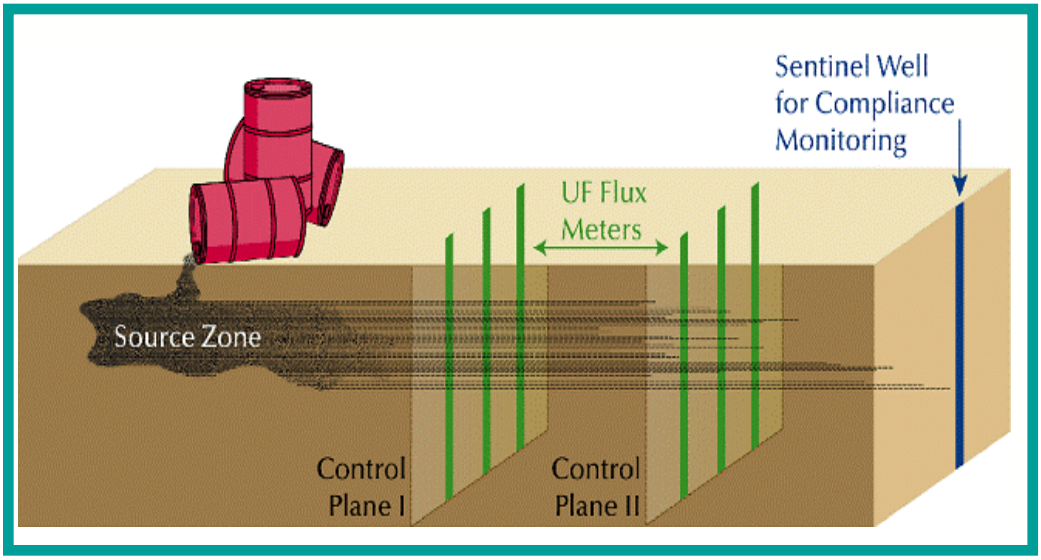
ESTCP
Cost and Performance Report

(ER-0114)



Field Demonstration and Validation of a New Device for Measuring Water and Solute Fluxes

April 2007

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT
ESTCP Project: ER-0114

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
bgs	below ground surface
BHD	borehole dilution (method)
CFB	Canadian Force Base
CU	clay unit
DCE	dichloroethene
DNAPL	dense nonaqueous phase liquid
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EW	extraction well
IHDIV-NSWC	Indian Head Division of the Naval Surface Warfare Center
LC-34	Launch Complex
LOX	liquid oxygen
LSU	Lower Sand Unit
MFGU	Middle Fine Grained Unit
MLS	multilevel samplers
MTBE	methyl tertiary butyl ether
MW	monitoring well
NAPL	nonaqueous phase liquid
NASA	National Air and Space Administration
NEX	Naval Exchange
NSWC	Naval Surface Water Center
PCE	perchloroethene
PFM	passive flux meter
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
SM-SI-GAC	surface-modified silver impregnated granular activated carbon
TCE	trichloroethene
UF	University of Florida

USU	Upper Sand Unit
VOA	volatile organic analysis

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

1.0 EXECUTIVE SUMMARY

The Department of Defense (DoD) has a critical need for technologies that provide cost-effective long-term monitoring of volatile organic chemicals, petroleum and related compounds, trace metals, and explosives. In recent years, the utility of contaminant flux and contaminant mass discharge as robust metrics for assessing site risks and site remediation performance has gained increasing acceptance within scientific, regulatory, and end-user communities. The passive flux meter (PFM) is a new technology that measures subsurface water and contaminant flux directly. This technology addresses the DoD need for cost-effective, long-term monitoring because flux measurements can be used for process control, remedial action performance assessments, and compliance monitoring.

Under the Environmental Security Technology Certification Program (ESTCP) Project No. ER-0114, the PFM was demonstrated and validated as an innovative flux monitoring technology at several locations, including the National Air and Space Administration's (NASA) Launch Complex 34 (LC-34) in Cape Canaveral, Florida; the Canadian Forces Base in Ontario, Canada (Borden); the Naval Construction Base in Port Hueneme, California; and the Naval Surface Warfare Center at Indian Head, Maryland. Projects at NASA, Borden, and Port Hueneme included objectives of evaluating the flux meter as a technology for direct in situ measurement of cumulative water discharge and contaminant flux under controlled flow and under natural gradient conditions. Tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), vinyl chloride, ethylene, and methyl tertiary butyl ether (MTBE) were the contaminants studied. At the Naval Surface Warfare Center at Indian Head, Maryland, the PFM was demonstrated and validated as a technology for measuring water and perchlorate fluxes. Data and results from all sites were compiled and interpreted to expedite regulatory and end-user acceptance and to stimulate commercialization.

1.1 SITE STUDY OBJECTIVES

- Demonstrate and validate the flux meter as an innovative technology for direct in situ measurement of cumulative water and contaminant fluxes in groundwater
- Demonstrate and validate a methodology for interpreting source strength from point-wise measurements of cumulative contaminant and water fluxes
- Compile field data to support technology transition from the innovative stage to regulatory and end-user acceptance and to stimulate commercialization.

On the first two objectives, this demonstration generated the necessary statistics to show that PFM-measured solute and water fluxes compared well to independent estimates generated through alternative methods (e.g., borehole dilution [BHD], multilevel samplers [MLS], and plume interception wells). Concerning the third objective, favorable results from this demonstration project led to subsequent PFM deployments at more than 25 sites in the United States, Canada, Australia, and Wales. Several recent deployments were executed by ENVIROFLUX, a newly established company licensed to use the PFM technology.

1.2 COST ASSESSMENT AND COMPARISON

Costs were calculated for the PFM method and compared to the BHD/MLS method for contaminant flux characterization. Cost estimates per linear ft for PFM deployments and BHD/MLS measurements indicate that the PFM method resulted in lower unit costs, depending on cost variability and the number of wells monitored. Both approaches exhibited similar costs in terms of materials and analytical costs, and these costs were scalable to larger and smaller deployments. When monitoring involved as few as 3 to 4 wells, costs were comparable. For sites involving 5 or more wells, PFMs were less expensive. In general, the BHD/MLS method demanded considerably more time on site than PFMs, which rendered it almost impractical when more than seven wells were involved. The cumulative monitoring given by PFMs generates flux estimates, which represent long-term transport conditions and are less sensitive to day-to-day fluctuation in flow and contaminant concentration whereas water and contaminant flux values derived from the alternative BHD/MLS method represent short-term evaluations that are not likely to satisfy DoD's need for cost-effective, long-term monitoring.

1.3 DEMONSTRATION CONCLUSIONS

At the CFB (Borden) site, it was demonstrated under controlled flow conditions that the PFM produced highly accurate measures of both water and contaminant fluxes. PFM-measured MTBE, PCE, and TCE fluxes compared closely to those predicted using the known groundwater flux and contaminant concentrations from a dense network MLS. Under the same controlled flow conditions, it was demonstrated that PFMs could be used to measure aquifer conductivities and thus provide critical hydrogeologic data to complement measured water and contaminant fluxes. At LC-34 (NASA), PFMs were tested in an aggressive environment of active bioremediation. PFM measured fluxes for TCE, DCE, vinyl chloride, and ethylene in a test cell confirmed expected flux variations with time. Measured water fluxes appeared less reliable, suggesting that the highly active biotic environment undermined PFM performance in terms of measuring groundwater specific discharge. From the Port Hueneme site, PFMs generated depth-varying measures of groundwater flux from wells of different construction. These measures were independently verified with data gathered from borehole logs, slug tests, and conductivity measurements. Pushed wells recorded lower groundwater and contaminant fluxes than drilled wells; however, flux-averaged concentrations did not vary significantly between well types. At the Indian Head site, PFMs were tested on perchlorate, a major inorganic contaminant of DoD concern. For this demonstration, a surfactant modified activated carbon was developed and then field-tested as a new PFM-sorbent for measuring groundwater and perchlorate fluxes. Measured water fluxes compared well to predictions derived from BHD tests and conventional water quality data. Measured perchlorate fluxes were reproducible between successive PFM deployments at most wells.

