consequently, ferrous iron must be analyzed immediately after sample collection and the Fe (II)

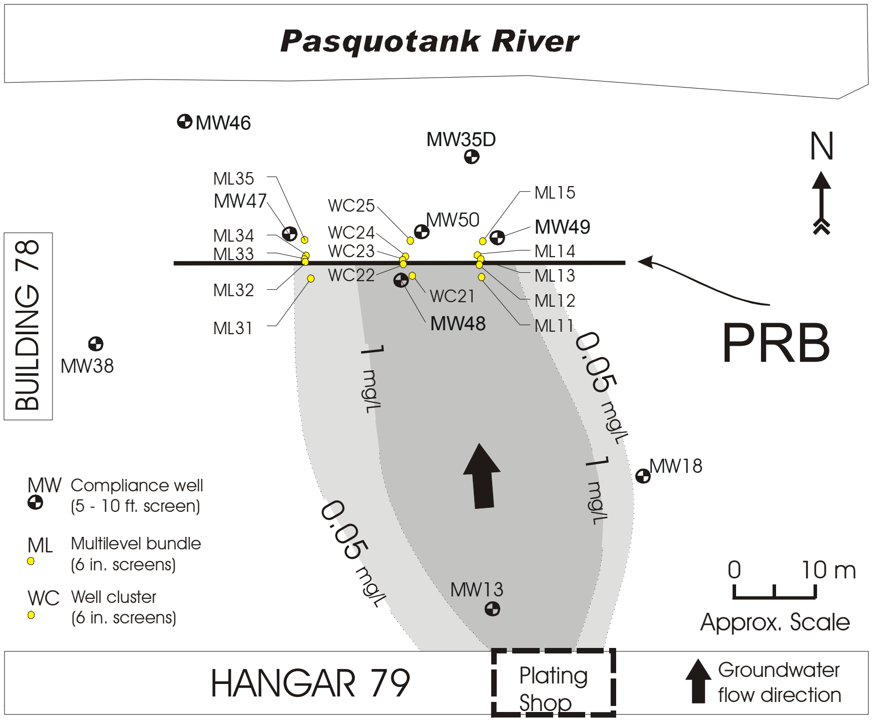


Figure 3-1. Plan View Map Showing Compliance Well, Bundle and Well Cluster Locations Relative to Granular Iron Barrier and Cr Plume (Elizabeth City) (June 1994 Data)

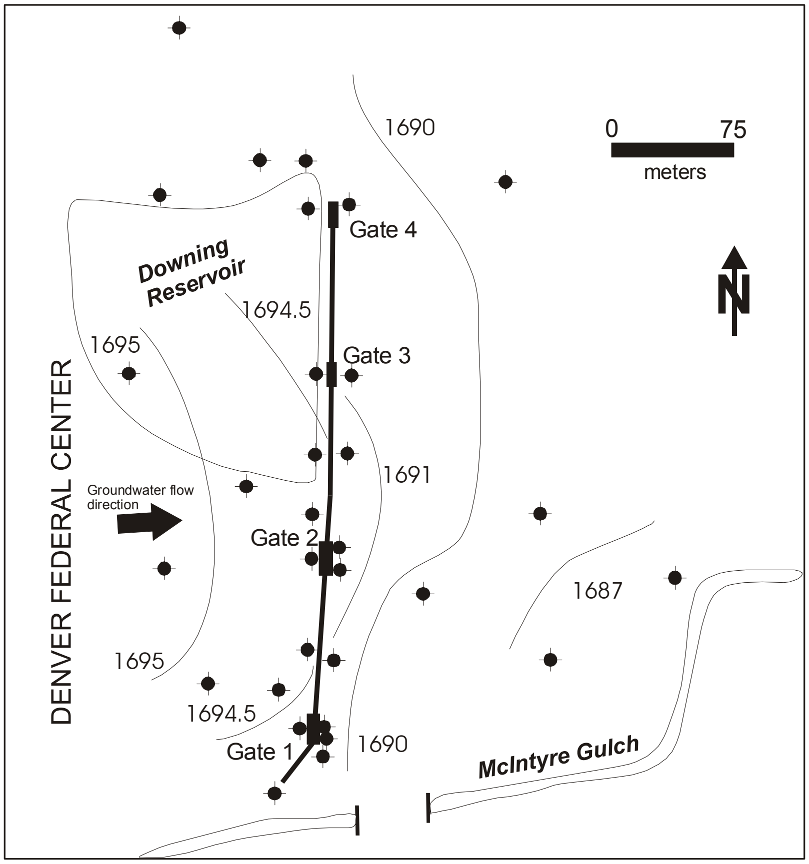


Figure 3-2. Plan View Map of the Denver Federal Center PRB

Table 3-1. Design Features of PRBs at Sites Evaluated by U.S. EPA

PRB Site Name, City, State	Pilot/Full Scale (Installation Date)	Type of Barrier [(a)]	Reactive Medium	PTZ [(b)] and Reactive Medium Thickness	Gate/ Barrier Width (ft)	Barrier Depth (ft)	Amount of Iron (tons)	Source of Iron	Notes
U.S. Coast Guard Support Center, Elizabeth City, NC	Full (June 1996)	CRB	100% Fe	N/A	2	24	280	Peerless	PRB length is 150 ft
Denver Federal Center, Lakewood, CO	Full (October 1996)	F&G (4 gates)	Reactive medium is 100% Fe; Pretreatment zones are 100% pea gravel	Each gate is 10 ft thick with 2 – 4 ft PTZ	Width of Fe: Gate 1 6’ Gate 2 4’ Gate 3 2’ Gate 4 2’	Gate 1 28’ Gate 2 31’ Gate 3 24’ Gate 4 24’		Peerless	All gates 40 ft in length

(a) F&G = Funnel and gate; CRB = Continuous reactive barrier

(b) Pretreatment zone (PTZ) is any medium used for homogenizing flow or chemically pre-treating the groundwater.

Use N/A for not available or not applicable.

Table 3-2. Site Hydrogeology and Hydraulic Parameters of the PRB at Sites Evaluated by U.S. EPA

PRB Site	Aquifer Conductivity (ft/day)	Groundwater Gradient (ft/ft)	Groundwater Velocity (ft/day)	Aquifer depth (ft bgs)	Water table depth (ft bgs)	Primary Contaminants and concentrations	Notes
U.S. Coast Guard Support Center, Elizabeth City, NC	1 – 30	0.0011 – 0.0033	0.4 – 0.6	24	5 – 6.5	Cr(VI) (<10 mg/L); TCE (<20,000 µg/L); c-DCE (<200 µg/L); VC (<70 µg/L)	
Denver Federal Center, Lakewood, CO	0.1 – 100	0.02	0.1 – 1	20 – 30	10 – 18	TCE (<700 µg/L); c-DCE (<360 µg/L); TCA (<200 µg/L); DCE (<230 µg/L)	From Pacific Western Technologies, LTD. (2000)

Table 3-3. Site Groundwater Geochemistry at Sites Evaluated by U.S. EPA

PRB Site	pH	Eh (mV)	DO (mg/L)	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Alkalinity (mg/L)	Cl (mg/L)	SO4 (mg/L)	NO3 (mg/L)	Silica (mg/L)	Notes
U.S. Coast Guard Support Center, Elizabeth City, NC	5.5 – 6.5	-100 to 400	0.2 – 3.0	250 – 400	5 – 20	5 – 10	30 – 70	20 – 60	5 – 60	<0.1 – 2.0	6 – 14	
Denver Federal Center, Lakewood, CO	7.1 – 7.9	-100 to 300	0.1 – 4.0	900 – 1200	90 – 110	17 – 32	290 – 590	48 – 81	<1 – 284	<0.1 – 3.9	12 – 15	

results should be checked against total iron measurements made on acidified samples using methods such as inductively coupled plasma spectroscopy or atomic absorption spectroscopy. The reducing and iron-rich environments often encountered at PRB sites are challenging for obtaining reliable electrode and colorimetric determinations of dissolved oxygen. At low DO levels, electrode response can be slow or unreliable and the presence of any iron oxidation artifacts can interfere with the rhodazine D colorimetric tests. While ORP measurements appear to be useful for tracking changes through time of the reductive capacity of zero-valent iron systems, ORP measurements must be carefully made in the field with frequent evaluations of electrode performance.

