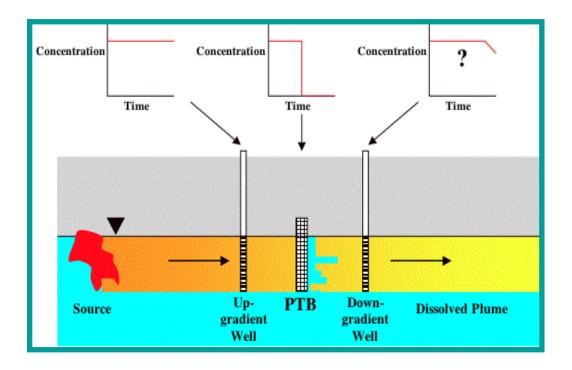
ESTCP Cost and Performance Report

(ER-0320)



Prediction of Groundwater Quality
Down-Gradient of In Situ Permeable
Treatment Barriers and Fully-Remediated
Source Zones

August 2008



ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT

Project: ER-0320

TABLE OF CONTENTS

			Page
1.0	EXE	CUTIVE SUMMARY	1
1.0	1.1	BACKGROUND	
	1.2	OBJECTIVES OF THE DEMONSTRATION	
	1.3	REGULATORY DRIVERS	
	1.4	DEMONSTRATION RESULTS	
	1.5	STAKEHOLDER/END-USER ISSUES	
2.0	TEC	HNOLOGY DESCRIPTION	3
	2.1	TECHNOLOGY DEVELOPMENT AND APPLICATION	3
	2.2	PROCESS DESCRIPTION	5
	2.3	PREVIOUS TESTING OF THE TECHNOLOGY	6
	2.4	ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY	6
3.0	DEM	IONSTRATION DESIGN	9
	3.1	PERFORMANCE OBJECTIVES	9
	3.2	TEST SITE SELECTION	9
	3.3	TEST SITE/FACILITY HISTORY/CHARACTERISTICS	10
	3.4	PHYSICAL SETUP AND OPERATION	
	3.5	SAMPLING/MONITORING PROCEDURES	12
	3.6	ANALYTICAL PROCEDURES	13
4.0	PER	FORMANCE ASSESSMENT	15
	4.1	PERFORMANCE DATA	15
	4.2	PERFORMANCE CRITERIA	18
	4.3	DATA ASSESSMENT	19
	4.4	TECHNOLOGY COMPARISON	19
5.0	COS	T ASSESSMENT	21
	5.1	COST REPORTING	21
	5.2	COST ANALYSIS	23
6.0	IMPI	LEMENTATION ISSUES	25
	6.1	COST OBSERVATIONS	
	6.2	PERFORMANCE OBSERVATIONS	25
	6.3	SCALE-UP	25
	6.4	OTHER SIGNIFICANT OBSERVATIONS	
	6.5	LESSONS LEARNED	
	6.6	END-USER ISSUES	
	6.7	APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANC	E 25

TABLE OF CONTENTS (continued)

			Page
7.0	REFERENC	CES	27
APPE	NDIX A	POINTS OF CONTACT	A-1

LIST OF FIGURES

		Page
Figure 1.	Schematic of Deployment Options for PTBs	4
Figure 2.	Schematic of the Groundwater Quality Issue Downgradient of a PTB	5
Figure 3.	Large-Scale Biobarrier PTB System at NBVC	11
Figure 4.	Sampling Locations Used in This Project	12
Figure 5.	MTBE Concentrations—Vertical Cross Section Along Plume Centerline.	17

LIST OF TABLES

		Page
Table 1.	Summary of Proposed Approach for Anticipating Dissolved	
	Groundwater Quality Changes Downgradient of PTBs	6
Table 2.	Performance Objectives.	9
Table 3.	Summary of Field Sampling Activities at NBVC	12
Table 4.	Analytical/Testing Methods	13
Table 5.	Hydraulic Conductivity Descriptive Statistics for NBVC Site	15
Table 6.	MTBE Groundwater Concentration Statistics in Monitored	
	Downgradient Zone from the 2004 and 2005 Sampling Events	16
Table 7.	Performance Metrics.	19
Table 8.	Minimum Data Collection/Data Reduction Needs and Incremental Effort	
	Required Relative to Routine Data Collection and Reduction for PTB	
	Sites	22
Table 9.	Cost Reporting Table—Incremental Costs Above Typical	
	Characterization and Data Reduction Activities.	23

ACRONYMS AND ABBREVIATIONS

bgs below ground surface BDL below detection limit

cm/s centimeter per second

DNAPL dense non-aqueous phase liquid

DO dissolved oxygen DoD Department of Defense

ESTCP Environmental Security Technology Certification Program

FID flame ionization detector

GC gas chromatograph

GW groundwater

 $\begin{array}{ll} \mu g/L & \text{micrograms per liter} \\ mg/L & \text{milligrams per liter} \end{array}$

mL milliliter mV millivolt

MTBE methyl tert butyl ether

NBVC Naval Base Ventura County

ND non detect

NEX Navy Exchange Service

NFESC Naval Facilities Engineering Service Center

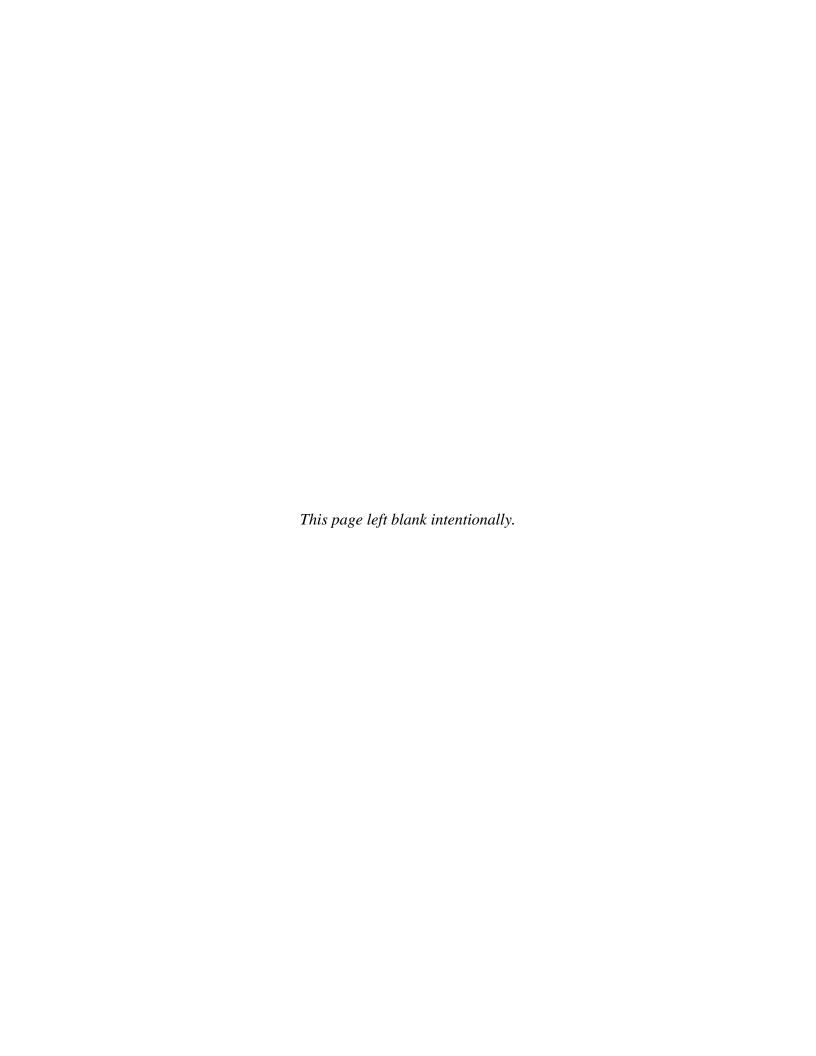
ORP oxidation reduction potential

PID photo-ionization detector PRB permeable reactive barrier PTB permeable treatment barrier