1.4 RECOMMENDATIONS

The current PFM design is effective in relatively shallow (<60 m) screened wells. The PFM should be redesigned and tested in deep wells and in karst/fractured rock wells. A study should be performed to determine if flux meters can be redesigned to provide direct in situ measures of contaminant biodegradation. Finally, a study should be conducted to determine if measured fluxes and hydraulic gradients at existing monitoring networks can be used to reconstruct site

fluxes from historical measures of water levels (hydraulic gradients) and contaminant concentrations.

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2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

This demonstration/validation study investigated the utility of a new method (Hatfield et al, 2002a, 2002b, and 2004) for the direct in situ measurement of cumulative water and contaminant fluxes in groundwater. The new method uses a down-hole permeable device, referred to as a passive flux meter (PFM). When deployed in a well, groundwater flows through the PFM under natural gradient conditions (see Figure 1). The interior composition of the PFM is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and/or inorganic contaminants present in fluid intercepted by the unit. The sorbent matrix is also impregnated with known amounts of one or more fluid soluble resident tracers, which are leached from the sorbent at rates proportional to fluid flux.

After a specified period of exposure to groundwater flow, the PFM is removed from the well or boring. Next, the sorbent is carefully extracted to quantify the masses of all contaminants intercepted by the PFM and the residual masses of all resident tracers. Contaminant masses are used to calculate cumulative time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative or time-average groundwater fluxes.

Figure 2 displays two hypothetical cross sections of a PFM configured as circular column (such as one installed in a monitoring well). In this figure, cross section A reveals a single resident tracer uniformly distributed over the cross section before any fluid has flowed through the meter. As water flows through the meter, soluble tracers are leached from the sorbing matrix and lost from the meter. Cross section B reflects the subsequent spatial distribution of tracer after exposure to a fluid flow field. Here, the tracer has been displaced to the right and leached from the section in a manner consistent with the assumption that fluid streamlines are parallel to the general direction of fluid flow. Multiple tracers with a range of partitioning coefficients are used simultaneously in a PFM to enable water flux measures over three orders of magnitude.

The mass of resident tracer remaining within section B of Figure 2 is used to estimate the cumulative fluid volume intercepted by this section of the meter. Assuming reversible, linear, and instantaneous resident tracer partitioning between the sorbent and water, the dimensionless cumulative volume ξ of water intercepted by the PMF at a specified well depth is obtained iteratively using the following equation (Hatfield et al, 2002b, and Annable et al, 2005):

$$\xi = \left\{ 1 - \left[Sin\left(\frac{\pi M_R}{2} + \xi\sqrt{1-\xi^2} \right) \right]^2 \right\}^{1/2} \qquad (2\text{-}1)$$

where M_R is the relative mass of tracer retained in the PFM sorbent at the particular well depth.

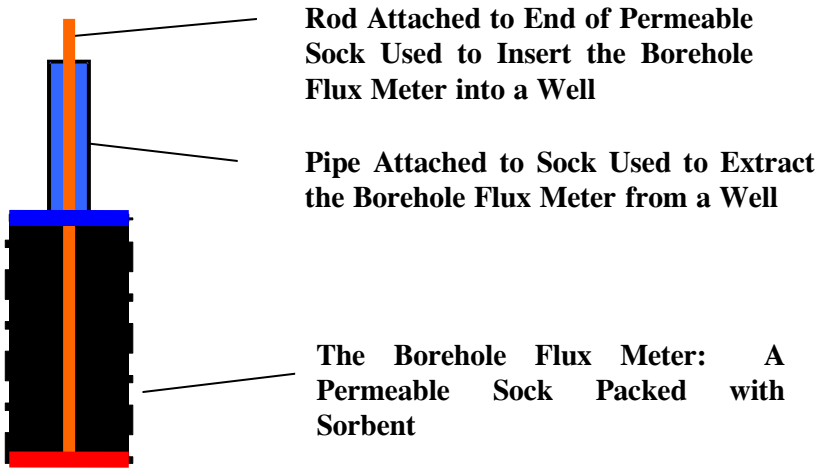

Figure 1. Schematic of a PFM Consisting of a Permeable Sock Filled with a Selected Sorbent.

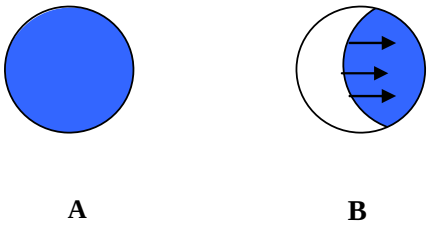

Figure 2. PMF Cross-Sections of Initial Condition (A) and Displaced Tracer Distribution (B) after Exposure to a Fluid Flow Field.

The water flux, q *[L/T]* (e.g., m/day), through the sorbent is calculated using:

$$q = \frac{2r\theta R_d \xi}{t} \qquad (2\text{-}2)$$

where r is the radius of the PFM cylinder; θ is the water content of the sorbent; R_d is the retardation factor of the resident tracer on the sorbent; and t is the sampling duration. Since in most field applications, flow is unknown, multiple resident tracers are used to represent a broad range of tracer retardation factors. Likewise, multiple tracers provide for flux meters designed for both long- and short-term sampling durations.

As indicated above, q, is the specific discharge of water flowing through the sorbent; however, the flux of interest is the specific discharge of groundwater, q_o. The specific discharge indicated by the residual mass of resident tracers, q, is proportional to the groundwater flux, q_o, in the immediate vicinity of the PFM. Hence,

$$q = \alpha' q_o \tag{2-3}$$

where α' is a factor that can be calculated from the geometry of the well and the estimated permeabilities of the aquifer, well screen, well packing, and sorbent (Klammler et al, 2006a).

The contaminant mass retained on the sorbing porous matrix can be used to estimate solute flux into the meter. The measured flux is valid over the dimensions of porous medium contributing flow to the device. Assuming reversible, linear, and instantaneous contaminant partitioning between the sorbent and water, the contaminant mass flux J_c *[M/L²/T]* (e.g., kg/m²/day) can be determined using Equation 2-4 from Hatfield et al, 2004,

$$J_c = \frac{qM_c}{\pi r^2 L(1 - M_{RC})\theta R_{dc}} \tag{2-4}$$

where M_c is the mass of contaminant sorbed and L is the length of the sorbent matrix or the vertical thickness of the aquifer interrogated. R_{dc} is the retardation factor of the contaminant on the sorbent, and M_{RC} is the relative mass of a hypothetical resident tracer retained after time period t where that tracer has a retardation factor equal to R_{dc}. M_{RC} is calculated using Equations 2-1 and 2-2, while q is determined from resident tracers.

Depth variations of both water and contaminant fluxes can be measured in an aquifer from a single PFM by vertically segmenting the exposed sorbent packing and analyzing for resident tracers and contaminants. Thus, at any specific well depth, an extraction from the locally exposed sorbent yields the masses of all resident tracers remaining and the masses of all contaminant intercepted. This data is used to estimate local values of cumulative water and contaminant fluxes.

2.2 PROCESS DESCRIPTION

Operationally, the PFM is very simple. A single individual can deploy, retrieve, and sample a flux meter, but two is better operationally. Several PFMs (30 to 40) can be installed or deployed in a number of wells in a single day. Figure 3 illustrates the deployment of six PFMs in six wells distributed over two transects located downgradient from a contaminant source but upgradient from a sentinel well. In this example, the upgradient PFM transect is used to assess source strength, while the downgradient transect is used to quantify changes in contaminant flux between transects that may be due to natural or enhanced attenuation.

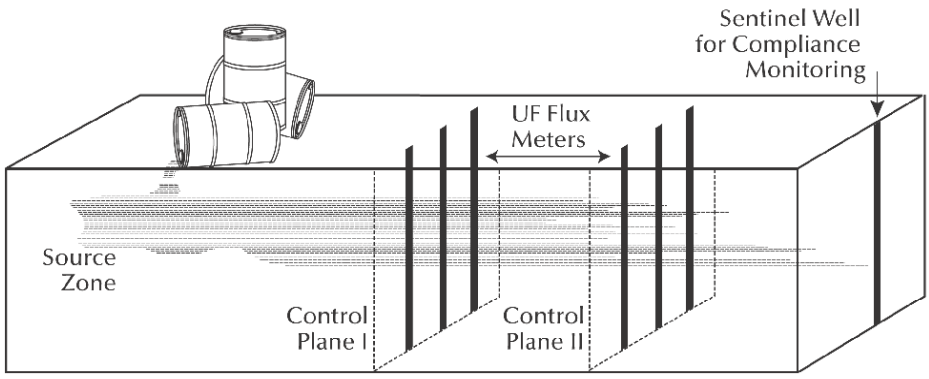

Figure 3. Deployment of Six Passive Flux Meters in Six Wells Distributed over Two Control Planes Located Downgradient from a Contaminant Source Zone.