3.1.2.2 Core Sampling and Analysis. To assess the extent of corrosion and mineral build-up on the iron surfaces, 5 cm i.d. cores were collected at the Elizabeth City PRB. Core barrels were driven using a pneumatic hammer to the desired sampling location and continuous, up to 110 cm, sections of iron or iron + soil were retrieved (Beck et al., 2002). Angle cores (30° relative to vertical) and vertical cores were collected in order assess the spatial distribution of mineral/biomass buildup in the reactive media. Prior to pushing the core barrel, an electrical conductivity profile was collected to verify the exact position of the iron/aquifer interface. The electrical conductivity measurements were instrumental in maximizing the efficiency of collecting cores that consistently captured the desired aquifer/iron interface. Core materials from the Elizabeth City site were jet black in color without any obvious signs of oxidation. Cementation of iron grains was not evident in cores from the Elizabeth City site (after 4 years). Immediately after collection the cores were frozen. In the laboratory, the frozen cores were partially thawed and then placed in an anaerobic chamber with a maintained H_2-N_2 atmosphere. Each core was logged and partitioned into 5 to 10 cm segments. Each segment was homogenized by stirring in the glove box and split into 4 sub-samples: (1) inorganic carbon analyses, (2) sulfur analyses/x-ray diffraction (XRD), (3) Scanning electron microscopy (SEM)/x-ray photoelectron spectroscopy (XPS) analyses, and, (4) microbial assays. All sub-samples were retained in airtight vials to prevent any air oxidation of redox-sensitive constituents prior to analysis.

Coulometric methods were used to determine the concentrations of inorganic carbon and sulfur on the iron grains. Sulfur partitioning determinations were made by conducting a series of chemical extractions to obtain information about the abundances of sulfide, disulfide, and sulfate precipitates on the iron grains. Compositional information was obtained by using x-ray photoelectron spectroscopy. Mineralogical analysis was performed using powder x-ray diffraction techniques. X-ray diffraction patterns were collected on fine-grained materials removed from the iron grains by sonication. Scanning electron and optical microscopy were utilized to determine the thickness of surface precipitates, evaluate physical morphology of the iron grains, and the extent of surface coverage. Prior to microscopic characterization, samples were set in epoxy resin, cured, and ground and polished using standard techniques. Samples splits were also analyzed for content and distribution of phospholipid fatty acids to evaluate the abundance and composition of microbial biomass.

It should be noted that while detailed studies of core materials from PRB sites are essential for: evaluating the geochemical and microbiological processes that impact performance, developing tools for improving technology selection decisions, and for site characterization investigations, such time-consuming and expensive studies are not likely to be routinely required as a component of most performance monitoring programs.

3.1.3 Results and Discussion. At Elizabeth City, concentrations of chromium above 5 μg/L have not been observed in any of the reactive barrier compliance wells since November 1996. Over the period of study, chromium concentrations have remained below 10 μg/L in wells located up to 20 m downgradient of the PRB. Similarly concentrations of chlorinated organic compounds (TCE, cis-DCE, vinyl chloride) at Elizabeth City are below regulatory target levels in downgradient compliance wells.

Success of the Elizabeth City zero-valent iron PRB for treating a hexavalent chromium plume over its first five years correlates with consistent patterns in the commonly measured field parameters (pH, specific conductance, and Eh). At this site, five years appears to be too short a period of time to observe a clear correlation between changes in geochemical parameters and declining performance. At Elizabeth City, subsurface regions of high pH do not necessarily correlate with regions of low Eh. Spatial and temporal variations in the concentration distribution of terminal electron accepting species (e.g., sulfate), specific conductance, and Eh suggest that both anaerobic iron corrosion and microbial activity play important roles in controlling the oxidation-reduction potential in iron barriers. Low Eh values (<-100 mV relative to the SHE) and decreases in the specific conductance of groundwater between upgradient contaminant plumes and sampling points within reactive iron media are consistently indicative of normally operating PRB systems. Anomalous behavior or trends in these parameters may be useful indicators of declining iron reactivity.

Mineral precipitates identified in the Fe^0 barrier at the USCG-SC are broadly consistent with those predicted to form based on the results of geochemical reaction path models that track the attainment of chemical equilibrium between selected volumes of groundwater and iron metal (Wilkin and Puls, 2001; Wilkin et al., 2002). Primary authigenic precipitates identified in the Elizabeth City PRB are calcium carbonates, iron hydroxy carbonate, carbonate green rust, hydrous ferric hydroxide, ferric oxyhydroxide, and iron monosulfides (mackinawite and greigite). Microscopy observations indicate that mineral accumulation mainly occurs on the surfaces of the iron particles collected near the upgradient aquifer/iron interface where steep gradients in pH and redox potential promote mineral nucleation and growth. After about 4 years of mineral precipitation and accumulation, a consistent coverage of surface material ranging in thickness from about 10 to 50 µm is observed on iron grains collected near the upgradient interface at Elizabeth City (horizontal penetration <8 cm). At greater penetration depths (horizontal penetration >8 cm), surface coatings are discontinuous and <5 µm thick. Accumulation of inorganic carbon precipitates and sulfur precipitates is greatest near the upgradient aquifer-Fe^0 interface. Abundance of surface precipitates decreases with increasing penetration into the iron. Concentrations of inorganic carbon in the reactive media at Elizabeth City are as high as 2000 mg/kg and authigenic sulfur values approach 1200 mg/kg.

A comparison of groundwater chemistry between upgradient and downgradient wells indicates that the iron media at Elizabeth City is a long-term sink for C, S, Ca, Si, Mg, and N. Solid phase characterization studies indicate average rates of inorganic carbon and sulfur accumulation of ~0.1 and ~0.05 kg/m^2y at Elizabeth City where upgradient waters contain up to 400 mg/L total dissolved solids (TDS). Carbon accumulation rates, based upon the solid-phase characterization studies, are in good agreement with estimates made through reactive transport modeling efforts (Mayer et al., 2001). However, the agreement between measured and modeled sulfur accumulation rates is not as good (D. Blowes, pers. communication). The reasons for this discrepancy between model predictions and field measurements are currently being examined.

At the Elizabeth City site, consistent patterns of spatially heterogeneous mineral precipitation and microbial activity are observed. Mineral precipitates and microbial biomass accumulate the fastest near the upgradient aquifer-Fe^0 interface. Porosity loss in the iron media due to precipitation of inorganic carbon and sulfur minerals was estimated by integrating the concentrations of inorganic carbon and sulfur as a function of distance in the iron and estimating the volume loss by using the molar volumes of zero-valent iron, calcium carbonate, iron carbonate, and iron sulfide. The rate of mineral accumulation and the rate of iron corrosion varies spatially, therefore so does the rate of porosity infilling. The highest concentrations of mineral precipitates and rates of porosity loss are found adjacent to upgradient interfaces. At Elizabeth City, a maximum of 5.9% loss of the initial available volume (50%) is estimated at 2.5 cm into the iron media after 4 years of operation. At distances >8 cm, volume loss decreases significantly to <0.1% of the initial available volume after 4 years.