UXO unexploded ordnance

VOA volatile organic analysis

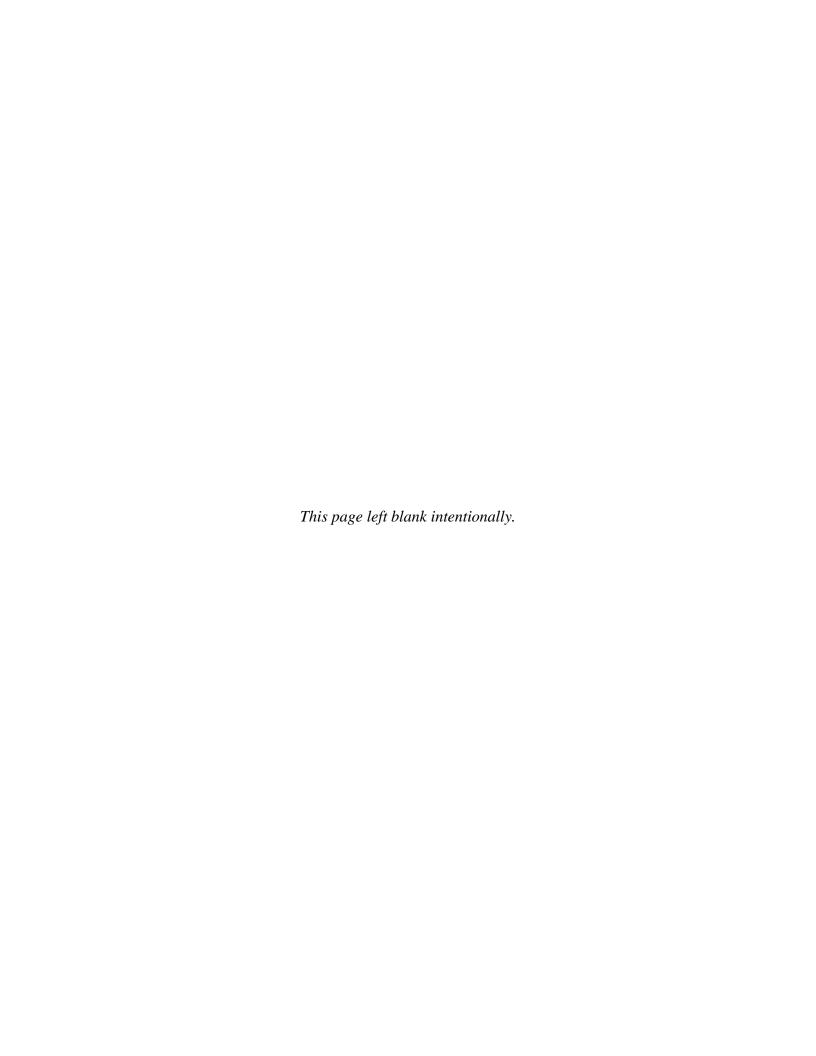
WL water level



ACKNOWLEDGEMENTS

The authors would like to thank Dorothy Cannon, James Osgood, William Major, Rebecca Biggers, and Ernie Lory from the Naval Facilities Engineering Service Center (NFESC), Port Hueneme, California, for their support during the field work phase of this project at the Naval Base Ventura County, Port Hueneme, California.

The authors would also like to thank the Environmental Security Technology Certification Program (ESTCP), especially Dr. Jeff Marqusee and Dr. Andrea Leeson, for funding and supporting this demonstration.



1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

In situ permeable treatment barriers (PTB) are designed so that contaminated groundwater flows through an engineered treatment zone within which contaminants are eliminated or the concentrations are significantly reduced. These systems are often considered for the containment of dissolved groundwater contaminant plumes or for controlling the discharge and larger scale impact of dissolved contaminants from source zones to aquifers. The performance of a PTB is typically judged by short-term changes in groundwater concentrations with time within the treatment zone and also in wells located some distance downgradient. Typically, expectations for groundwater concentration changes with time are based on a single site-wide average linear groundwater velocity estimate. For example, clean groundwater would be expected to be observed from 0 ft to 365 ft downgradient of a PTB after one year at a site having a 1 ft/day average linear groundwater velocity. Previous Environmental Security Technology Certification Program (ESTCP)-sponsored studies have concluded that this approach does not agree well with observations at PTB sites and that a better understanding of the subsequent improvements in downgradient groundwater quality with time is needed. Realistic projections of how the downgradient concentrations will change with time are important, or else incorrect performance conclusions might be drawn in the short term, leading to premature abandonment of the PTB technology and unnecessary investment in other remedial options.

1.2 OBJECTIVES OF THE DEMONSTRATION

The objectives of this project were to: a) propose a practicable approach that can be used to project reasonable order-of-magnitude estimates of groundwater quality improvements with time downgradient of a PTB, b) conduct detailed monitoring and characterization downgradient of a well-understood PTB site, and c) illustrate and reflect on the use of the proposed approach for the PTB system studied in this project. These objectives were met by this demonstration project.

1.3 REGULATORY DRIVERS

A PTB is installed to prevent further downgradient discharge of impacted groundwater and to meet prescribed numerical standards for groundwater cleanup downgradient of the PTB. When selecting a PTB system, it is critical that all stakeholders understand how groundwater quality changes will occur with time and distance downgradient of the PTB and how long it might take to achieve standards at different distances downgradient of the PTB.

1.4 DEMONSTRATION RESULTS

Detailed monitoring and characterization of groundwater concentration changes with time downgradient of a full-scale methyl tert-butyl ether (MTBE) biobarrier PTB system were conducted at the Naval Base Ventura County (NBVC) to illustrate the issue discussed above. This included discrete depth groundwater sampling at 37 locations and analysis of more than 680 groundwater samples for MTBE during three sampling trips (1226, 1324, and 1709 days after the biobarrier treatment zone was well-oxygenated and seeded); conventional slug tests (in 2-in and 4-in wells) and constant drawdown pumping tests (in 3/4-in wells) conducted at existing full-

length monitoring wells; water level measurements in monitoring wells; constant draw-down mini pumping tests conducted at 1-ft (0.3-m) intervals during direct-push sampling; soil cores collected at 20 locations; and 245 laboratory permeameter tests with at least a 1-ft (0.3-m) resolution on the soil cores.

Variations in horizontal groundwater velocity were reflected in the movement of clean water downgradient from the NBVC PTB. Overall, the highest concentrations (180 micrograms per liter [μ g/L] to 880 μ g/L) of MTBE persisted longest in the areas of lower hydraulic conductivity (and hence lower groundwater velocity). These findings further demonstrated that use of a single site-wide estimate of groundwater velocity (i.e., 3.5 x 10^{-4} centimeter per second [cm/s] or 1 ft/day) for NBVC would lead to unreasonably low predicted concentrations at shallower depths and unreasonably high predicted concentrations at deeper depths. For samples collected from a typical groundwater monitoring well (which mixes concentrations across deep and shallow zones at this site), the single site-wide velocity estimate would significantly overestimate the apparent movement of clean water downgradient of the NBVC PTB.

The recommended site-specific assessment approach for PTB systems is one that focuses on characterization of vertical variations in horizontal hydraulic conductivity. This can be done at most sites through coring followed by lab tests, or by using in situ discrete pump tests, both of which were demonstrated at the NBVC site. Using this information along with hydraulic gradient data, well construction information (i.e., screened interval data), pretreatment concentrations, and treatment zone concentration data, estimates of downgradient groundwater quality change with time can be produced assuming that horizontal groundwater flow is the dominant dissolved chemical transport mechanism. A spreadsheet-based tool (DGCHANGE v1.0) was developed to help users perform these calculations and better visualize the projected concentration versus time behavior in the aquifer and at the wells.

1.5 STAKEHOLDER/END-USER ISSUES

At about the time that this study was initiated, Battelle (2002) issued a report that inventoried PTB applications and reviewed the data available from a number of sites. The authors of that report commented that "...it may be several years before a noticeable decline in contaminant concentrations is observed at a down-gradient compliance point, as indicated by the difficulty in discerning a clean front emerging from various existing permeable reactive barriers (PRBs)." Given this apparent slow rate of clean groundwater propagation downgradient of the treatment zone, the authors also recommended that "...it may be important to determine, through monitoring and understanding of the site, possible causes of persistent down-gradient contamination, in order to allay regulatory concerns." This project produced an approach for anticipating groundwater quality changes with time downgradient of PTBs. It also produced a supporting spreadsheet-based calculation tool that uses site-specific data as inputs and generates graphs and tables that visually describe the anticipated groundwater quality changes with time downgradient of PTBs.

