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# Long-Term Monitoring of Permeable Reactive Barriers

## Progress Report

L. Liang, N. E. Korte, G. R. Moline,  
and O. R. West

Environmental Sciences Division  
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Environmental Sciences Division

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## LIST OF ABBREVIATIONS

AFB	Air Force Base
ASTD	Accelerated Site Technology Deployment
BCL	below casing level
BGL	below ground level
BTC	breakthrough curves
BOC	below top of casing
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ETI	EnviroMetal Technologies, Incorporated
GC	gas chromatography
IC	ion chromatograph
ICP/MS	inductively coupled plasma/mass spectrometer
ITRC	Interstate Technology and Regulatory Cooperation
NFESC	Naval Facilities Engineering Service Center
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
PI	principal investigator
PRBs	permeable reactive barriers
RTDF	Remediation Technologies Development Forum
SCFA	Subsurface Contaminants Focus Area
SERDP	Strategic Environmental Research and Development Program
SI	saturation index
SI	screened interval
TCE	trichloroethylene
TPI	Tri-Agency PRB Initiative
TTP	Technical Task Plan
VOC	volatile organic compound
OBER	Office of Basic Energy Research
USGS	U.S. Geological Survey

## EXECUTIVE SUMMARY

This report presents data acquisition activities performed during FY 2000 and satisfies a deliverable listed in the Technical Task Plan (TTP) for ORO-9-SS-30.

Field activities focused on both chemical sampling and hydraulic monitoring at permeable reactive barrier (PRB) sites at a few U.S. Department of Energy (DOE) facilities. These insitu PRBs have been selected based on the types of contaminants present, the types of reactive media (all contain zero-valent iron, Fe(0)), the groundwater geochemistry, and other properties. Chemical sampling and analysis have been performed mostly by site owners, with assistance from the project researchers through recommendations of the types of the field analytes. Chemical data have been collected from the Y-12 Plant site in Oak Ridge, Tennessee; Monticello mill tailing site, Utah; Rocky Flats site, Colorado; and Kansas City Plant, Missouri. These water chemistry data represent a broad range of geochemical conditions and will serve as a database for the development of a generic, predictive model on the deterioration of the PRBs. Geochemical modeling of the data show that the charge balance is generally good, with an error within 7%.

Additional chemical data have been collected from controlled field experiments at the Y-12 Plant site, where two columns filled with reactive iron, Fe(0), media were set up side-by-side to treat insitu groundwater. The purpose of the column investigation is to examine iron deterioration, ionic species removal, and mineral precipitation under accelerated reaction conditions. The columns have been in operation for 4 months, and preliminary results showed that at a flow rate close to the field condition equilibrium has been established in groundwater/Fe(0) systems. At a higher flow rate, where accelerated reaction could be observed, the residence time was critical to creation of the equilibrium condition. A steady state condition has been achieved, and the results on chemical speciation are useful to interpret transient flow or preferential flow in the field. The system (with fast flow) is being fine tuned to reach an equilibrium condition. Sampling and monitoring of these reactive columns will continue in FY 2001.

Hydraulic investigation has been conducted with a colloidal borescope at five different sites, and a simple reconnaissance was performed with the data to characterize field flow direction and velocities. These sites include Dover Air Force Base (AFB), Delaware; the Y-12 Plant site, Oak Ridge, Tennessee; Lowry AFB, Denver, Colorado; Elizabeth City site, North Carolina; and Monticello site, Utah. Experiments were repeated at the Y-12 Plant site, and data are compared to those collected in the previous year. Data from the Dover and Lowry sites are compared with data obtained with a HydroTechnics™ flowmeter. The results from HydroTechnics are approximately one order of magnitude lower than both average regional measurements based on conductivities and observed gradients, and direct measurements made with the borescope at the Dover site. The borescope data demonstrate that there are zones in the aquifer that are relatively stagnant. A field multiple tracer test was conducted at the Monticello site, Utah, and extensive analysis is being performed. Preliminary results show that transport rates and directions are heterogeneous in nature at this site. The transport rates and directions do not seem to agree with the hydraulic gradients, indicating that preferential pathways within the barrier are significant. Consequently, the hydraulic data alone (i.e., measurements of water levels and hydraulic gradients) are not adequate to provide a good overall assessment of the barrier performance and transport characteristics. Detailed analyses on the breakthrough data are being performed to estimate velocities, residence times, and transport directions.

A critical component of the strategy for accomplishing this project is collaboration with the U.S. Department of Defense (DoD) and the U.S. Environmental Protection Agency (EPA). The

interagency efforts have included face-to-face meetings, regular conference calls, joint reviews of documents, joint publications, and collaborative fieldwork. A website has been set up under the Federal Remediation Technologies Roundtable at <http://www.frtr.gov/prb/> and a two-page brochure has been drafted to clarify the objectives and scope of this interaction. A document on monitoring and analysis protocol will be drafted based on the available data in year 2001. Coordination with the DOE site users is very important to the success of the project, and we will rely as much as we can on the site monitoring programs. Recognizing that each site may alter their existing barrier configuration to meet regulatory requirements, we will try our best to obtain data that are meaningful and provide generic understanding to the geochemical and hydraulic performance of the PRBs. We will continue working with DoD and EPA partners and Remediation Technologies Development Program/Interstate Technology and Regulatory Cooperation (RTDF/ITRC) working groups to share the lessons learned from the sites and to obtain feedbacks for drafted reports.

# 1. INTRODUCTION

## 1.1 PROJECT OBJECTIVES

The purpose of this project is to conduct collaborative research to evaluate and maximize the effectiveness of permeable reactive barriers (PRBs) with a broad-based working group including representatives from the U.S. Department of Energy (DOE), U.S. Department of Defense (DoD), and the U.S. Environmental Protection Agency (EPA). The Naval Facilities Engineering Service Center (NFESC) and its project partner, Battelle, are leading the DoD effort with funding from DoD's Environmental Security Technology Certification Program (ESTCP) and Strategic Environmental Research and Development Program (SERDP). Oak Ridge National Laboratory (ORNL) is coordinating the DOE effort with support from Subsurface Contaminant Focus Area (SCFA), a research program under DOE's Office of Science and Technology. The National Risk Management Research Laboratory's Subsurface Protection and Remediation Division is leading EPA's effort. The combined effort of these three agencies allows the evaluation of a large number of sites. Documents generated by this joint project will be reviewed by the participating agencies' principal investigators, the Permeable Barriers Group of the Remediation Technologies Development Forum (RTDF), and the Interstate Technology and Regulatory Cooperation (ITRC). The technical objectives of this project are to collect and review existing field data at selected PRB sites, identify data gaps, conduct additional measurements, and provide recommendations to DOE users on suitable long-term monitoring strategies.

The specific objectives are to (1) evaluate geochemical and hydraulic performance of PRBs, (2) develop guidelines for hydraulic and geochemical characterization/monitoring, and (3) devise and implement long-term monitoring strategies through the use of hydrological and geochemical models. Accomplishing these objectives will provide valuable information regarding the optimum configuration and lifetime of barriers at specific sites. It will also permit development of site-specific monitoring and performance plans, thus optimizing operation and maintenance (O&M) costs while increasing confidence of both regulators and end users in applying the barrier technology.

This project is funded through DOE's Office of Science and Technology, SCFA (TTP number ORO-9-SS-30). ORNL is planning and implementing the technical scope and has prepared this annual report to summarize field data acquisition, column testing, and geochemical modeling activities in FY 2000.

## 1.2 BACKGROUND

One of the major problems that hinders the broad application of PRB technology is the lack of consolidated performance data for a variety of barriers in different geological and geochemical settings (Liang et al. 2000). Although many types of reactive media may be used in a PRB, our focus is on the barriers containing zero-valent iron [i.e., Fe(0)], which has been found to be effective for dechlorination of volatile organic compounds (VOC) (e.g., trichloroethylene, TCE) and metals [e.g., U(VI)]. The nature and rates of chemical processes that potentially cause Fe(0) fouling and the subsequent effect on the performance of the iron media in treating dissolved contaminants in groundwater, such as chlorinated solvents and metals, are not well understood at the field scale. Modifications in groundwater pH and redox potentials, surface oxidation and mineral precipitation, and rate-inhibiting effects of co-contaminants will all impact the reactivity of the media, affecting the life of PRBs. The current estimates of the lifetime operation of a PRB is between 5 and 50 years (Kinser et al. 1997). This rough estimate makes it difficult to accurately determine the O&M costs over the life of a PRB. A fundamental understanding of media fouling, as induced by mineral precipitation, is needed to achieve practical solutions to mitigate these adverse effects and extend the life of the barrier.

Recent experience has shown that at most field sites where Fe(0) media were used, PRBs will require some O&M (Kinser et al. 1997). Minimally, water samples need to be taken to determine contaminant levels in and around the PRB (ITRC 1999). In general, there is significant variation of the amount and quality of performance-monitoring data that are being collected at PRBs. As a result, sites are unable to assess accurately the routine monitoring costs they expect to encounter. Monitoring costs of more than \$300,000 a year have been estimated for some sites. Such cost and performance uncertainties led to development of this interagency effort to provide a better understanding of processes that contribute to PRB failure and O&M costs.

At present, there are no accepted protocols that end users and regulators can rely on to evaluate the suitability of a site for a PRB and to monitor and evaluate barrier performance once it is installed. Hydraulic evaluation may be performed by conducting tracer tests that determine flow velocity within and around barriers, providing data for evaluation of subsequent permeability change. However, the tests can be intensive and costly. Various flowmeters (e.g., colloidal borescope, heat-pulse, electro-magnetic) are available for determining flow direction and velocity, yet systematic field testing of these instruments in and around barriers has not been sufficient to demonstrate which, if any, of these devices should be adopted by site managers and regulators.

This report reflects work performed by ORNL for DOE, but final data interpretation, recommendations, and protocols will be a collaborative effort performed by DOE, DoD, and EPA.

## **2. CHEMICAL SAMPLING AND GEOCHEMICAL MODELING**

In FY 2000, specific PRB sites were identified for data collection. Limited fieldwork was also performed in order to develop sampling and analysis procedures and a chemical database for the project. Considerable effort was also expended to contact sites and to develop mechanisms that foster the interagency collaboration. Chemical sampling activities include (1) review of site monitoring data and making suggestions, if necessary, to include key chemical parameters that have not been collected; (2) design, setup, and monitoring a set of Fe(0) columns that are plumbed directly to site groundwater (Y-12 Plant site) for the purpose of investigating accelerated chemical reactions that corrode iron, resulting in accumulation of precipitated minerals in the pore spaces; and (3) geochemical modeling to interpret field and column data.

### **2.1 SITE DATA**

In this project, data are being obtained from several DOE sites that were selected on the basis of certain established characteristics (see previous deliverable on-site-selection strategy, Korte and Liang, 1999). These sites are described briefly in the following sections. Additionally, managers of other sites have agreed to cooperate with this project by tailoring their monitoring programs to the needs of this project and by agreeing to share data as they are obtained. These sites include the Mound and East Trenches installations at Rocky Flats, the aboveground system at Lawrence Livermore National Laboratory, and the uranium removal sites at Durango and Fry Canyon.

#### **2.1.1 Y-12 Plant**

The zero-valent iron barrier installation at Pathway 2 of the S-3 Disposal Ponds at the Y-12 Plant in Oak Ridge, Tennessee, is a focus site for this project. The barrier was installed by MSE Technology

Applications, Inc., in December 1997 to intercept and remove U(VI) thereby mitigating the migration of uranium to nearby Bear Creek (Watson et al. 1999). This site was selected for this project because of its proximity to ORNL and the existence of another related project for which leveraging funds can be used. Previous research at the site has included coring and hydraulic testing with tracers and the colloidal borescope (Watson et al. 2000). Hence, considerable information is already available regarding both precipitates present and groundwater hydraulics. Uranium is present at this site and the groundwater geochemistry will provide a significant contrast with respect to the Monticello site. Tables 2.1, 2.2, and 2.3 show monitoring data at Pathway 2; the first two tables show data for upgradient monitoring wells and the last table shows sulfate concentrations in a number of selected monitoring wells. Data for other sampling wells are available and have been used in the geochemical modeling discussed in Section 2.3.

**Table 2.1. Field measurements for well TMW-5 from 1997–2000 (Watson et al. 2000)**

Date	Fe <sup>2+</sup> (ppm)	S <sup>2-</sup> (ppm)	Alkalinity (ppm)	Dissolved O2 (ppm)	Conductivity μS/cm	Temperature (deg. C)	Eh	pH
10-Dec-97	0.27	0.006	220		1900	18.80		6.75
10-Dec-97					2120	18.60		
06-Mar-98	0.01	0.004		3.00	2120	16.00	277.2	6.60
25-Jan-99	0.02	0.000		1.47	1605	16.80	215.4	6.75
14-Apr-99	0.02	0.004		2.37	1820	16.09	-105.0	6.70
21-Oct-99	0.02	0.000		2.18	1668	16.87	182.0	6.79
24-Jan-00	0.04	0.000		4.72	1574	14.60	31.8	6.80
17-Apr-00	0.05	0.000	n/a	2.77	1972	17.56	78	6.77

**Table 2.2. Cation analysis (ppm) in well TMW-5 from 1998–2000 (Watson et al. 2000)**

Date	Al	Ca	Fe	K	Mg	Mn	Na	Ni	Si	Zn
5-Mar-98	<0.15	366.37	<0.1	6.41	22.99	0.092	10.22			0.024
1-Jan-99	<0.15	361.00	<0.1	361.00	20.52	0.075	8.90	0.505	3.83	<0.005
4-Apr-99	<0.15	345.20	<0.1	2.92	21.59	0.056	9.29	0.447	3.15	0.056
10-Aug-99	<0.15	334.20	<0.1	1.86	21.83	0.075	8.29	0.236	4.02	1.580
20-Oct-99	<0.15	336.90	<0.1	<0.4	21.86	0.080	9.42	0.255	3.81	0.012
26-Jan-00	<0.15	337.50	<0.1	2.42	21.86	0.070	10.11	0.189	3.70	0.019
14-Apr-00	0.2185	342.40	0.11	2.92	22.75	0.056	9.12	0.190	5.28	<0.005

**Table 2.3. Ion chromatography analysis of sulfate (ppm) in groundwater from select sampling wells (Watson et al. 2000)**

Date	Monitoring Well						
	TMW-5	TMW-6	TMW-7	TMW-9	TMW-11	TMW-12	TMW-13
12/10/97	52.52	13.96	0	63.92	147.19	389.68	
12/15/97		74.16	43.34	17.60	120.52	254.30	
12/19/97		48.17	94.61	115.74	2.49	137.43	
2/12/98		85.73	0	0	62.47	105.67	73.42
week of 3/4/98	39.41	107.14	2.69	2.55	72.63	79.07	60.70
week of 4/20/98		133.52	29.6	107.97	145.42	172.79	46.76
week of 5/11/98		94.94	24.73	2.13	104.72	97.40	35.83
week of 6/1/98		86.83	38.07	8.37	110.95	79.46	45.1
9/1/98-9/4/98		96.86	5.22	41.83	72.02	135.54	61.86
11/4/98-11/9/98		19.19	2.70	61.43	87.72	107.10	63.48
week of 1/25/99	46.83	91.27	0.72	67.89	91.80	94.98	
Apr-99	53.78	93.39	1.56	59.67	119.00	82.11	
Jul-99	49.05	76.93	2.30	55.09	77.38	76.48	
10/20/99	49.01	80.34	1.64	131.70	101.76	62.77	
Jan. 00	48.98	74.27	1.14	80.13	61.25	52.69	
Apr.00	48.45	90.12		36.07	65.95	69.56	

### 2.1.2 Monticello

The PRB construction at Monticello, Utah, was completed in July 1999. The existing monitoring program [partially funded by Accelerated Site Technology Deployment (ASTD) Program and by EM-40] provides unique groundwater geochemical data from the PRB site that we have been able to use. In general, hydraulic conditions at many sites make it difficult to determine flux through a reactive barrier. However, at Monticello, the PRB is installed across the entire length of a hydrogeologic valley, thereby enabling more reliable quantification of groundwater flux through the barrier. If the groundwater flux through a barrier is known, it is possible to relate the groundwater geochemistry to the type and quantities of precipitates within the barrier. It is also possible to conduct a field validation of geochemical models. In addition, the groundwater at the Monticello site is oxidizing and has high levels of uranium and a high concentration of total dissolved solids. These characteristics make the site more susceptible to precipitation and clogging which, in turn, enhances its desirability for careful monitoring and evaluation.

Monitoring of the Monticello barrier will also provide needed field data to resolve an ongoing scientific controversy regarding the mechanism of uranium removal from groundwater by zero-valent iron. The mechanism has significant implications with regard to long-term use of the barrier and whether removal of the spent iron media might be required in the future. Uranium is the primary contaminant of interest at Monticello. Focusing on this site, therefore, should yield considerable information that can be applied throughout the DOE complex. An example of the kinds of data from Monticello is listed in Table 2.4; such data will be used for geochemical modeling as described in Sect. 2.3. Data for other locations (e.g., upgradient, through the Fe(0) media, and downgradient) are available for geochemical modeling (Monticello 2000). A decision will be made in the future on the need for coring and the funding to be used for this field effort.

**Table 2.4. Field parameters, cationic, and anionic concentrations  
from a selected number of wells (Monticello 2000)**

WELL ID	Alk mg/L	As ppm	Ca ppm	Cl ppm	DO ppm	Fe ppm	K ppm	Mg ppm	Mn ppb	Mo ppb	Na ppm	NO3 ppm	ORP mV	pH	Se ppm	SO4 ppm	Temp °C	U ppb	V ppb
R1-M1	283	9.4			0.44					96			133		18.9		10.8	706	450
R1-M2	280	11.2	303	151	0.74	11.5	23.6	77.3	845	84.9	367	98200	107	6.52	17.2	1220	10.7	609	424
R1-M3	303	10	322	172	0.64	12.3	21.4	83.3	560	70.2	353	93200	-9	7.17	26.9	1270	10.5	722	357
R1-M4	384	6.3	410	207	0.52		14.5	108		35.6	326	66000	205	6.3	53	1320	10.5	526	330
R1-M5	391	5.8			0.32					37.8			122	6.39	50.4		10.3	536	304
R2-M1	107	0.4			0.16					21.8			-312	8.02	3.5		10.6	18.7	1
R2-M2	265	0.4	265	156	0.21	5600	21	78.3	583	28.5	365	42400	48	7.26	12.8	1230	10.9	145	1
R2-M3	343	0.4			0.4					32.4			-149	7.01	17.4		10.9	228	1
R2-M4	195	0.4	239	174	0.4	4480	16	77.8	431	24.3	347	24300	-121	7.63	14.1	1230	11.3	101	1
R2-M5	331	0.4			0.25					33.3			-173	6.93	26.1		10.1	346	1

### 2.1.3 Kansas City

The zero-valent iron barrier at the Kansas City Plant, Kansas City, Missouri, has already been subjected to hydraulic testing and coring by the project team (Kansas City 2000). This site also has some unique features that render it particularly useful for this program. Data obtained to date have demonstrated that flow is not directly through the barrier and that bypass of contaminants is occurring on both sides. Flow direction reversals have also been observed. These characteristics will enhance evaluations of hydraulic monitoring methods by providing a site that is difficult to measure and interpret.

Another potentially important feature of the Kansas City barrier is the fact that a pea gravel layer was not used in front of the iron. Pea gravel has been found to confound measurements of calcium within barriers. Some chemical data have been obtained from the project manager for geochemical analysis and modeling.

### 2.1.4 Other Sites

Site visits were also made to Rocky Flats, Colorado, where a groundwater collection/vault system was installed. Site managers have promised to collect the geochemical and mineralogical data needed for this program. Moreover, they have also offered to provide samples of water or barrier material as requested. The type of data available from Rocky Flats is shown in Table 2.5; data provided from this site will need to be consolidated and put into a form that will be useful for geochemical modeling.

**Table 2.5. Field parameters analyzed for well R1-2 on March 7, 2000, at mount site, Rocky Flats, Colorado (Rocky Flats, 2000)**

Type of analysis	Description	Characteristic	Units
Alkalinity	Alkalinity	214	ppm
Sample method	Bailer	Peristaltic pump	
Calcium	Calcium	40	mg/L
Purge date	Date	03/07/00	Date
Waterdepth	Depth of water source where samples are collected		ft
DO	Dissolved oxygen (mg/L)	2.66	mg/L
EH	EH measurement	-48.5	mv
Ferrous iron	Ferrous iron	0.07	mg/L
Purge method	How the well is purged	Peristaltic pump	
pH	pH (6.0 to 9.0 S.U.)	8.66	S.U.
Headspace	PID reading	0	ppm
Purgevol	Purge volume	800	ml
Well bore	Reading at well bore	0	ppm
Breathing zone	Reading in breathing zone	0	ppm
Color	Sample color	Clear	
Odor	Sample odor	None	
SC	Specific conductants (MS/CM)	605.7	mg/L
Temp(H <sub>2</sub> O)	Temp(H <sub>2</sub> O)	8.2	C
Totdepth	Total depth		ft
Turbidity	Turbidity	5.6	ntu

The project investigators have been involved with the PRB project at Paducah, Kentucky, through the design phase and comments on monitoring plans. ASTD funds are being used to install a 100-ft barrier in a gravel aquifer at a depth of 80 to 120 ft below the surface. This site is unique because of its depth and rapid groundwater flow rate. However, because the barrier is not in place yet, few data are available. The site could be a focus site if additional funds for monitoring the barrier are provided to Paducah. (Such funds have been requested based on a recent review by a Deployment Assistance Team organized by SCFA.) The type of multiple tracer testing that has been conducted at the Monticello site (see Sect. 3) would be applicable here as well. Indeed, of all of the sites reviewed, the Paducah location is the most challenging in terms of evaluating hydraulic control. The site is also challenging for geochemical modeling because of the high contaminant concentrations and oxidizing conditions in the aquifer.