Microbiological impacts are important to understand in order to better predict how long PRB systems will remain effective. The presence of a large reservoir of iron coupled with abundant substrate availability (i.e., hydrogen) supports the metabolic activity of iron-reducing, sulfate-reducing, and/or methanogenic bacteria. About 35 core samples collected from the USCG-SC PRB were analyzed for content and distribution of phospholipid fatty acids (PLFA). These organic compounds can be used as lipid biomarkers to provide a quantitative means to evaluate viable microbial biomass, community composition, and nutritional status. Biomass concentrations after 4 years at Elizabeth City ranged between about 5 and 875 pmoles of PLFA per gram of dried iron, or between 1.02×10^5 and 1.78×10^7 cells per gram of iron matrix. The highest concentrations of microbial biomass were again found at the upgradient aquifer/iron interface. Analysis of PLFA structural groups suggests the dominance of anaerobic, sulfate-reducing and metal-reducing bacteria. Low concentrations of microbial biomass in mid-barrier and downgradient samples suggest that the environment at these locations is more challenging to bacterial growth and survival, which is likely due to substantial decreases in biologically available electron acceptors such as sulfate and cis-DCE

The principal factors that determine the amount of mineral precipitation and biomass accumulation in reactive iron media are seepage velocity and groundwater chemistry. After 5 years of operation, the Elizabeth City barrier has developed a consistent pattern of spatially heterogeneous mineral precipitation and microbial activity. The development of precipitation and biomass fronts result from the abrupt geochemical changes that occur at upgradient interface regions coupled with groundwater transport of dissolved solutes. Complete filling of available pore space has not occurred after 5 years, suggesting that flow characteristics may not be affected by the accumulation of authigenic components. Even relatively thin coatings of mineral precipitates that do not affect flow patterns, however, may affect the reactivity of iron particles with respect to the degradation of chlorinated organic compounds by diminishing electron flow and the efficiency of reductive degradation processes.

A thorough cost analysis of the Elizabeth City PRB (and 21 other sites) was also undertaken to complement the long-term performance study by U.S. EPA. Full results for this study will be included in a forthcoming U.S. EPA report in early 2003. In this analysis, it was found that the largest savings from use of PRB technology comes in reduced operation and maintenance (O&M) costs. The magnitude of these savings is dependent on the life of the PRB and changes in the monitoring program over time. Up front capital costs vary with installation type, size of plume, contaminant concentrations, complexity of natural site conditions, and other factors. Comparisons were made to PRB and pump-and-treat (p&t) technologies where comparable levels of data were available for the same site. In some cases capital costs were greater for PRBs than p&t, while in others, capital costs were less for PRBs. Costs for O&M were consistently less for PRBs compared to p&t. Indeed, when expressed as fraction of construction costs, PRB O&M costs were 0.12 times construction costs while p&t O&M costs were 0.41 times construction costs. Interestingly, the Elizabeth City site had approximately the same construction costs for both PRB and p&t, but O&M costs were $85,000 and $200,000, respectively. This difference is actually greater because the largest fraction of the O&M costs for PRBs is monitoring and the $85,000 figure was for the first year of operation. Current annual monitoring costs are $30,000. This is because the wall is now monitored with much less frequency and analyzed parameters have been optimized. This is typical for PRBs and indeed recommended by the ITRC (ITRC, 1999).

3.2 Denver Federal Center (Lakewood, CO)

3.2.1 Site Description. In the fall of 1996, the Federal Highway Administration (FHWA) and General Services Administration (GSA) installed a permeable reactive barrier at the eastern edge of the Denver Federal Center in Lakewood, Colorado to treat a contaminant plume containing volatile organic compounds, primarily TCE, cis-DCE, TCA, and DCE (Figure 3-2). The DFC PRB has a funnel-and-gate design configuration. The funnel component of the PRB employs metal sheet pile that was driven into unweathered bedrock or into resistant, weathered layers of the local bedrock. The DFC PRB has 4 reactive gates, each 12.2 m long, 7.5 to 9.5 m deep, and from 0.6 m (Gate 3 and 4) to 1.8 m (Gate 1) wide. The design thickness varied because of anticipated differences in contaminant fluxes to the PRB at different locations along the plume front (McMahon et al., 1999; Parsons Engineering Science, 2000).

3.2.2 Methods

3.2.2.1 Groundwater Sampling. Groundwater was sampled from monitoring wells using peristaltic pumps. In all cases, low-flow purging and sampling methods were used to minimize chemical and hydrological disturbances in an around the monitoring wells. Groundwater was pumped through a flow-through cell equipped with calibrated electrodes for pH, oxidation-reduction potential (ORP), specific conductance, and dissolved oxygen. Stabilization of electrode readings was tracked as a function of time (every 1 minute). Filtered samples (0.45 µm) were collected for the analysis of anions and cations. Unfiltered samples were collected for the analysis of volatile organic compounds and dissolved gases.

Colorimetric methods were used in the field for dissolved oxygen, Fe(II), and hydrogen sulfide. Ferrous iron and sulfide concentrations were measured using the 1,10 phenanthroline and methylene blue indicators, respectively. Dissolved oxygen was determined by using tests kits that utilize the indigo carmine indicator (DO>1 mg/L), but more typically the rhodazine D (DO<1 mg/L) colorimetric indicator was employed. Alkalinity determinations were conducted in the field by titrating samples with standardized sulfuric acid to the bromcresol green-methyl red endpoint. Unlike the Elizabeth City PRB, ground water collected from within and around the DFC PRB frequently contained concentrations of hydrogen sulfide of up to about 1 mg/L.

Quality assurance and quality control practices for field measurements at the DFC were the same as those used at the Elizabeth City PRB as described in section 3.1.2.1. These QA procedures for electrode measurements included frequent checks of the electrodes against buffer solutions (pH, ORP, specific conductance) and measurements of prepared standard solutions.

3.2.2.2 Core Collection and Analysis. To assess the extent of corrosion and mineral build-up on the iron surfaces, 5 cm i.d. cores were collected at the DFC PRB. Core barrels were driven using a pneumatic hammer to the desired sampling location and continuous, up to 110 cm, sections of iron, iron + soil, or iron + pea-gravel were retrieved. Angle cores (30° relative to vertical) and vertical cores were collected in order assess the spatial distribution of mineral/biomass buildup in the reactive media. Prior to pushing the core barrel, an electrical conductivity profile was collected to verify the exact position of the iron/aquifer interface. Core materials from the Denver Federal Center were jet black in color without any obvious signs of oxidation. In 2001, after 5 years of operation, some of the iron cores collected from the DFC showed signs of cementation, nodules of cemented iron grains 1 to 3 cm in diameter were recovered in some of the retrieved cores. Iron grains from the upgradient interface of DFC Gate 2 were noticeably enriched in a black-colored, gel-like material. This core consistency was not observed at other DFC gates or at the Elizabeth City PRB. Immediately after collection the cores were frozen. In the laboratory, the frozen cores were partially thawed and then placed in an anaerobic chamber with a maintained H_2-N_2 atmosphere. Each core was logged and partitioned into 5 to 10 cm segments. Each segment was homogenized by stirring in the glove box and then split into 4 sub-samples: (1) inorganic carbon analyses, (2) sulfur analyses/x-ray diffraction (XRD), (3) Scanning electron microscopy (SEM)/x-ray photoelectron spectroscopy (XPS) analyses, and, (4) microbial assays. All sub-samples were retained in airtight vials to prevent any air oxidation of redox-sensitive constituents prior to analysis.

Coulometric methods, wet chemical extractions, x-ray photoelectron spectroscopy, x-ray diffraction, and high-resolution microscopy were used to examine the chemical properties of iron core materials retrieved from the DFC PRB. Similar methods were used at the Elizabeth City PRB as described in section 3.1.2.2. Samples splits were also analyzed for content and distribution of phospholipid fatty acids to evaluate the abundance and composition of microbial biomass.

3.2.3 Results and Discussion. Microscopy observations indicate that mineral accumulation mainly occurs on the surfaces of the iron particles collected near the upgradient aquifer/iron interface where steep gradients in pH and redox potential promote mineral precipitation (Wilkin et al., 2002). After about 4 years of mineral precipitation and accumulation, a consistent coverage of surface material ranging in thickness from about 10 to 50 µm is observed on iron grains collected near the upgradient interface at the DFC (horizontal penetration <20 cm). Therefore, coverage of iron particles by mineral precipitates extends to greater penetration depths at the DFC as compared to the Elizabeth City PRB. The principal reason for this is related to a higher average total dissolved solids concentrations at the DFC that results in greater net rates of mineral precipitation. At greater penetration depths (horizontal penetration >20 cm), surface coatings are again discontinuous and <5 µm thick. Accumulation of inorganic carbon precipitates and sulfur precipitates is greatest near the upgradient aquifer-Fe^0 interface. Abundance of surface precipitates decreases with increasing penetration into the iron. Greater buildup of mineral precipitates and microbial biomass was identified in one gate of the three investigated at the Denver Federal Center (Gate 2). Concentrations of inorganic carbon in DFC Gate 2 are as high as 8000 mg/kg and total sulfur values approach 4500 mg/kg, or about a factor of about 4x the maximum amounts observed in DFC Gate 1, DFC Gate 3, and the Elizabeth City PRB (based on core analysis results from 2000, about 4 years after installation).