2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

This project did not involve the demonstration of a developing cleanup technology, as is common for most ESTCP projects. Rather, it was conducted to supplement our understanding of PTB systems through:

- The detailed monitoring of groundwater quality changes with time and distance downgradient of a well-monitored PTB system in order to better understand the dynamics of treated water movement and the reasons groundwater quality improvements do not occur as quickly as typically anticipated
- The testing of a practicable approach to anticipate groundwater quality changes with time and distance downgradient of PTB systems in order to develop reasonable performance expectations.

For those readers interested in the development and application of PTBs, the Battelle (2002) and Interstate Technology and Regulatory Council (2005) reports are valuable sources of information. In brief, in situ PRB and in situ biobarriers are examples of technologies that will be referred to more generally in this document as "in situ" (PTBs). As shown in Figure 1, these treatment systems may be installed at the edge of the source of a dissolved groundwater contaminant plume, at the leading edge of a dissolved groundwater contaminant plume, or anywhere in between. These systems are designed such that contaminated groundwater flows through an engineered treatment zone within which contaminants are eliminated or the concentrations are significantly reduced. The hydraulic design of the system may rely on natural groundwater flow or may involve pumping to direct the contaminated groundwater through a treatment system (i.e., a "funnel and gate" system). The treatment system may utilize chemical reactions (e.g., iron barriers), biochemical reactions (e.g., aerobic or anaerobic biodegradation), or physical-chemical processes (e.g., air sparging to induce volatilization).

These systems are often considered for the containment of dissolved contaminant plumes, especially in cases where: a) near-term complete source zone treatment is unlikely and long-term containment is necessary or b) preventing the continued growth of a dissolved groundwater contaminant plume is necessary. Situations like this are often encountered at complex dense non-aqueous phase liquid (DNAPL) spill sites or at sites where sources are distributed over large areas (e.g., unexploded ordnance [UXO] sites). Relative to the typical pump-and-treat/hydraulic containment alternatives, natural-gradient (non-pumping) PTB systems are attractive because they are less maintenance-intensive and above-ground treatment and discharge systems are not required. Cost comparisons and performance-risk analyses of PTB and pump-and-treat systems often favor PTBs, except in deeper groundwater settings (i.e., >100 ft below ground surface [bgs] to groundwater), where the PTB installation costs begin to offset the savings from the lower operation and maintenance costs.

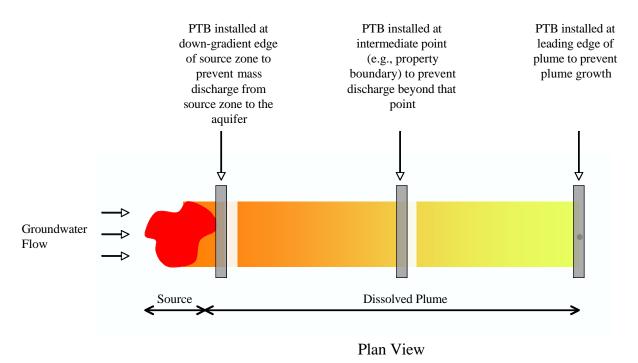
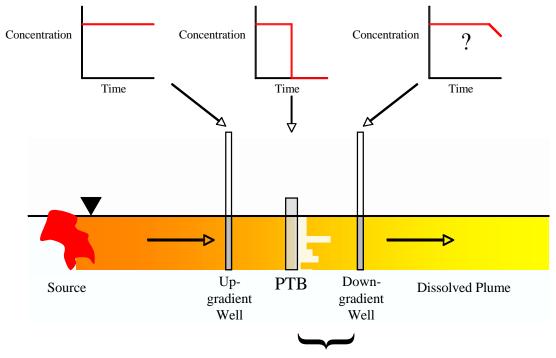


Figure 1. Schematic of Deployment Options for PTBs.

In all cases, prediction as well as monitoring of the dynamic movement of the clean/treated groundwater (e.g., distance versus time relationships for the clean groundwater) is needed. This is critical because the economic analysis for designing, operating, and maintaining these downgradient detached plume treatment options will depend on the duration of treatment (i.e., the projected annual and lifetime costs for each treatment option will depend on whether the projected duration is 5 years, 50 years, or 100 years). Typically, expectations for groundwater concentration changes with time are based on a single aquifer-wide average linear groundwater velocity estimate. For example, improvements in groundwater quality would be expected between 0 ft and 365 ft downgradient of a PTB after one year at a site having a 1 ft/day average linear groundwater velocity. Previous studies (i.e., Battelle 2002) have concluded that this approach does not agree well with observations and that a better understanding of the subsequent improvements in downgradient groundwater quality with time is needed.

Gaining a better understanding of this behavior is also of interest because the performance of a PTB may be judged by the short-term changes in dissolved concentrations with time immediately downgradient of the PTB. It is important to have realistic projections of how the concentrations will change with time as shown in Figure 2, or incorrect performance conclusions might be drawn in the short-term.



Anticipating Treated Water Movement and Down-gradient Water Quality Improvements
Observed in Monitoring Wells - The Focus of This Study

Figure 2. Schematic of the Groundwater Quality Issue Downgradient of a PTB.

2.2 PROCESS DESCRIPTION

As discussed above, this project was conducted to better understand the dynamics of treated water movement downgradient of PTBs and to identify reasons groundwater quality improvements do not occur as quickly as typically anticipated. It involved detailed data collection downgradient of a well-monitored PTB system and the use of that data to test a simple, practicable approach to anticipate groundwater quality changes with time and distance downgradient of PTB systems.

The proposed approach is summarized in Table 1. In brief, it involves:

- Collection of pre-PTB groundwater concentration data in order to form a conceptual model of the initial dissolved groundwater concentration distribution
- Collection of hydrogeologic data in order to form a layered conceptual model of the groundwater system and the flow direction
- Entry of this data into an Excel spreadsheet-based tool that estimates changes in groundwater quality with time and space, and concentration versus time in selected monitoring well locations.

Table 1. Summary of Proposed Approach for Anticipating Dissolved Groundwater Quality Changes Downgradient of PTBs.

	Components of the		
	Approach	Measurement and Discussion	Analysis
1	Determination of groundwater flow direction and horizontal hydraulic gradient	Groundwater level measurements should be collected from at least three groundwater monitoring wells located in the vicinity of the proposed (or existing) PTB. The number of wells and their positions should be selected based on recommendations provided in Dahlen (2004) in order to minimize error.	Groundwater level measurements are contoured to determine the groundwater flow direction and to calculate the horizontal hydraulic gradient. (It is assumed that vertical gradients at most PTB sites will be small, although that may not always be the case.)
2a	Determination of vertical variations in horizontal hydraulic conductivity	This can be accomplished through soil coring and subsequent testing of soil properties, through in situ testing of hydraulic properties across discrete vertical intervals, or some combination of the two. If making in situ measurements, groundwater samples should be collected at the same time from the intervals being characterized.	The data must be sufficient to create a layered conceptual model of the section of the aquifer of interest and to assign quantitative properties (hydraulic conductivity, effective porosity, and fraction of organic carbon).
2b	Determination of groundwater concentration distribution and the concentration of chemicals of concern leaving the PTB	Groundwater sampling downgradient of PTB location followed by chemical-specific analysis to determine the initial distribution of chemical concentrations. Ideally, samples are collected at the same vertical intervals as the hydraulic conductivity data discussed above.	These initial contaminant concentrations are input into the spreadsheet tool (discussed below) as the initial (t=0) concentrations.
3	Estimation of rate of downgradient propagation of treated water leaving the PTB and corresponding changes in groundwater quality in wells or discrete sampling points	Estimates are based on the data from the three items listed above.	Data are entered into an Excel spreadsheet that calculates advection-dominated transport model results as a first-order approximation of the real behavior of the system.