An aboveground vault system has been installed at the Livermore Site 300 during the fall/winter of 1999/2000. The site manager has been contacted and has consented to send data and to modify their monitoring program to meet the needs of this project.

In summary, these activities are expected to provide ORNL with geochemical data from diverse sites. The diversity of the data will ease the preparation of the generic predictive geochemical models as outlined in the TTP.

## 2.2 FLOW-THROUGH COLUMNS AT Y-12 PLANT

The column work at the Y-12 Plant site has been designed to examine iron deterioration, ionic species removal, and mineral precipitation under accelerated reaction conditions occurring in a PRB. Depending

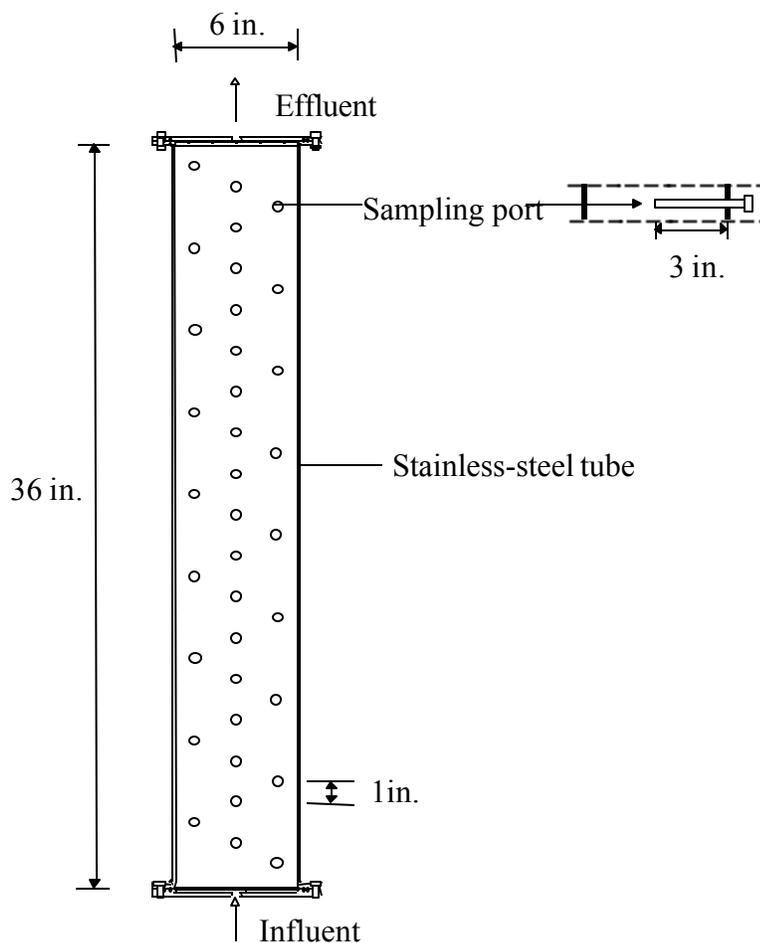
on the hydrogeological setting and the means of installation, heterogeneous flow will occur in and around a PRB. Consequently, the amount of water flowing through the media will vary, resulting in different levels of iron corrosion and mineral precipitation in the media. Because of the lack of control of water flow at field sites, the mass balance of chemical species is unknown, which presents problems for a reasonable prediction on the life of the reactive media. This study emphasizes the change of water chemistry and the associated change of hydraulic performance. The change of iron reactivity toward contaminant degradation and removal has been studied previously at a field pilot-scale facility (Liang et al. 1997; West et al. 1997) and elsewhere (Battelle 2000b; Roberts 2000).

The column testing design for this project will yield unique data. Most column testing with zero-valent iron has employed either synthetic solutions or water that was removed from the site and transported to columns located in a laboratory. In the latter case, preventing aeration and other changes in the groundwater is virtually impossible. For this study, the testing will be performed with water pumped directly from the aquifer, permitting a much better comparison between column results and the in situ installation.

Another feature of column testing performed by other researchers is that it has been assumed that the faster flow rates employed in the laboratory could be extrapolated directly to the slower flow rates observed in the field. (It is generally not practical to run laboratory experiments at field-comparable flow rates because the experiments would require too much time.) Whether the more rapid column testing has any effect on geochemical reactions or the loss of colloids from the iron is unknown but is being determined by the field column work in this project. These data, therefore, will assist both with the application of geochemical models and with the design and performance evaluation of treatability results at other locations.

Two columns are being used in this study with flow rates of ~1 ft/d and ~20 ft/d, respectively. The lower flow rate was chosen because it represents the average groundwater flow rate at many field sites. The higher flow rate is comparable to that observed at the Y-12 Plant site during a bromide (Br<sup>-</sup>) tracer test. Other studies show that at a flow rate of 25 ft/d, the pH will stabilize at the final sampling ports near the effluent end of the column (Battelle 2000b). That is, the groundwater has reached equilibrium with the media at this point. We are operating the high and low flow rate columns concurrently so that we can have a better understanding of the impact of a wide range of flow velocities representative of full-scale field systems and identify any potential problems associated with an in situ barrier.

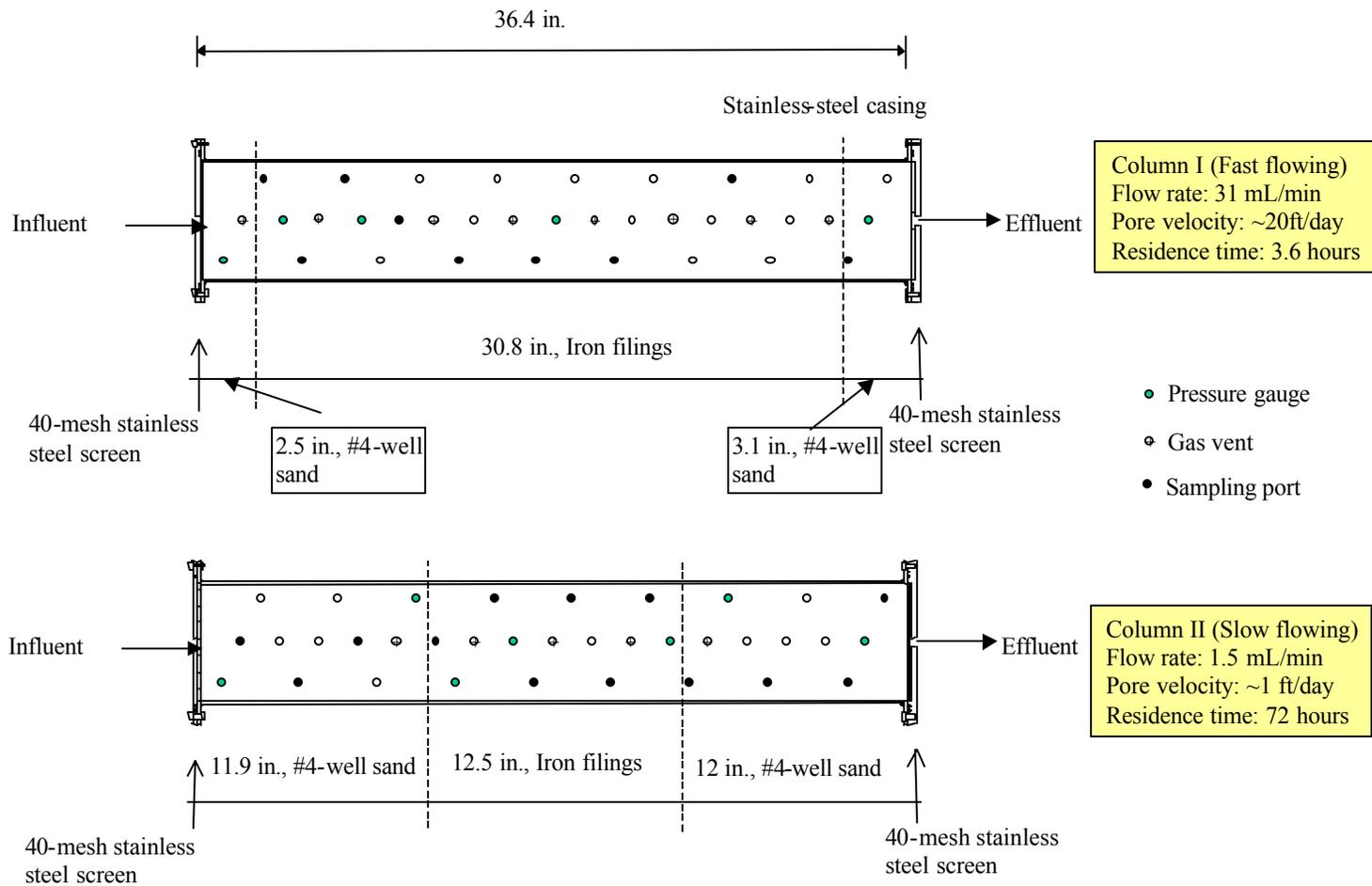
Both columns consist of stainless steel tubes with multiple sampling ports spaced at 1-in. intervals along the 36-in. length and 6-in. diameter column (Fig. 2.1). For the column with a 20 ft/d flow rate (Column I), 30.8 in. of iron were placed between ~2.5-in. and 3.4-in. layers of sand at the influent and effluent ends of the column, respectively (Fig. 2.2). For the column with 1 ft/d flow rate (Column II), 12.5 in. of iron was placed in the midsection of the column between ~12 in. of sand both upgradient and downgradient of the iron (Fig. 2.2).



**Fig. 2.1. Column design.**

The iron filings were obtained from Peerless, which is the same supplier of the iron used in the Y-12 barrier (mesh size  $-8 + 50$ ), and the sand was the standard well sand #4. The columns were wet-packed vertically so that trapped air at the grain surfaces were removed before the columns were put into operation. The columns were laid horizontally after packing, after which pumping of groundwater commenced. Anticipating  $H_2$  production through reaction of  $Fe(0)$  with water, we placed venting ports along the top edge of the columns. Pressure gauges were installed at the interface between sand and iron and at various other points (see Fig. 2.2 for locations).

The columns were set up at the end of July 2000, and the projected duration of the experiment is about 12 months. The purpose of Column I is to speed up flow and simulate a long time of PRB operation compressed into a short period. This requires the column to reach equilibrium condition at the effluent end. Depending on the final flow rate used for this column, 1-year operation may represent 5 to 20 years operation if the flow rate is set at 5 to 20 times of the baseline flow rate. The slow flowing column is set to baseline conditions so that any artifacts (such as colloid mobilization induced by higher flow rate) could be factored in the results of this study.



**Fig. 2.2. Locations of pressure gauges, vents, and sampling ports in relation to iron and sand packing.**

### 2.2.1 Bromide-Tracer Test

At the beginning of the column studies, we conducted Br<sup>-</sup> tracer tests in each column to determine their hydraulic performance. Pulse sources of Br<sup>-</sup> were injected into the columns and effluent water samples were collected and analyzed with Br<sup>-</sup>-specific ion probes (Orion) that were calibrated against standard solutions.

Figure 2.3 shows the breakthrough curves from tracer tests conducted in Column I (fast flowing column) on Day 2 and Day 24. On Day 2, the tracer test was prematurely terminated and the full breakthrough curve was not captured. Nonetheless, the early breakthrough of a small tracer peak is indicative of reduced saturated pore space in the column. This result is in agreement with previous observations of extensive gas production in iron columns (Liang et al. 1996, 1997). After a week of operation, gas production subsided and early breakthrough of the Br<sup>-</sup> tracer was not observed (data not shown). By Day 24 the flow in Column I was characterized by a well-defined peak in the tracer test results shown in Fig. 2.3, where the peak breakthrough of the tracer occurred at slightly greater than 1 pore volume (pv) with little peak spreading caused by dispersive/diffusive effects. Slight retardation and tailing of the tracer in the column were observed, but the near symmetric aspect of the breakthrough curve indicated that flow in the column is well described as plug flow. The tracer was completely recovered during the test.

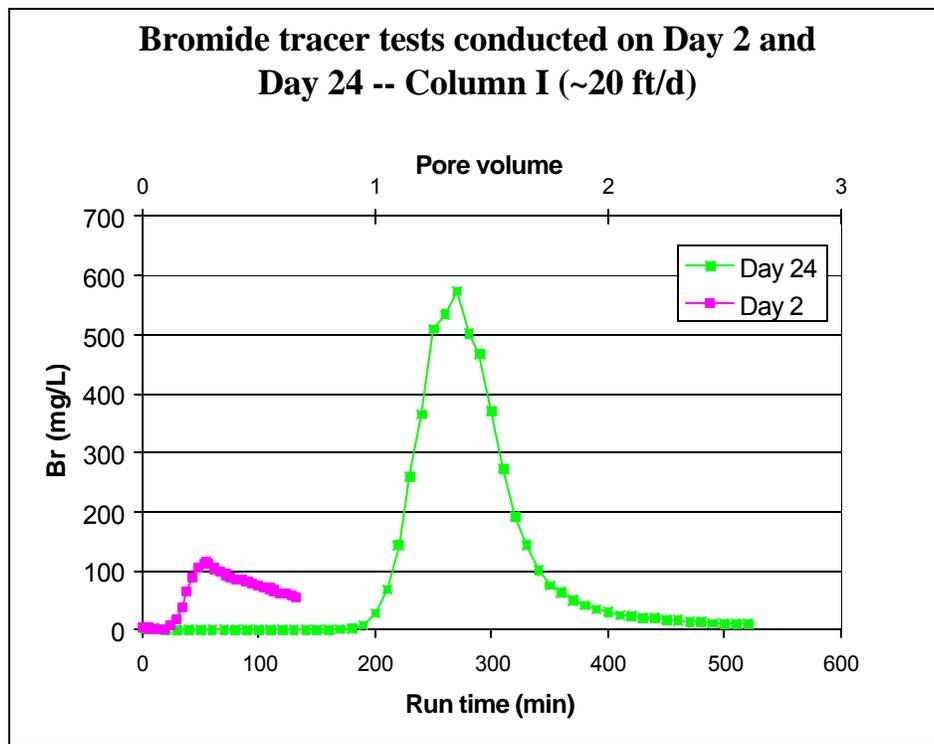
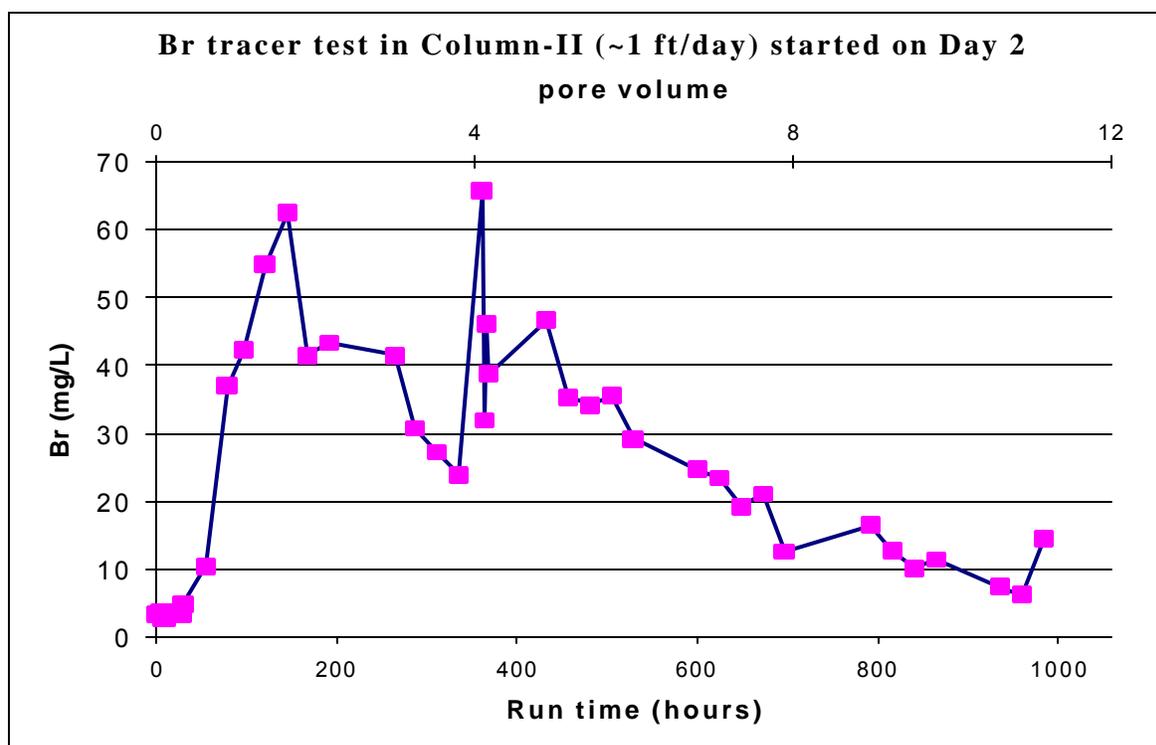


Fig. 2.3. Bromide tracer tests conducted on Day 2 and Day 24 in Column I (~ 20 ft/d).

We suspect that the well-defined breakthrough curve observed on Day 24 compared with that on Day 2 may be a result of reduced H<sub>2</sub> gas production over the period of operation. Additionally the fast flow rate

may have allowed the gas bubbles to vent out of the column along with the water flow, which may not be occurring in the slow flowing column (see below) or in field installations where flow rates are slow.

The Br<sup>-</sup> tracer breakthrough in the slow flowing Column II (Fig. 2.4) does not exhibit a well-defined peak as in the fast flowing Column I. An initial breakthrough peak occurred at ~1 pv, but the spread of the tracer was broad and tailing was extended. The recovery of the tracer was greater than 100%; we attribute this to interference by Cl<sup>-</sup>, which is exacerbated by low Br<sup>-</sup> concentrations. Future analysis of Br<sup>-</sup> for tracer tests will be performed using ion chromatography instead of ion-specific electrode probes to prevent artifacts introduced by Cl<sup>-</sup> interference. Because of the slow flow, H<sub>2</sub> gas generated in Column II may be trapped around the iron grains. We have assumed that gas bubbles would coalesce and migrate upwards toward the gas sampling ports. At various vent ports, however, we attempted to collect gas samples for H<sub>2</sub> analysis but could not collect significant volumes. Instead, we observed a gas phase at the water sampling ports (which are placed at the center line of the column). At extended operation (>40 days), we started seeing occasional stoppage of the flow. The flow usually resumed after the gas phase was vented.



**Fig. 2.4. Bromide tracer test in Column II (~ 1 ft/d) started on Day 2.**

## 2.2.2 Chemical Parameter Measurements

The purpose of the column tests is to investigate the geochemical reactions in water as it passes through iron media. These reactions lead to surface oxidation and passivation, mineral precipitation, and alterations of pH and redox potentials, all of which directly affect the performance of iron media. We have been collecting aqueous geochemical and microbial data and plan to identify surface precipitates from solid samples. We will integrate these different types of information and use them as input to geochemical models and verification for modeling results. We will also use the data and modeling results to assess the potential for barrier fouling caused by abiotic or biotic processes.

During the column tests, groundwater samples have been taken periodically and analyzed for basic chemical (e.g., pH, Eh, temperature, dissolved oxygen, specific conductance, alkalinity), ionic (major cations and anions, ferrous iron, sulfide), and microbial parameters (types and population, etc.). Standard probes were used for pH, Eh, temperature, and specific conductance. Alkalinity was determined by titration with a standard HCl solution to pH 4.5. An attempt was made to separately determine the total alkalinity and OH-alkalinity by titrating solutions to pH end points of 4.5 and 8.3. Dissolved oxygen (DO), ferrous iron, and sulfide ion were determined by colorimetric methods (DO was analyzed by an indigo-carmin method, where the dissolved O<sub>2</sub> reacts with the indigo-carmin that produces the color, and S<sup>2-</sup> was analyzed by methylene blue methods, both from Chemetric chemical kits). Ferrous iron was analyzed by a 1,10-phenanthroline method (using Hach kits). Cation analysis was performed with an inductively coupled plasma/mass spectrometer (ICP/MS), and anionic species were determined with an ion chromatograph (IC).

### 2.2.2.1 Influent water chemistry

Table 2.6 lists the influent chemical composition for both columns. At the start up of the tests, the pH of the influent was slightly alkaline. After a month of operation, the pH stabilized at about 6.7, the dissolved oxygen at ~0.32 ppm, and conductivity ~1.2 mS/cm. The alkalinity increased from the initial value of 186 to ~310 mg/L (as CaCO<sub>3</sub>). Data from nearby groundwater monitoring wells from December 1997 to April 2000 showed pH varied from 6.6 to 6.80, Eh from -105 to 277 mV, conductivity 1.6 to 2.1 mS/cm, sulfide from 0 to 0.006 ppm, ferrous iron from 0.01 to 0.05 ppm, and alkalinity ~220 ppm (Table 2.1-1). Because of the periodic recharge of rainwater, the observed variation of influent chemical parameters is expected and consistent with other monitoring data.