PFM retrieval or extraction from wells is quite simple and can be conducted by a single individual. PFMs require no electrical utilities; hence, they can be deployed in remote locations. Given existing wells, the requirements for mobilization, training personnel in PFM installation and extraction, and assuring personnel health and safety are comparable to traditional water sampling. A listing of key criteria used to design a PFM is provided in Table 1.

Table 1. Key Design Criteria for the PFM.

Parameter	Comments
Sampling period	The specified duration of continuous flux measurements
Sorbent	Must be resistant to microbial degradation
Retardation factors of resident tracers	A suite of tracers is needed such that residual mass of one or more exists at the end of the sampling period and for the range of potential groundwater flows
Contaminant retardation factor	Retardation factors should be sufficiently high to retain the contaminant on the sorbent
Inside radius of the well screen	If a well screen exists
Outside radius of the well screen	If a well screen exists
Inside radius of the well	If no well screen exists
Permeability of the well screen	It is desirable that the screen be at least six times more permeable than the most permeable zone of the aquifer
Permeability of sorbent	It is desirable that the sorbent be at least 36 times more permeable than the permeable zone of the aquifer
Maximum permeability of the aquifer	Under natural gradient should yield a groundwater discharge greater than 1 cm/d
Minimum permeability of the aquifer	Under natural gradient should yield a groundwater discharge greater than 1 cm/d

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

Significant prior testing of the technology was limited to laboratory tests (Campbell et al, 2006; Hatfield et al, 2002b and 2004; and Klammler et al, 2006b). However, several recent field-scale tests were conducted by team members from the University of Florida (UF) and Purdue University. These tests were conducted at a subsurface test facility on the Canadian Forces Base (CFB), Borden, Ontario, Canada (Annable et al, 2005, and Klammler et al, 2006a); at various

dense nonaqueous phase liquid (DNAPL) sites at Hill Air Force Base (AFB) (OU-2), Utah (Brooks et al, 2006); Fort Lewis, Washington; Patrick AFB and Cape Canaveral, Florida. Finally, Purdue University recently led a demonstration study where PFM-measured water and perchlorate fluxes were measured by the Naval Surface Water Center (NSWC) at Indian Head, Maryland. (Lee et al, 2006).

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The flux meter is the only technology available that provides simultaneous direct measures of both water and contaminant fluxes. The prominent alternative technology is to quantify groundwater contaminant concentrations through multilevel samplers, then calculate contaminant fluxes using groundwater fluxes measured from BHD tests conducted at multiple depths.

The flux meter possess the advantage of providing a long-term monitoring solution that generates time integrated estimates of both groundwater and contaminant flux. Hence, transient fluctuations in contaminant concentrations and groundwater flows are directly integrated in PFM-measured fluxes and are not an issue of concern as they are with traditional instantaneous monitoring methods. Field measurements do not require training beyond that currently needed in collecting groundwater samples. However, unlike typical groundwater sampling protocols, wells used for flux measurements are not purged; thus, disposal of contaminated purge water is not an issue. Note that the duration of flux monitoring must be long enough that measurements are not significantly influenced by hydraulic perturbation resulting from installation. Finally, the flux meter offers an additional advantage of not requiring power; thus, it can be used in remote locations. Clearly, all other continuous monitoring technologies require power (such as a down-hole flow meter).

The primary limitation of the technology is that it could encourage the gathering of more samples at any single well because it is quite easy to acquire multiple samples with depth (such as over the vertical extent of the well). Proper design of the flux meter should include aligning the vertical length of the sorbent material to cover the screen length of the well, so that samples acquired are representative of the depth intervals within the screen. A second limitation is that the method quantifies water fluxes by releasing resident tracer into the environment. Obtaining regulatory approval for the release of resident tracers could be time consuming. Selecting nontoxic, benign tracers could minimize permitting issues.

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3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The performance objectives, a critical component of this demonstration, provided the basis for evaluating the performance and costs of the technology. Performance objectives were the primary performance criteria (see Sections 4.1 and 4.2) established for evaluating the PFM. Meeting these performance objectives was considered essential for successful technology demonstration and validation.

Table 2 lists the PFM performance objectives applied at all four field sites. Future field application of this technology was assumed contingent on rigorous statistical comparison of solute and groundwater flux data between the flux meter and conventional groundwater measuring devices. Thus, as part of these demonstrations, statistics were developed and comparisons were drawn between solute and water fluxes derived from the PFM and flux data generated through alternative field measurements.

Table 2. Performance Objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)
Qualitative	1. Ease of Use	Operator acceptance
	2. Acceptability of sample analysis	Environmental laboratory acceptance
	3. Regulatory acceptability of method	General acceptance
Quantitative	1. Sensitivity	+/- 15%
	2. Minimum detection	< 2 cm/day
	3. Accuracy	+/- 25%

3.2 SELECTING TEST SITE

Under ESTCP Project No. ER-0114, the PFM was demonstrated and validated at several locations including three sites within CFB in Ontario, Canada (Borden); at NASA's LC-34 in Cape Canaveral, Florida; at the Naval Base Construction Base in Port Hueneme, California; and at the Naval Surface Warfare Center at Indian Head, Maryland.

The CFB Borden site was selected because of an existing infrastructure that provided maximum likelihood of technology demonstration and validation under controlled conditions. Testing occurred at three locations within 100 m of each other. The sheet-pile isolated flow cell was used as a subsurface controlled-flow gate in one test. The controlled-release plume, located in an adjacent forest area was used in a plume characterization test. Finally, a plume interception well located at the end of the controlled-release plume was used in a third test.

NASA's LC-34 site was selected for testing the PFM in a biologically simulated environment. Pre-demonstration cores were conducted by NASA and GeoSyntec to select a site within a TCE source zone and within a controlled flow cell domain.

The Port Hueneme site was selected for testing the PFM in a shallow, unconfined, sandy aquifer contaminated with MTBE and in clusters of wells that differed in design (with and without filter packs) and completion techniques (drilled versus pushed).

The Indian Head site was selected for testing the PFM in an aquifer contaminated with perchlorate and contained a well-defined dissolved plume in a shallow, permeable, unconfined aquifer (see Section 3.3). This perchlorate site was among the few known to exist among Department of Defense (DoD) facilities on the Eastern Seaboard.

3.3 TEST SITE HISTORY/CHARACTERISTICS

The CFB Borden site is a unique research facility established by John Cherry and the University of Waterloo research group (Cherry et al, 1996). Site geology was composed of a surficial sand layer that is approximately 3.5 m thick and overlies a clayey aquitard. Aquifer conductivities range from 0.1-15 m/d. The first of the three demonstration/validation tests used an on-site test gate for subsurface flow in which groundwater flow could be controlled, MTBE concentrations could be monitored using MLSs, and both water and MTBE fluxes could be measured using PFMs installed in wells of different construction. The test gate was 25 m long and 2 m wide and opened on one end. The saturated thickness of the aquifer in the gate was about 1.77 m (this includes 35 cm of capillary fringe). Steady flow was established from four pumping wells located in the closed end.

The second and third field tests took place in the controlled release plume. Here, John Cherry released a DNAPL mixture consisting of 45% PCE, 45% TCE, and 10% chloroform by weight. This mixture was released on April 9, 1999, from a single release point located 1.8 m below ground surface and 0.9 m below the water table. The DNAPL source generated a dissolved plume approximately 80 m long. The Waterloo group characterized this plume with a dense network of MLSs. The MLS data were used in this demonstration to generate alternative estimates of contaminant flux and flux-average contaminant concentrations that were then compared to PFM measures.

NASA's LC-34 was constructed to support the Saturn I and IB missile launches. Launch operations involved the use of nitrogen, helium, liquid oxygen (LOX) and RP-1 fuel. During this time, Saturn rocket engines were cleaned while on the launch pad with solvents containing TCE. Engine parts were also cleaned with TCE on racks located in the shop situated on the western side of the Engineering Support Building.