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

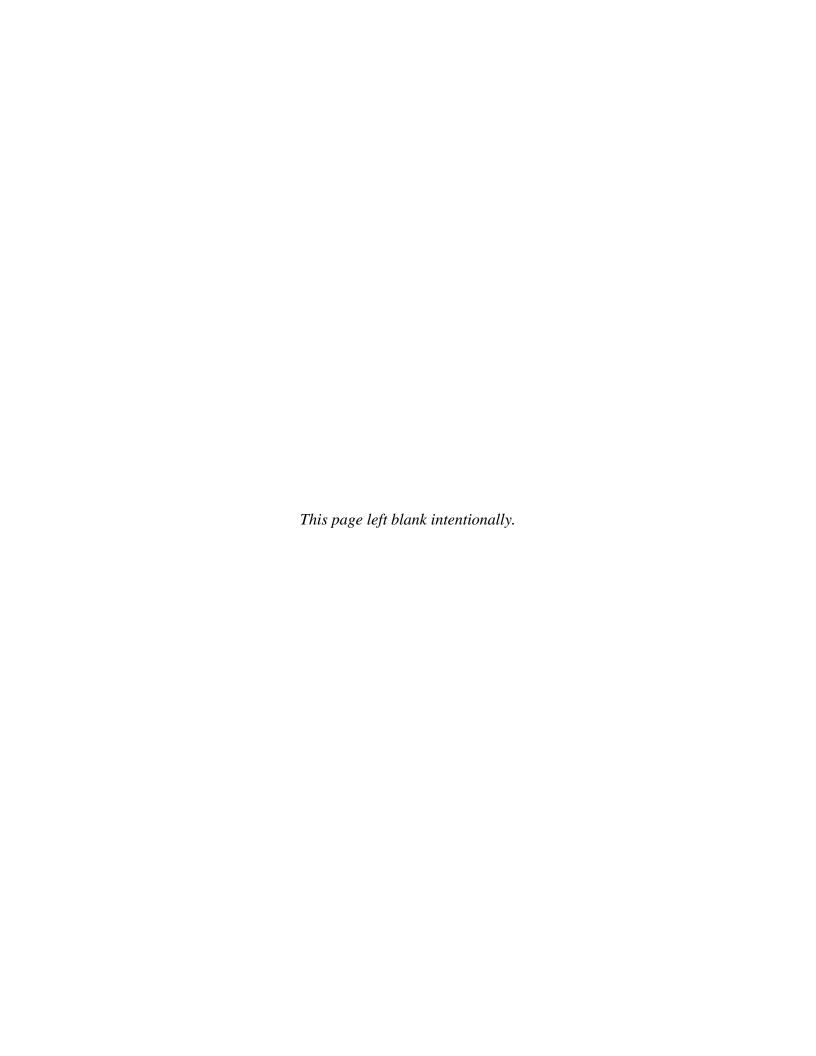
This approach was not tested prior to this demonstration project.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantage of this technology is that it addresses the identified need for an approach to estimate downgradient water quality improvements with time so that realistic PTB performance expectations can be set and decision makers are better prepared to interpret the performance data.

The limitation of this technology is that it involves the use of a relatively simplistic model of treated water movement downgradient of a PTB. Sites are characterized as being layered with

homogeneous hydraulic and chemical transport properties within each layer, gradients are assumed to be horizontal, and there is no vertical transport between the layers (i.e., no back-diffusion). Thus the tool is not applicable at sites where this simplification is not appropriate.



3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The performance objectives for this project are captured in Table 2.

Table 2. Performance Objectives.

Type of Performance	Primary Performance		Actual Performance
Objective	Criteria	Expected Performance Metric	(Objective met?)
Qualitative	Develop a practicable approach that can be used to project reasonable order-of-magnitude estimates of groundwater quality changes with time downgradient of a PTB	 Data collection requirements utilize available technology (i.e., sampling methodologies) and do not significantly increase base-case characterization costs. Calculation tool for projection of performance can be used by most environmental professionals, regulators, and project managers. 	Yes, the approach incorporates use of conventional characterization tools and the calculation tool is in spreadsheet format.
Semi- Quantitative	Be able to project reasonable order-of-magnitude estimates of groundwater quality changes with time downgradient of a PTB	Comparison of projected concentration versus time and distance relationship with that observed at the NBVC site.	Yes, the approach leads to better estimates of downgradient concentration changes with time than conventional approaches.
Quantitative	Collect data set for the NBVC site that can be used to test the approach and provide insight to factors controlling groundwater quality changes with time	 The data satisfies data quality objectives, and the density of samples is sufficient to be useful for testing models of varying sophistication, including the tool developed in this project. 	Yes, data set is the most comprehensive ever collected downgradient of a PTB.

3.2 TEST SITE SELECTION

For this project, the desired test site was one that met the following criteria:

Criteria	Reasoning
- A PTB is installed and has been operational	Necessary as the objective of this
for at least 6-12 months	demonstration is to demonstrate and assess
- The operational history of the PTB is known	water quality changes downgradient of an
 Detailed monitoring of the PTB system has 	operational and fully effective PTB
been conducted and the data is available	
- Groundwater samples collected from within	
the PTB treatment zone indicate significant	
and consistent concentration reduction	
- The hydrogeology of the site is reasonably	
well-characterized and it has been	

Criteria	Reasoning
demonstrated that flow is through, not	
around the PTB	
 Access to sampling locations downgradient 	
of the PTB	
- Relatively shallow groundwater (to	Necessary so that cost-effective, direct-push
minimize project costs)	drilling and well installation techniques can be
- Base personnel are present to facilitate the	used and so that groundwater sampling can be
logistics associated with sampling events	achieved with peristaltic pumps
- The estimated groundwater average linear	Necessary to ensure that downgradient water
velocity is greater than 10 ft/yr (3 m/yr)	quality changes can be observed within the
	lifetime of this project

3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

The MTBE biobarrier PTB system shown in Figure 3 was installed at the NBVC, Port Hueneme, California, to fully treat a 500-ft (150-m) wide dissolved MTBE plume. It was installed just past the downgradient edge of the gasoline-impacted source zone at the Navy Exchange Service (NEX) service station and became operational in September 2000. The system consisted of a line of gas injection wells designed to create a well-oxygenated zone spanning the width of the MTBE plume while still allowing unimpeded flow of groundwater through the system. Performance data was collected through mid-2002 during another ESTCP demonstration project. The biobarrier ultimately achieved a reduction of MTBE concentrations in groundwater to <5 µg/L within the well-oxygenated treatment zone.

The geology throughout the vadose zone and upper unconfined aquifer consists of unconsolidated sands, silts, and clays with minor amounts of gravel and fill material. Silty fill material extends from ground surface to about 7-9 ft (2.1–2.7 m) bgs.

Below that, silty fine- to medium-grained sands transition to predominantly medium-grained sands, which extend to approximately 20 ft (6.1 m) bgs, at which point a clay aquitard is encountered. Depth to the groundwater table is approximately 9 ft (3 m) bgs, with seasonal variations of approximately 1 ft (0.3 m). The gasoline-containing source zone soils are generally found in the sandy layer from about 9-12 ft (2.7–3.7 m) bgs. The dissolved MTBE groundwater plume of interest to this study was contained within this upper aquifer.

In general, groundwater within this aquifer flows to the southwest with gradients ranging from approximately 0.001 to 0.003 ft/ft (0.001 to 0.003 m/m). Transmissivity values ranging from 19,000 to 45,000 gal/day/ft have been reported, which correspond roughly to hydraulic conductivity estimates of 250 to 600 ft/day (0.088 to 0.21 cm/s). Groundwater flow velocity estimates range from 270 to 1,900 ft/yr (80 to 580 m/yr), assuming an effective porosity of 0.35 ${\rm ft}^3$ -H₂O/ft³ (0.35 m³-H₂O/m³).



Figure 3. Large-Scale Biobarrier PTB System at NBVC. (The fenced-in area is approximately 600-ft long.)

Tracer studies conducted in the vicinity of the field site demonstrated groundwater velocities ranging from about 280 to 560 ft/yr (85 to 170 m/yr), with the velocity increasing from the top to the bottom of the aquifer (Amerson and Johnson, 2003). An average linear groundwater velocity of about 300 ft/day (91 m/yr) is consistent with the dissolved plume length and time since the gasoline release.

3.4 PHYSICAL SETUP AND OPERATION

This project did not involve the installation of any equipment or the modification of the PTB discussed above. It involved primarily soil and groundwater sampling and the development of a spreadsheet tool. A Geoprobe direct-push rig was used for soil core and groundwater sample collection. Most analyses were conducted on site using field laboratory analytical equipment.