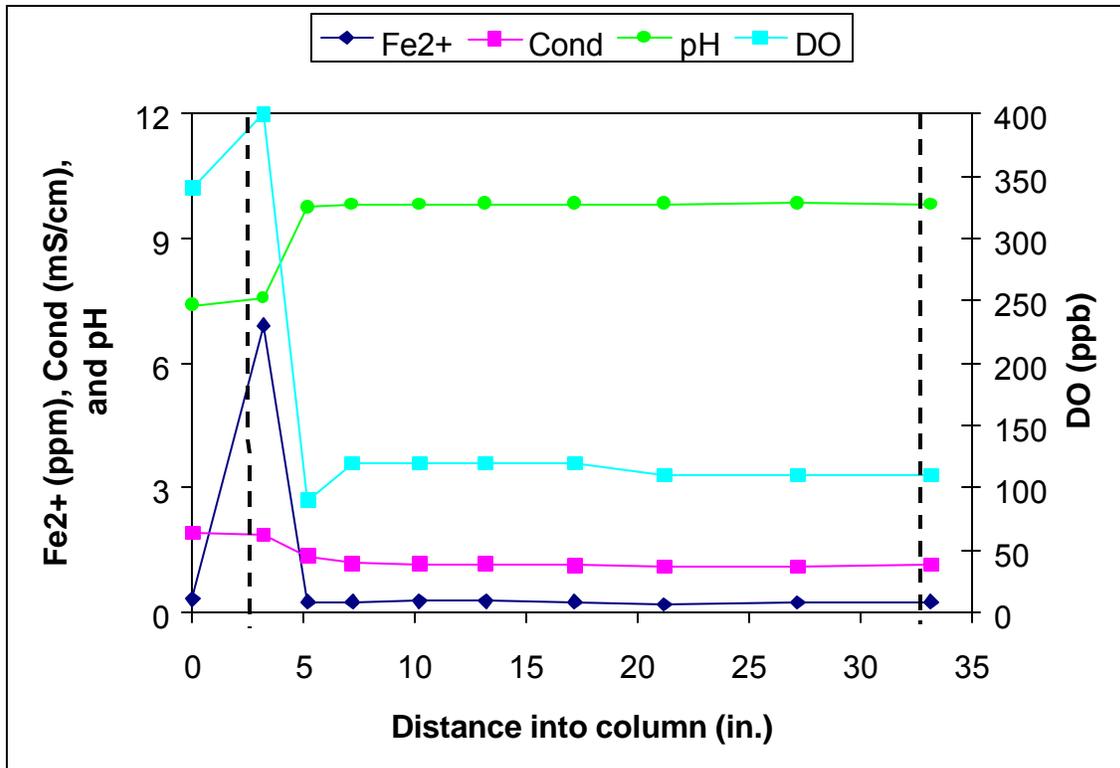
**Table 2.6. Field parameters of influent chemistry**

Date	pH	Eh (mV)	DO (□g/L)	Temperature (° C)	Conductivity (mS/cm)	Fe <sup>2+</sup> (mg/L)	Sulfide (mg/L)	Alkalinity (mg/L CaCO <sub>3</sub> )
07-26-00	7.39	--	430	24.2	1.91	0.32	0	186
08-03-00	7.01	128	--	20.3	1.19	0.0	--	--
08-24-00	6.71	--	320	20.4	1.16	0.05	0.01	319
10-04-00	6.73	218	--	17.1	1.19	0.01	--	304
Major cation concentration by ICP analysis								
	Fe <sub>T</sub> (ppm)	Si (ppm)	Ca <sup>2+</sup> (ppm)	Sr <sup>2+</sup> (ppm)	Mg <sup>2+</sup> (ppm)	Na <sup>+</sup> (ppm)	K <sup>+</sup> (ppm)	
07-26-00	0.054	4.14	363.5	0.694	18.6	8.82	1.34	
08-24-00	0.0	2.02	215.3	0.480	18.6	3.97	2.23	

### 2.2.2.2 Column I results

During the period of operation of Column I from July 26, 2000, to October 4, 2000, the flow rate was about 30 mL/min or ~20 ft/d. Figure 2.5 shows the chemical parameters analyzed immediately after the samples were collected on Day 1 in Column I. The pH increased from the initial value of ~7 to ~9.8 in the iron media, and this pH was maintained through Column I. It is worth noting that although samples were collected during active pumping, most samples came from the pore water that had been equilibrated with Fe(0) during the wet packing on Day 0.

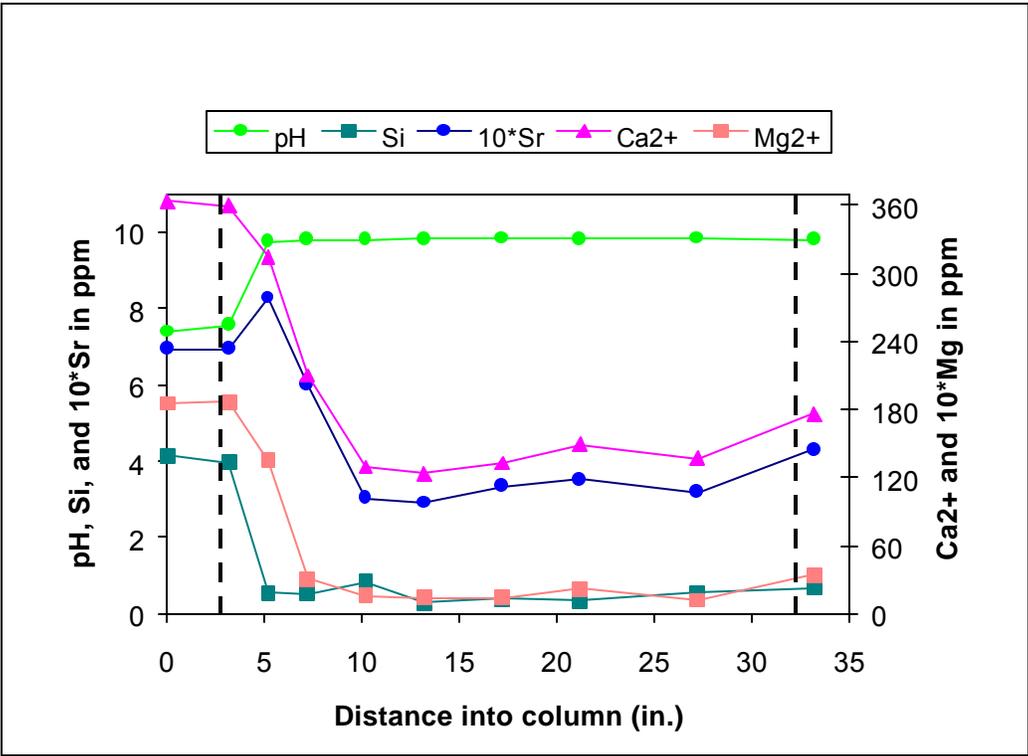
The variation in the alkalinity data is quite large (data not shown), which we attribute to analytical artifacts. For this particular set of data, the titration was performed a couple of days after the sample collection. Because of the high pH of the samples, atmosphere exchange of CO<sub>2</sub> may have increased the apparent alkalinity in some of the water samples. The dissolved oxygen was substantially decreased from the influent 430 ppb to about 100 ppb within the iron media. Ferrous iron was about 7 mg/L in the iron at the interface of sand and iron near influent but remained near 0 in samples with elevated pH.



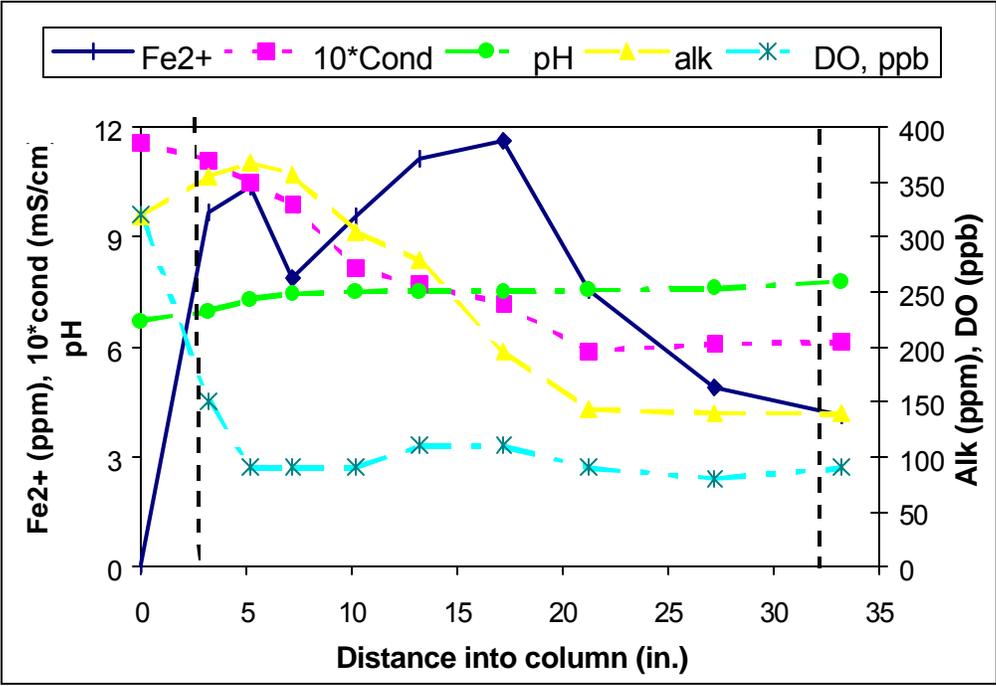
**Fig. 2.5. Field parameters (ferrous iron, conductivity, pH, and dissolved oxygen) in Column I on Day 1 (7/26/2000).** Iron medium is bounded by dashed lines.

Figure 2.6 shows the change of cation concentration in the media. We plotted pH data with the cations in the same figure for comparison. All major divalent ions are removed from water as pH increased to ~9.8. Si was also removed from water in the iron media. The decrease in the ionic species agreed well with conductivity data, which show a general decreasing trend in waters from the iron media (Fig. 2.5).

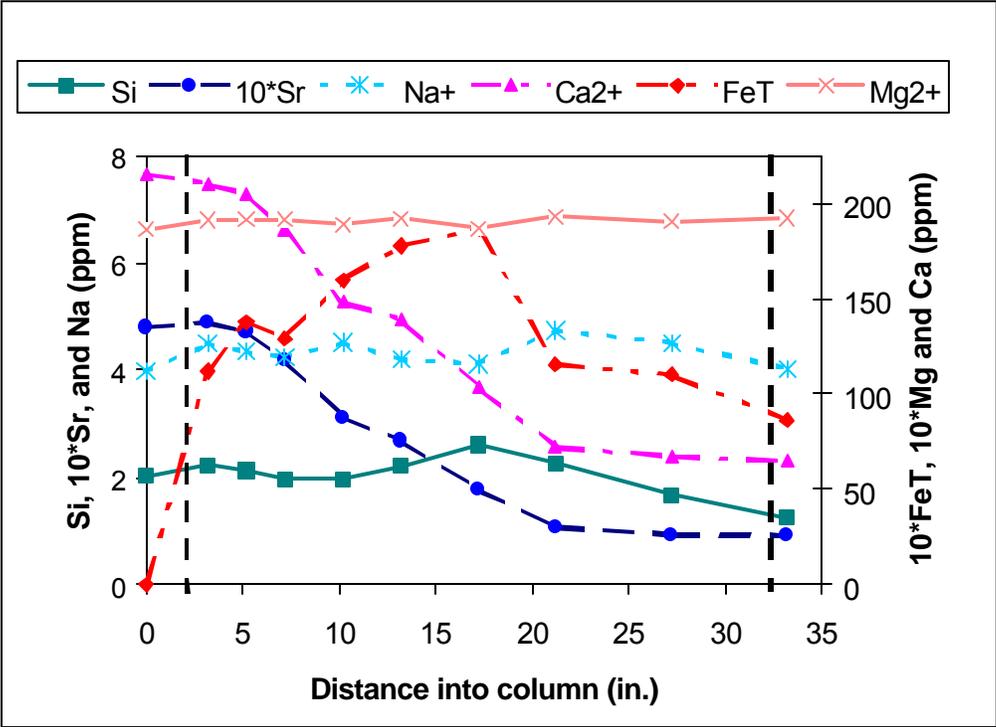
Four weeks after the start of groundwater flow through Column I, we performed another round of chemical sampling. These results are plotted in Fig. 2.7 and are more representative of conditions expected for a steady-state flow-through system than those obtained on Day 1. The influent water chemistry data, especially influent pH (Table 2.6) were more in line with those from long-term monitoring (Table 2.1-1). The chemical and cation data show significant differences from those on Day 1. The pH in the iron media did not increase significantly from the influent pH. Calcium and Sr decreased along the iron column, but the Mg concentration was maintained at the level observed in the influent water. Ferrous iron followed the trend of the total iron, increasing from near zero at the influent end of the column to a peak level and then decreasing toward the effluent end. Sodium concentrations remained constant throughout the column, as no major chemical reactions are expected to add/remove Na ions. Compared with data from Day 1, it appears that Mg<sup>2+</sup> removal from influent water is associated with higher pH, whereas removal of Ca<sup>2+</sup> and Sr<sup>2+</sup> from the influent is less affected by the change of solution pH. Thus we speculate that precipitation of magnesium hydroxide, Mg(OH)<sub>2</sub>, is a major removal mechanism for Mg<sup>2+</sup>, whereas Ca<sup>2+</sup> and Sr<sup>2+</sup> are precipitated out mainly as carbonate minerals. We will use geochemical modeling and minerals identified in the pore space to verify our hypothesis as the project progresses. However, because the fast flow conditions do not allow water to equilibrate with Fe(0) (as reflected in the pH values), the removal of dissolved ions could be kinetically inhibited, a hypothesis which is under current investigation.



**Fig. 2.6. Cations in Column I (20 ft/d) on Day 1 (7/26/2000).** Iron medium is bounded by dashed lines.



(a)



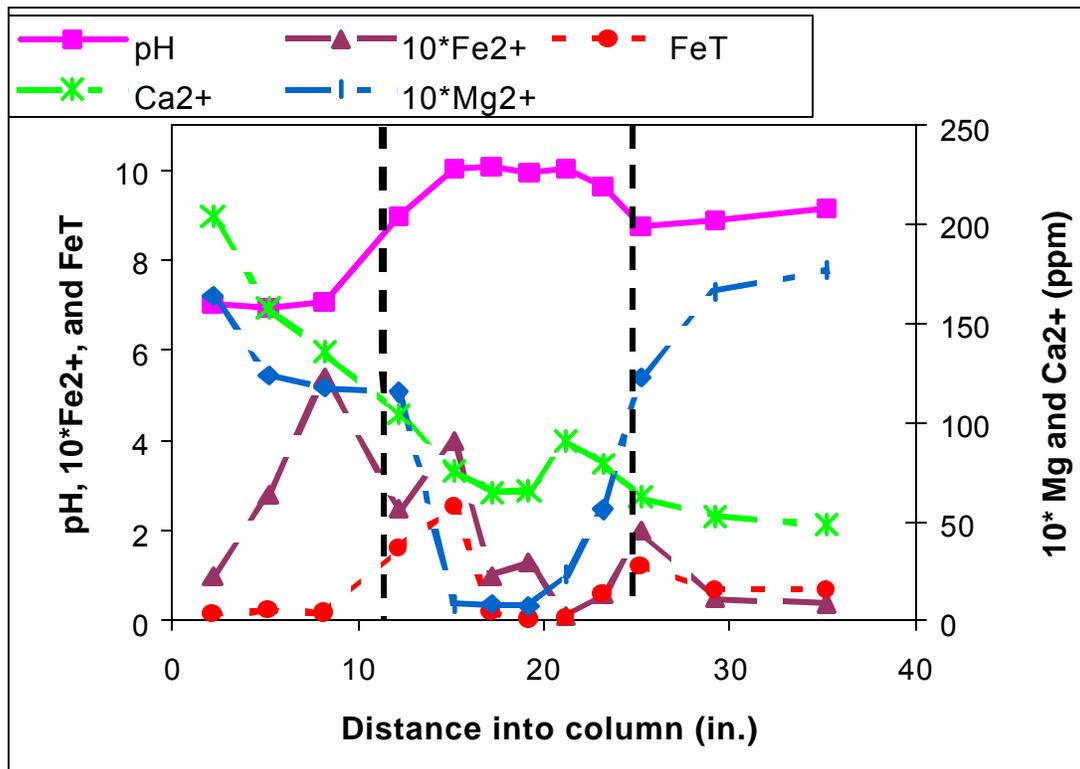
(b)

Fig. 2.7. Field data (a) and cation data (b) in Column I (20 ft/d) on Day 30 (8/24/2000). Iron medium is bounded by dashed lines.

### 2.2.2.3 Column II results

Similar chemical parameters were collected for Column II during the start of the tests (Day 1) and extended operation (Day 58). The flow during this period was about 1 ft/d.

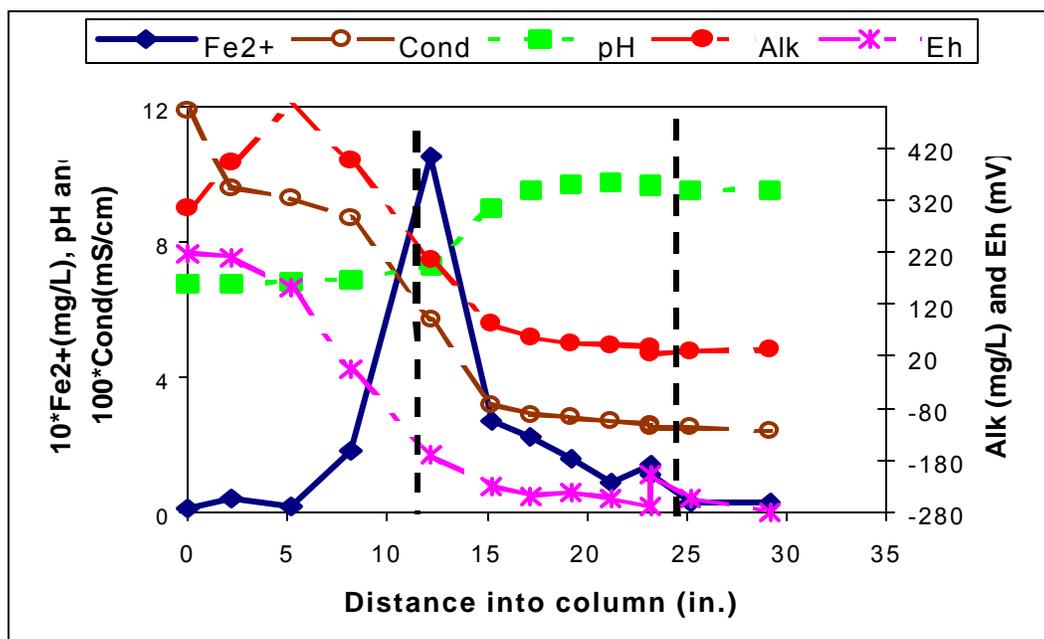
The Day 1 samples were taken from water that had been equilibrated with the iron filings in the column packed the previous day, although active pumping was applied during sampling. Figure 2.8 shows pH, alkalinity, and cation concentrations on Day 1. Similarly to data obtained for Column I, the alkalinity data contain artifacts because they were not analyzed immediately after the sampling. The pH increased to ~10 in the Fe(0) media from the influent value of ~7.3. Calcium and Sr follow a similar trend, and Mg is substantially removed from water sampled within the iron media. The chemical parameters in the downgradient sand layer almost mirror the data in the upgradient sand layer, except somewhat lower in values. We would expect a perfectly symmetrical match of these data if the water were stagnant. Active pumping during sampling, particularly for water samples collected later during the day of sampling should provide mixing of water from up stream with the water initially present in the pore space, which accounts for the lower pH, alkalinity, and the other chemical parameters.



**Fig. 2.8. Field and major cation data from Column II (1 ft/d) on Day 1 (8/1/2000).** Iron medium is bounded by dashed lines.

On day 58 (Fig. 2.9), groundwater had been pumped continuously since the start of the experiments. The flow rate was ~1 ft/d. In the upgradient sand layer, the pH increase was small and Eh and conductivity of the samples decreased as water flowed toward the iron layer. A slight increase of alkalinity was observed from the influent port to the midsection of the sand layer, followed by a decrease toward the iron layer. Ferrous iron increased and peaked in the iron layer. However, ferrous iron decreased continuously in iron media, corresponding to increasing pH. In the downgradient sand layer, all chemical parameters hold the

values at the iron–sand interface. This trend is expected, because no major chemical reactions occurring in the downgradient sand would significantly alter the water chemistry.



**Fig. 2.9. Field data on Day 58 (9/27/2000) from Column II (1 ft/d).** Iron medium is bounded by dashed lines.

#### 2.2.2.4 Summary of column study results

These preliminary results suggest that the flow rate in Column I (~20 ft/d) is too fast for the water-Fe(0) system to reach a condition of stable equilibrium during the short residence time available (~ 3 hrs). However, our data indicate that the changes we observe along the length of Column I are reproducible and probably represent steady-state conditions. Therefore, it is likely that the dominant water-Fe(0) reactions are kinetically inhibited, an inference that we intend to explore further in this project.

One of the most sensitive parameters (and simplest to measure), pH, appears to be a good indicator of the kinetically limited reactions. For example, for the Y-12 groundwater system the influent pH of ~6.7 to 7.0 rises to ~ 9.8 under equilibrium conditions (e.g., Column II). However, in Column I although the pH rises steadily along the length of the iron media in the column, it only achieves a value of ~7.8 (at ~20 ft/d flow) at the effluent end. Therefore, these results suggest that knowing site groundwater chemistry and the reactions likely to occur, one may be able to use pH measurements as a tool for designing a PRB and as an indicator of how closely an existing PRB has achieved a state of chemical equilibrium.

The purpose of Column I is to speed up flow and simulate a long time of PRB operation compressed into a short period of time. This requires the column to reach an equilibrium condition by the effluent end. Since this has not occurred with a flow rate of 20 ft/d, we will need to slow down the flow rate. We have changed the flow rate to ~10 ft/d and the equilibrium state still has not been attained. In order to keep a high flow rate and still get to equilibrium, we may have to extend the length of the Fe(0) media for such a study. Current work is being done to optimize the length of the column and the flow rate to get the desired equilibrium conditions.

Both columns are continuously monitored and data will be used in the geochemical modeling discussed in Sect. 2.3.

## 2.3 MODELING

Depending on the geological environment of the PRB installation, the nature and the rates of chemical reactions will be important to the long-term performance of a PRB. Geochemical modeling will be applied to the field data to determine the important geochemical behavior of pH, pE (or oxygen content), and ionic constituents (e.g., carbonate, sulfides, etc.) that result in clogging.