A comparison of groundwater chemistry between upgradient and downgradient wells indicates that the iron media at the DFC is a long-term sink for C, S, Ca, Si, Mg, N, and Mn. Solid phase characterization studies indicate average rates of inorganic carbon and sulfur accumulation of ~2 and ~0.8 kg/m^2y at the DFC where upgradient waters contain up to 1200 mg/L total dissolved solids (TDS). At the DFC, consistent patterns of spatially heterogeneous mineral precipitation and microbial activity are observed. Mineral precipitates and microbial biomass accumulate the fastest near the upgradient aquifer-Fe^0 interface. Porosity loss in the iron zones due to precipitation of inorganic carbon and sulfur minerals was estimated by integrating the concentrations of inorganic carbon and sulfur as a function of distance in the iron and estimating the volume loss by using the molar volumes of zero-valent iron, calcium carbonate, iron carbonate, and iron sulfide. The rate of mineral accumulation and the rate of iron corrosion varies spatially, therefore so does the rate of porosity infilling. The highest concentrations of mineral precipitates and rates of porosity loss are found adjacent to upgradient interfaces. At the DFC, a maximum of 14.2% loss of the initial available volume (50%) is estimated at 2.5 cm into the iron media after 4 years of operation in Gate 2. At distances >10 cm, volume loss decreases to <8% of the initial available volume after 4 years. In Gate 1 of the DFC, the precipitation front is spread out over a greater distance, which may be the result of higher average flow rates in Gate 1 (0.38 m/d) compared to Gate 2. A maximum of 6% porosity lost is estimated for Gate 1 near the upgradient/aquifer interface after 4 years, decreasing to <0.5% porosity lost at horizontal penetrations >10 cm.

Microbiological impacts are important to understand in order to better predict how long these PRBs will remain effective. About 35 core samples collected from the DFC PRB was analyzed for content and distribution of phospholipid fatty acids (PLFA). These organic compounds can be used as lipid biomarkers to provide a quantitative means to evaluate viable microbial biomass, community composition, and nutritional status. The highest accumulations of microbial biomass were found at the DFC Gate 2 near the upgradient iron/aquifer interface, where concentrations were as high as 4,100 pmoles of PLFA per gram of dried iron (8.36×10^7 cells/gm). The analysis of PLFA structural groups suggests the dominance of anaerobic, sulfate-reducing and metal-reducing bacteria. Lower concentrations of microbial biomass in mid-barrier and downgradient samples suggest that the environment at these locations is more challenging to bacterial growth and survival, which is likely due to substantial decreases in biologically available electron acceptors such as sulfate.

At the DFC, Gates 1, 3, and 4 have been successful in removing VOCs to concentrations at or below MCLs. The reactive gates similarly affect contaminant concentrations in downgradient compliance wells located within 2 m of the gates. Breakthrough of contaminants of Gate 2 occurred soon after the system was constructed in October 1996. At the Denver Federal Center, successful performance in Gate 1 and Gate 3 is reflected in long-term patterns of pH, specific conductance, and Eh. In Gate 2 of the DFC, detection of 1,1-DCE at downgradient sampling points has been linked to impacts of the funnel-and-gate system on groundwater flow and/or perhaps residual contamination in downgradient sediments. Contaminant breakthrough, particularly of 1,1-DCE is likely related, either directly or indirectly, to anomalous build-up of authigenic precipitates and biomass on the reactive iron surfaces, which would lead to decreased efficiency of contaminant degradation reactions. In addition to mineral/biomass accumulation in Gate 2, potential indicators of decreased performance are increased Eh values, decreased dissolved hydrogen values, and increases in relative specific conductance values between upgradient monitoring points and monitoring points within the reactive media.

4.0 EVALUATION OF PRBS AT DOE SITES

The two sites evaluated under the DOE study are Y-12 Plant, Oak Ridge, TN and the Uranium Mill Tailings Site, Monticello, UT. The features of the PRBs at these two sites are described in Tables 4-1, 4-2, and 4-3 and the results of the evaluation are described in this section.

4.1 Y-12 S-3 Ponds/Pathway 2 PRB

4.1.1 Site Description. The Y-12 Pathway 2 PRB is located at the U.S. Department of Energy's Y-12 National Security Complex in Oak Ridge, Tennessee. The trench-style barrier was constructed in November 1997 to intercept contaminated groundwater upgradient of a shallow creek (Figure 4-1, Watson et al., 1999). The plume at this location (referred to as S-3 Ponds/Pathway 2, Watson et al., 1999) contains on the order of 1 mg/L of uranium and between 20 and 150 mg/L of nitrate. The hydrogeologic setting at this site is rather complex, consisting of densely fractured shale-carbonate bedrock overlain by low-permeability clay-rich residuum (highly weathered shale) and fill materials emplaced during construction of the Y-12 plant. Transport through both bedrock and residuum is fracture-controlled, with geologic strike following an east-west direction. Further adding to the complexity is the presence of a former streambed channel containing permeable alluvial deposits and likely acting as preferential flowpath for groundwater in the area.

The trench is approximately 225 feet long, 2 feet wide, and 30 feet deep (Figure 4-1). The base of the trench is seated at the point of refusal of backhoe penetration, or the approximate top of competent bedrock. The PRB was constructed using a trench-and-fill operation, where the trench was initially stabilized using guar gum and subsequently broken down by circulating an enzyme through the trench after filling (Watson et al., 1999). The PRB was designed to intercept and channel shallow groundwater through a section of the trench filled with Fe(0) (Figure 4-1a). The reactive portion of the PRB is a 26-ft long trench filled with Peerless™ Fe(0) filings from the base of the trench to a depth of about 10-12 feet below ground surface, corresponding to seasonal high water levels. Sections of pea gravel were placed upgradient and downgradient along the long axis of the reactive section, providing high permeability zones to facilitate capture and discharge of groundwater. Because the Fe(0) and gravel zones were estimated to be more permeable than the surrounding sediment, it was anticipated that groundwater would flow along the long axis of the PRB (Figure 4-1a). The trench was subsequently extended and a sump was installed at the distal end to further drive flow along the length of the trench, after an early tracer test demonstrated significant cross-barrier transport.

Highlights of monitoring activities conducted at this site are presented below, while more detailed results can be found in Watson et al. (1999), Watson et al. (2000), Phillips et al. (2000), and Moline et al. (2002). Geochemical modeling specific to this site is described in Liang et al. (2002).

4.1.2 Methods. The performance of the Y-12 S-3 Ponds/Pathway 2 PRB was evaluated using an integrated approach which consists of monitoring contaminant levels, changes in water chemical parameters, and hydrologic tests (e.g., water level measurements and tracer tests). Material coring was conducted at the PRB site and the iron cores were used for mineralogical analysis. Monitoring and groundwater sampling was achieved through more than 50 single and multilevel piezometers and wells installed in and around the PRB before and during barrier construction (Figure 4-1b). Groundwater samples were analyzed for major cations, anions, field parameters (e.g., pH, specific conductance, temperature, dissolved oxygen, Eh, S^{2+}, Fe^{2+}, and alkalinity), and contaminant concentrations. Details regarding analytical methods can be found in Watson et al. (1999), Phillips et al. (2000), and Moline et al. (2002).