This project was conducted over a 2-year period. Soil and groundwater sampling and hydrogeologic characterization events occurred in April and May 2004, July and August 2004, and August 2005. For reference, this is 1226, 1324, and 1709 days, respectively, after the seeding of the biobarrier in December 2000 (oxygenation began in September 2000). Development of the calculation tool, testing, and refinement began following the second field event and extended through the remainder of the project.

3.5 SAMPLING/MONITORING PROCEDURES

All sampling procedures were in compliance with the Demonstration Plan's Quality Assurance Project Plan. Field investigations occurred in April and May 2004, July and August 2004, and August 2005. Activities are summarized in Table 3, and sampling locations are shown in Figure 4.

Table 3. Summary of Field Sampling Activities at NBVC.

			Sampling Events		
			April/May 04	July/Aug 04	Aug 05
Number o	f temporary GW san	npling locations	33	18	37
	Number of GW samples collected and analyzed (excluding quality assurance/quality control samples)			197	298
A: £	Temporary GW locations Permanent wells	Constant drawdown pumping tests	74	66	
Aquifer characterization		WL recovery tests	88		
tests		Constant drawdown pumping tests		67	
		Slug tests		8	
Number of soil of	Number of soil cores collected for lab permeameter testing			61	
Number of permeameter tests performed				245	

Notes:

GW - groundwater WL - water level

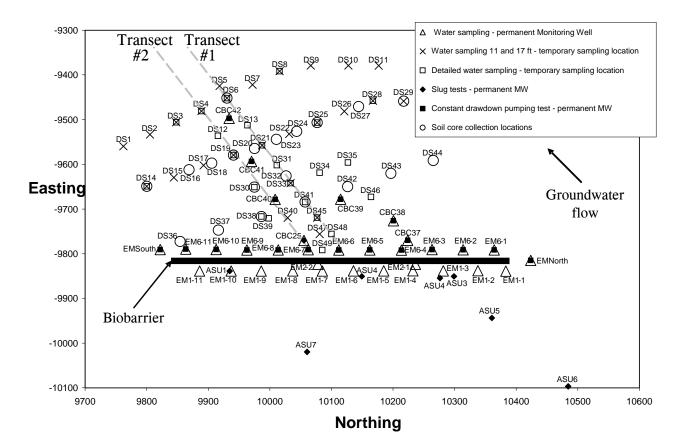


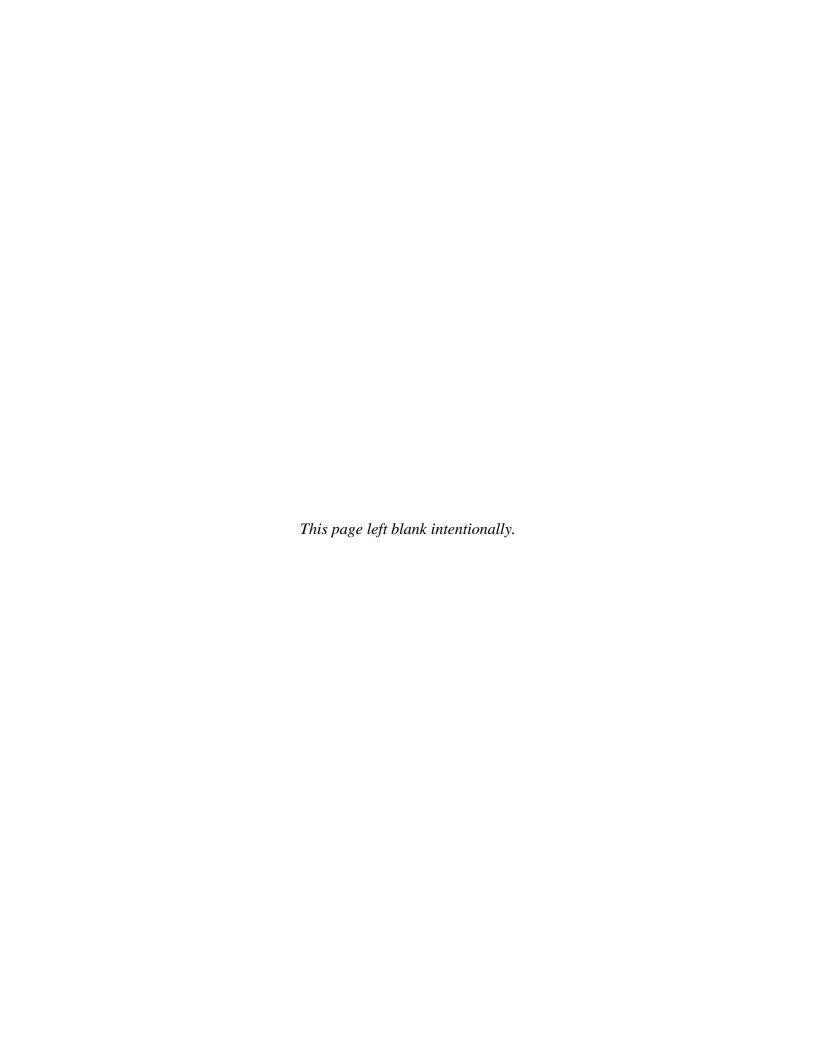
Figure 4. Sampling Locations Used in This Project. (All distances along the axes are in feet.)

3.6 ANALYTICAL PROCEDURES

Table 4 summarizes the analytical methods used as described in the Demonstration Plan.

Table 4. Analytical/Testing Methods.

Measurement	Description of Analyses
Dissolved oxygen (DO)	DO concentrations were measured using a flow-through cell and a YSI Model 550A DO meter with an accuracy of ±0.3 milligrams per liter (mg/L) or ±2% of the reading, an air saturation range of 0 to 200% and a temperature range of -5°C to +45°C. DO concentrations were monitored until a stable reading was obtained and until a sufficient volume of water from the well or groundwater sampling point was purged (approximately 1 L). Meter calibration was conducted by a one-point calibration in air, as is standard for this instrument.
MTBE concentration in groundwater	Heated headspace method: 30 milliliter (mL) sample warmed in 40 mL volatile organic analysis (VOA) vial to 35°C followed by 0.5 mL injection of headspace onto an SRI 8610C gas chromatograph (GC) equipped with a DB-1 type capillary column and photo-ionization detector (PID) and flame ionization detectors (FID). The GC was calibrated to known dissolved MTBE concentrations across the concentration range of interest (approximately 0.001 mg/L to 10 mg/L). A three- to five-point calibration was used, with at least one calibration concentration within each order of magnitude. The reporting level for this study was generally about 0.005 $\mu g/L$, based on calibration data.
Oxidation reduction potential (ORP)	ORP was measured using an Orion Quikchek Model 108 ORP meter with a relative millivolt (mV) range/resolution: ±999mV/1mV and relative accuracy: ±5mV. ORP meter function was confirmed using an ORP standard solution. Due to the slow response time for the meter, it was determined in the field that the most stable ORP measurements were made when a static sample was collected and the meter was allowed to stabilize within the sample.
Specific discharge	For 0.75-in (1.9-cm) diameter permanent monitoring wells and direct-push groundwater sampling locations, specific-discharge tests were conducted using an electronic water level indicator, a volumetric cylinder, a peristaltic pump, and a stop watch. First, the water level is measured in the well/drive-rod until stable. Then the polyethylene tubing inlet is lowered 3 in (7.6 cm) to 6 in (15 cm) below the stable water level, and the peristaltic pump is run at a speed capable of drawing the water down to that level (this was apparent by slugs of air coming up in the tubing). At this point, the flow is measured by recording the time required to collect a specified volume of water.
Slug tests	Slug testing was performed in permanent monitoring well installations with well diameters 2 in (5.1 cm) or greater. Slug tests utilized either one or two 4-ft (1.2-m) long slugs to obtain a minimum 1-ft (0.3-m) displacement within each monitoring well. A submersible transducer/data logger was used to monitor water level recovery during each test.
Laboratory permeameter tests	Laboratory hydraulic conductivity tests were conducted on all soil cores using both constant- and falling-head permeameters. Each core was cut into 1-ft (0.3-m) intervals or smaller, based on visual changes in the geology of the soil core. Each interval was then tested. Sections that took longer than 30 min to saturate were not analyzed. For these intervals, the hydraulic conductivity was assigned a value less than the lowest conductivity recorded for the laboratory methods (10 ⁻⁵ cm/s)



4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

The following briefly summarizes key data collected during this demonstration. A complete compilation and analysis of the data can be found in the Final Report from this project as well as in Maass (2005).