From a chemical point of view, an elevated dissolved oxygen level in groundwater will be a major factor contributing to the oxidation of Fe(0) in a reactive barrier. Clogging of the reactive barrier will also result from the precipitation of metal oxides/hydroxides, carbonates, sulfates, and sulfides (Phillips et al. 2000). Groundwater with a limited pH buffering capacity will develop high pH in the Fe(0) barrier, suppressing microbial activity and resulting in slow biofouling on Fe(0) particle surfaces. Chemical precipitation resulting in hydroxides and carbonates at the elevated pH, however, may be significant in solid buildup in pore spaces. In contrast, groundwater with high alkalinity will likely buffer pH at near-neutral values within the barrier and create conditions conducive to biofouling and clogging from the surface precipitation of sulfides and carbonates (Liang et al. 2000).

We have used the geochemical equilibrium modeling code, PHREEQC (Parkhurst and Appelo 1999), to perform “forward” (also known as reaction path) and “inverse” modeling. Forward modeling consists of two components: First, aqueous speciation and mineral saturation indices (SI) can be calculated based on mole-balance and mass-action equations that define the ion-association model at equilibrium (the PHREEQC database has been used in this work). Using this approach, we can evaluate the quality of field data through the charge balance error calculation, which allows us to identify if a major chemical component is missing from the analysis or has been measured incorrectly. Secondly, we can use forward modeling to examine the impact of perturbations to an equilibrium system resulting from dissolving a given amount of reactive minerals in groundwater.

Inverse modeling attempts to determine sets of mass transfers of mineral and gas phases that account for changes in water chemical compositions between an initial and a final state, within specified compositional uncertainty limits. Thus, if we are certain about the chemistry of influent and effluent groundwater and the identity of potential reactive phases (both dissolving and precipitating), we can calculate the mass transfer of a set of plausible reactants and products that account for the changes in groundwater chemistry. It is important to recognize that inverse modeling does not involve an assessment of thermodynamic stability of the phases selected for mass-balance calculations.

### 2.3.1 Forward Modeling

We have used the forward modeling approach to examine the quality of field data and the potential for mineral precipitation at a few sites. Table 2.7 shows a few examples of influent groundwater at selected PRB sites.

**Table 2.7. Background or upgradient groundwater compositions from a few selected PRB sites at DOE and DoD facilities (concentration units are in mg/L, unless it is otherwise designated)**

	Dover area 5 <sup>a</sup> Gate1-6/99	Portsmouth <sup>b</sup> X625-3/98	Moffett field <sup>c</sup> 6/96	Monticello <sup>d</sup> 10/99	Y-12 Plant <sup>e</sup> Pathway2-1/99
Upgradient well ID	U4S	FC-1	WIC-2	R1-M3	TMW-05
PH	5.07	5.9	7.15	6.51	6.75
Eh (mV)	596	119	236	159	215
DO	4.15	0.097	3.2	0.44	1.47
Alkalinity as CaCO <sub>3</sub>	6	55	292	237	220
Ca	4.5	74.9	147	275	361
Cl	30	21.87	71	123	54.92
Fe	0	0.336	NA	0.009	0.02
Mg	7.1	34.6	47	69.1	20.52
Mn	1.7	0.368	NA	0.516	0.08
Nitrate	8	2.97	2.1	118	903.6
Si	10	14.5	NA	NA	3.83
Na	20	93.8	57	326	8.9
S as SO <sub>4</sub>	9.3	496	269	1170	46.83
K	NA	2.02	2.8	18.9	3.61
H <sub>2</sub>	NA	1.50% saturation	NA	NA	NA

NA - Not available.

<sup>a</sup>Gavaskar et al., 1999.

<sup>b</sup>Liang et al., 1997.

<sup>c</sup>Battelle, 2000a.

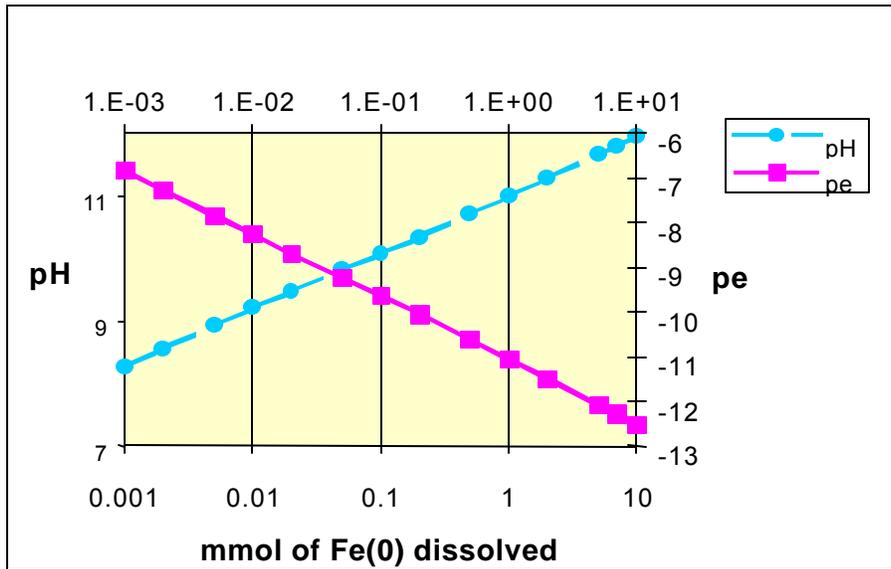
<sup>d</sup>Monticello, 2000.

<sup>e</sup>Watson et al., 1999.

Equilibrium calculations were performed with PHREEQC using input data from Table 2.7 to evaluate the charge balance, the expected Eh, ionic strength, and SI. In general, the charge balance is good with errors less 7%, except in the Dover groundwater where the ionic strength and alkalinity are low. It is reasonable to assume that the alkalinity measurement was underestimated for this particular water sample, because greater analytical uncertainties are involved when groundwater alkalinity is less than 10 mg/L (Table 2.8). The modeling results show that several carbonate minerals (aragonite and calcite) might be supersaturated in groundwater at Moffett field and at the Y-12 Plant, whereas silica minerals are at near saturation in water from Dover and Portsmouth sites. Additionally, a few ferric oxyhydroxides are supersaturated in groundwater samples from the Monticello and the Y-12 Plant sites, because the chemical analysis showed the presence of iron and high DO in these waters. This illustrates the need for good chemical analysis, which allows more accurate modeling results.

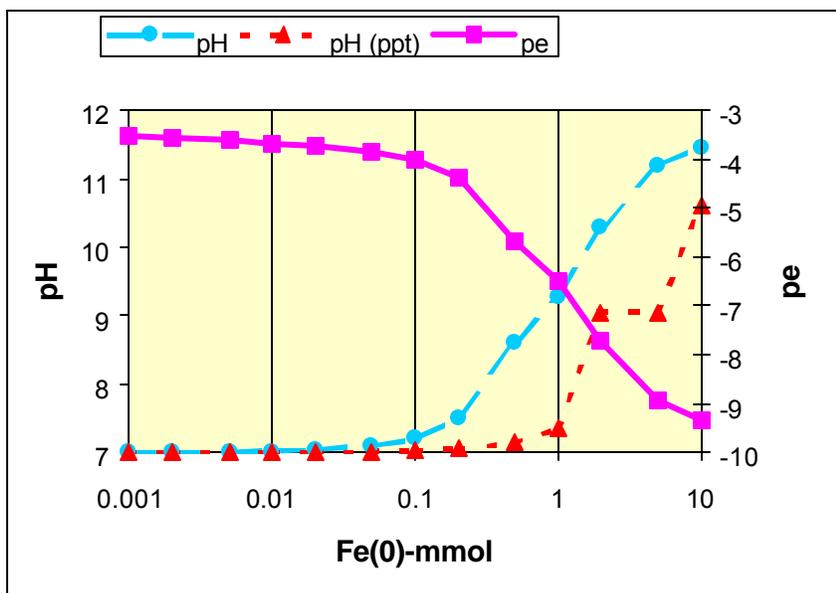
**Table 2.8. PHREEQC equilibrium calculation performed on data listed in Table 2.7.**  
Here the ionic strength and alkalinity units are in mEq.

	Dover area 5 Gate1-6/99	Portsmouth X625-3/98	Moffett field 6/96	Monticello 10/99	Y-12 Plant Passway2-1/99
Upgradient	U4S	FC-1	WIC-2	R1-M3	TMW-05
pH	5.07	5.9	7.15	6.51	6.75
pe	15.5	-4.4	13.4	13.9	13.8
Eh (mV)	920	-261	795	821	814
Ionic strength (mEq)	2.09	16.4	18.7	43.6	30
Alkalinity (mEq)	0.12	1.1	5.8	4.7	4.4
Charge balance, %error	10.57	-6.98	1.18	-0.68	-3.23
Modeling results on mineral saturation index (SI)					
Aragonite	--	--	0.11	-0.54	-0.03
Calcite	--	--	0.26	-0.39	0.11
Chalcedony	-0.23	-0.06	--	--	--
Dolomite	--	--	0.36	--	-0.66
Goethite	--	--	--	4.2	5.4
Hematite	--	--	--	10.41	12.8
Quartz	0.2	0.37	--	--	--
SiO2(a)	-1.07	-0.9	--	--	--



**Fig. 2.10. Modeling of pH and pe vs iron dissolution in 5 mM NaCl with PHREEQC for an unbuffered solution.**

Another example of forward modeling is illustrated in Figs. 2.10 and 2.11 in which we predict the changing equilibrium conditions of groundwater as we allow increasing amounts of Fe(0) to dissolve in the influent groundwater. Figure 2.10 shows pH and pe change in a 5 mM NaCl solution as a function of the amount of Fe(0) dissolved in the water. Because the solution is poorly buffered, the pH of the solution will rise to ~11 if 1 mM (56 mg/L) Fe(0) is allowed to dissolve. If the influent groundwater contains high alkalinity (Fig. 2.11), the buffering capacity of the sample will limit the increase of pH as Fe(0) is dissolved.



**Fig. 2.11. Modeling Fe(0) dissolution with PHREEQC for a buffered solution containing 3.9 mM CaCO<sub>3</sub> and 4.5 mM Cl.**  
 Note: Model results with mineral precipitation are plotted as triangles [pH(ppt)].

Figure 2.11 shows results of a theoretical dissolution experiment similar to that shown in Fig. 2.10, except the influent solution has an alkalinity value 3.9 mM (as CaCO<sub>3</sub>) in addition to 4.5 mM NaCl. In this solution, the pH only rises to ~9 rather than ~11 as in the previous example as a result of dissolution of 1 mM Fe(0). However, with an alkalinity value of 3.9 mM, the solution is not stable with respect to siderite (FeCO<sub>3</sub>), and we predict that precipitation of this mineral phase will occur. If we allow siderite to precipitate, the equilibrium concentration of Fe(II) is substantially decreased and the equilibrium pH is reduced to ~7.5 [Fig. 2.11, pH(ppt)]. If we allow 10 mM Fe(0) to dissolve, the unbuffered solution will show a large increase in pH to 12 (Fig. 2.10), whereas the pH will rise to ~10 with carbonate precipitation in the buffered system [Fig. 2.11, pH(ppt)].

The modeling results show that the buffering capacity of the influent groundwater is very important in determining the equilibrium pH. For the selected sites in Table 2.3-1, the alkalinity values span from 0.12 mM to ~6 mM. If we allow 0.5 mM of Fe(0) to dissolve [this amount of Fe(II) has been measured at the Portsmouth and the Y-12 Plant sites], and at the same time permit various minerals to precipitate, the expected final pH will vary from 9 to 11 over the range of alkalinity values considered (Fig. 2.12). Note that siderite predominately precipitates from solution when sufficient HCO<sub>3</sub><sup>-</sup> is available in the influent water (i.e., high alkalinity), whereas Fe(OH)<sub>2</sub> precipitates primarily from low-alkalinity groundwater.

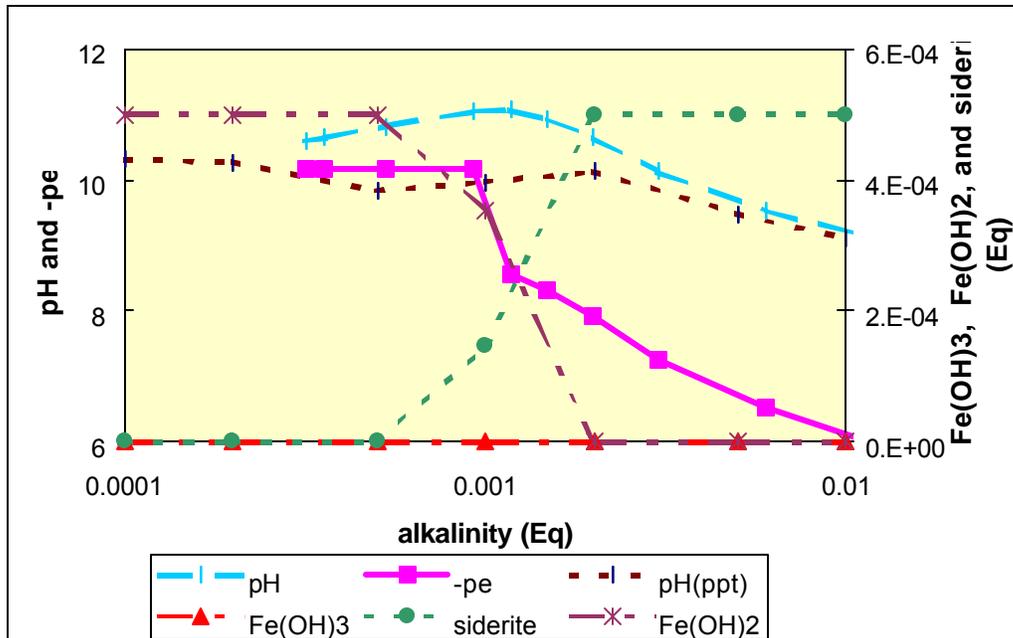


Fig. 2.12. Modeling with PHREEQ with varying alkalinity with 0.5 mL dissolved Fe(0).

Using a similar approach, we allow either 1 mM or 10 mM iron to dissolve in the influent water from the sites represented in Table 2.7 and predict the pH at equilibrium. Table 2.9 shows the results of the calculation. In each of the groundwaters considered, the pH change is small when 1 mM of Fe(0) is allowed to dissolve and re-equilibrate with the water while at the same time permitting carbonates and oxides to precipitate. Dissolution of 10 mM Fe(0) increases the pH from the influent values of  $\leq 7$  to 7.5–11. The equilibrium prediction for 10 mL Fe(0) compares well with the measured pH values in downgradient wells (Table 2.9). Discrepancies exist between the model result and field measurement for the Portsmouth site. We believe that the low observed pH value in downgradient water is a result of the fast flow of that system, in which water was at steady state rather than equilibrium conditions. Alternatively, these results could be interpreted as reflecting a smaller amount of iron in equilibrium with the water.

Table 2.9. Predicted equilibrium pH assuming 1 mM and 10 mM Fe(0) dissolved in the influent water (Table 2.7) compared with measured downgradient pH

		Dover area 5	Portsmouth	Moffett field	Monticello	Y-12 Plant	
Date sampled		June/99	March/98	June/96	Oct/99	Jan/99	
Measured upgradient	Well	Gate1-U4S	X625-FC-1	WIC-2	R1-M3	TMW-05	
	Influent pH	5.07	5.9	7.15	6.51	6.75	
	Calculated pH given Fe(0) <sub>diss</sub>	1 mM	5.85	6.28	7.03	6.67	6.80
		10 mM	10.46	11.04	10.64	7.66	7.47
Measured downgradient	Well	F7D	T1-4	WW-8B	R2-M4	DP20M	
	Measured pH	10.59	7.2	9.6	7.88	7.52	

### 2.3.2 Inverse Modeling

As discussed earlier in this section, in inverse modeling one aqueous solution is assumed to mix with other aqueous solutions and to react with minerals and gases to produce the observed composition of a

second aqueous solution. Thus, it calculates mixing fractions for the aqueous solutions and mole transfers of the gases and minerals that produce the composition of the second aqueous solution. Because inverse modeling is based on material transfer and balance, multiple numerical solutions are possible when a sufficient number of phases are being considered. In general, one seeks to perform the modeling by considering those phases that have been identified or are reasonably expected to be present.

When pure water is allowed to react with Fe(0), the chemical composition of the system is well defined. For groundwater with a complex chemical composition, dissolving Fe(0) could invoke precipitation of a variety of minerals, and one must rely on the minerals identified from direct observations to constrain the system. We have attempted to calculate the amount of Fe(0) needed to dissolve in an influent groundwater in order to obtain the composition of effluent groundwater and the mass of the associated precipitates from such systems. Unless the minerals that have been identified from Fe(0) cores recovered from in situ PRBs are available to us, the inverse modeling remains as an exercise only because the systems are not constrained.

This quantitative geochemical modeling activity is intended to provide a predictive capability for the behavior of PRBs under different geochemical conditions. The goal is to use a manageable set of indicator chemical parameters to monitor the performance of the zero-valent iron media and use a comprehensive set of observed phases to calculate the mass accumulation of precipitates that may fill pore spaces in a PRB and restrict the flow, thus affecting the hydraulic performance of the barrier.

### **3. HYDRAULIC MONITORING ACTIVITIES**

Because one of the knowledge gap is understanding system hydraulics at PRB sites, most of the sites have embarked on hydraulic monitoring programs involving one of a number of commercially available flowmeters, water level monitoring, single-well tests, pumping tests, and/or tracer tests. These hydraulic monitoring approaches have not been consistently applied, hence, results have been variable.

Different approaches are also evident. The DoD has installed HydroTechnics meters at several sites, whereas the DOE has employed the colloidal borescope. The EPA sites have used electromagnetic flowmeters. Little has been done to determine whether one approach is better than another or where one approach is most likely to succeed.

#### **3.1 HYDRAULIC MONITORING WITH THE COLLOIDAL BORESCOPE**

At the present time, the interagency collaborators on this project are sharing data and obtaining additional data with several flowmeters at multiple sites. The HydroTechnics meter requires a fixed installation that cannot be moved from site to site. Thus, the colloidal borescope has been deployed at multiple sites that have HydroTechnics meters. The borescope and the KV Associates portable heat pulse meter have also been compared at one site. The instruments have different advantages and shortcomings. For example, the borescope is portable but may require several hours to obtain sufficient data in a flow zone. Nevertheless, the instrument can be deployed in any 2-in. well and can be moved up and down in the screened interval in order to find a suitable flow zone. The HydroTechnics meter has to be installed in a fixed location and cannot be easily retrieved if a malfunction is suspected. For example, two HydroTechnics meters are installed at the Travis Air Force Base PRB. One indicates a flow direction consistent with the PRB design and the potentiometric surface as determined from water level measurements. The other HydroTechnics meter, however, indicates flow is approximately 180° in the direction opposite the potentiometric surface.

Our effort in FY 2000 in hydraulic performance evaluation has focused on obtaining comparable borescope data at the sites where previous data have been obtained and the sites that our DoD and EPA partners have other types of flowmeters employed. The colloidal borescope was deployed at several sites, including: Dover AFB in Dover, Delaware; Y-12 Plant site, S3-Pond site, Oak Ridge, Tennessee; Elizabeth City site, North Carolina; and Monticello site, Utah. At the Dover site, the data collected with the borescope will be compared with velocity and directional data obtained with other instruments. At the Y-12 Plant site, measurements were repeated at locations initially measured one year ago. Measurements at the Elizabeth City PRB were made at the request of the EPA, which funded the work. Finally, borescope measurements were made as part of the comprehensive hydrologic investigation being made at the Monticello PRB.

In general, it is necessary to collect data for several hours of because experiments have shown that insertion of any device into a borehole generates a large quantity of extraneous particles that have no relationship either to the mobile pollutant load or the aquifer hydraulics (Kearl et al. 1992). Thus, from several minutes to several hours are needed for the flow field to stabilize after insertion of the borescope.

### 3.1.1 Dover Site

Monitoring points investigated during this field effort were, U1-S, U3-S, U3-D, U4-S, U4-M, U4-D, U5-S, U5-D, U12-S, U13-S, F1-S, F10, F14-S, P1-S, U7-D, U8-M, U8-D, and U9-D. A simplified site map showing the points investigated and the direction of groundwater flow identified with the borescope is found on Fig. 3.1.

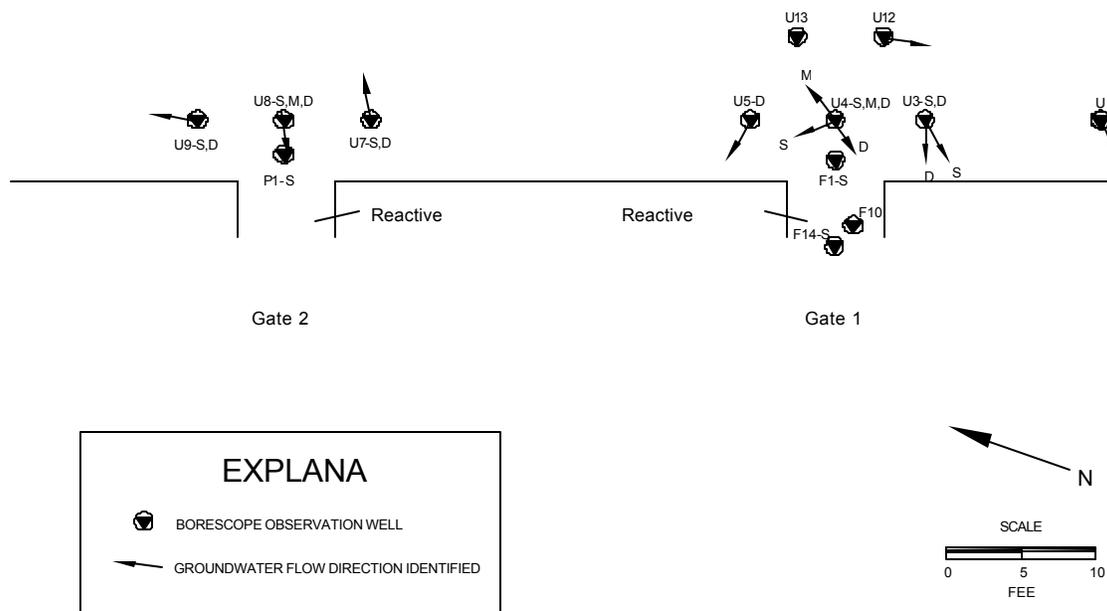


Figure 2. Borescope observation locations, Permeable Reactive Barrier, Area 5, Dover AFB

**Fig. 3.1. Borescope observation locations, permeable reactive barrier, Area 5, Dover AFB, Delaware.**

The following list provides the wells and intervals (ft) that were tested at the Dover site. At each wellbore, the borescope was lowered to the target depth and data were recorded until flow stabilized. In some cases, only swirling nondirectional flow was observed even after an hour of waiting for stabilization. In those cases, the borescope was moved to another depth interval. The range of observations are shown by comparing U1-S, where the first zone tested gave a reliable flow field, with U3-D in which 7 zones were tested before finding an acceptable zone. There were also some wells in which only swirling, non-directional flow was observed.