The area utilized for flux testing was located underneath the Engineering Support Building and contained TCE as a nonaqueous phase liquid (NAPL). Site geology is composed of surficial sand and shell deposits that extend to a depth of 45 ft where clay is encountered. The Clay Unit (CU) is typically 2 ft thick but can be very thin, e.g., 0.5 ft. The surficial unit can be divided into three parts—the Upper Sand Unit (USU), the Middle Fine Grained Unit (MFGU), and the Lower Sand Unit (LSU). The aquifer exists within the MFGU, at a depth 22 to 30 ft below ground surface (bgs). The MFGU is a fine-grained sand layer with significant clay content. The top surface of the MFGU is irregular and the thickness of the unit varies significantly over short distances (from 1 ft to 17 ft). The sediments in the surficial aquifer are relatively permeable. Vertical permeabilities range from 10^{-3} to 10^{-2} cm/s. The hydraulic conductivity ranges from 1.44×10^{-2} to

$1.21x10^{-2}$ cm/s in the USU, from $8.28x10^{-2}$ to $5.43x10^{-2}$ cm/s in the MFGU, and $1.21x10^{-2}$ to $4.10x10^{-2}$ cm/s in the LSU. The difference between the three upper units and the CU is 4 to 6 orders of magnitude (CU: 10^{-7}-10^{-8} cm/s). Previous measurements of vertical hydraulic conductivity of the CU range from $1.5x10^{-7}$ to $4.5x10^{-8}$ cm/s with an average of $5.89x10^{-8}$ cm/s.

The Port Hueneme site was located downgradient from the Naval Exchange (NEX) Service Station. This service station served as a retail outlet for gasoline and automotive services for military personnel working at the base. Gasoline was the only type of contamination reported to have been released from this site. A total of 10,800 gal of leaded regular and premium unleaded gasoline (containing MTBE and 1,2-dichloroethane additives) was released to the subsurface in 1984 and 1985. A semi-perched aquifer became contaminated as a result of this release. The depth to groundwater in the perched aquifer from ground surface was about 8 to 9 ft. PFM testing was conducted in well cluster B, an area constructed for side-by-side testing of multiple wells constructed in clusters and with different completion methods. These well clusters permitted side-by-side comparisons of PFM-measured groundwater discharges and MTBE mass fluxes.

The Indian Head site was on the southeast side of Building 1419 (Hog Out Facility) of the Indian Head Division of the Naval Surface Warfare Center (IHDIV-NSWC), Indian Head, Maryland. This facility was used to clean out ("hog out") solid propellant containing ammonium perchlorate from various devices, including spent rockets and ejection seat motors. The hog out process and former waste handling/disposal methods resulted in a perchlorate plume in groundwater near Building 1419.

At the site, the top 2 to 4 ft of surficial deposits consisted of fill material including organic material, gravel, and silty sand. The underlying 11 to 13 ft consisted of mottled light to olive brown clayey to sandy silts. The clay and sand fraction of the silts varied horizontally and vertically. Fine-grained sand seams 1 to 2 inches in thickness were seen in many boring locations, but these seams were not continuous from boring to boring. At a depth of approximately 15 ft bgs, a 1 to 1.5-ft thick layer of sand and gravel was encountered. This layer was found to be continuous throughout the area near the test plot. The sand and gravel layer was underlain by a gray clay layer, which extended to a depth of at least 20 ft bgs (the maximum depth studied). Depth to groundwater ranged from approximately 6.5 ft to 10.25 ft bgs. The average hydraulic gradient was 0.023 ft/ft. Slug test results indicated an average hydraulic conductivity of approximately 0.012 ft/min within the aquifer. Based on these values, the estimated groundwater flux was 0.4 ft/day (~12 cm/day).

3.4 PHYSICAL SETUP AND OPERATION

The focus of this research effort was to demonstrate/validate the PFM using field experiments at four selected field sites. Each experiment was designed to provide independent estimates of both groundwater and contaminant fluxes that could be compared to fluxes measured by PFMs.

For the three field tests at Borden, either 3.2 or 5.1 cm fully screened polyvinylchloride (PVC) monitoring wells were used. For the first test in the controlled flow gate, two transects of three 5.2 cm fully screened wells were installed downgradient from yet another transect of three MLS wells. In one PFM transect, well screens were installed with 2.54 cm sand packs. The idea here

was to draw comparisons between water and contaminant fluxes measured in wells with and without sand packs and again compare PFM-measured contaminant fluxes to those estimated using MLS concentrations and the known groundwater flux in the gate.

In the second field test, flux monitoring was conducted in a controlled-release plume. A single transect of flux wells was installed immediately downgradient from MLS well transect No.13. Seventeen 3.2 or 5.1 cm shallow fully screened monitoring wells were installed, in which PFMs were later inserted. The wells were installed using standard techniques and without sand packs, which allowed the formation to collapse around the well screens. PFM-measured contaminant fluxes and flux-averaged contaminant concentrations were compared to fluxes and concentrations estimated from data derived from MLS well transect No.13.

For the third field test, a ring of eight 3.2 cm fully screened monitoring wells were placed evenly apart at a radial distance of 35 cm from an active plume interception well. The objective was to compare integrated PCE, TCE, and water fluxes obtained from the ring of PFMs to water and contaminant mass discharges measured at the head of the interception well.

At NASA LC-34, an experimental flow cell was used consisting of three injection and three extraction wells and five MLS wells within the cell. The flux monitoring was conducted in three wells installed upgradient of the central extraction well (EW)-2. All wells were screened over the interval 16 to 26 ft bgs. The MLS wells had five sampling locations distributed over this interval. Flux was directly measured using PFM. These fluxes were compared to those calculated using known groundwater fluxes and measured contaminant concentrations from MLS wells. In addition, by integrating PFM-measured fluxes over the flow cell cross section, comparisons were made to water and contaminant mass discharge rates measured at EW wells. There were four sampling events over the course of the bioremediation study. The first deployment took place during water recirculation after approximately 4 weeks of steady water flow. This provided a measured background flux prior to bioremediation. At this point and for all subsequent measurements, TCE and degradation by-products were quantified. The next two flux monitoring events occurred during ethanol injection performed to stimulate biological activity (Phase II), and the third event (Phase III) occurred after injection of microbes specifically identified as TCE degraders. The final phase occurred after several weeks with no additional treatment in the intervening time. The work at the LC-34 site was conducted over a 1-year period for a total of four phases of the bioremediation study.

At the Port Hueneme site, PFMs were deployed in selected wells in cell cluster B, which contained wells that differed in design (with and without filter packs) and completion techniques (drilled versus pushed). Four well clusters had been previously installed in cell B, where each cluster shared the same five well types (Kram et al, 2001). These wells clusters were located in close proximity to each other, allowing groundwater flow and MTBE flux to be compared. PFMs were deployed in these wells at the same time and for the same duration. Results were compared for both groundwater flow and MTBE flux. Clusters contained commonly installed well types, including a generic well design consisting of a 20-40 mesh sand pack surrounding 0.010-inch slotted schedule 40 PVC pipe, and often installed by direct-push wells consisting of 0.010-inch slotted schedule 40 PVC pipe with and without filter packs. PFMs were tested in all of these wells.

At the Indian Head site, PFMs were installed in several existing 2-inch monitoring wells. The site was divided into two zones: near-source zone and plume. Perchlorate fluxes were measured in wells representing a broad range of ambient concentrations. Water samples were taken in advance of PFM installation to ensure that meter performance was evaluated over a broad range of perchlorate fluxes. The plume zone was further subdivided into the mid-plume zone around monitoring well 4 (MW-4), and the toe of plume around MW-2 and -3. MW-1 was used to estimate local perchlorate flux in the near-source zone. All monitoring wells had 10-ft screens, and two 5-ft socks were installed in each well to cover the whole screened interval. The PFMs were deployed twice, once for a period of 3 weeks and the second for a period of 6.3 weeks. Before any well was used for flux measurements, it was developed (usually immediately after installation) and then left for approximately 1 week to equilibrate with the flow field before a PFM was inserted. Each PFM was constructed on site, then immediately inserted in a selected well.