Table 4-1. Design Features of PRBs at DOE Sites

PRB Site Name, City, State	Pilot/Full Scale (Installation Date)	Type of Barrier (a)	Reactive Medium	PTZ (b) and Reactive Medium Thickness	Gate/ Barrier Width (ft)	Barrier Depth (ft)	Amount of Iron (tons)	Source of Iron	Notes
Y-12 Plant, Oak Ridge, TN	Full Scale (November, 1997)	CRB	PTZ is 100% pea gravel; 100% Fe in reactive cell	2 ft. across barrier	26-ft reactive cell;	22-30 ft.	80	Peerless	Reactive cell placed within gravel-filled capture trench, guar gum used during installation
Uranium Mill Tailings Site, Monticello, UT	Full Scale, (June 30 1999)	F&G	PTZ is 13% Fe/pea gravel; 100% Fe in reactive cell	8 ft. total; 2 ft. PTZ, 4 ft reactive zone and 2 ft gravel down gradient	97-ft and 240-ft slurry walls; 100 ft. reactive gate	12-24 ft.		Peerless	Air sparging system was installed in the down gradient in the gate section

(a) F&G = Funnel and gate; CRB = Continuous reactive barrier

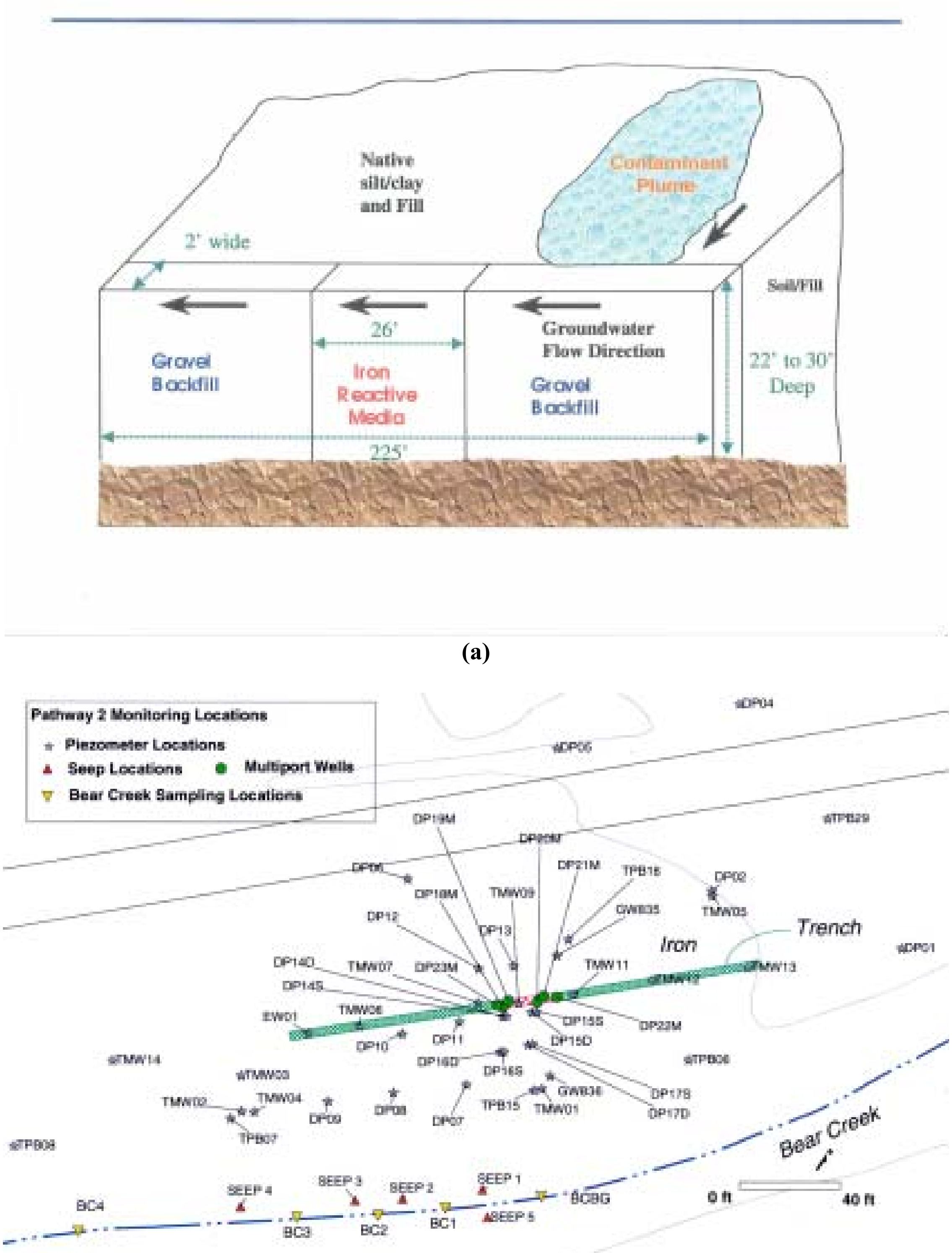
(b) Pretreatment zone (PTZ) is any medium used for homogenizing flow or chemically pre-treating the groundwater. Use N/A for not available or not applicable.

Table 4-2. Site Hydrogeology and Hydraulic Parameters of the PRB at DOE Sites

PRB Site	Aquifer Conductivity (ft/day)	Groundwater Gradient (ft/ft)	Groundwater Velocity (ft/day)	Aquifer depth (ft bgs)	Water table depth (ft bgs)	Primary Contaminants and concentrations (μg/L unless otherwise specified)	Notes
Y-12 plant, Oak Ridge, TN	2.9 - 0.0029	0.02; increases during storm events	6-20	Approx. 30 ft of highly-weathered fill & overburden	10-15 ft., with seasonal and storm variations	U (100 – 2700), Tc (<600 pCi/L), NO_3 (10 – 1400 mg/L)	Groundwater flow through the reactive cell is both parallel and transverse to the barrier.
Uranium Mill Tailings Site, Monticello, UT	10-89		2-24	Approx. 8 ft. of alluvial deposits	6-9 ft.	U (245 - 916), Se (3.5 - 350), V (0.237 - 481), Mn (6.7 – 872) and As (1.1 – 13.6)	K determined from slug tests; velocity from tracer tests

Table 4-3. Site Groundwater Geochemistry at DOE Sites

PRB Site	pH	Eh (mV)	DO (mg/L)	Electric condutivity (umhos/cm)	Ca (mg/L)	Mg (mg/L)	Alkalinity (mg/L)	Cl (mg/L)	SO4 (mg/L)	NO3 (mg/L)	Silica (mg/L)	Na (mg/L)	Notes
Y-12 plant, Oak Ridge, TN	5.7-7.0	-300 to 304	0.2-5.4	626-4308	105-547	17.2-63	91-1100	15-186	2-147	38-822	0.9-8.3	5-57	High nitrate & TDS ground water
Uranium Mill Tailings Site, Monticello, UT	6.0 – 6.88	-158 to 244	0.16 – 5.5	2450 – 2540	216 – 295	53.3 – 75.1	206 – 480	82.7 – 173	0.014 – 1180	118	NA	248 – 326	High TDS ground water



(a)

(b)

Figure 4-1. Schematic (a) and Plan View (b) of Y-12 Pathway 2 PRB. Monitoring Network also Shown in (a). (From Watson et al., 1999)

Three bromide-tracer tests have been conducted at the Y-12 PRB: at 10 months, 2 and 4 years after the PRB was constructed. Cores from the PRB were collected at approximately the same time intervals as the tracer tests. These solid samples were stored in Ar-purged polyvinyl chloride tubes and processed soon after the collection for mineralogical analysis by x-ray diffraction (XRD) and scanning electron microscopy (SEM).

To obtain more quantitative information, laboratory and field column experiments were conducted using the Y-12 site groundwater and careful control of flow rates. Groundwater from a well upgradient of the PRB was pumped through two large-volume (6-in diameter, 36-in length) columns and a small volume column was set up in the laboratory to study gas production during Fe(0) treatment. The results of the column study can be found in Kamalpornwijit et al. (2002).

4.1.3 Results and Discussion. Uranium is removed by Fe(0) within the reactive zone of the PRB. Variations in U concentrations with time do not follow any specific trends but appear to be mainly from fluctuations in influent concentrations. The deep sampling ports from wells DP20 and DP21 (Figure 4-2), where high U concentrations were observed, are actually located below the Fe(0) media zone (within the saprolite), based on collocated cores collected in September 2001. Although the reactive zone of the PRB is effective in removing U, contaminant levels in groundwater within the downgradient gravel zone are comparable to upgradient levels. Flow through the PRB is not occurring along the length of the PRB alone, and the downgradient gravel zone is likely receiving more groundwater from elsewhere (in the direction across the PRB) rather than through the reactive zone.