<u>well</u>	<u>interval (ft)</u>
U1-S	18, 18.5, 19
U3-S	18
U3-D	32, 33, 33.5, 34, 34.5, 35, 35.5
U4-S	18, 19
U4-M	25, 26
U4-D	32, 33
U5-S	18, 18.5, 19, 19.5
U5-D	31, 32, 33, 34
U12-S	18

<u>well</u>	<u>interval (ft)</u>
U13-S	18, 19, 19.25
F1-S	18, 19, 19.5
F10	18, 19, 20, 21, 22, 23
F14-S	18, 19
P1-S	18, 18.5, 19, 19.25, 19.5
U7-D	32, 33, 34
U8-M	25
U8-D	31, 32, 33
U9-D	32, 33, 34

### 3.1.1.1 Results

Following are descriptions of the observations made at each of the wells listed. The resulting data are summarized in Table 3.1.

**Table 3.1. Summary of data obtained from each well tested**

Well	Depth of flow zone(s) (ft)	Predominant direction	Average velocity (ft/d)	Comments
U1-S	18.5	SW	4.8 – 9.6	Poor, but usable flow zone
U3-S	18	NW	6-12	
U3-D	35.5	WSW	7.7-15	
U4-S	19	NW	6.5-13	
U4-M	26	NNE	1.8-3.6	Inconsistent direction and velocity in all 4 intervals
U4-D	32	SW	1-2.1	
U5-S	None	None	None	
U5-D	34	WNW	7.8-15.7	
U12-S	18	S	5.9-11.9	Swirling and turbid flow
U13-S	None	None	None	
F1-S	None	SW	None	Marginal data, but preponderance of particles were flowing SW
F10	None	W	None	Rapid swirling flow, bent well casing
F14-S	None	None	None	Swirling, nondirectional flow
P1-S	None	None	None	Swirling, nondirectional flow
U7-D	34	ENE	7.7-15.5	Data limited by power outage
U8-M	None	None	None	Water too turbid
U8-D	33	WSW	3.6-7.1	Data record may be too brief
U9-D	34	N	5.9-11.7	Deflection off sheet piling?

### 3.1.1.2 Monitoring points of wells at Dover site

The monitoring point of well U1-S had a screened interval (SI) 15.0 to 20.0 ft below top of casing (BTOC). Of the three zones investigated in this well (18.0 ft, 18.5 ft, and 19.0 ft), a well-defined flow zone was identified at 18.5 ft. This zone had a very consistent corrected azimuth of 228 degrees or southwest with an average corrected velocity of 4.8 to 9.6 ft/d.

The monitoring point of well U3-S had an SI 10.0 to 20.0 ft BTOC. One interval, 18.0 ft, was investigated with overnight data acquisition. This zone did not produce an exceptionally good flow file, but a trend with an average azimuth of 221 degrees was produced. The standard deviation of the azimuth was 86 degrees. Velocities were inconsistent throughout the data acquisition period indicating a non-laminar flow zone. The length of time the direction sustained itself does suggest that the directional data are usable.

The monitoring point of well U3-D had an SI 31.0 to 36.0 ft BTOC. Seven zones (32.0 ft, 33.0 ft, 33.5 ft., 34.0 ft, 34.5 ft, 35.0 ft, and 35.5 ft) were investigated in this lower completion monitoring well. Of these intervals, a relatively good zone was identified at 35.5 ft BTOC. The average azimuth was 250 degrees or west-southwest. Velocities oscillated somewhat with the average corrected values ranging from 7.7 to 15.4 ft/d.

The monitoring point of well U4-S had an SI 16.0 to 21.0 ft BTOC. Intervals at 18.0 and 19.0 ft were investigated in this monitoring well. A usable flow zone was identified at 19.0 ft. The average direction was west-northwest with an azimuth of 320 degrees. There was some variation throughout the test period. Average corrected velocities ranged from 6.5 to 13.0 ft/d.

The monitoring point of well U4-M had an SI 24.0 to 29.0 ft BTOC. Two zones were investigated in this monitoring well, 25.0 ft and 26.0 ft. A north-northeastern flow direction with an average azimuth of 30 degrees was identified at 26.0 ft. The velocity was low compared with other wells tested with corrected averages of 1.8 to 3.6 ft/d. This flow zone indicated the opposite direction of that found in the upper screened interval. An explanation for this apparent contradiction may be that backflow is created by deflection of the sheet pile as water flows toward the gate. Another possible explanation is that the nested monitoring wells are causing unnatural flow zones to be created.

The monitoring point of well U4-D had an SI 31.0 to 36.0 ft BTOC. Two intervals were examined in the lower completion of this monitoring well, 32.0 ft and 33.0 ft. Overnight data acquisition at 32.0 ft produced a relatively good 12-hour data file with an average direction of southwest with an azimuth of 217 degrees. The average corrected velocity was relatively low and ranged from 1.0 to 2.1 ft/d.

The monitoring point of well U5-S had an SI 10.0 to 20.0 ft BTOC. Four intervals were tested in the upper completion of this monitoring well, 18.0 ft, 18.5 ft, 19.0 ft, and 19.5 ft. No consistent flow zones were found. The nested well construction may be disturbing the natural flow field and preventing determination of a suitable flow file. This well completion was directly downgradient of the lower completion. The well screen, therefore, may have been obstructed by riser pipe from the lower completion.

The monitoring point of well U5-D had an SI 30.0 to 35.0 ft BTOC. Of the four intervals that were tested (31.0 ft, 32.0 ft, 33.0 ft, and 34.0 ft), the 34.0-ft interval produced a relatively good flow file for 2 hours. Velocities varied somewhat, but the average direction remained fairly constant with a direction of west-northwest with an azimuth of 283 degrees. In the upper completion of this monitoring well (18.0 ft, 18.5 ft, 19.0 ft, and 19.5 ft), no consistent flow zones were found. This well completion was directly downgradient of the lower completion which may have caused some obstruction of flow.

The monitoring point of well U12-S had an SI 15.0 to 20.0 ft BTOC. The 18.0-ft interval was the only interval tested in this upper completion monitoring well. This interval, which was observed overnight, produce a very good flow file with an azimuth of 172 degrees, or just slightly east of due south. The average corrected velocity ranged from 5.9 to 11.8 ft/d.

The monitoring point of well U13-S had an SI 15.0 to 20.0 ft BTOC. Three intervals (18.0 ft, 19.0 ft, and 19.25 ft) were tested. These produced only swirling flow. Water in the well was also very turbid, inhibiting further testing.

The monitoring point of well F1-S had an SI 15.0 to 20.0 ft BTOC. Three intervals were investigated in this upper completion well: 18.0 ft, 19.0 ft, and 19.5 ft. No good flow zones were found. However, a review of the files indicated that most flow was toward the southwest, which is consistent with groundwater flowing into the gate.

The monitoring point of well F10 had an SI 15.0 to 36.0 ft BTOC. Several intervals were investigated in this well. This well's casing was bent such that the borescope could not be advanced below 23 ft. None of the six zones, (18.0 ft, 19.0 ft, 20.0 ft, 21.0 ft, 22.0 ft, and 23.0 ft) produced a consistent flow zone. Observations of the flow field indicated very high velocities with a westerly trend.

The monitoring point of well F14-S had an SI 15.0 to 20.0 ft BTOC. Only two intervals were investigated in this well: 18 ft and 19 ft. Only swirling, nondirectional flow was observed.

The monitoring point of well P1-S had an SI 15.0 to 20.0 ft BTOC. Five intervals were investigated: 18.0 ft, 18.5 ft, 19.0 ft, 19.25 ft, and 19.5 ft. Only swirling, nondirectional flow was observed.

The monitoring point of well U7-D had an SI 31.0 to 36.0 ft BTOC. Three intervals were tested: 32.0 ft, 33.0 ft, and 34.0 ft. The zone at 34 ft was observed overnight. Unfortunately, a power outage limited the data acquisition. The flow file that was obtained had a direction of east-northeast with an average azimuth of 61 degrees and a corrected velocity of 7.7 to 15.5 ft/d. Testing of a deeper interval was planned but was abandoned because the water had such high turbidity.

The monitoring point of well U8-M had an SI 24.0 to 29.0 ft BTOC. A zone at 25.0 ft was investigated, but only swirling, nondirectional flow was observed.

The monitoring point of well U8-D had an SI 30.0 to 35.0 ft BTOC. Three zones, 31.0 ft, 32.0 ft, and 33.0 ft, were investigated. The interval at 33.0 ft produced a flow file that indicated an average azimuth of 241 degrees and an average corrected velocity of 3.6 to 7.1 ft/d. It should be noted that the velocity and direction appeared to be changing as the 100-minute data acquisition period was completed. There was insufficient time remaining to determine whether a significant change was occurring.

The monitoring point of well U9-D had an SI 15.0 to 20.0 ft BTOC. Intervals at 32.0 ft, 33.0 ft, and 34.0 ft were investigated in this lower completion. The 34.0-ft zone produced a flow file that had an average azimuth of 350 degrees and an average corrected velocity of 5.7 to 11.7 ft/d. Velocities and direction were very consistent throughout the data acquisition period. The direction of flow may indicate deflection from the sheet piling.

### **3.1.1.3 Discussion of Dover results**

Figure 3.1 presents the flow directions measured in this study. At Gate 1, the wells generally have flow toward the gate, although there is a significant anomaly with the nested well U-4 in which flow at depth appears to be through the gate, whereas flow in the middle and shallow region of the aquifer appears to be 45 to 180 degrees offset.

At Gate 2, flow in U-8-D does appear to be directly through the gate. Useful flow fields were not obtained for the other completions in this nested well. Data for wells U7 and U9 are anomalous but that may, in part, be the result of problems that occurred during data collection (Table 3.1). Data from well U-1 demonstrate that flow at this location, as expected, is bypassing the barrier. In general, therefore, those wells placed directly in front of the feature being evaluated (i.e., the gate or the edge of the barrier) showed flow directions consistent with the site conceptual model. The directions observed in U3 and U5 also indicate flow toward the barrier that would presumably be captured by the gate.

Two explanations are offered for the apparent anomalous flow directions. The first is based on observations from the nested well completions. Flow observed in the lower completion was consistent with the regional flow direction, however, the upper completions may be affected by the nearby middle and lower completions. The resulting turbulent flow may make the measured directions unreliable. This is a suggested explanation for the anomalous flow files obtained from the middle and upper completion of U-4, and the inability to obtain useful flow files from the upper and middle completions at U-8.

A second explanation for anomalous flow files could be the proximity of the wells to the barrier itself. Figure 3.2 shows the data in Fig. 3.1 superimposed on simulated groundwater particle lines obtained from a figure in the Design, Construction and Monitoring Report for the site (Gavaskar et al. 1999). Figure 3.2 demonstrates the bending of flow lines near the barrier. While the simulated flow lines indicate laminar flow, this is an idealized representation. The actual flow field is certainly more complex—particularly close to the barrier. Thus, the borescope observations probably reflect some turbulence caused by the proximity to the barrier.

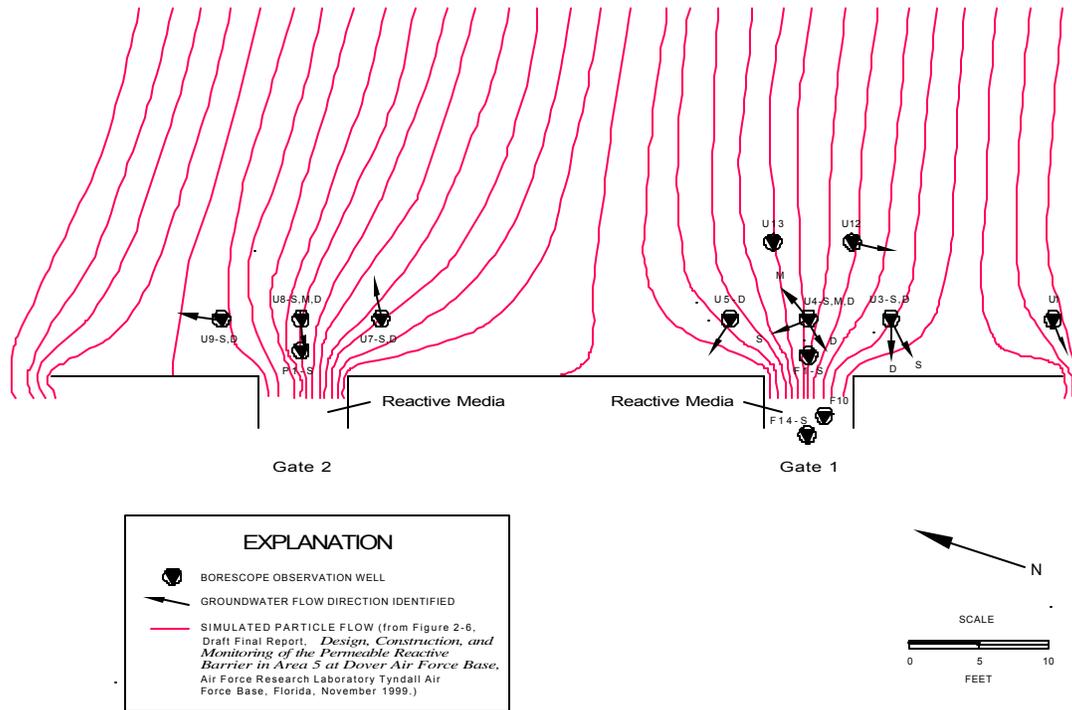


Figure 3. Simulated groundwater particle lines and borescope observation locations, Permeable Reactive Barrier, Area 5, Dover AFB

**Fig. 3.2. Simulated groundwater particle lines and borescope observation locations, permeable reactive barrier, Area 5, Dover AFB.**

It should also be noted that data from the HydroTechnics meters did not show flow directly through the gates. As noted in Gavaskar et al. (1999), “it is possible that the flow direction changes from the regional southwest gradient to the PRB-induced westward gradient only when the water gets very close to the funnel walls.” This consideration is apparently supported by data from the borescope as well.

### 3.1.1.4 Summary at Dover site

Considering the data as a whole, borescope-measured flow velocities varied by approximately one order of magnitude from 1 to 2 ft/d to 15 ft/d. These values are consistent with those based on observed gradients and conductivity as reported previously (Gavaskar et al. 1999, Table 6-7). Velocity through the gates, as reported by Gavaskar et al. (1999), was mostly in the range of 2 to 6 ft/d. Considering that the borescope measures the fastest zones, the agreement of these results is reasonable.

Gavaskar et al. (1999) also reported velocities obtained with the HydroTechnics flowmeter. Those results are approximately one order of magnitude lower than both average regional measurements based on conductivities and observed gradients and direct measurements made with the borescope. The borescope

data demonstrate that there are zones in the aquifer that are relatively stagnant. Because the HydroTechnics meter cannot be moved after installation, it simply may be installed in a location where flow is not significant.

### **3.1.2 Y-12 Plant**

The primary purpose of this investigation was to determine groundwater flow directions and velocities from selected monitoring points within and near the S-3 reactive barrier pilot project at the Y-12 Plant. Another objective was to compare observed data with that obtained during a field study previously done in December 1998. Monitoring points investigated during this field effort were DP07, DP09, DP11, DP13, TMW07, TMW09, and TMW11 (see Watson et al. 1999, for locations).

#### **3.1.2.1 Results**

Following are well-by-well descriptions of the measurements made.

At the monitoring point for well DP07, a well-defined flow zone was identified at 15.0 ft. This zone trended east-northeast with an approximate average corrected velocity of 3 to 4.74 ft/d. No flow zones were found during the December 1998 field studies hence no comparisons can be made.

At the monitoring point for well DP09, three zones were investigated: 16.0 ft, 19.0 ft, and 20.0 ft. No well-defined zones were identified. A reasonably good zone that had been present at 16.0 ft during the December 1998 fieldwork could not be reproduced.

At the monitoring point for well DP11, six zones (15.6 ft, 16.6 ft, 17.5 ft, 18.5 ft, 19.5 ft, and 20.5 ft) were investigated, and no acceptable flow zones were identified. Swirling, nondirectional flow and a low colloid density were the most significant observations.

At the monitoring point for well DP13, flow zones at 20.5 ft and 21.0 ft were investigated. The flow zone found during the December 1998 fieldwork was still present and showed a southwestern flow direction for about three hours. However, data were collected overnight and the flow direction fluctuated to a more westerly direction and then drifted to the east.

At the monitoring point for well TMW07, five zones were investigated in this temporary monitoring well: 18.0 ft, 19.0 ft, 20.0 ft, 25.5 ft, and 26.0 ft. A southwestern flow direction was identified at the 26.0-ft interval with an average corrected velocity of 1.7 ft/d. This zone was not observed in the December 1998 fieldwork.

At the monitoring point for well TMW09, intervals at 18.0 ft and 27.0 ft were examined. An overnight data collection at 27.0 ft produced a good 17-hour file with an average direction of 265 degrees and average corrected velocity of 4.6 to 9.1 ft/d. This zone compared favorably to the December 1998 test, which produced an average direction and velocity of 233 degrees and the 5 to 12 ft/d, respectively. Also noteworthy were organisms that were approximately 1 micron in size that were seen in the well at 18.0 ft. None were observed in the lower part of the well, which is a contradiction to the observations made in December of 1998. At that time they were observed throughout the screened interval and at a much higher density. Larger organisms, that were 50 to 100 microns in length and were observed in the well during December of 1998, were absent during this observation period.

At the monitoring point for well TMW11, four intervals were tested: 18.0 ft, 22.0 ft, 26.0 ft, and 28.0 ft. Two good flow zones were found. The first, at 22.0 ft, had an average direction of 301 degrees with an average corrected velocity of 6.7 to 13.5 ft/d. The remaining flow zone was identified at 26.0 ft. The

average direction was 291 degrees with an average corrected velocity of 9.9 to 19 ft/d. Both flow zones displayed very low colloid density. No flow zones were found in the December 1998 fieldwork, however the general lack of colloids in the well was also noted during that time.

### 3.1.2.2 Comparison of 1998/1999 results

The 1999 measurements at the Y-12 Plant site provided one of the few opportunities thus far to evaluate flowmeter results on a year-to-year basis. Unfortunately, site conditions were considerably different during the two measurement periods. Heavy rains fell during the 1998 fieldwork. Water levels were several feet higher, upwelling was observed in some wells and insufficient colloid density in others. Nevertheless, from 1998 to 1999, the data for DP11, DP13, and TMW09 showed excellent agreement (Table 3.2). For two of the other four wells, no flow zone was found in 1998 because of a lack of colloids caused by the recent rainfall and rise in water level. DP09 has the most anomalous result in that a flow zone was found in 1998 and not in 1999. Again, these data indicate the borescope's most serious limitation (i.e., it takes a long time to acquire data). Additional testing at this site is planned for future periods.

**Table 3.2. Repetitive measurements collected with the borescope at the Y-12 Plant site in 1998 and 1999**

Well	Observation
DP07	1998, no flow zones; 1999, flow zone at 25.0 ft
DP09	1999, flow zone at 16 ft; 1999, no flow zones found
DP11	1998/1999, no flow zones identified
DP13	1998/1999, flow zone found at 21 ft
TMW07	1998, no flow zones (or colloids); 1999, flow zone at 26 ft
TMW09	1998, flow zone at 27 ft (5 to 12 ft/d); 1999, same zone had (4.6 to 9.1 ft/d)
TMW11	1998, no flow zones (or colloids); 1999, flow zones at 22 and 26 ft (6.7 to 19 ft/d)

### 3.1.2.3 Y-12 Plant summary

In summary, the primary objectives for the field study were to (1) evaluate previous use of the borescope by evaluating whether the same flow zones were present from year-to-year and (2) evaluate the amount of bacterial activity in the upper and lower portions of the screened intervals for the specific wells.

There appears to be a general lack of colloids in the trench. This observation was also noted in the December 1998 fieldwork. Some depths that had flow zones in the December 1998 study did not produce repeatable flow zones in 1999. One zone in TMW09 that was identified at 27.0 ft had similar results during both field efforts. Whether the observed differences were the result of effects of the instrument or the variable site conditions will require additional measurements to determine. Finally, the monitoring points that were identified as having high bacterial activity in December 1998 showed much less activity. This microbial activity was limited to the upper portions of the monitoring points or was not present.

### 3.1.3 Elizabeth City

The EPA requested deployment of the colloidal borescope during a period of time when significant additional work was being conducted at the PRB. Because the colloidal borescope measures the stable colloid flow existing in an undisturbed well, activities that cause extraneous particles to be entrained within the wellbore prevent measurements from being taken. Unfortunately, tracer testing, drilling, and sampling being conducted by EPA personnel prevented several of the wells from being tested. More data

could have been obtained if the borescope had been deployed the week before or the week following the other fieldwork.