At all sites, tracers used were in some cases volatile so the time between construction and insertion was kept to a minimum. The construction of each flux device involved packing the carbon sorbent (with tracers) with multiple impermeable dividers in a sock. Each PFM of 1.5- to 1.6-m length required about 30 minutes to construct and install. The PFMs remained in the field from 3 days to 7.3 weeks, depending on the experiment. In most cases, personnel left the site only to return at a later date for PFM retrieval. During retrieval, the PFM was removed from the well and segmented vertically for sorbent subsampling. Each 20 to 25 cm interval of sorbent was homogenized and subsampled for analysis. The process of extraction and subsampling required about 20 minutes per meter. Approximately 8 hours were required to sample 25 PFMs.

3.5 SAMPLING/MONITORING PROCEDURES

At the Borden site, PFM demonstration/validation experiments focused on a sampling density that was adequate to provide a reasonable comparison to the fluxes measured or estimated by other means. For characterizing the controlled release plume, horizontal spacing of PFMs and vertical sampling of PFM sorbent corresponded with the MLS network density. PFMs were spaced horizontally at 1 m intervals; the vertical resolution of sorbent sampling was 20 to 25 cm. Sampling within the controlled flow flume used 0.5-m spacing and 20-cm vertical resolution over the entire saturated zone. Two rows of wells were deployed. Extraction well flow rates were measured twice a day, and water samples were collected once a day during the PFM installation. For the experiment comparing PFM measured fluxes with those derived from the plume interception well, a vertical sampling resolution of 10 cm was used over the entire saturated zone. Twice daily the interception well flow rate was measured and water samples were gathered for subsequent TCE/PCE analyses.

At NASA's LC-34 site, flux meters were installed in three wells with 10-ft screen intervals. Subsamples were taken in intervals of 60 cm (or less) to correspond with the multilevel sampling network. During PFM deployment, samples were collected from the multilevel sampler network at the beginning and end of the PFM installation period. Also, extraction well samples were collected from the three extraction wells. Flow rates and water levels were monitored during PFM deployment to determine cumulative water flow.

At Port Heuneme and Indian Head test sites, PFM testing experiments used screened wells. Subsamples were taken in vertical intervals of approximately 30 cm to provide depth-resolved flux distributions. Groundwater samples were collected from wells prior to PFM installation. These samples were used to calculate perchlorate fluxes based on estimated groundwater fluxes from prior measures of hydraulic conductivity and current measures of hydraulic gradients.

Sample Collection. Two types of samples were collected at all sites: groundwater samples from wells and sorbent samples from PFMs. Sample handling procedures were as follows.

Water Samples. Wells were pumped or bailed prior to sampling. Groundwater samples were collected in 40-mL volatile organic analysis (VOA) vials, placed in coolers containing dry ice, and transported to Purdue University or UF. Sample analysis for alcohol tracers was less than a 14-day holding time.

Sorbent Samples. Sorbent samples were collected from the extracted PFMs. The 150 to 160-cm PFMs were segmented into 5 to 60-cm subsections and transferred to containers. Samples were thoroughly mixed and subsampled into 250-mL wide-mouth jars, placed in a cooler, and transported to Purdue University or UF. Sample analysis was completed within a 28-day holding time.

3.6 ANALYTICAL PROCEDURES

All samples were analyzed at laboratories at UF or Purdue University. Volatile organics, including alcohol tracers, were analyzed by direct liquid injection on gas chromatographs. Detection limits were approximately 1 mg/L. Headspace analysis was used in the event that low concentrations were encountered. Detection limits for headspace analysis was approximately 50 µg/L. Perchlorate was analyzed with ion chromatography according to Environmental Protection Agency (EPA) Method 314.1. The detection limit for perchlorate was 1µg/L

Data quality was maintained and checked throughout the project. Details on approaches implemented to maintain data quality were provided in the quality assurance/quality control (QA/QC) plan in Appendix C of UF and Purdue University, 2006a and the protocol report (UF and Purdue University, 2006b). Initial and continuing calibration procedures for analytical instrumentation, quality control checks, and corrective actions were conducted to maintain reproducible experiments. These procedures were fully described in the QA/QC Plan in Appendix C of UF and Purdue University, 2006a. Simple regression analysis was used to assess the quality of data collected at single wells. More sophisticated spatial analysis was performed with data collected to assess the spatial mean and variance of contaminant/water fluxes evaluated over transects or within a plume.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

The quality of groundwater and contaminant flux estimates based on PFM installations at the four sites was compared to alternative measures of these quantities. Future field application of this technology would likely depend on rigorous statistical comparison of solute and groundwater flux results between the PFM and conventional methods of measuring or calculating water and contaminant fluxes; therefore, statistics were developed to characterize the "expected" flux and the flux "estimation variance." The installation and interpretation of the flux meter data was generally the same in all field experiments. For example, in the controlled release plume experiment at the Borden site, water fluxes were compared with estimates based on recent BHD tests performed immediately prior to or immediately following flux meter measurements whereas contaminant fluxes and flux-averaged concentrations were compared with estimates based on MLS data collected during the flux meter deployment period.

Several metrics were identified to assess PFM performance in the field. Table 3 indicates criteria applied for the Borden site; however, analogous criteria (not shown) were applied to the remaining three sites. Because the typical range for contaminant fluxes in the field could be five orders of magnitude (for water fluxes the range was two orders of magnitude), achieving the identified performance metrics would greatly reduce the uncertainty of contaminant flux assessments. Clearly, a significant uncertainty reduction would be valuable to regulators and site managers. For example, for the gate and plume characterization experiments conducted at Borden, a successful comparison resulted if groundwater and contaminant fluxes were estimated within 15-20 and 25-35%, respectively. The higher uncertainty associated with contaminant flux measurements was allowed due to the nature of the MLS-based estimates. Again, recalling the Borden extraction well experiments as an example, water and contaminant flux were known with more certainty. Acceptable comparisons with the flux meter results were set at 15 and 25% for groundwater and contaminant flux, respectively.

4.2 PERFORMANCE CRITERIA

Table 4 describes the performance criteria generally used to evaluate the performance of the flux meter at all sites. Both qualitative and quantitative performance criteria were used and were categorized as either primary (which are the project's performance objectives) or secondary criteria.

Table 3. Expected Performance and Performance Confirmation Methods at Borden.

Performance Criteria	Expected Performance Metric	Performance Confirmation Method*
PRIMARY CRITERIA (Performance Objectives) (Qualitative)		
Ease of use	Minimal training required	Experience from demonstration operations
PRIMARY CRITERIA (Performance Objectives) (Quantitative)		
Groundwater flux estimates within the plume	Estimate within 20%	Comparison with BHD estimates
Contaminant flux estimates within the plume	Estimate within 35%	Comparison with MLS-based estimates
Groundwater flux estimates within the gate	Estimate within 15%	Comparison with extracted volume rate
Contaminant flux estimates within the gate	Estimate within 25%	Comparison with MLS-based estimates
Induce groundwater flux estimates within the capture well	Estimate within 15%	Comparison with extracted volume rates
Contaminant flux estimates within the capture well	Estimate within 25%	Comparison with extracted mass rates
Process waste generated	8 gallons	Observation
SECONDARY PERFORMANCE CRITERIA (Qualitative)		
Reliability (CU)	No failures	Recordkeeping
Safety (all) - Hazards - Protective clothing	Contaminated sorbents Level D	Experience from demonstration operation
Versatility (all) Short-/long-term averaging	Consistent results	Experience from demonstration operation

* Refer to Appendix B or Appendix D of the Technical Report for further details.

Table 4. Performance Criteria.

Performance Criteria	Description	Primary or Secondary
Groundwater flow estimates	Compare groundwater flow based on the PFM to other measures	Primary
Contaminant flux estimates	Compare contaminant flux based on the PFM to other measures	Primary
Process waste (all)	Identify any process waste quantities produced using the PFM; compare this with other approaches	Secondary
Factors affecting technology performance	Identify limitations of the PFM in terms of site conditions (groundwater velocity, media properties, temperature, salinity)	Primary
Reliability	Robustness of the approach—how much error was introduced by installation and extraction	Secondary
Ease of use	Evaluate difficulties in installation and extraction; characterize the level of expertise needed. Can monitoring be reduced?	Primary
Versatility	Potential for difficult environments	Secondary
Safety	Identify potential for hazards beyond that of normal water sampling	Secondary

4.3 DATA ASSESSMENT

For the Borden site, Table 5 lists criteria used to evaluate PFM performance and data showing expected and actual performance. Criteria are both qualitative and quantitative and are categorized as being primary (consistent with project's performance objectives) or secondary.