Lack of flow through the long-axis of the PRB was confirmed by all tracer tests at the site. A concentrated Br solution was injected into well TMW11, which is located in the upgradient gravel zone about 2-ft from the gravel/Fe interface (see Figure 4-1a). High Br levels were detected at the “deep” port of DP22 within 24 hours, but Br was not detected in significant levels in the shallow and intermediate ports of DP22 which are only ~4 ft from the injection well (Figure 4-2). Br signals disappeared from the injection well within 24 hours so groundwater was flowing freely through this well but not through the reactive zone of the PRB. Aside from the deep port of DP22, Br was only detected at high levels within the reactive zone in the deepest ports of DP21 and DP20, both of which turned out to be located within saprolite below the PRB. Angled coring of the PRB from the upgradient gravel zone to Fe(0) zone intersecting well DP22 (Figure 4-2) revealed significant cementation in the Fe(0) within the shallow zone, consistent with the tracer test which showed blocked flow between the injection well and the shallow and intermediate ports of DP22. The primary crystalline phases found in the solid samples using XRD analysis are aragonite, green rust, siderite and quartz. However, the most abundant solid phase based on thin sections of the cemented Fe(0) filings was amorphous iron oxyhydroxides; work is ongoing to identify and quantify this amorphous phase. High nitrate levels in the influent groundwater is likely leading to the significant corrosion of the Fe(0) material and subsequent precipitation of Fe-oxides in the reactive zone. Precipitation of carbonate phases further contribute to cementation and clogging within the reactive zone of the PRB. Geochemical modeling is currently being used to integrate the mineralogical analysis with the groundwater geochemistry, and to determine whether rapid clogging of the PRB could have been predicted. Results of the geochemical analyses, as well as comparisons of field results with the column study (Kamalpornwijit et al., 2002) are the subject of forthcoming publications (Liang et al., 2002; Moline et al., 2002).

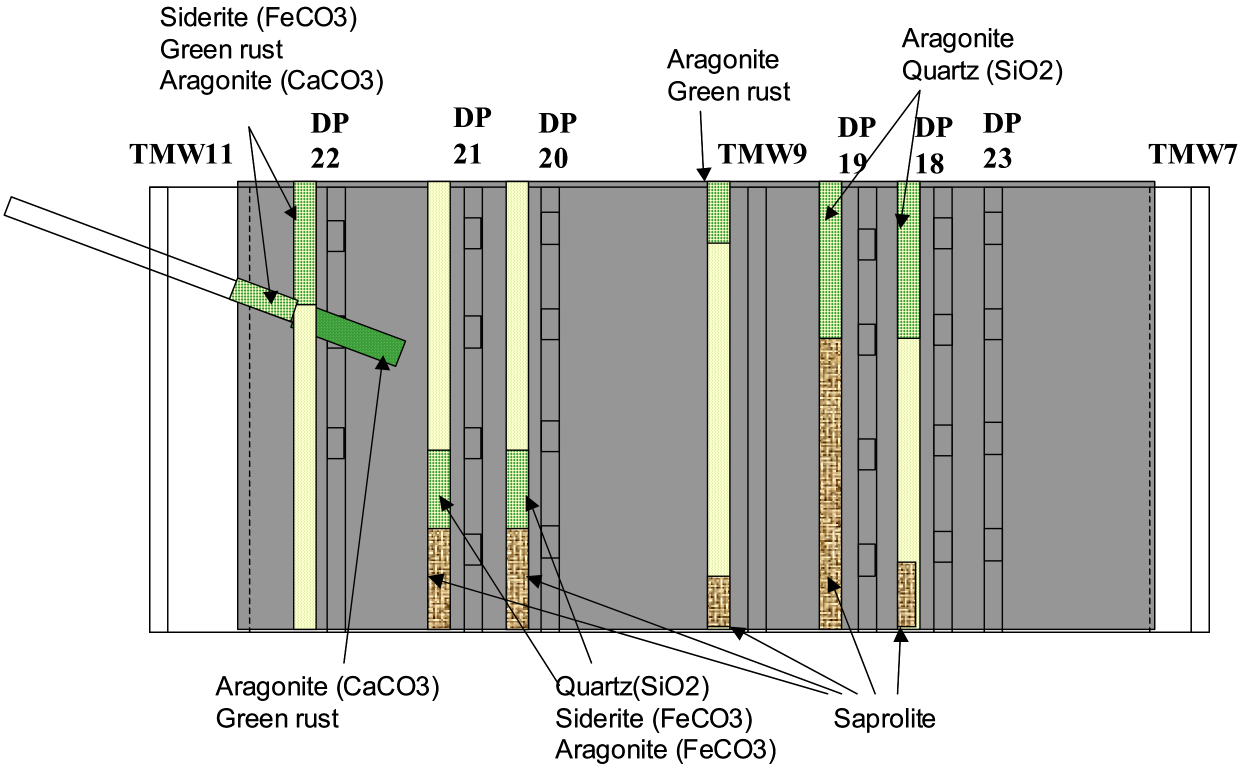


Figure 4-2. Schematic Summary of Coring Results; Cores Collected 4 Years After PRB was Installed. Gray rectangular area corresponds to Fe(0) zone, TMW11, DP22 etc are monitoring wells. Dotted and diamond-shaded areas correspond to loose and cemented filings

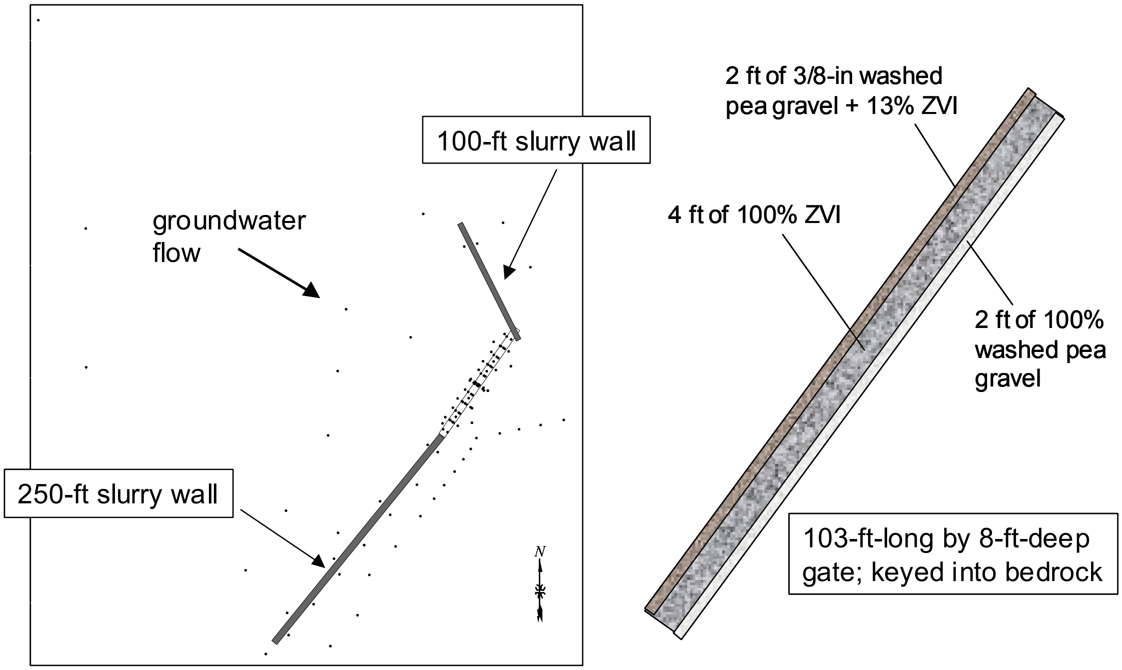


Figure 4-3. Plan View of Monticello PRB and Detailed Schematic of Permeable Section