### **3.1.3.1 Results**

Wells MW47, MW49, and MW52 were sufficiently turbid from sampling activities that borescope measurements were precluded. Attempts were made to obtain data, but during the fieldwork period, these wells never became clean enough to observe colloids.

Well MW13 is located upgradient of the PRB, just downgradient from the former plating shop—the source area for the contamination. The screened interval is at 10 to 15 below ground level (BGL). The intervals tested were 12, 12.5, 13.25, 13.5, and 14 feet below casing level (BCL). There was a good flow zone at 13 feet. The direction was NE to NW with an approximate velocity of 4.4 ft/d. The data from 12 ft and 14 ft indicated flow that is less stable than desired for accurate measurements. The data from the latter zones do indicate, however, similar velocity and flow directions that typically had an easterly component.

Well MW46 is located downgradient of the PRB and is due north of the west end of the wall. The well location is also approximately 20 ft south of the Pasquotank River, and the water level in the well appears to reflect the river stage. When a northwesterly wind began to blow, wave action appeared to have an effect on the observed flow direction. The screened interval is 14 to 24 ft BGL. Intervals tested were at 15, 16, 17, 18, 18.5, 19.5, 20, 20.5, and 21 ft. The best data were obtained from the interval at 21 ft. The predominant flow direction was NW with a velocity of approximately 4.9 ft/d. An interval at 20.5 feet provided data of questionable value because the standard deviation for the flow direction is so large. The velocity is in the same range as at 21 ft, but the flow direction appears to be opposite.

Well MW48 is located approximately 3 feet upgradient and at the center of the PRB. The “induced flow distribution” for this well, as determined by measurements performed by an EPA researcher on-site at the same time, indicated that there would be a good flow zone at 19 to 20 ft. Intervals tested were 19.5, 20, 20.5, 21, 21.5, and 22 ft BCL. The interval at 20 ft yielded the best borescope data. However, the velocity was initially very high and then decreased by approximately a factor of five. In general, only long-term data are considered meaningful, hence the easterly flow direction and approximate velocity of 6 ft/d are believed to best represent the conditions at this interval. Data at 21.5 ft showed a distinct direction to the SE, but the flow velocity fluctuated throughout the test. Data collected at 22 ft also showed a SE flow direction and similar velocity.

Well MW50 is located northeast of MW48 on the downgradient side of the barrier. The screened interval is 25 to 30 ft. Intervals tested were at 25, 25.5, 26, 26.5, 27, 27.5, and 28 ft. The interval at 25 ft produced a relatively stable flow direction to the SE with an approximate velocity of 5.2 ft/d. The tests for 25.5 and 26 ft, although brief (60 to 80 minutes), showed easterly flow directions with average velocities of approximately 4 to 5 ft/d. The other intervals showed too much fluctuation in both direction and velocity to yield useful data.

### **3.1.3.2 Elizabeth City data discussion**

The purpose of the testing was to evaluate flow directions and velocities at the Elizabeth City PRB. Unfortunately, other fieldwork being conducted at the same time that the borescope was deployed prevented the acquisition of sufficient data to provide a comprehensive view of the site. Similarly, it was not possible to perform an adequate comparison with the “induced flow distribution” testing that was occurring at the same time. Nevertheless, the data do permit the following observations:

- In the only well where both the borescope and the induced flow distribution tests were performed, the instruments agreed on the location of the most permeable zone.
- Two wells that were not adjacent to the PRB yielded useful data. The flow directions in these wells corresponded to the regional flow direction based on other testing.
- Two wells were tested that were adjacent to the PRB. The flow directions were not compatible with the regional flow direction. For example, the data indicate that the water in MW51 may be flowing back into the wall from the downgradient side. The direction for well MW48 indicates flow away from the wall. Unfortunately, more data are needed to interpret these flow directions. Anomalous or complex flow patterns near and within the PRB have been noted at several other sites. Apparently, the flow regime created by the PRB is too complex to be interpreted based on only a few borescope measurements.
- Velocities measured with the borescope were approximately an order of magnitude greater than the design velocity for the site (0.5 ft/d). Typically, borescope velocities are a factor of four or less greater than average velocities measured with pumping tests and single well tests.

### 3.1.4 Lowry AFB PRB

#### 3.1.4.1 Data from the Lowry site

Measurements were made over a 5-day period from October 25 to October 29, 1999.

The following wells and intervals were tested at the Lowry site. As noted above, the borescope was lowered to the target depth and data were recorded until flow stabilized. In some cases, only swirling non-directional flow was observed even after an hour of waiting for stabilization. In those cases, the borescope was moved 6 in. in order to obtain measurements from another zone.

The list below provides the wells and intervals (ft) that were tested at the Lowry site. The range of observations are shown by comparing N-2, where the first zone tested gave a reliable flow field, with U-6 in which 12 zones were tested and only swirling, nondirectional flow was observed. The resulting data are summarized in Table 3.3.

<u>well</u>	<u>interval (ft)</u>
N-1	10.0, 10.5, 11.0
N-2	10.0
N-3	10.0, 11.0, 12.0, 13.0
N-5	10.0, 10.5, 11.0, 11.5, 12.5, 13.0, 13.5, 14.0
N-6	10.0, 10.5
N-9	10.0, 11.0, 11.5, 12.0, 12.5, 13.0
U-1	10.0, 10.5, 11.0, 11.5
U-6	9.5, 9.75, 10.0, 10.25, 10.5, 10.75, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5
U-7	10.0, 10.5, 11.0, 11.5, 12.0, 12.5
U-9	10.0, 11.0, 11.5, 12.0, 12.5
U-10	10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0

**Table 3.3. Summary of data obtained from each well tested**

Well	Depth of flow zone(s) (ft)	Predominant direction	Average velocity (ft/d)
N-1	11	NNW	6.15
N-2	10	NNW	4.38
N-3	None located	Swirling flow only	Not applicable
N-5	None located	Swirling flow only	Not applicable
N-6	10.5	NW	6.01
N-9	13	ESE	11.29
U-1	11	NE	4.54
U-6	None located	Swirling flow only	Not applicable
U-7	10, 12.5	N, N	3.76, 2.237
U-9	12.5	E	2.16
U-10	None located	Swirling flow only	Not applicable

### 3.1.4.2 Discussion and summary

Data collection at the Lowry site was constrained by time, budget, and security reasons. In other words, longer tests are sometimes desirable as is testing of more zones in the wells. Nevertheless, several excellent flow zones were found. For example, the data from U-9, as shown in Table 3.3, are a classic depiction of the data that is desired for a particular flow zone. For 1 or 2 hours there was swirling flow as the particles disturbed within the wellbore settled. After 1 to 2 hours, the flow zone stabilized and unidirectional flow with a constant velocity was observed. These data for U-9 show the advantage sometimes derived from leaving the instrument in the well overnight. Unfortunately, more wells could not be tested in this manner because of time and security reasons. However, N-6 demonstrates that an overnight measurement would not always have provided smoother data. Here the data show swirling flow for approximately 30 minutes at which point easily interpretable, unidirectional flow became evident.

Data from U-1 and N-9 indicate flow toward the nearby stream. Data from N-1, N-2, U-7, and U-9 indicate flow that will probably be captured by the funnel and gate system, although flow in U-9 is directly toward one of the wing walls.

Average velocity measurements were in the range of 2 to 11 ft/d. These measurements will be compared with data obtained from HydroTechnics flowmeters already installed on-site. However, as shown by the borescope data, there is significant heterogeneity, which may complicate comparison of the two flow measurement methods. Indeed, it may be useful to return to the site in the future and evaluate how well the borescope can replicate this series of measurements.

### 3.1.5 Monticello

Borescope measurements were made in several wells at the Monticello site. These data were taken in preparation for a multiple-tracer test that was conducted several weeks thereafter. In general, the borescope is being used to support the hydraulic testing at the Monticello barrier in the following ways:

- Flow directions and velocities within the barrier are being evaluated to determine residence time, whether there are preferential flow paths, and whether flow is directly through the barrier.
- Flow directions and velocities upgradient of the barrier are being used to evaluate the capture zone and the magnitude of preferential flow zones.

- Flow directions and velocities downgradient of the barrier are being used to evaluate whether preferential flow zones have an influence on flow through the barrier.

Repetitive borescope measurements will be made during, at least, the next two years to supplement water level data, to evaluate whether clogging is occurring, and to evaluate the magnitude of seasonal changes in flow direction and residence time.

Interpretation of the measurements made to date was incomplete at the time this report was prepared. The borescope data will be evaluated in conjunction with the data from the tracer test and provided in a subsequent report. It should be noted, however, that a qualitative review of the borescope results indicated that flow to and through the barrier was faster than the design flow. Based on this information, sampling intervals for the tracer test were adjusted. These adjustments were appropriate and eased the performance of the tracer test.

## **3.2 TRACER TESTS**

The hydraulic characteristics of several PRBs have been investigated with tracer tests. Results to date have been mixed. Some of the tests have failed or yielded inconclusive results. Moreover, the tests have been relatively expensive. In order to better define where tracer testing is appropriate, and how best to conduct the tests, a multiple-tracer test has been performed for the Monticello, Utah, mill tailings site. Additionally, the site has specific goals to accomplish through the tracer test: (1) To establish the current hydrologic performance of the reactive barrier and (2) to provide a baseline against which to assess changes in barrier performance over time.

### **3.2.1 Background**

Installation of the reactive barrier was completed on June 30, 1999, and quarterly water level monitoring began in October 1999 using the array of piezometers installed during and following construction. Water level measurements indicate the formation of groundwater mounding behind the reactive barrier, more pronounced at the southern end of the gate portion of the barrier. The extent of this mounding is difficult to ascertain because of the paucity of monitoring locations away from the barrier. Much of the hydraulic head drop across the barrier occurs immediately at the upgradient interface of the barrier and, secondarily, immediately upon crossing the exit wall of the barrier. This has led to some concern that either smearing of fine-grained materials or vibrational compaction from installation of the sheet pilings has created a low-permeability layer that is creating resistance to flow at the barrier wall.

Mounding will occur if the groundwater flux captured by the slurry walls is greater than the capacity for the gate to handle the increased flow through that cross-sectional area, and a new equilibrium water table is established. The mounding has the potential to create a flow bypass farther upgradient, however, as flow is diverted toward the outer edges of the slurry walls. A second possibility is that groundwater that would ordinarily flow through the coarse alluvial deposits with minimal resistance could be forced through relatively permeable zones within the underlying bedrock because of resistance to flow through the gate, creating underflow as a result of changing hydraulic conditions upgradient of the barrier. Thus any plan for evaluating the hydrologic performance of the reactive barrier needs to take into account the potential for bypass and underflow of the barrier, as well as evaluating transport through the gate portion of the barrier itself.

### 3.2.2 Multi-Tracer Selection

Tracer tests afford the opportunity to assess transport velocities through the barrier and residence times within each layer of the barrier. In addition, the application of tracers in multiple locations can provide a picture of the spatial variations in transport characteristics and the degree of vertical and lateral mixing of groundwaters moving through the barrier. Ideally, the tracers used will have the following characteristics:

- a. Easily introduced into the subsurface.
- b. No detrimental impact on the barrier.
- c. Nonhazardous to the environment.
- d. Straightforward sampling and analytical methods.
- e. Multiple tracers can be detected and differentiated in a single analysis.
- f. Inexpensive and easy to obtain.
- g. Low reactivity and, therefore, high likelihood of detection, minimal retardation, and rapid flushing through the system after injection.

These characteristics ensure that the introduced tracers can be detected above natural background levels, that sufficient flushing has occurred to enable repeat testing over time using the same tracers, and that cost and effort are minimized, while protecting the barrier integrity and the environment.

A wide variety of groundwater tracers are available to choose from, many of which have the characteristics listed above and have been field-tested. Two considerations that narrowed the selection of tracers for this test were the reactive nature of the barrier materials and the desire to conduct on-site analysis for presence of the tracers during the test period. Tracers that behave conservatively in natural geologic materials may react with Fe(0) media and therefore need to be tested in advance to ensure their detection downgradient. Moreover, field analytical methods are much more restrictive than those available in the laboratory.

We first tested fluorescent dyes (rhodamine-WT and fluorescein), which are inexpensive and can be detected at very low concentrations through fluorescence spectroscopy or by using field fluorimeters. Batch tests with Fe(0) showed that these dye tracers were highly reactive in the Fe(0) media, and are therefore not suitable for field deployment around Fe(0) installations. Simple anionic tracers (iodide and bromide) were the next choice because they are also inexpensive and can be analyzed using standard ion chromatography (IC) or ion-specific probes. The probes have the benefit of easy field analysis, although they lack the sensitivity and accuracy of IC methods. A chief concern, however, was the potential for cross-interference between the bromide and iodide if both tracers appeared in the same wells.

Noble gases, such as helium, neon, and argon, have been used as dissolved gas tracers. The benefits of using noble gases are that (1) they are nonreactive in all environments, (2) they can be analyzed using simple gas chromatography (GC) methods, (3) multiple gases can be analyzed from a single sample, and (4) there is no volume displacement during injection, as the gas is introduced by passive diffusion into the groundwater in the injection well. The disadvantages are that (1) loss of the gas can occur at a number of points during the sampling and analysis process, resulting in reduced concentrations or false non-detects, and (2) additional time is required to bring injection concentrations to equilibrium. A further disadvantage is potential loss of dissolved gas into the vadose zone in shallow systems or loss to any trapped gas phase in the saturated zone, resulting in reduced concentrations and lower apparent transport rates.

In the end, we chose to use helium and neon as the primary tracers, using a passive-diffusion injection system and field GC for analysis because of their inherent nonreactivity. However, because of the potential for loss of gases for the reasons stated in the preceding discussion, we also chose to inject

bromide and iodide tracers along with the gases as a backup, using an ion-specific probe for rapid field analysis to monitor tracer transport throughout the test.

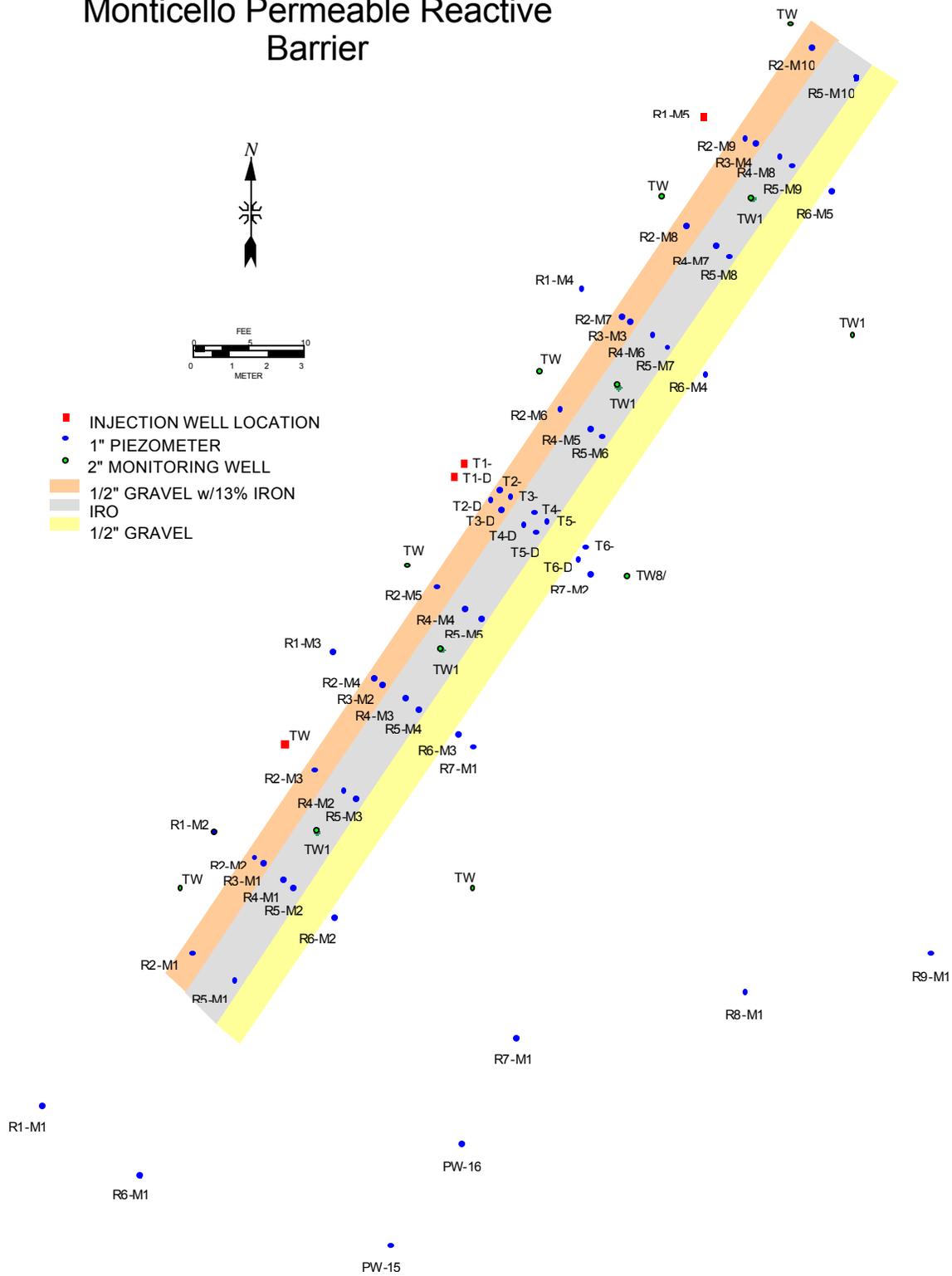
### **3.2.3 Tracer Injection**

We injected different tracers into four separate locations immediately upgradient of the barrier: wells TW-2 (bromide and helium), T1-S (neon), T1-D (iodide and argon), and R1-M5 (bromide and helium) (Fig. 3.3). The choice of these locations provided a lateral and vertical distribution in order to assess variability in transport characteristics along the barrier and the degree of mixing within and around the barrier. The decision to use identical tracers at either end of the barrier was considered reasonable because of the low likelihood that lateral transport across the length of the barrier over the short distance through the barrier would occur.

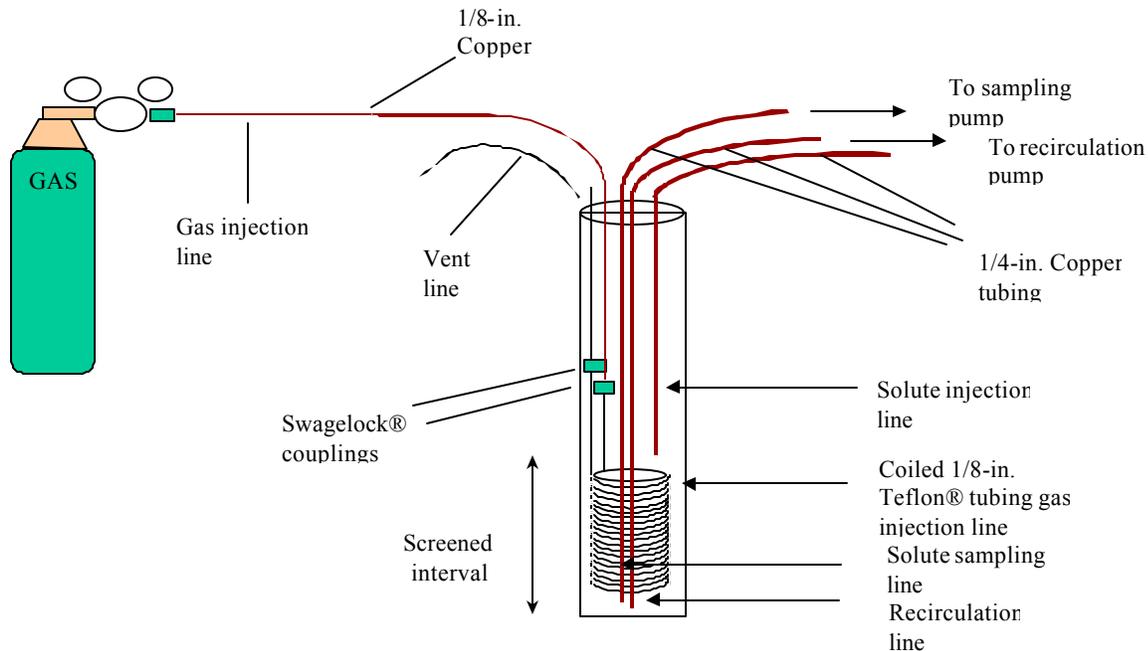
For the anionic tracers, we applied continuous flux-controlled injection controlled by a Campbell datalogger using peristaltic pumps (Fig. 3.4). A concentrated tracer solution was pumped into the injection well and continuously recirculated within the well casing. Specific conductance of the water in the wellbore was monitored using a flow-through device and recorded by the datalogger. The conductivity had been calibrated to tracer concentration by analyzing samples taken from the injection well during injection. A constant, predetermined concentration in the injection well can be maintained by setting a target conductivity and a tolerance based on the background conductivity of the groundwater plus the increase in conductance as a result of the addition of tracer at the predetermined level. When the concentration in the well drops below the critical concentration, the datalogger triggers the opening of a solenoid valve, that allows tracer solution to drip into the recirculation loop until the concentration once again increases above the critical concentration. The datalogger controlled the input of tracer solution and recorded the conductivity throughout the test.

The dissolved gas tracers were introduced by continuous injection using a diffusion method (Fig. 3.4). A coil of 1/8-in. Teflon tubing was inserted into the screened portion of the injection well. The gas tracer was continuously pumped through the injection tubing at a low flow rate and vented to the atmosphere. This allowed the gas to diffuse into the groundwater surrounding the injection tubing, coming to a constant equilibrium concentration, with the exception of minor fluctuations due to temporary variation.