Table 5. Expected and Actual PFM Performance at the Borden Site.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Ease of use	Minimal training required	Experience from demonstration operations	Approximately 15-20 minutes required to construct and install each PFM in a well; another 15 minutes needed to retrieve and sample. Each test installation required 2-8 hours on site followed by 2-4 hours of sampling.
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Groundwater flux estimates within the plume	Estimate within 20%	Comparison with borehole dilution estimates	Average absolute difference of 9.4% and standard deviations of 5.7%
Contaminant flux estimates within the plume	Estimate within 35%	Comparison between MLS-based flux-averaged concentrations and PFM flux-averaged concentration	Average differences in flux-average concentrations were 13.2% and 13.0% for TCE and PCE, respectively.
Groundwater flux estimates within the gate	Estimate within 15%	Comparison with extracted volume rate	For screened wells with filter pack, the maximum error was 7.7% at the well level; for the gate cross section, the error in the integrated estimate was 0.7%. For screened wells the maximum error was -11.2% at the well level; for the gate cross section, the error in the integrated estimate was -2.3%.
Contaminant flux estimates within the gate	Estimate within 25%	Comparison with MLS and well-based estimates of MTBE flux	Minimum and maximum differences at a single well were 4.06 and 93.16% respectively. For the gate cross section, the difference between integrated fluxes ranged from 1.18 to 16.63%.
Induce groundwater flux estimates within the capture well	Estimate within 15%	Comparison with extracted volume rates	Integrated measures within 2% of extraction flow rate
Contaminant flux estimates within the capture well	Estimate within 25%	Comparison with extracted mass rates	Integrated TCE flux within 9% and PCE 32% of extraction well mass flow rates
Process waste generated	25 gal	Observation	15 gal
SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	No failures	Recordkeeping	100% reliable (no failures)
Safety (all) - Hazards - Protective clothing	Contaminated sorbents Level D	Experience from demonstration operation	Level of protection similar to groundwater sampling methods; minimal vapor exposure with samples on activated carbon
Versatility (all) - Short-/long-term averaging - Other applications	Yes Fractured rock, radionuclides	Experience from demonstration operation	One suite of PFM deployed for 51 days. All devices were in shallow 2-m wells.

Table 6 lists criteria used to evaluate PFM performance and data for NASA's LC-34 site showing expected and actual performance. Criteria are both qualitative and quantitative and are categorized as being primary (consistent with the project's performance objectives) or secondary.

Table 6. Expected and Actual PFM Performance at NASA's LC-34 Site.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Ease of use	Minimal training required	Experience from demonstration operations	Approximately 20-min installation per 5-ft unit (sampling time approximately 15 min)
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Water flux estimates	Estimated within 20%	Comparison to induced flow rate	Percent differences for preremediation ranged from 6 to 19%. Post remediation ranged from 4 to 30% after biostimulation differences were up to 67%.
Contaminant flux estimates during background flood	Estimate within 25%	Comparison with MLS-based estimates	Integral average flux plane differences between flux meters and MLS ranged from 0 to 23%. Point-to-point TCE flux comparison differences ranged from 7 to 113%. Average difference for local flux was 41%.
Contaminant fluxes during the bioremediation phase	Estimate within 45%	Comparison with extracted volume rates	Integral average flux plane differences between flux meters and MLS ranged from 17 to 186%. Point-to-point TCE flux comparison differences ranged from 0 to 200%. Average difference for local flux was 125%. Comparison between integrated flux from well and PFM flux plane varied from 32 to 190%.
Process waste generated	25 gal	Observation	Approximately 4 gal of waste activated carbon generated for each deployment; disposed of by NASA
SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	No failures	Recordkeeping	100% reliable (no failures)
Safety (all) - Hazards - Protective clothing	Contaminated sorbents Level D	Experience from demonstration operation	Level of protection similar to groundwater sampling methods; minimal vapor exposure with samples on activated carbon
Versatility (all) - Short-/long-term averaging - Other applications	Yes Fractured rock, radionuceides	Experience from demonstration operation	Problems were encountered with material integrity. More durable fabrics may be warranted. Most deployments were for 1-week durations but in a highly reactive environment. Simultaneous measures of multiple contaminants were made.

Table 7 lists criteria used to evaluate PFM performance and data at the Port Heuneme site showing expected and actual performance. Criteria are both qualitative and quantitative and are categorized as being primary (consistent with project's performance objectives) or secondary.

Table 7. Expected and Actual PFM Performance at the Port Hueneme Site.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method*	Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Ease of use	Minimal training required	Experience from demonstration operations	Approximately 15-20 min required to construct and install each PFM in a well; another 15 min needed to retrieve and sample
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Comparison of water flux between wells	Estimate within 25%	Direct comparison	Usually within a factor of 2 for all pushed wells
Comparison of water flux to slug test results and BHD	Estimate within 25%	Direct comparison to fluxes based on the gradient and slug test conductivity or BHD	Usually within a factor of 2 to 3
Comparison of MTBE flux between wells	Estimate within 25%	Direct comparison	Pushed well measured significantly lower fluxes than 2-in wells
Comparison of MTBE flux averaged concentration between wells	Estimate within 25%	Direct comparison	No significant differences between wells
Process waste generated	25 gal	Observation	15.3 gal
SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	No failures	Recordkeeping	1 failure out of 43 events (2%)
Safety (all) - Hazards - Protective clothing	Contaminated sorbents Level D	Experience from demonstration operation	Level of protection similar to groundwater sampling methods; minimal vapor exposure with samples on activated carbon
Versatility (all) - Short-/long-term averaging - Other applications	Yes Fractured rock, radionuclides	Experience from demonstration operation	Most deployments were for short durations (1-2 weeks)

Table 8 lists criteria used to evaluate PFM performance and data at the Indian Head site showing expected and actual performance. Criteria are both qualitative and quantitative and are categorized as being primary (consistent with project's performance objectives) or secondary.

Table 8. Expected and Actual Performance at the Indian Head Site.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Ease of use	Minimal training required	Experience from demonstration operations	Level of training similar to water sampling
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Water flux estimates	Estimate within 25%	Compare PFM measured water fluxes between wells and sampling events	Between events, measures at a given well agreed within 21 to 35%.
Contaminant flux estimates	Estimate within 25%	Compare PFM measured contaminant fluxes between wells and sampling events	Between events, measures at MW1 and MW4 agreed within 22 and 0%, and 193% for MW3.
Vertical variations in water and contaminant flux between wells	Estimate within 40% (for water fluxes alone)	Compare flux statistics between wells	Between wells, water flux variances were within 40% of each other. Contaminant flux variances varied as expected in proportion to the mean flux, indicating significant site heterogeneity.
Process waste generated	25 gal	Observation	3.2 gal
SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	No failures	Record keeping	100% (no failures)
Safety (all) - Hazards - Protective clothing	Contaminated sorbents Level D	Experience from demonstration operation	On the same order as water sampling
Versatility (all) - Short-/long-term averaging - Other applications	Yes Fractured rock, radionuclides	Experience from demonstration operation	Consistent perchlorate fluxes were quantified over short- (3-week) and long-term (6-week) deployments

4.4 TECHNOLOGY COMPARISON

Transition of any technology from the innovative testing phase to a point where it receives regulatory and end-user acceptance requires validation against conventional techniques. Groundwater fluxes measured by PFMs were compared with (1) BHD test results or (2) flux estimates made using slug test conductivity values and site hydraulic gradients, or (3) known groundwater discharges within controlled flow systems. PFM-measured contaminant fluxes were compared to fluxes estimated from site data on groundwater concentrations (from wells or MLSs) and values of groundwater specific discharge (from controlled flow systems or estimated from measured aquifer conductivities and hydraulic gradients).

For the Borden field tests, the analysis of PFM measurements of groundwater flux were compared to known fluxes and to measurements acquired by BHD test. Where the plume characterization test was conducted, previous studies reported groundwater fluxes ranging from 5 to 8 cm/d. The average PFM measured fluxes was 6.62 cm/d with an estimated coefficient of variation of 0.33. Measured water fluxes were based on PFMs deployed for 7.3 weeks with no evidence of significant resident tracer degradation.