4.2 Former Uranium Milling Site, Monticello, UT

4.2.1 Site Description. A zero-valent iron funnel-and-gate system was installed in July 1999 to treat contaminated groundwater at a former uranium milling site in Monticello, UT (Figure 4-3; Morrison et al., 2001, 2002). The contaminant plume, which consists primarily of uranium and other heavy metals, lies within alluvial deposits underlain by a mudstone/siltstone aquiclude. Results of pumping and slug tests conducted within the alluvial aquifer prior to barrier installation indicated a hydraulic conductivity of about 10^{-2} cm/s (Morrison et al., 2002), although discrete measurements ranged over four orders of magnitude. The Monticello PRB was installed across an alluvial valley and consists of a 103-ft long permeable section containing a 4-ft thick layer of Fe(0) (-8+20 mesh Peerless), a 2-ft layer of 77% pea gravel /13% Fe (0) mix upgradient and a 2-ft m pea gravel pack downgradient of the Fe(0) layer (Figure 4-3). The permeable section is bounded by two (250 ft and 100 ft long) 8-ft thick slurry walls; the south wall was keyed into the alluvial valley while the north slurry wall stops ~50 ft from the alluvial valley wall. The bottom of the PRB was keyed at least ~1 ft into the underlying aquiclude ~15-20 ft below ground surface. The top of the Fe(0) is approximately 0.5 ft below ground surface, covered by a geotextile and topped to grade by native material.

4.2.2 Methods. A network of 52 wells was installed during PRB construction to provide a means for collecting groundwater samples as well as evaluating the hydraulic characteristics of the PRB. Routine contaminant and geochemical groundwater monitoring was conducted by the DOE/Grand Junction Program Office; details regarding procedures can be found in Morrison et al. (2001) and Morrison et al. (2002). Hydraulic characterization activities conducted by ORNL at the Monticello PRB site included groundwater flow velocity measurements using a colloidal borescope, a multiple tracer (bromide, iodide, neon and helium) test. The borescope measurements and tracer test were performed approximately one year after the PRB was installed. A more detailed description of the borescope and tracer test procedures can be found in Liang et al. (2001).

4.2.3 Results and Discussion. Data collected in August 1999 through October 2000 show uranium, selenium, vanadium, arsenic, molybdenum, and nitrate decrease significantly within the Fe(0) zone of the PRB when compared to upgradient levels (DOE-GJPO, 2002). Uranium concentrations are predominantly lower in wells immediately downgradient of the PRB, although some exhibited levels comparable to upgradient values. These high U concentrations were attributed to leaching from contaminated aquifer sediments (Morrison et al., 2001), and by-pass of contaminated groundwater around the ends of the slurry walls (Morrison et al., 2002).

The bromide and iodide tracer test results showed significant heterogeneity and preferential flow path development within the PRB. Velocities on the order of 2 ft/day were initially anticipated based on the results of groundwater modeling. However, actual velocities based on the bromide and iodide breakthroughs in the PRB wells ranged from 2.4 to 18 ft/day, with residence times ranging from 22 to 90 hours. Gas tracers were not detected in any of the wells, even in wells where co-injected bromide and iodide tracers were being detected. It is unclear whether this was due to analytical difficulties (e.g., loss of gases during sample collection) or if the gaseous tracers were actually being stripped by a gas phase at the upgradient section of the PRB.

Water levels show groundwater flow perpendicular to the long-axis of the PRB, but the tracer test revealed significant lateral transport. The borescope measurement showed flows that were even directed upgradient for a few wells. The discrepancies among the estimated flow characteristics were caused by the scale that different methods evaluate with. Potentiometric surfaces simply show average gradients, and may not be sensitive to heterogeneity within the scale of a typical PRB thickness (i.e., a few feet). However, they are useful for assessing larger regional flow patterns, and for delineating gross features such as groundwater mounding, zones of dewatering, potential for vertical transport, and large permeability changes such as at the influent face of the PRB. Tracer tests provide definitive evidence of transport, and will average over the distance between monitoring wells and, as such, are scalable. The borescope method measures localized velocities and is subject to perturbations from structures such as the PRB walls or even from the borehole itself. The scale of the measurement needs to be taken into account to interpret field data.

5.0 MONITORING AND REGULATORY ISSUES WITH PRBS

5.1 Compliance and Performance Monitoring

A permeable reactive barrier (PRB) monitoring program typically consists of both compliance and performance monitoring. The objective of the compliance monitoring program is to ascertain compliance with applicable state standards at designated compliance point(s). This monitoring is typically driven by regulatory requirements. The contaminated site and the compliance point(s) are the focus of the monitoring.

The objective of the performance monitoring program is to verify that the PRB is operating as designed. Performance monitoring generally is focused on the PRB system itself (including impermeable funnel walls, if present), rather than the entire site or the compliance boundaries. The program should be designed to verify proper installation of the PRB and identify any changes in the system that would affect treatment effectiveness. Ability to identify changes, such as loss of reactivity, decrease in permeability, changes in contaminant residence time within the reaction zone, and short circuiting or leakage through the funnel walls should be taken into account when designing a performance monitoring program.

5.1.1 Compliance Point. The compliance point typically is chosen at a location downgradient of the treatment system, where the water quality is expected to meet the groundwater quality standards or criteria. The chosen location for the compliance point must also ensure protection of downgradient receptors.

Identification of a compliance point at PRB sites can in many cases be complicated by the location of the PRB. At a majority of the cases, the PRB has been placed within the contaminated plume rather than at the leading edge of the plume. In cases where the PRB is within the plume, downgradient points initially are contaminated. Sampling of wells located downgradient of the PRB will reflect the initial contamination within the aquifer, including any contamination desorbing from the aquifer soil or diffusing from finer sediments. It may take several months or even years for downgradient wells to show any improvement in water quality, depending on the specific site’s characteristics. Therefore, when a PRB is installed within a contaminant plume, additional monitoring wells generally are installed within the PRB itself (near the downgradient edge of the reactive medium) to monitor contaminant removal. If the thickness of the reactive media is not sufficient to incorporate monitoring wells, the wells can be located very near the downgradient edge, while taking into account any difference in geochemical makeup between the reactive medium and aquifer. Given the time lag in achieving an improvement in downgradient water quality, regulators and site owners should consider establishing a temporary compliance point within the reactive medium or near the downgradient edge of the PRB, for some period of time after installation. This allows an evaluation of the treatment system's ability to remove contaminants from the groundwater to levels that meet the established regulatory standard or criteria. The location of the compliance point can be re-evaluated and changed to a more suitable downgradient location (protective of downgradient receptors) once the water quality in the downgradient aquifer begins to reflect the treatment occurring within the PRB.

5.1.2 Sampling Parameters. Compliance monitoring parameters for PRBs typically include the contaminants of concern (e.g., TCE), as well as any potentially deleterious reaction products (e.g., cis-1,2 DCE). In addition, general water quality monitoring (field) parameters, such as pH, alkalinity, specific conductance, dissolved oxygen, redox potential, and temperature, typically are measured with each sampling round. Water levels also are an important parameter to identify groundwater flow paths and hydraulic capture of the treatment system.

Performance monitoring focuses on parameters useful in the evaluation of the geochemistry associated with the treatment system. There is some overlap in parameters between the compliance and performance monitoring programs. The overlap includes monitoring of the contaminants of concern, byproducts, general water quality parameters, and water level data. In addition, the native groundwater species, such as alkalinity, calcium, chloride, iron, magnesium, manganese, nitrate, potassium, sodium, sulfate, silica and TDS, can be monitored as indicators of short- and long-term PRB performance. Standard U.S. EPA methodologies should be employed for all analysis.

5.1.3 Sampling Frequency. Monitoring frequency should be determined on a site by site basis. The frequency of monitoring typically depends on the groundwater flow velocity and the location of the PRB. Monitoring frequency should consider the amount of contaminated ground water that will flow through the treatment system over a given period of time. At sites where the PRB is placed at the leading edge of the plume, monitoring may not be necessary until the contaminant plume reaches the PRB.