# Monticello Permeable Reactive Barrier



**Fig. 3.3. Well locations at the reactive barrier at Monticello site, Utah.**



**Fig. 3.4. Gas and solute tracer injection system.** The recirculation loop is continuously powered by a peristaltic pump. Concentrated tracer solution is dripped into the recirculation line through a solenoid valve controlled by a Campbell datalogger. Control of the valve is based on changes in conductivity in the wellbore that occur as the tracer is variably injected and diluted by ambient flow.

Some problems were encountered early in the test that required adjustments to the field plans. First, there were problems with the power hookup to the site that prevented starting the recirculation pumps in advance. Ideally, the recirculation pumps are allowed to run for 24 hours to allow the system to stabilize, to obtain current background conductivity measurements and gauge the variability, to calibrate the rate of tracer concentrate drip into the system using distilled water, and to obtain a rough estimate of the groundwater flux through the injection wells. However, because of the power difficulties, this early starting of the recirculation pumps would have required a delay in the start of the tracer injections and resulted in a shorter test. Thus, it was decided to use the historical conductivity measurements and initial estimates of injection rate and not to delay the start.

The recirculation loop is continuously powered by a peristaltic pump. Concentrated tracer solution is dripped into the recirculation line through a solenoid valve controlled by a Campbell datalogger. Control of the valve is based on changes in conductivity in the wellbore that occur as the tracer is variably injected and diluted by ambient flow.

The result was that, while the injection systems worked according to plan, injection concentrations varied more than anticipated and injection concentrations were 2 to 3 times higher than planned. The total mass of tracer injected was not affected, only the time period over which it was injected. Additionally, problems that developed with one of the conductivity probes were not detected until the tracer test had begun.

A second problem encountered was that we were unable to detect the gas tracers in the downgradient wells. The most likely cause was degassing during sampling, based on the observation of air bubbles in the sampling tubes leading to the pumps. Because we co-injected anionic tracers and were able to

conduct a field analysis for bromide tracer, use of the gas tracers was abandoned early in the test period in favor of sole reliance on the anionic tracers.

Finally, one of the original injection wells (R1-M2) was abandoned after one day when it was determined that groundwater flux through the screen was very low based on the very slow drop in conductivity after bringing the well up to the initial injection concentration. A second well, TW-2, was chosen as an alternate, and tracer injection began in that well on the second day of the test, following completion of the injection in T1-D.

Tracer injection was planned to occur over a period of 5 days, followed by a recovery period of approximately 7 days. The injection and recovery periods were adjusted, however, based on the transport behavior as the tracer started breakthrough. Total time of the field test, including setup and baseline sampling was two weeks.

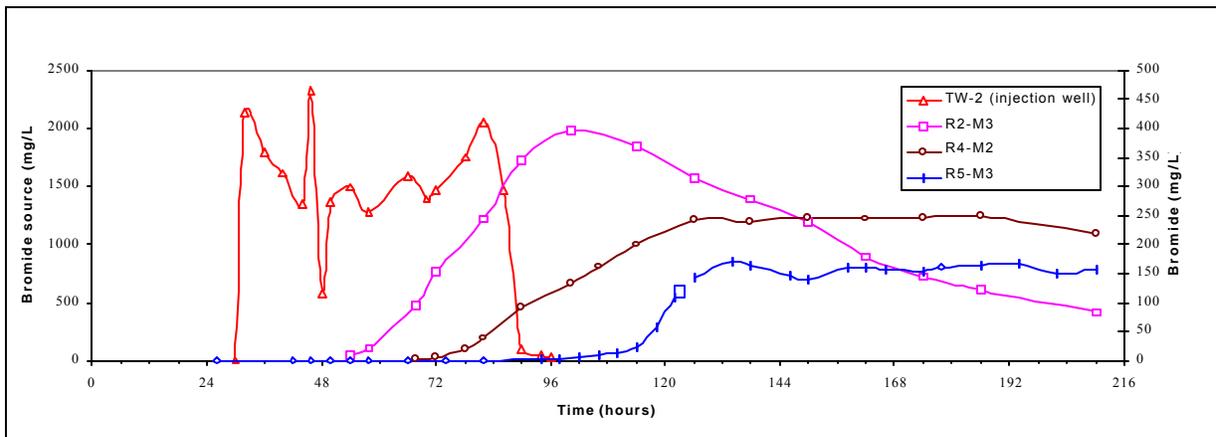
### **3.2.4 Sampling Collection and Analysis**

Monitoring took place in multiple locations within and downgradient of the permeable barrier to determine transport rates and directions. In this way, transport rates and residence times within each of the barrier layers could be determined. Sampling was performed using peristaltic pumps and low-purge methods in order to minimize disturbance to the flow-field. Sampling occurred in 51 wells along 9 transects across the barrier, including several newly installed wells located upgradient, within, and downgradient from the barrier (Fig. 3.3).

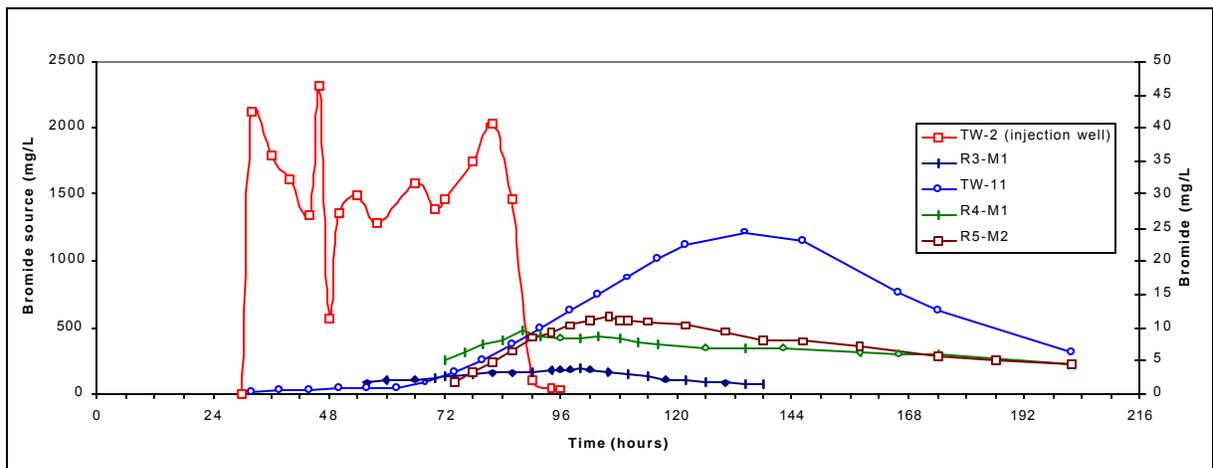
All wells were sampled prior to injection to ascertain that there were no significant background concentrations of the tracers or any other analytes that may interfere with the tracer analyses; these include the basic water quality parameters [i.e., major cations and anions, Fe(II), S(II), pH, Eh, DO, and alkalinity].

Samples for the anionic tracers were collected in 40-mL EPA vials that were carefully labeled as to location and time and stored immediately in an ice chest in the field. Analyses were performed on-site using ion-selective electrodes. Samples were split and shipped back to ORNL for laboratory analysis for both bromide and iodide tracers using ion chromatography. Initially, only selected samples were analyzed to confirm the accuracy of field-determined concentrations (approximately 10%) and to test samples where concentrations were either below the detection limit for field methods or where there was difficulty getting the probe to stabilize during the analysis.

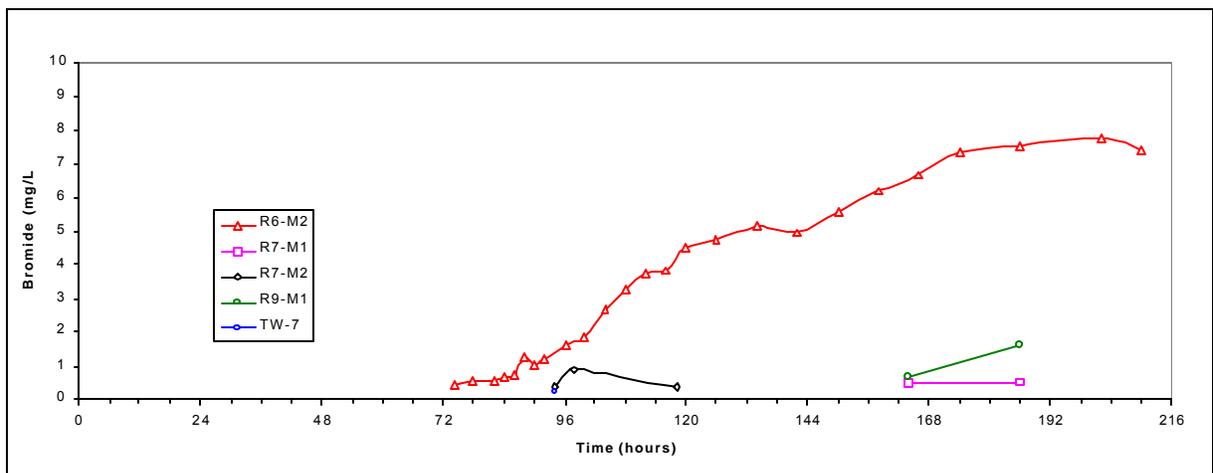
Based on the results of selective analysis, it was determined that the field analyses could not be considered valid. Concentrations were overestimated, particularly in the higher ranges, most likely because they exceeded the calibration range of the instruments. In addition, the probes incorrectly identified the anionic species in a few wells, so that what was initially identified as bromide was, in fact, iodide. At this time, approximately 80% of the samples have been analyzed by IC methods. These data are contained in Table 3.1, and the resulting breakthrough curves (BTCs) are shown in Figs. 3.5, 3.6, and 3.7.



(a)

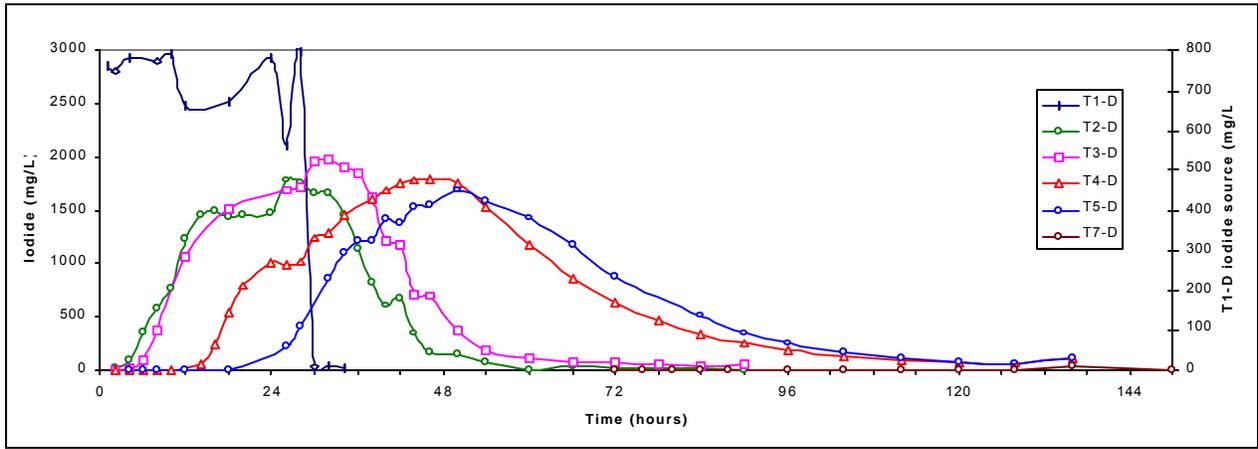


(b)

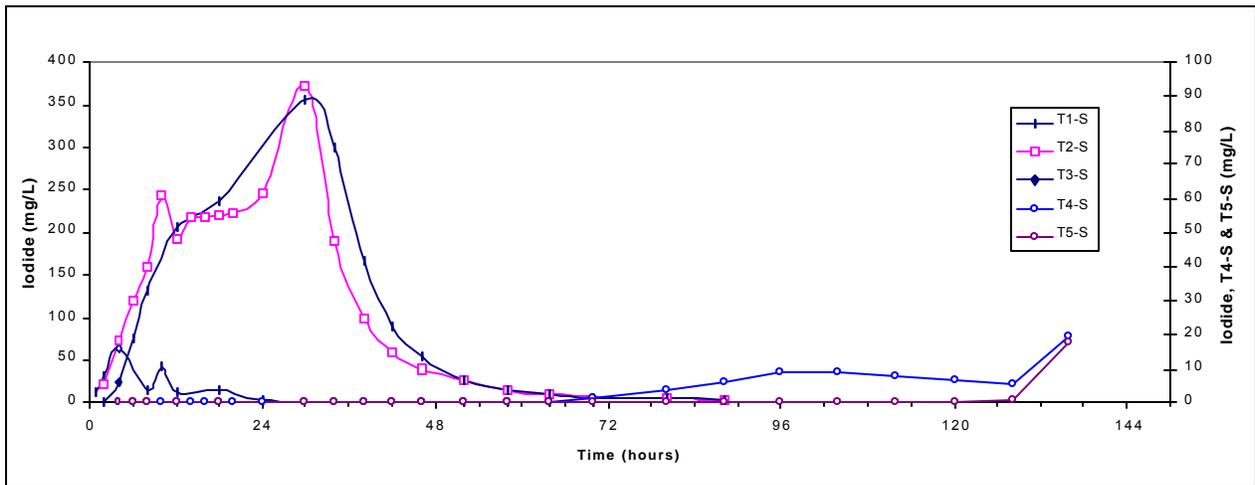


(c)

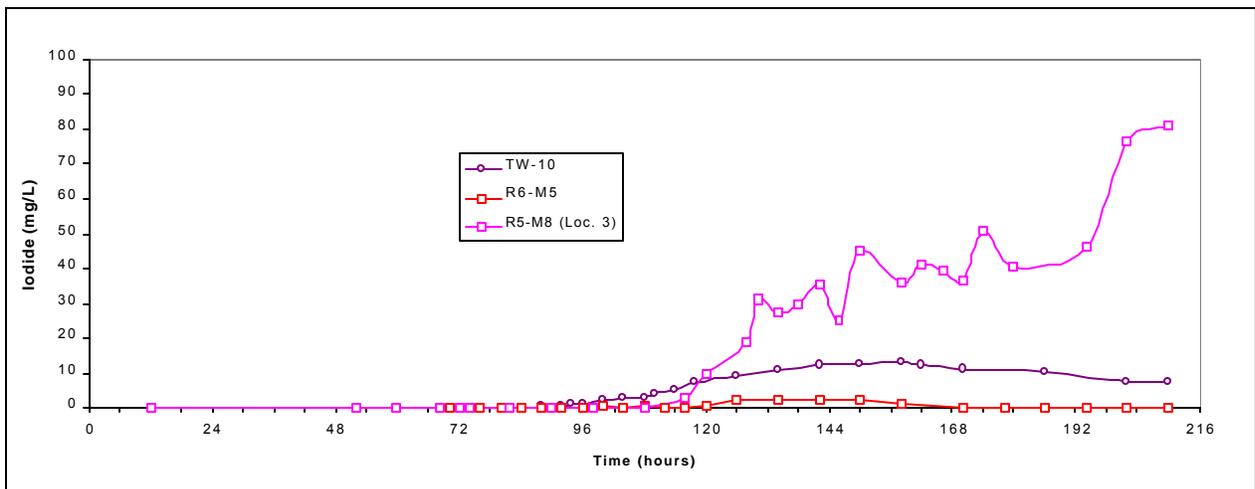
**Fig. 3.5. Bromide tracer breakthrough curves for location 1 [(a) center transect, (b) southwest trend, (c) exit wells].** Time scale is hours from the start of the tracer test. Note that the injection at this location was delayed relative to injection at the other two locations.



(a)

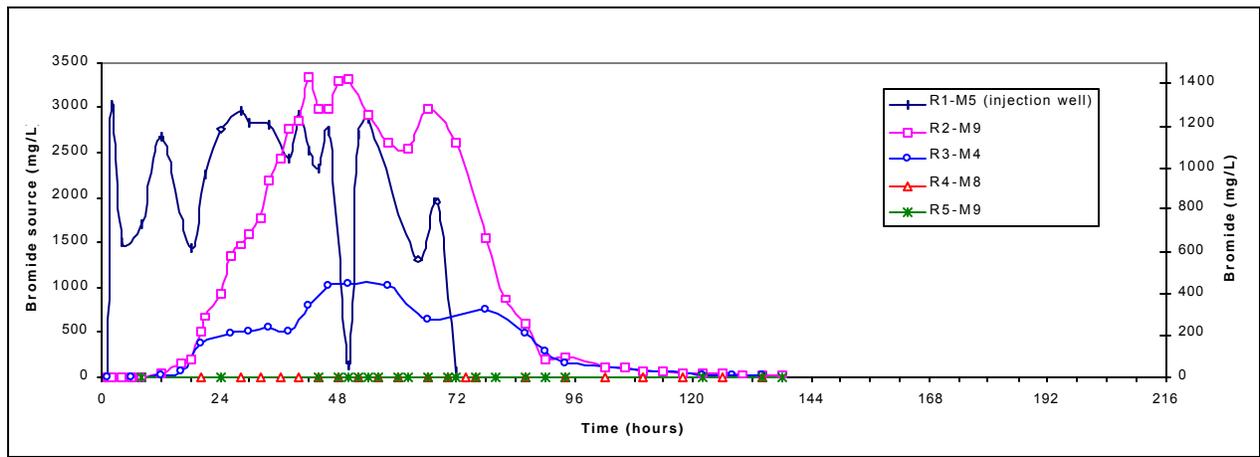


(b)

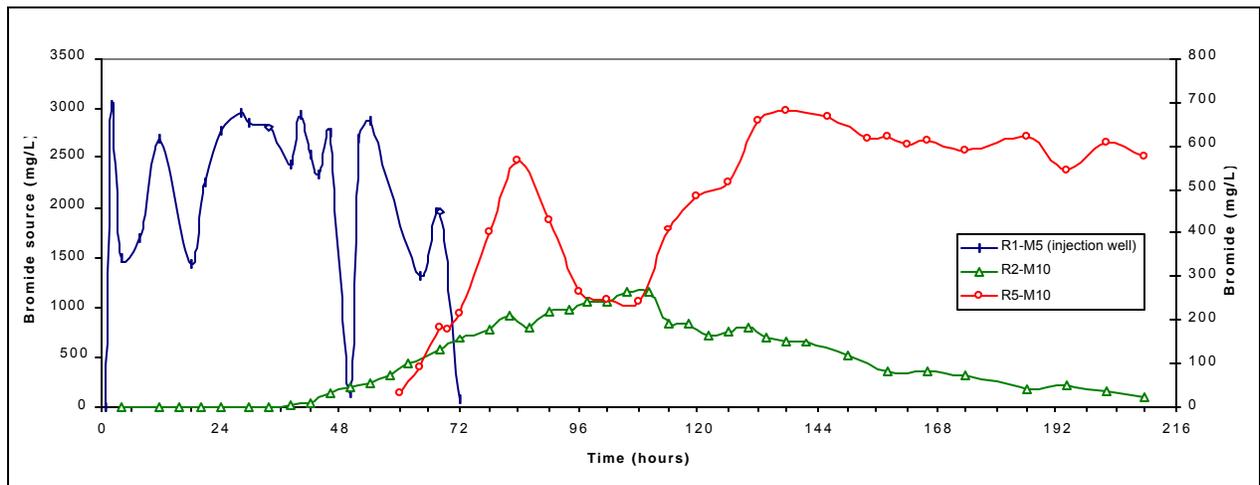


(c)

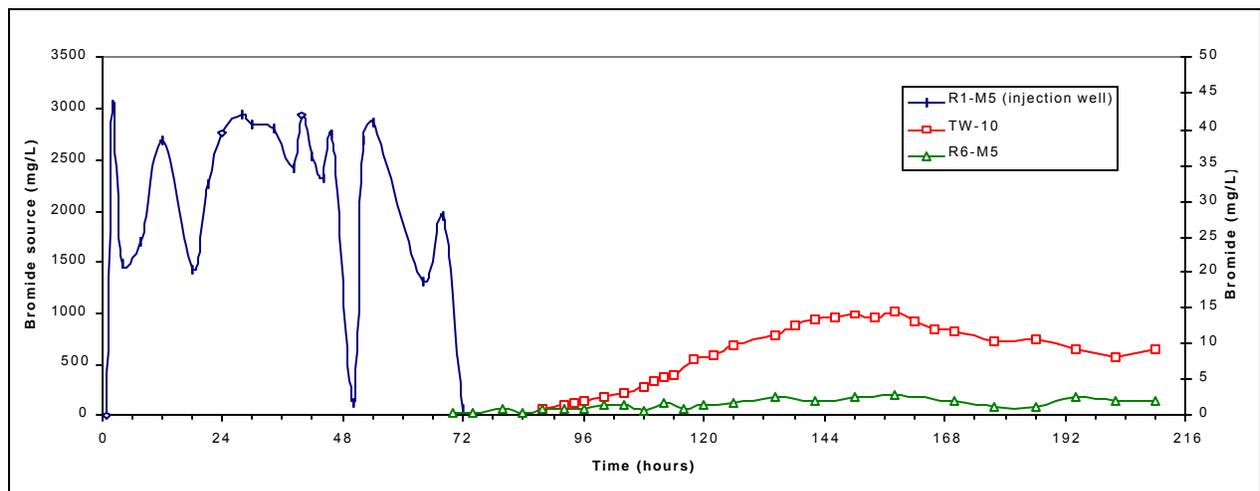
**Fig. 3.6. Iodide tracer breakthrough curves for location 2 [(a) center transect, deep wells; (b) center transect, shallow wells; and (c) exit wells].** Time scale is hours from the start of the tracer test.