A BHD was also conducted in one of the PFM wells. A strong linear correlation was obtained between PFM-measured fluxes and BHD test results (see Figure 4). The average absolute relative difference in measurements was 9.4%. Furthermore, these results were well within the performance criterion of less than 20% difference specified in Table 5.

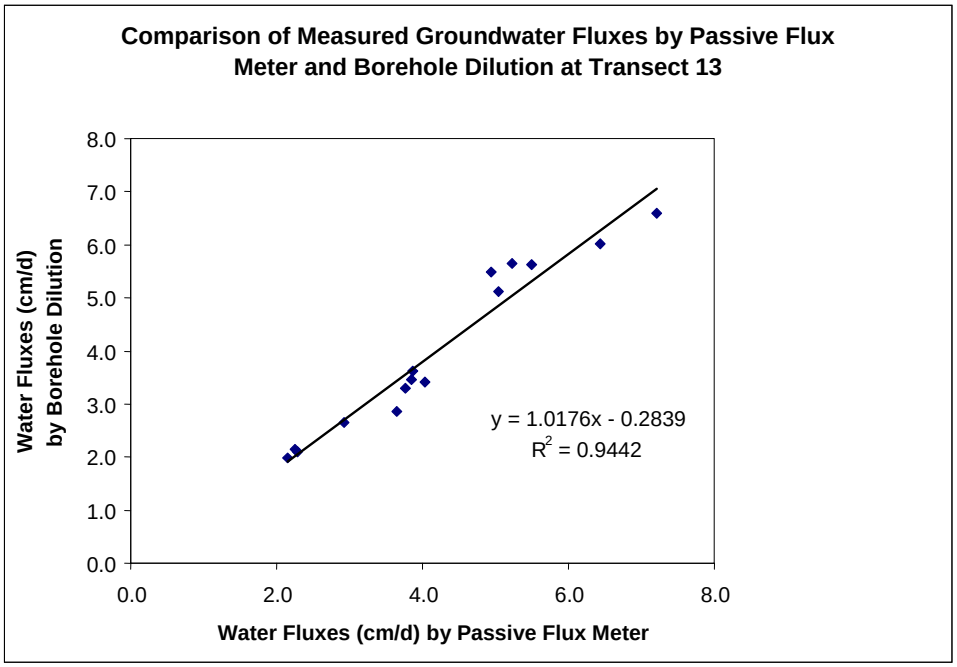

Figure 4. Comparison of Measured Groundwater Fluxes Inside a Screen Well by PFM and BHD over the 13th Sampling Transect (CFB, Borden), April 2002.

It was expected that that the PFM would measure water fluxes within 15% of the induced flow rate in the gate. Actual performance was better. Maximum absolute differences between the measured fluxes at any given well and the induced flux in the gate (8.23±0.66 cm/d) were less than 11.2%. The maximum coefficient of variation for measured water fluxes was 0.6 in wells constructed with a filter pack and less than 1.3 for simple screened wells. The integrated water fluxes obtained from averaging results of three PFMs installed in the same type of well were even closer to the induced flow rate: -2.3% for screened wells and 0.7% for wells constructed with filter packs. For the last field test involving the plume interception well, an acceptable comparison with the flux meter results was specified at 15%. According to Table 5, water fluxes were estimated within 2% of the extraction flow rate.

Concerning PFM-measured contaminant fluxes, it was proposed for the gate study that PFM-measured MTBE fluxes must be compared to fluxes calculated from the induced specific discharge in the gate and in the average MTBE concentration generated from measurements taken from wells and MLS in the gate. It was anticipated that PFMs could measure contaminant fluxes within 25% of the calculated flux, based on MLS data and well concentrations (see Table 5). Actual PFM performance was better. Total MTBE fluxes, obtained from spatially integrating PFM measurements from FA wells (those without sand packs) compared within 16.63% of

integrated calculations from MLS's. For the FB wells containing sand packs, total MTBE fluxes were within 1.18% of integrated calculations using depth-average MTBE concentrations from six flux wells and three MLS wells.

In the contaminant plume, a higher level of uncertainty associated with contaminant flux measurements was anticipated due to the nature of MLS-based estimates. Field data revealed that MLS contaminant concentrations were comparable to the flux-averaged TCE and PCE concentrations derived from PFM measurements in the plume. Coefficients of variation for MLS and PFM concentration data were both greater than 1.0, which would indicate significant variability. Relative concentration differences between MLS and PFM data were 3.2% for TCE and 13% for PCE when averaged over the 13th MLS-sampling transect. These differences are well within the performance criterion of 35% indicated in Table 5. However, concentration differences in excess of this criterion were recorded between individual wells.

For the third field test, a 25% error was considered acceptable between the measured contaminant mass flows at the well head and the integrated PFM measurements. TCE and PCE were respectively measured by PFMs to within 9 and 32% of mass flow rates at the well head.

At NASA's LC-34 site, PFM-measured water fluxes were expected to be within 20% of the controlled flow rate through the test cell. Percent differences prior to bioaugmentation ranged from 6 to 19%. After KB-1 bioaugmentation, the accuracy of water flux estimates decreased but differences remained within 67%. Following site remediation, percent differences ranged from 4 to 30%. Site bioactivity appeared to degrade the resident tracer ethanol; as a result, this tracer was no longer suitable for estimating water flux. The less degradable and more highly sorbed alcohols appeared to give more reliable assessments of water flux.

PFM-measured contaminant fluxes were expected to be within 25% of MLS-based estimates prior to remediation and within 45% during bioremediation. Prior to remediation, integral average flux plane differences between flux meters and MLS ranged from 0 to 23%. Point-to-point TCE flux comparisons differences ranged from 7 to 113%. The average difference for local flux was 41%.

During biostimulation and after bioaugmentation, contaminant flux estimates varied significantly. Differences in flux plane averages given by PFMs versus MLSs ranged from 17 to 186%. Point-to-point TCE flux differences ranged from 0 to 200%. The average difference for local flux was 125%. The difference between integrated fluxes taken at the extracted well and over the PFM flux plane varied from 32 to 190%. PFM measurements indicated significantly higher vinyl chloride and ethene fluxes than those derived from extraction well data and MLS samples. It could be that the PFM sorbent (activated carbon sorbent) functioned as an effective trap for highly volatile and gaseous compounds. It might also be the case that the sorbed TCE and DCE degraded to vinyl chloride and ethene while sorbed on the activated carbon.

At Port Heuneme, groundwater fluxes measured by PFM (Table 6) were compared with (1) BHD test results and (2) flux estimates made using pneumatic slug test conductivity values and an average hydraulic gradient of 0.002. It was expected that both methods would compare within 25%; however, for most cases, the fluxes varied within a factor of 2 to 3. Groundwater fluxes

estimated by aquifer conductivities and hydraulic gradients compared well to PFM measurements in ¾-inch wells and less so for the 2-inch wells. The drilling process used to install the 2-inch well would loosen soil in the vicinity of the well. It was hypothesized that PFMs could be more sensitive to local conductivity changes than the pneumatic slug test. Between wells, PFM-measured fluxes were within a factor of 2 of each other, which was reasonable given site heterogeneity. This suggested that the performance criterion of 25%, established prior to the demonstration, did not adequately reflect the impacts of site heterogeneity and that the criterion should have been amended to a larger and much more reasonable of range of 2-5.

A comparison of contaminant flux measurements between wells was also made. Pushed wells measured significantly lower fluxes than 2-in wells. Because natural aquifer heterogeneity induced larger than expected flow variations between well (see above), it came as no surprise that contaminant fluxes would not compare between wells (regardless of well type). Again, the performance criterion specified in advance should have been relaxed (increased) to reflect ill-considered site heterogeneity. Finally, comparison of flux-average concentrations showed no significant difference between well types. For this performance criterion, the allowance was a 25% deviation between wells.

At the Indian Head site, the primary goal of the study was to demonstrate the applicability of a new PFM-sorbent surface modified silver impregnated granular activated carbon (SM-SI-GAC) for field-scale measurement of groundwater and perchlorate fluxes. PFM measured water fluxes compared well with fluxes calculated from BHD tests. Whereas measured contaminant and water fluxes both showed good reproducibility between two deployments. The criterion for allowable water flux differences between events was 25%. The actual performance at any given well agreed within 21 to 35%. A similar allowance between events was specified for measured perchlorate fluxes. The actual differences were 22, 193, and 0% for perchlorate fluxes at MW1, MW3, and MW4, respectively. Field tests demonstrated that SM-SI-GAC can be used as a PFM sorbent at sites with perchlorate concentrations ranging from 7 to 64 mg/L. Results also indicated that the SM-SI-GAC was stable physically, chemically, and biologically for a maximum of 44 days and that the alcohol tracers and captured perchlorate on it were not biodegradable.