Geologic/Hydrogeologic Characterization Data. Geologic/hydrogeologic characterization data is summarized in Table 5. Overall, these data suggest hydraulic conductivities that are lowest at shallow intervals and highest at deeper intervals throughout the aquifer interval of interest. This range of values is consistent with previous findings, including the Amerson and Johnson tracer study (2003) and estimates of hydraulic conductivity collected during the installation of the MTBE biobarrier in 2000. The data are also generally in agreement with visual observations of the soils cores.

Table 5. Hydraulic Conductivity Descriptive Statistics for NBVC Site.

			Hydraulic Conductivity (cm/s)					
	Interval		Adjusted					
	(ft bgs)	Average	Median*	Median	Minimum	Maximum		
	8	2.0E-2	1.0E-5	1.0E-5	1.0E-5	4.0E-1		
	9	2.2E-4	1.0E-5	1.0E-5	1.0E-5	4.2E-3		
	10	7.9E-3	1.0E-5	1.0E-5	1.0E-5	8.2E-2		
Laboratory	11	6.9E-3	3.8E-3	9.0E-4	1.0E-5	8.2E-2		
Permeameter	12	1.0E-2	1.3E-2	8.5E-3	1.0E-5	3.5E-2		
Tests	13	1.6E-2	1.4E-2	1.3E-2	1.0E-5	6.8E-2		
	14	2.3E-2	1.5E-2	7.5E-3	1.0E-5	2.1E-1		
	15	3.8E-2	3.4E-2	2.8E-2	1.0E-5	1.1E-1		
	16	3.9E-2	4.0E-2	1.9E-2	1.0E-5	2.0E-1		
	17	3.6E-2	4.1E-2	3.1E-2	1.0E-5	1.3E-1		
	18	5.1E-2	5.1E-2	4.2E-2	1.0E-5	1.4E-1		
	19	7.6E-2	7.6E-2	5.6E-2	1.0E-5	3.7E-1		
]						
	Interval		Adjusted					
	(ft bgs)	Average	Median*	Minimum	Maximum	N		
	8							
Discrete	9							
Interval Field	10	1.1E-2	1.1E-2	1.1E-2	1.1E-2	2		
Mini-Pump	11	7.8E-3	3.1E-3	1.3E-3	2.1E-2	5		
Tests at	12	6.4E-3	1.6E-3	6.9E-4	2.5E-2	5		
Direct-Push	13	2.5E-2	9.3E-3	1.6E-3	7.3E-2	5		
Locations	14	7.3E-3	6.3E-3	1.6E-3	1.7E-2	5		
	15	2.1E-2	5.2E-3	3.6E-3	4.9E-2	5		
	16	4.0E-2	4.3E-2	4.8E-4	7.9E-2	5		
	17	3.4E-2	1.7E-2	1.0E-3	7.9E-2	5		
	18	3.2E-2	6.3E-3	5.1E-4	7.9E-2	5		
	19	3.8E-2	2.4E-2	1.4E-3	7.9E-2	5		

^{* &}quot;Adjusted median" represents the median of values after the exclusion of values considered to be outliers for that layer.

Groundwater Flow Direction and Hydraulic Gradient. Depth to groundwater across the site was approximately 8 ft, with seasonal fluctuations of up to 1 ft. Using depth-to-water measurements and survey data, groundwater elevations were calculated and were used to develop water level contour maps and to determine flow direction and hydraulic gradient across the site for each measurement event. The data indicate groundwater flow to the southwest, with hydraulic gradients ranging from 0.003 ft/ft to 0.004 ft/ft. Using a range of hydraulic conductivities from 10^{-5} cm/s to 2.1×10^{-1} cm/s, a hydraulic gradient of 0.004 m/m, and a moisture content of 0.3 m³-H₂O/m³-soil, groundwater velocities at the site were estimated to range from 1.3×10^{-7} cm/s (3.8 x 10^{-4} ft/day) to 2.7×10^{-3} cm/s (7.9 ft/day).

Groundwater Quality Changes in Space and with Time. Pre-biobarrier PTB operation groundwater quality data were obtained by Bruce et al. (2003) from 13 monitoring well locations in August of 2000. These data, collected at 15 ft and 20 ft bgs, indicated that dissolved MTBE concentrations were as high as $12,000 \,\mu\text{g/L}$ in the core of the dissolved plume.

Table 6 summarizes groundwater quality changes with depth and time throughout the area sampled in this project. Figure 5 provides a sample contour plot illustrating changes in concentration with time and distance along the MTBE dissolved plume centerline.

Table 6. MTBE Groundwater Concentration Statistics in Monitored Downgradient Zone from the 2004 and 2005 Sampling Events (1226–1324 days and 1709 days after biobarrier seeding, respectively).

	2004 MTBE concentrations (μg/L)			2005 MTBE concentrations (µg/L)		
Depth (ft bgs)	Minimum	Maximum	Median	Minimum	Maximum	Median
9	BDL	BDL	BDL	ND	ND	ND
10	ND	507	19.5	ND	63	3
11	ND	654	29	ND	170	3
12	ND	876	78	ND	176	9
13	ND	484	39.5	ND	102	5
14	BDL	480	18.5	BDL	52	3
15	BDL	67	13	ND	28	3
16	BDL	53	9	ND	8	3
17	BDL	226	10	ND	7	3
18	BDL	84	11	ND	9	3
19	1	111	13	ND	8	3

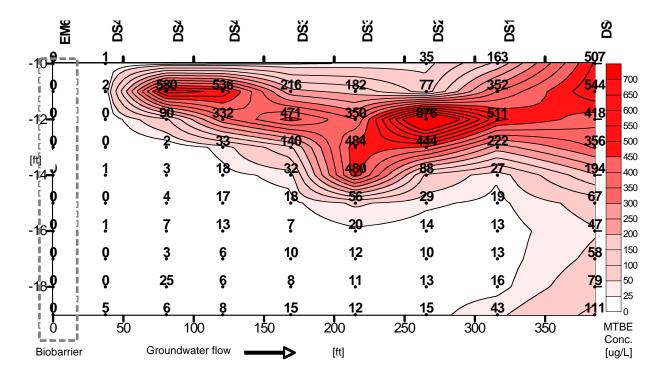
Notes:

BDL - below detection limit

ND - non detect

bgs - below ground surface

2004 Data Collected 1226 to 1324 Days After Biobarrier Seeding



2005 Data Collected 1709 Days After Biobarrier Seeding

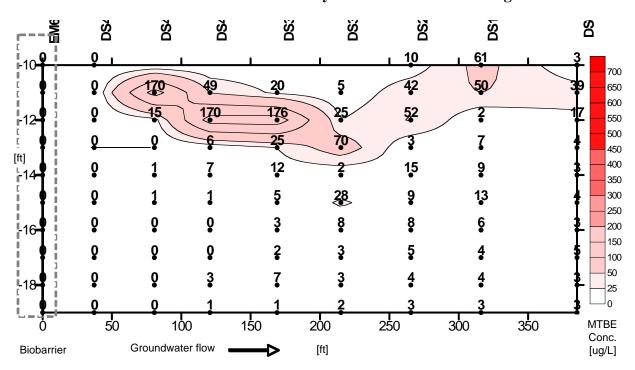


Figure 5. MTBE Concentrations—Vertical Cross Section Along Plume Centerline.

Key observations from the field data set include:

- Dissolved MTBE concentrations were typically greatest at shallower depths and decreased with increasing depth down to 20 ft bgs. The greatest dissolved MTBE concentrations were located along the plume's central axis.
- With time, treated water from the biobarrier can be seen to be migrating downgradient, resulting in a decreasing trend in concentration.
- Changes in concentration with time occur more rapidly in the deeper and higher conductivity sections of the aquifer. Concentrations persist longer in the shallower and less conductive sections of the aquifer.