(a)

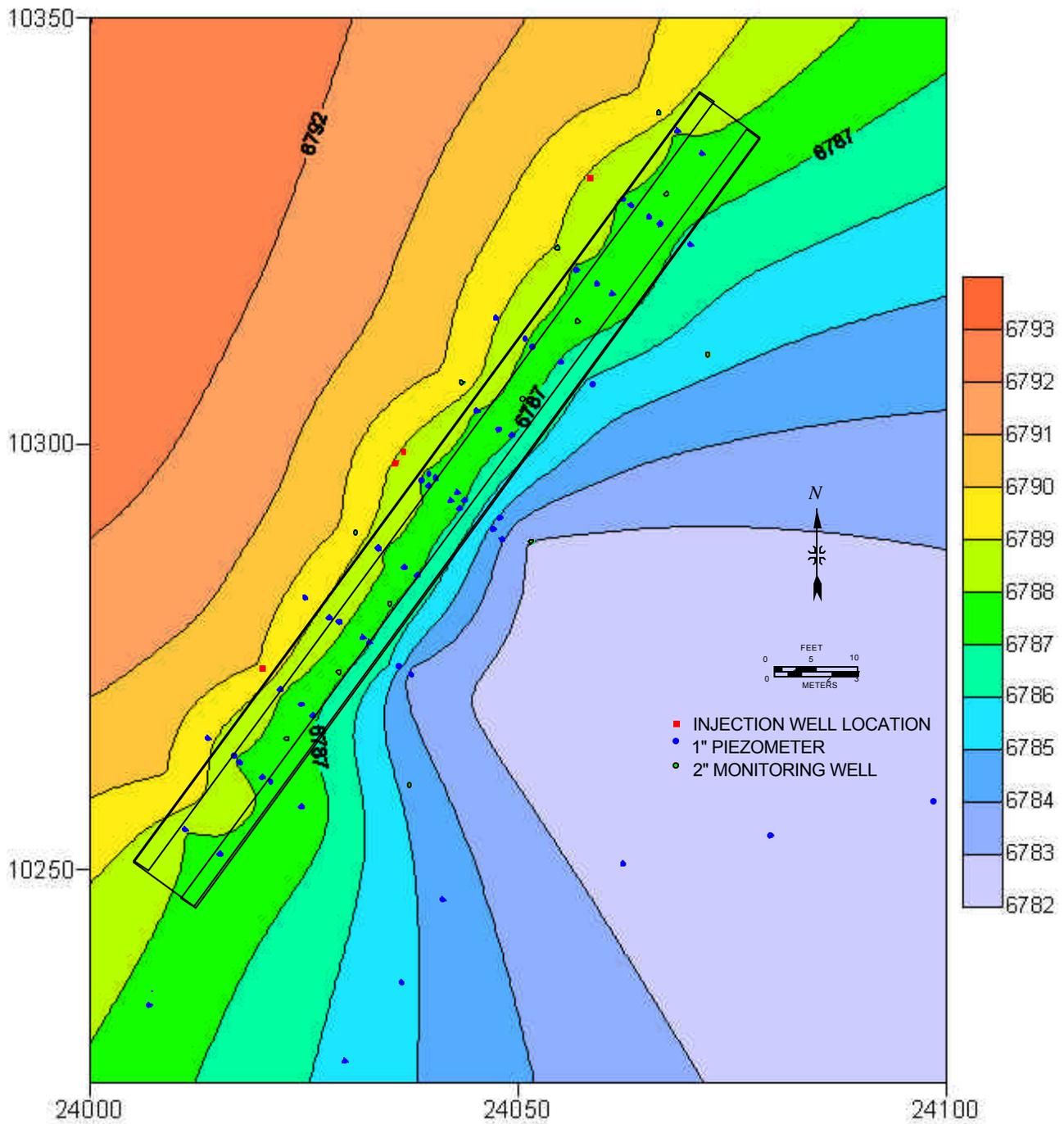


(b)



(c)

**Fig. 3.7. Bromide tracer breakthrough curves for location 3 [(a) center transect, (b) lateral pathway, and (c) exit wells]. Time scale is hours relative to the start of the tracer test.**



**Fig. 3.8. Potentiometric map for the area surrounding the reactive barrier.**  
 Note that there is a steep drop in hydraulic head across the barrier. The hydraulic gradient would indicate flow perpendicular through the barrier and then focused toward the central axis of the valley upon exiting the barrier.

### 3.2.4.1 Water level monitoring

To establish groundwater flow patterns, water levels in wells in and around the barrier were measured daily throughout the course of the field tracer test. Water levels were obtained manually using a water-level meter. Figure 3.8 shows the potentiometric surface in and around the barrier, including the rapid drop in hydraulic head at the formation/barrier interface on both sides of the barrier. Based on the hydraulic gradient, groundwater is anticipated to move directly through the barrier in an essentially perpendicular direction.

Water levels were measured just prior to the start of tracer injections and again a week later. The levels were unchanged in most locations, and no more than 0.1 ft different in the remaining locations, indicating that the frequent sampling was having very little impact on the flow field.

### 3.2.5 Preliminary Data

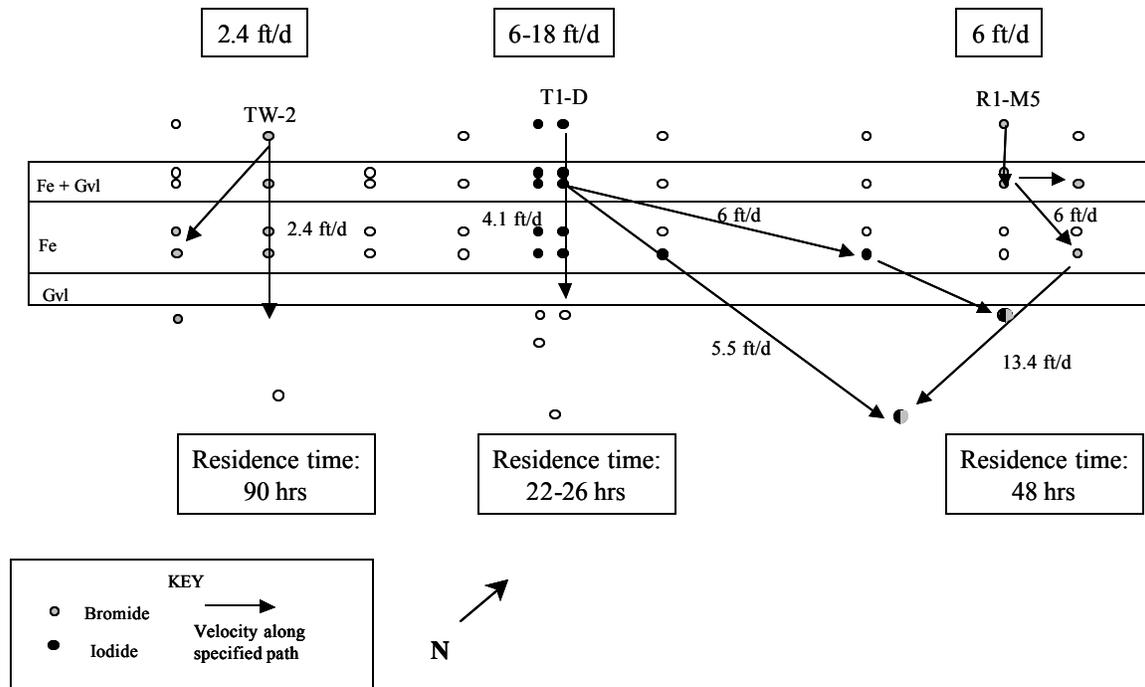
At the time of this report, some analysis of the data has been done to ascertain the range of velocities, residence times, and transport directions. However, final analysis requires analysis of the remaining samples, after which a more quantitative approach will be applied. This supplemental information will be provided at a later date. Average advective velocities were determined from the time difference between the start of injection and the time associated with the midpoint of the rise of the BTC. Midpoints from one BTC to that of an adjacent well were used to determine residence times within the Fe layers. These calculations assume that the iodide and bromide tracers are acting conservatively. However, tailing of the BTCs suggests some sorption most likely occurred, which would result in retardation. Thus, the velocities and residence times must be considered minimum or maximum values, respectively (i.e., values for nonreactive species would move faster).

Preliminary analysis indicates significant variability in transport velocities, transport directions, and residence times across the barrier (Fig. 3.9). Further, the transport behavior suggests significant heterogeneity within the barrier itself, either because of nonuniform placement of the barrier materials, creating preferential flowpaths, or subsequent permeability changes resulting from one or more chemical processes. Further analysis incorporating the geochemical data may help to identify the latter.

In location 1, the average velocity is 2.4 ft/d with a residence time in the Fe(0) media of approximately 90 hours. That is the slowest location, consistent with both the slug tests and the borescope measurements. Transport was primarily perpendicular to the barrier, although there was significant transport toward the southwest, consistent with directions predicted by the borescope measurements (Figs. 3.5 and 3.9).

In location 2, the average velocity varies from between 6 ft/d to 18 ft/d, with the faster velocities apparently in the shallower zone. This result is also consistent with the borescope measurements that detected higher velocities in the 9- to 11-ft depth range (Fig. 3.6). Transport in this zone is more complex (Fig. 3.9), with rapid breakthroughs going straight through the barrier but also significant lateral transport to R5-M8 (80 ppm) in zone 3 and TW-10 (10 ppm). Residence times in the Fe(0) barrier are estimated between 22 and 26 hours.

In location 3, transport is also complex, with velocities estimated at 6 ft/d into and through the Fe(0) barrier, giving a residence time of 48 hours based on a transport pathway from R2-M9 just inside the gravel/Fe(0) layer to R5-M10 just before the flow exits the Fe(0) layer (Fig. 3.7). Bromide did not move straight through the barrier, but diverted laterally toward the slurry wall in the gravel/Fe(0) mix, and showed up in small concentrations (1max) in TW-10 (Fig. 3.9).



**Fig 3.9. Schematic drawing of tracer transport through the barrier, showing approximate velocities, directions, and residence times based on the tracer breakthrough curves.**

The complexity of the transport patterns may become clear when the remaining samples are analyzed by IC (analysis is near completion) and on completion of transport modeling that is planned for this fiscal year. Overall, transport rates and directions are quite heterogeneous at this site, and the fact that they do not agree with the hydraulic gradients indicates preferential pathways within the barrier itself. Consequently, the hydraulic data alone (i.e., water level measurements and hydraulic gradient determination) are not adequate to provide a good overall assessment of the barrier performance and transport characteristics.

Preliminary data show that there is some correlation between the velocities from the injection wells into the first barrier wells and the well/borehole tests. At this time, there is no evidence to suggest that a low permeability layer exists at the formation/Fe(0) barrier interface. Little to no tracer transport was observed in the new wells installed immediately upgradient of the barrier and located lateral to the injection wells. In addition, the rapid transport of the tracers into the barrier precludes the existence of a significant blockage to flow at the formation/barrier interface. The tracer moves through the barrier, but not at the rates or in the directions anticipated based on previous modeling work or on water level data alone.

Based on the field experience, we could improve a few things so that future tracer tests would show a significant decrease in cost and effort. One suggested improvement is automating the injection and sampling systems to operate by a battery run on solar-power recharge. This automated system has been used successfully for extended tracer tests conducted on the Oak Ridge Reservation. By automating the sampling, the field staffing could be reduced to a minimum and the wells could be over-sampled rather than relying on real-time in-field analysis. This opens the door to a wider selection of tracers, providing potentially more cost savings. Selected samples could be analyzed in the laboratory under much more

controlled conditions, and once the transport patterns were established in a gross sense, additional samples could be analyzed to fill in the breakthrough curves and the surplus samples could simply be discarded. This also eliminates the need to fix the time range of the test in advance when the behavior is not known a priori and allows the test to be adjusted in length if necessary to capture tailing effects.

## 4. INTERAGENCY COLLABORATION

A critical component of the strategy for accomplishing this project is collaboration with the DoD and EPA. This subsection summarizes interagency activities and describes the mechanisms for ensuring continued collaboration. The interagency efforts have included face-to-face meetings, regular conference calls, joint reviews of documents, joint publications, and collaborative fieldwork.

### 4.1 MEETINGS AND CONFERENCE CALLS

Following the first face-to-face meeting in conjunction with the EPA-sponsored *In Situ Abiotic Treatment Conference* held at the end of August 1999 in Dallas, Texas, the group met again in February 2000 at Battelle in Columbus, Ohio. At this meeting, the group agreed that:

- The three agencies bring to the study a variety of PRB designs and site conditions. By continuing their respective evaluations and sharing the results, the three agencies hope to cover as many sites as possible and, at the same time, leverage each other's resources to achieve a broader understanding of PRB performance issues.
- Focus on geochemistry (longevity) and hydrogeologic aspects at various sites.
- Formalize the three agencies' efforts by preparing information brochures for the public and bringing out a common product (recommendations report) at the end of the project. The three agencies' cooperation is to be known as Tri-Agency PRB Initiative (TPI).
- Current focus is on excavated PRBs. Later years may focus on new construction techniques, such as jetting and hydrofracturing.

The team also agreed to publish joint reports. The possible products of the interagency cooperation includes a web-formatted fact sheet containing tri-agency PRB performance initiatives and a two-page hard-copy flyer showing the tri-agency effort. In addition to their individual reports, each agency will contribute to a final report.

Following the meetings, the website was set up under the Federal Remediation Technologies Roundtable at <http://www.frtr.gov/prb/> and the two-page brochure was drafted (enclosed in the Appendix). Another face-to-face meeting was held in Monterey, California, in May 2000. Because of DOE's travel restrictions, the principal investigators (PIs) from this project were not present but participated through a telephone conference call.

Conference calls have been held regularly every 2 months. These activities have emphasized results of monitoring and analysis methods at various sites in order to identify additional research needs and to reach a consensus regarding recommendations for sites that install PRBs. These discussions have highlighted some important issues, such as the following:

- uncertainties with regard to hydraulic monitoring
- the need for multiple rinses with acetone to remove water from core samples
- unexplained variability with respect to core recovery
- poor mass balances for calcium removal
- uncertainty with respect to the mechanism by which iron removes uranium

Subsequent deliverables will provide details and recommendations as these and related issues are resolved. The next face-to-face meeting is planned in conjunction with the Remedial Technology Development Forum (RTDF) conference that is being planned for April or June 2001.

## 4.2 PUBLICATIONS

Participants agreed that documents submitted for publication would be reviewed by the PIs from each agency. To that end, one EPA document and two DoD documents have been reviewed by DOE. A DOE report due in January 2001 will be submitted for review to DoD, EPA, and the ITRC PRB group.

As mentioned in Sect. 4.1, the group agreed to issue a joint guidance document on the long-term field implementation and monitoring of PRBs for current and potential users of the technology. The joint report will include a 5-page summary for each site studied that describes the field hydraulic performance and longevity experiences, field methods, results, and lessons learned. This report will discuss the long-term monitoring recommendations of the TPI, including (1) evaluations on monitoring parameters, frequency, and methods used for sampling and analysis of groundwater, iron cores, hydraulic measurements, etc.; (2) how these can be used to evaluate long-term reactive and hydraulic performances; and (3) how the lessons learned in this study can be applied for better designs at future sites.

In addition, DOE has led the preparation of an interagency journal publication. The manuscript, entitled "Geochemical and microbial reactions affecting the long-term performance of in situ iron barriers," has been published in *Advances in Environmental Research*. The senior author is L. Liang and the co-authors are N. Korte and B. Gu, all of ORNL; R. Puls of EPA; and C. Reeter of DoD. This publication establishes a geochemical baseline for long-term monitoring. As such, it is a key part of the strategy for accomplishing this project.

## 5. SUMMARY

The project is making good progress in acquiring geochemical and hydrological data. Preliminary modeling has been performed to evaluate the quality of the field data. Examination of a few influent geochemical data sets has shown that the error associated with the charge balance is within 7%, which is generally regarded as acceptable if the error is <10%. More work is needed to correlate the geochemical data with hydraulic performance data. Additionally, the type of mineral precipitation in iron core needs to be collected or analyzed, if necessary. Field column experiments are ongoing, and data collected so far show that pH is a good indicator on the equilibrium conditions of the barriers.

Hydraulic investigation has been a focus in the project. In this fiscal year, we applied a colloidal borescope at five different sites to characterize field flow direction and velocities. Comparative experiments were performed with respect to data collected in previous year (at the Y-12 Plant site) and against other types of flowmeters (HydroTechnics at the Dover and Lowry sites and electromagnetic at

Elizabeth City). The results from HydroTechnics are approximately one order of magnitude lower than both average regional measurements based on conductivities and observed gradients and direct measurements made with the borescope at the Dover site. The borescope data demonstrate that there are zones in the aquifer, that are relatively stagnant. A field multiple-tracer test was conducted at the Monticello site, Utah. Preliminary results show that transport rates and directions are heterogeneous in nature. Because transport rates and directions do not agree with the hydraulic gradients, preferential pathways within the barrier are significant. Consequently, the hydraulic data alone (i.e., measurements of water levels and hydraulic gradients) are not adequate to provide a good overall assessment of the barrier performance and transport characteristics. Additionally, it does not appear that there is any evidence suggesting that a low- permeability layer exists at the formation/Fe(0) barrier interface. At the moment, the breakthrough data are being analyzed to estimate for velocities, residence times, and transport directions. The hydraulic data collected at these facilities will be carefully analyzed and published in the open literature.

A document on the monitoring and analysis protocol will be drafted based on the available data. Coordination with the DOE site users is very important to the success of the project, and we will rely as much as we can on the site monitoring programs. When necessary, we will sample field barriers to fill in the data gaps. Recognizing that each site may alter their existing barrier configuration to meet regulatory requirements, we will try our best to obtain data, that are meaningful and provide generic understanding to the geochemical and hydraulic performance of the PRBs. We will continue working with DoD and EPA partners and RTDF/ITRC working groups to share the lessons learned from the sites and to obtain feedbacks for drafted reports.

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## 7. APPENDIX – BROCHURE OF TRI-AGENCY INITIATIVE



### The Tri-Agency Permeable Reactive Barrier Initiative



U.S. DoD and DOE representatives conduct a joint evaluation of the hydraulic performance of PRBs at former Lowry Air Force Base



U.S. EPA continues to monitor the performance of the PRBs at the Coast Guard Station in Elizabeth City and Denver Federal Center

The permeable reactive barrier (PRB) technology represents a passive option for long-term treatment of groundwater contamination. PRBs are a potentially more cost-effective treatment option for a variety of dissolved contaminants, such as certain types of chlorinated solvents, heavy metals, and radionuclides. Because these contaminants are present at several government (and private) sites, the **U.S. Department of Defense (DoD)**, **U.S. Department of Energy (DOE)**, and **U.S. Environmental Protection Agency (EPA)** are cooperating to evaluate the field performance of several PRBs under a variety of site conditions.

#### Objectives

The objectives of the Tri-Agency PRB Initiative are to leverage the technical and financial resources of the three agencies in order to:

- Examine the field performance of multiple PRBs
- Conduct additional field investigations to address any information gaps
- Issue a joint guidance document on the long-term field implementation and monitoring of PRBs for current and potential users of the technology.

A survey of existing PRBs indicated that the two main challenges facing the technology are (1) evaluating the *longevity* (geochemistry) of a PRB and (2) ensuring/verifying its *hydraulic performance*. Therefore, this initiative will focus primarily on these two challenges. In 2001, the three agencies will publish a combined report that summarizes the results and conclusions of this initiative and the recommendations for PRB implementation and long-term monitoring. In addition, each agency will prepare a final report detailing the methodology and results of the investigations at their respective sites. The Tri-Agency PRB Initiative has established an Internet site at <http://www.frtr.gov/prb/> to facilitate the transfer of information to potential users. This site will be updated whenever significant new information or results become available.

## Key Participants

- The **Naval Facilities Engineering Service Center (NFESC)**, Port Hueneme, California and its project partner, **Battelle**, Columbus, Ohio are leading the DoD effort. Other DoD participants include the Army Corps of Engineers (ACE), Air Force Center for Environmental Excellence (AFCEE), and Air Force Research Laboratory (AFRL). DoD's Environmental Security Technology Certification Program (ESTCP) and Strategic Environmental Research and Development Program (SERDP) are sponsoring this project. The DoD field divisions and their local contractors provide site access and some field support.
- **Oak Ridge National Laboratory (ORNL)**, Oak Ridge, Tennessee is coordinating the DOE effort. DOE's Office of Science and Technology (OST)/ Subsurface Contaminant Focus Area (SCFA) provides support for this project. DOE site managers, industrial partners, and university researchers support ORNL in the field investigation.
- The **National Risk Management Research Laboratory's** Subsurface Protection and Remediation Division in Ada, Oklahoma is leading the EPA effort. Other participants include U.S. Coast Guard, U.S. Geological Survey, Federal Highway Administration, General Services Administration, and General Electric Co.

The **Federal Remediation Technology Roundtable** will serve as the forum for general dissemination of project data and results via its Internet site at <http://www.ftrr.gov/>. The **Remedial Technologies Development Forum (RTDF)** Permeable Barrier Action Team and the **Interstate Technology and Regulatory Cooperation (ITRC)** Permeable Barriers Subgroup provide review support and help disseminate the project results to the regulatory and user community.

## Technical Approach

Local site managers independently conduct routine monitoring at all installed PRBs. However, this initiative will focus on a closer investigation of a few sites (e.g., former Naval Air Station Moffett Field, former Lowry Air Force Base, Dover Air Force Base, Watervliet Arsenal, DOE's Monticello site, Bear Creek Valley at Oak Ridge Y-12 plant, Kansas City Plant, Denver Federal Center, and the Coast Guard Site in Elizabeth City). These sites provide a good sampling of different PRB designs, hydrogeologic features, and groundwater chemistries. Other sites may be added if their attributes present suitable features of interest in terms of longevity and hydraulic performance.

Longevity evaluation tools are likely to include inorganic analysis of groundwater, reactive media core collection and analysis, geochemical modeling, and long-term column testing. Hydraulic performance evaluation tools are likely to include aquifer hydraulic property measurements, multiple tracer testing, modeling, and innovative flow measurement tools, such as heat sensors and colloidal borescope. These planned activities may be subject to modification in the future depending on ongoing lessons learned, project priorities, and availability of funds.

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