As a general guide, monitoring for compliance purposes should be completed on a quarterly basis. This schedule also allows evaluation of seasonal changes. After the first year or two the PRB system should be evaluated based upon compliance, performance and stability. A reduction in the monitoring frequency may be appropriate where the system is operating as originally designed, on a consistent basis.

5.1.4 Sampling Methods. Sampling within and around a PRB requires special techniques in order to collect representative samples. Groundwater samples should be collected in such a way that the residence time of the growth in the PRB is not shortened. Passive sample collection methods are preferred for the collection of samples. Low flow sampling methods or micro purge techniques should be used for sampling wells, especially those in close proximity to or within the reactive zone. An example of a passive sampling compounds (VOCs) is the technique for volatile organic compounds of passive diffusion bag samplers. Vroblesky (2001) provides guidance on the use of diffusion bag samples.

Field parameter measurements should be conducted with a flow through cell and monitoring instruments for continuous measurement and to minimize any interferences associated with the introduction of oxygen into the sample. Field instruments can also be employed as in wells (down-hole probes) for the collection of field parameter data. Down-hole probes can be inserted in wells either at the time of the sampling episode or left in a well on a continuous basis (Sivavec et al., 2001).

5.1.5 Monitoring Well Location. The location of monitoring wells is a critical element in determining whether the PRB is meeting compliance and performance criteria. The ground water model for the site typically is utilized for locating monitoring wells around a PRB. In general, wells are located upgradient and downgradient and, if possible, within the PRB itself. In addition, wells at each end of the PRB are necessary to verify hydraulic capture and evaluate potential plume by-pass. Where a PRB includes impermeable sections (funnel walls), monitoring the impermeability of that barrier typically is appropriate. The monitoring wells are generally sized to be just large enough to accommodate the sampling equipment. Smaller wells, such as 1-or-2-inch diameter wells, are preferred to limit the amount of water that is extracted for sample collection, thereby allowing the efficient collection of a representative sample that minimizing changes to the groundwater residence in the PRB system.

It is important to achieve complete vertical and horizontal delineation of the contaminant plume and its relation to the PRB. Monitoring wells should be screened at depths where the highest level of contamination is migrating through the aquifer. It is preferable to screen all the wells in the vicinity of the barrier at the same depth interval.

Monitoring well locations must be evaluated on a site by site basis. It is important, when considering the number and location of wells, that all aspects of the contaminant plume are characterized and conceptually understood. Ground water modeling conducted for the site is an essential tool for determining the placement of monitoring wells. The appropriate locations and number of monitoring wells will be dictated by the size and geometry of the contaminate plume, the size of the PRB, groundwater flow rate, the heterogeneity of the geologic formation, and outside influences on ground water flow in the vicinity of the PRB.

Elder et al. (2001) used computerized modeling to evaluate the locations of monitoring wells at PRB sites. MODFLOW and adaptive particle tracking were used to identify flow through a heterogeneous aquifer with both continuous and funnel and gate PRBs. Monitoring well networks were identified that provided the fewest monitoring points with the highest probability of detecting the median, 75th and 90th percentiles of effluent concentration. For continuous reactive barriers, a horizontal monitoring spacing of 15 feet and a vertical spacing of 9 feet was recommended by Elder et al. (2001). For funnel-and-gate system there is recommended a horizontal spacing of 6 feet and a vertical spacing of 12 feet.

5.2 Contingency Sampling Plan

A contingency sampling plan should be developed whenever a PRB is the chosen remedial alternative. A contingency sampling plan addresses alternative sampling and investigative techniques that would be used in a situation where the PRB fails to meet compliance or performance criteria. Techniques or methods which should be considered as part of the contingency sampling plan include, changes in monitoring frequency, tracer testing, coring and analysis of the reactive media from the PRB, as well as long term column testing using site groundwater.

5.3 Other Regulatory Issues

5.3.1 Biostat. The use of guar gum (a natural food thickener) as a reactive medium or as a support for trench excavation, is gaining increased popularity for the installation of PRBs. Stabilizing the guar gum prior to installation typically includes the addition of a biostat to slow microbial breakdown of the mixture. The addition of the biostat into the aquifer has raised regulatory concerns. The biostat has the potential to contaminate groundwater, both from the original compound used and any degradation products. It is important to understand the fate and transport of any biostat before it is utilized in these applications. In some instances regulators have prohibited the use of biostat (Huber et al., 2001) while in other instances, additional monitoring requirements have been imposed.

5.3.2 Contingency Plans. In many cases, a contingency plan is required in the event that the PRB fails to meet the compliance criteria. Contingency plans may range from modification of the PRB system to use of an alternative technology. For instance, the contingency plan could include such options as extensions to the PRB system or the ability to install a second PRB downgradient of the initial PRB system. Alternative technologies could include the ability to operate a pump-and-treat system. The need for a contingency plan should be evaluated during the design of a PRB system.

6.0 SUMMARY OF CONCLUSIONS

The study by the three U.S. government agencies (DoD, DOE, and U.S. EPA) and the ITRC (a DoD study partner) covered more types of PRBs and site characteristics than would have been possible for any one agency alone. Through periodic teleconferences and meetings, the agencies were able to quickly transfer new ideas and lessons learned in a way that maximized the effectiveness of the three studies.

PRBs have emerged as an entire new class of technologies. Just as with pump-and-treat systems, different hydraulic capture configurations and different permeable barrier media are making it possible to address a number of contaminants of concern under a number of different site characteristics. Because zero-valent iron barriers were the first and most common PRBs installed, the tri-agency study focused primarily on iron barriers. Especially for the longevity evaluation, it was important to focus on sites with a history of at least a few years of operation. All the PRBs evaluated in this study were of the trench type (excavate-and-fill type). The more innovative PRB installations, where the reactive medium is injected into the ground using special methods, such as jetting or hydraulic fracturing, were not evaluated. The performance of injected PRBs is more difficult to evaluate in the field and was beyond the scope and resources of these studies. However, the general conclusions of this study are expected to be applicable to several different types of PRBs, a technology that typically relies on passive groundwater capture and treatment.

In the short term, the key performance issue is the ability of the PRB to prevent the target contamination from progressing beyond the plume cutoff location and thus reducing the risk to downgradient receptors. In the long term, the key performance issue is one of longevity; in other words, the question of how long a PRB may be expected to retain its reactive and hydraulic performance. Although post-installation monitoring was the primary tool used by the three agencies in this study, both short-term and long-term issues are best addressed in the pre-installation design stage at any prospective PRB site. Therefore, many of the study's recommendations relate to the measures that can be taken in the design of a PRB. A PRB is a more or less permanent installation, much more so than a pump-and-treat system. Once a PRB is installed, modifications can be relatively expensive; therefore, it is more important to get the PRB designed and installed right.

Pre-installation monitoring (site characterization) is an important tool in achieving a good design. Post-installation monitoring is required to verify compliance and to identify long-term performance trends. Lessons learned from this study in terms of the monitoring tools available and their effectiveness provide important pointers for future sites.

Some general conclusions concerning long-term performance of PRBs gleaned from this study are the following:

- ❑ Adequate site characterization, especially to improve understanding of the hydraulic flow regime at a prospective PRB location, is imperative to maximize the potential for success of a PRB meeting cleanup goals.

- ❑ Low-flow or passive sampling approaches are required for collecting representative data from PRBs.

- ❑ Over long periods of groundwater exposure, the reactivity of the granular zerovalent iron declines due to precipitation of native groundwater constituents.

- The ability of easily measurable water quality indicator parameters, such as pH and ORP, to provide early warning of reduced PRB performance in the long-term is unclear and requires further study.

- In geologic settings where low flow (fine textured formations) conditions exist, extra care should be taken to insure good hydraulic connection between the native aquifer material and the permeable reactive zone during system installation.

- Increased microbial activity and biomass in the immediate vicinity of a barrier wall may contribute to loss of reactivity and/or permeability over time.

- Additional studies are needed to monitor PRB longevity and improve lifetime predictions based on site-specific hydrologic, geochemical, and microbiological conditions.

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