In reviewing these data, it is important to note that the NBVC site would typically be considered a relatively simple and homogeneous site. Using the average hydraulic conductivity value from conventional well slug tests (0.4 cm/s, Table 5), a gradient of 0.004 m/m, and an effective porosity of 0.3 m³-H₂O/m³-aquifer, the conventional expectation would be that all wells within about 2,000 ft downgradient of the biobarrier would have non detect levels within a year of the start-up of the biobarrier. Yet, it is clear that MTBE persists in groundwater longer than this, and that the migration of clean water and persistence of MTBE are linked to the vertical variations in hydraulic conductivity.

Spreadsheet-Based Tool DGCHANGE v1.0. DGCHANGE v1.0 is a spreadsheet-based modeling tool developed to predict order-of-magnitude changes in groundwater quality with time downgradient of a PTB. With this tool, the user enters aquifer characteristics (layer thicknesses, layer hydraulic conductivities, groundwater gradient, initial dissolved concentrations), and the output is presented graphically as a) cross-section plots along the plume centerline showing concentration versus depth and distance for user-specified times, b) changes with depth and time at fixed distances downgradient, and c) expected concentrations versus time in conventional wells located at selected distances downgradient of the PTB. The output visually communicates the variations in clean water movement with depth and how those variations might be reflected in conventional monitoring well data.

4.2 PERFORMANCE CRITERIA

This ESTCP project does not involve the demonstration of a technology; instead, it involves the development and demonstration of an approach for estimating groundwater quality improvements downgradient of a PTB, as discussed in Section 2.0. Consistent with that, the performance criteria and metrics established for this project are summarized in Table 7. There were no significant deviations from the Demonstration Plan.

Table 7. Performance Metrics.

Primary Performance Criteria (qualitative and		Performance Confirmation	
quantitative)	Expected Performance Metric	Method	Actual
Data set collected at NBVC is useful for testing and revising approach for estimating	Data set reasonably characterizes the changes in hydraulic conductivity with depth in the aquifer and includes sufficient flow direction and hydraulic gradient data.	Summary tables of hydraulic property results and maps of groundwater elevations	Same as expected performance criteria
downgradient water quality changes with time, and for use by others in developing more sophisticated tools	Data set shows concentration versus distance and time behavior downgradient of the PTB, ranging from very low (or non detect) concentrations at the PTB to unaffected concentrations some distance downgradient of the PTB.	Plots of MTBE concentration versus distance at different sampling times	Same as expected performance criteria
Utility of approach	Illustrate approach for estimating downgradient water quality changes with time	Use data from NBVC site and present inputs and outputs	Same as expected performance criteria
	Comparison of projected and measured concentrations downgradient of the PTB Predictive tool incorporated in a	Reasonable order- of-magnitude agreement Spreadsheet	
	spreadsheet	created and Users Guide written	
	Comparison of characterization requirements for the proposed approach and current characterization requirements	Supplemental data collection does not increase typical characterization costs by more than $10-20\%$.	

4.3 DATA ASSESSMENT

This data set is the most comprehensive data set available focused on groundwater quality changes with time downgradient of a PTB. It is sufficient to assess the practicability of approaches for projecting groundwater quality changes with time downgradient of PTBs.

4.4 TECHNOLOGY COMPARISON

The conventional approach for projecting groundwater concentration changes with time utilizes a single aquifer-wide average linear groundwater velocity estimate. For example, improvements in groundwater quality would be expected after one year between 0 ft and 365 ft downgradient at the NBVC PTB site (as the average linear groundwater velocity cited in most site reports is about 1 ft/day). The data clearly show that this is not the case at this site.

The approach evaluated in this project couples determination of horizontal hydraulic conductivity changes with depth, flow direction, and hydraulic gradient with a simplistic spreadsheet-based tool (DGCHANGE v1.0). This approach appears practicable and produces groundwater quality changes with time that are reasonably consistent with the observed site behavior. In addition, the spreadsheet-based tool visually communicates the projections in a number of different views, including a vertical cross section that communicates changes with time along the dissolved plume centerline, a tabular presentation illustrating concentration changes with depth and time at a fixed location, and graphs of expected vertically averaged concentrations with time in conventional monitoring wells.

It should be noted that modeling of the downgradient migration of clean water was also performed using MODFLOW-2000 and MT3D, as these more sophisticated modeling tools are sometimes used to model groundwater transport downgradient of PTBs. A complete description and discussion of that exercise can be found in Maass (2005), only the key points of which are discussed here.

The MODFLOW/MT3D model was run for two scenarios: "low dispersion" and "typical dispersion." The former was selected to correspond with those conditions modeled using DGCHANGE v1.0. The latter was based on dispersion input parameters estimated from common rules-of-thumb for groundwater contaminant transport modeling (as dispersion coefficients are rarely measured and are typically estimated). The low dispersion scenario produced the same results as those generated by DGCHANGE v1.0. The typical dispersion scenario resulted in complete vertical mixing across all layers, which is not consistent with field observations. Thus, neither the simple nor more complex conventional modeling approaches would have reasonably predicted the migration of clean water and the concentration versus time changes observed at downgradient monitoring wells.

5.0 COST ASSESSMENT

5.1 COST REPORTING

This ESTCP project did not involve the demonstration and cost-tracking of a technology. Instead, this project was conducted to better understand the dynamics of treated water movement downgradient of PTBs and reasons groundwater quality improvements do not occur as quickly as typically anticipated.

The approach evaluated in this project involves:

- Collection of pre-PTB groundwater concentration data in order to form a conceptual model of the initial dissolved groundwater concentration distribution
- Collection of hydrogeologic data in order to form a layered conceptual model of the groundwater system and the flow direction
- Entry of this data into an Excel spreadsheet-based tool that estimates changes in groundwater quality with time and space, and concentration versus time in selected monitoring well locations.

It is important to note that the spatial density of data collected during the field work in this project greatly exceeded the level necessary to apply the approach outlined above; therefore, the sampling density and costs for this project should not be used as a basis for estimating costs at other sites. The high spatial data density was necessary for the following reasons: 1) One of the project goals was to obtain a detailed concentration data set downgradient of a well-understood PTB system in order to illustrate with data the differences between real behavior and conventional projections. 2) A larger data set can be used to test proposed minimum data needs.

Much of the data needed in the approach evaluated is routinely collected either during the initial site assessment or prior to final design of the PTB system; therefore, the cost assessment below focuses on incremental costs relative to routine data collection and reduction for PTB sites. Table 8 summarizes the minimum data collection/data reduction needs and the incremental effort required relative to routine data collection and reduction for PTB sites. Table 9 identifies incremental costs above typical characterization and data reduction activities.

At most sites, the characterization of vertical variations in hydraulic conductivity at one to three locations should be sufficient, and it is unlikely that most aquifers will be conceptualized as having more than 10 distinct layers. Thus, the incremental data collection costs should be negligible in comparison with baseline site characterization and PTB design costs for most sites.

Table 8. Minimum Data Collection/Data Reduction Needs and Incremental Effort Required Relative to Routine Data Collection and Reduction for PTB Sites.

Data Collection/ Data Reduction Need	Purpose	Incremental Effort Relative to Routine Data Collection and Reduction for PTB Sites
Depth to groundwater measurements and reduction to groundwater elevations Groundwater concentration measurements at different locations and depths Determination of vertical variations in hydraulic conductivity and use of this data with measured hydraulic gradients	Groundwater flow direction and hydraulic gradient determination Determine groundwater plume width and thickness, and initial concentrations downgradient of PTB Determine vertical variations in horizontal groundwater flow velocity	No incremental cost or effort—this is a component of conventional PTB selection and design activities No incremental cost or effort—this is a component of conventional PTB selection and design activities This may not currently be part of typical PTB selection and design activities, but PTB designers should be collecting soil cores as part of the design process, so the only additional effort here is the characterization of the core material. Also, as was done in this work, it may be relatively easy at some sites to measure hydraulic conductivity in situ via constant drawdown pumping tests at discrete depths while collecting groundwater concentration samples with direct-
Use of spreadsheet-based analysis tool, DGCHANGE v1.0	Project order-or-magnitude groundwater quality changes with time downgradient of PTB	push tools. Less than 16 hr of time to review site data, enter it in spreadsheet, produce expected performance projections, and write brief summary

With respect to use of the predictive tool, DGCHANGE v1.0, this, at most, involves a few hours once the site-specific data are available. Again, the incremental cost should be negligible in comparison with total project costs for most sites. The software is provided free.

Table 9. Cost Reporting Table—Incremental Costs Above Typical Characterization and Data Reduction Activities.

Cost Category	Subcategory	Incremental Costs				
Fixed Costs						
Capital costs	Mobilization/demobilization	\$0				
	Planning/preparation	\$1,000				
	Equipment	\$0				
	Other	\$0				
	Subtotal	\$1,000				
Variable Costs						
Operation and maintenance	Labor	\$0				
	Testing – outside lab	\$5,000				
	Utilities/fuel	\$0				
	Instrument cost	\$0				
	Subtotal	\$5,000				
Other Costs						
Other technology-specific costs	Review data and use spreadsheet-based	\$5,000				
	tool to project downgradient water					
	quality changes with time and distance					
	Total Costs	\$11,000				

5.2 COST ANALYSIS

As the costs given above are incremental, relative to baseline site characterization costs, they are relatively insensitive to site-specific factors. The costs will increase as the thickness of the dissolved plume increases and the number of aquifer layers increases, as more samples will be required for hydraulic conductivity analysis. However, PTBs are generally installed in shallow settings and usually not in very complex hydrogeologic settings, so the incremental costs for most sites should be similar to those given above.



6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

As discussed in Section 5.0, the spatial density of data collected during the field work in this project greatly exceeded the level necessary to apply the approach outlined above; therefore, the sampling density and costs for this project should not be used as a basis for estimating costs at other sites. The costs would have been greater at a site with a deeper or thicker groundwater plume, and at any site where direct-push sampling is not feasible.

6.2 PERFORMANCE OBSERVATIONS

The performance of this project met all acceptance criteria for the project's performance objectives.

6.3 SCALE-UP

This demonstration project was conducted at full scale (and at a full-scale PTB site).

6.4 OTHER SIGNIFICANT OBSERVATIONS

The technology demonstrated in this project is relatively easy to implement as it leverages the basic data collection activities that occur at all PTB sites.

6.5 LESSONS LEARNED

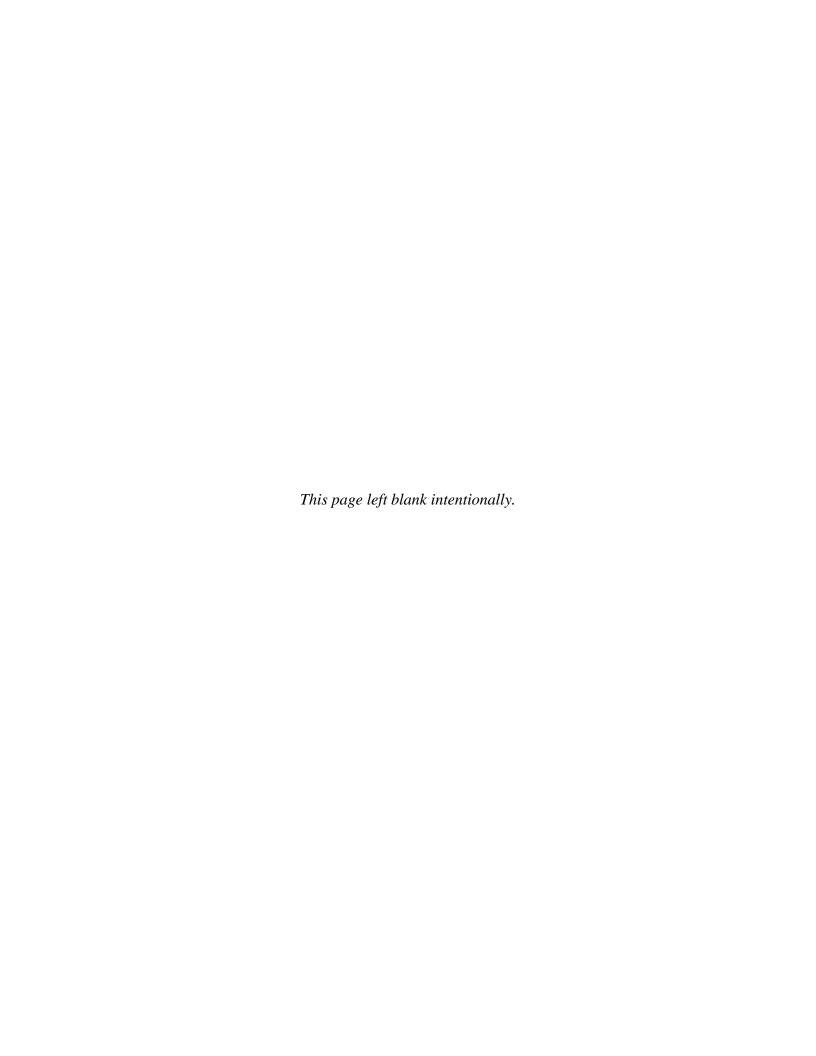
Site characterization and data reduction activities at PTB sites should emphasize site conceptual models involving layered settings with vertical variations in horizontal groundwater velocities. Increased insight to downgradient water quality changes with time and distance can be achieved at relatively low cost at sites where practitioners can concurrently collect groundwater samples and hydraulic conductivity information while performing depth-discrete sampling.

6.6 END-USER ISSUES

A manuscript for publication in Ground Water Monitoring and Remediation is being prepared.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

This technology can be applied under current regulatory guidance and does not require any additional approvals, licenses, etc. beyond those already required for site characterization activities.



7.0 REFERENCES

- ESTCP. 2003. Final Report: In Situ Bioremediation of MTBE in Groundwater (prepared by Naval Facilities Engineering Service Center and Arizona State University).
- Amerson, I., and R. Johnson. 2003. Natural Gradient Tracer Test to Evaluate Natural Attenuation of MTBE under Anaerobic Condition. Jour. GWMR, (23)1:54-61.
- Battelle. 2002. Final Report: Evaluating the Longevity and Hydraulic Performance of Permeable Reactive Barriers at Department of Defense Sites. Prepared for NFESC, Port Hueneme, California.
- Bruce, Cristin L., Johnson, Paul C., and Miller, Karen D. 2003. In-Situ Bioremediation of MTBE in Groundwater, ESTCP Cost and Summary Report. ESTCP Project No. CU-0013, Technical Report TR-2216-ENV. Port Hueneme, California.
- Dahlen, Paul R. 2004. Characterization of Petroleum Hydrocarbon Impacts to Arizona Groundwater Resources from Leaking Underground storage Tanks. Ph.D. Diss., Arizona State University.
- Interstate Technology & Regulatory Council Permeable Reactor Barriers Team. February 2005.

 Permeable Reactive Barriers: Lessons Learned/New Directions.
- Maass, Pamela B. 2005. Improved-Quality Groundwater Migration Down-Gradient of In Situ Permeable Reactive Barriers. M.S. Thesis, Arizona State University.



APPENDIX A

POINTS OF CONTACT

		Phone				
7.1. 600 1		Fax	- ·			
Point of Contact	Organization	E-Mail	Role			
Team Members						
Dr. Paul Johnson	Arizona State University	480-965-9115 (voice)	Principle Investigator			
	College of Engineering and	480-965-0557 (fax)				
	Applied Science	paul.c.johnson@asu.edu				
	P.O. Box 875506					
	Tempe, AZ 85287-5506					
Pamela Maass Carlson	CH2M Hill	480-966-8188 (voice)	Co-Principle Investigator			
	2625 S. Plaza Drive, Suite 200	480-966-9450 (fax)				
	Tempe, AZ 85282	pcarlson@ch2m.com				
Dr. Paul Dahlen	Arizona State University	480-965-0055 (voice)	Co-Principle Investigator			
	College of Engineering and	480-965-0557 (fax)				
	Applied Science	paul.dahlen@asu.edu				
	P.O. Box 875306					
	Tempe, AZ 85287-5306					
Department of Defense (DoD) Project Contact						
Dr. Andrea Leeson	ESTCP Program Office	703-696-2118 (voice)	Program Manager			
	901 N. Stuart Street, Suite 303	703-696-2114 (fax)	_			
	Arlington, VA 22203	andrea.leeson@osd.mil				



ESTCP Program Office

901 North Stuart Street Suite 303 Arlington, Virginia 22203 (703) 696-2117 (Phone) (703) 696-2114 (Fax)

e-mail: estcp@estcp.org www.estcp.org