At all test sites, only small volumes of waste carbon were produced. Furthermore, between the four test sites only one flux meter failed. This represented 0.5% failure rate. For the most part, PFMs were not tested in difficult environments such fractured media (one of the versatility criteria); the current design would need to be modified for rock wells. PFMs were tested over a range of deployment periods ranging from 1 day to 51 days (another versatility criterion). Significant tracer degradation was encountered only at NASA's LC-34 site and only after PFMs were deployed in an environment where there were ongoing efforts to stimulate contaminant biodegradation.

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5.0 COST ASSESSMENT

5.1 COST REPORTING

The passive flux meter is the only technology that provides simultaneous measures of both water and contaminant fluxes. The most prominent alternative technology is to measure groundwater contaminant concentrations through MLSs, then calculate contaminant fluxes using groundwater fluxes estimated from BHD tests. This combined BHD/MLS method is the only alternative that provides depth varying estimates of both water and contaminant fluxes that are comparable to PFM measurements.

To evaluate costs of using PFMs and the BHD/MLS method for site characterization, we followed the guidelines of the EPA document "Innovation in Site Characterization: Interim Guide to Preparing Case Studies" (EPA-542-B-98-009). We reported costs associated with the passive flux meter and the alternative BHD/MLS method. Reported fixed costs included general categories of capital costs needed for PFM deployment in regard to planning and preparation. In addition, we reported operational and variable costs including costs associated with per diem, labor, consumables, training, mobilization/demobilization, residual waste handling, sampling, and analysis. Finally, costs were expressed in totals per linear foot and, where appropriate, per sample. Many of the costs associated with the alternative technology were the same as those identified for the passive flux meter and were included in cost comparisons. The BHD/MLS method has some capital and training expenses associated with purchasing and using equipment to perform BHD tests and with acquiring equipment to collect multilevel samples. Both PFMs and the BHD/MLS method required fully screened wells so the cost of well installation was the same and not considered in this analysis. Finally, the additional cost of installing MLSs was not considered.

5.2 COST ANALYSIS

The major categories of costs that have been tracked are provided in Tables 9 and 10 for the two technologies of characterizing subsurface water and contaminant fluxes. To create these tables, we assume PFMs are deployed in 10 wells each having a screen interval of 10 ft. This represents 100 linear ft of well screen. PFMs are constructed in 5-ft long units; therefore, 20 PFMs are deployed. The vertical sampling interval for the PFMs is assumed to be 1 ft; thus, a total of 100 data points of both Darcy and contaminant flux results are generated. Table 10 provides cost estimates for the alternative technology, BHD/MLS. Here again we assume a network of 10 wells in which multiple BHD tests are performed to measure Darcy fluxes at 10 depths over each well screen. In addition, at each well location MLSs are used to gather groundwater samples at the same 10 depths for subsequent water quality analyses. Thus, from 10 wells the BHD/MLS method produces a total of 100 flux measurements by BHD and 100 aqueous contaminant concentrations from MLSs.

Table 9. Cost-Tracking for PFM Deployment. (Costs considered here are for site characterization assuming 10 wells are sampled with 10 ft of screen in each well.)

COST CATEGORY	Subcategory (10 wells – 100 linear ft)	Costs ($)
FIXED COSTS		
CAPITAL COSTS	Operator Training—for passive flux meter installation and sampling. Cost of $2,500 per person. Amortize over 10 deployments.	$500
	Planning/preparation (assume 8 hours, $80/hr) Organizing supplies, site access, deployment duration, sorbent/tracers selection and approval	$640
	Equipment: Sorbent preparation mixing equipment and PFM packing equipment ($10,000 capital) amortize over 10 major deployments	$1,000
	Environmental safety training ($1,000/yr/person). Amortize over 10 deployments for two people	$200
		Subtotal $2,340
VARIABLE COSTS		
OPERATING COSTS	Operator labor—two people required to construct and install passive flux meters and to collect, prepare, and ship samples. One day for deployment and a second day for retrieval. (8hr/day X 2 people X 2 days X $80/hr)	$2,560*
	Mobilization/demobilization—assumes two trips to and from the site, each requiring 0.5 days of travel plus travel costs for two people. $80/hour labor, air fare, travel costs up to ~$800 per person.(4 trips X 4hrs/trip X 2 people X $80/hr +4 X ~$800)	$5,760*
	Hotel for 2 people for 2 nights during PFM deployment and 2 nights during PFM retrieval assuming $150/night per diem. (4 nights X 2 people X $150/night)	$1,200
	Raw materials—sorbent and resident tracers ($166.70/well)	$1,667
	Consumables, supplies—sorbent, socks, ancillary components of the PFM, and sample vials ($183.33/well)	$1,833
	Residual waste handling—consumed sorbent and socks ($333.33/well)	$3,333
	Sampling and analysis for contaminants and resident tracers retained on passive flux meter sorbent ($100/sample or $1,000/well)	$10,000*
		Subtotal $26,353
OTHER COSTS	Data analysis—6 hours required ($160/well)	$1,600
		Subtotal $30,293
TOTAL TECHNOLOGY COST		$30,293
Unit cost per linear foot (ft)		$303/ft

* Mobilization/demobilization, labor, and analytical costs can vary up to 50% as principal cost drivers

Table 10. Cost-Tracking for BHD/MLS Deployment. (Costs considered here are for site characterization assuming 10 MLS with 1-ft vertical sampling interval.)

COST CATEGORY	Sub Category (10 MLS – 100 samples)	Costs ($)
FIXED COSTS		
CAPITAL COSTS	Operator Training for BHD ($5,000). Amortize over 10 sampling events	$500
	Planning/Preparation (assume 8 hours, $80/hr)—organizing supplies, site access, deployment duration, sorbent/tracers selection, and approval	$640
	Equipment—borehole dilution, MLS sampling equipment, and PFM packing equipment ($5,000). Amortize over 10 sampling events.	$500
	Environmental safety training ($1,000/yr/person) Amortize over 10 sampling events.	$200
		Subtotal $1,840
VARIABLE COSTS		
OPERATING COSTS	Operator labor—two people are required to sample the MLS network 15 min per sample per person (100 samples X 1/4 hr X $80/hr) or ($200/well)	$2,000*
	Mobilization/demobilization—assume 1 trip to site each 0.5 days of travel plus travel costs for two people. $80/hour labor, air fare, travel costs up to ~$800 per person. (2 trips X 4 hrs X 2 people X $80 +2 X ~$800)	$2,880*
	Hotel for 2 people for 16 nights for BHD tests assuming $150/night per diem. Total costs = (number of nights in a hotel X $150/night). Number of nights in a hotel = (2+number of wells X 1.4 days of BHD/well) X 2 people. For 10 wells, this is 16 nights. Thus, (16 nights X 2 people X $150/night)	$4,800
	Conduct BHD tests at 100 locations. Each test requires approximately 2 hours. (100 locations X 2 hrs X $80/hr or $1,600/well)	$16,000
	Consumables, supplies—sample vials, gloves, tracers ($66.70/well)	$667
	Residual Waste Handling Purge water for MLS sampling ($333/well)	$3,333
	Sampling and analysis for contaminants in water samples ($100/sample)	$10,000*
		Subtotal $39,680
OTHER COSTS	Data analysis. ($160/well)	$1,600
		Subtotal $43,120
TOTAL TECHNOLOGY COST		$43,120
Unit cost per linear foot (ft)		~$430/ft

* Mobilization/demobilization, labor, and analytical costs can vary up to 50% as principal cost drivers.

Cost impacts can be determined by varying the principal cost drivers of Tables 9 and 10 which include mobilization, demobilization, labor, and analytical costs. A 50% increase or decrease in each of these estimated drivers would alter the PFM total costs by ~33%. Similarly, a 50% increase or decrease in each of these estimated drivers for the BHD/MLS costs would alter the total cost by ~20%. Therefore, the unit cost per linear foot for the PFM method could range from $202 to $404; the unit cost per linear foot for the BHD/MLS method could range from $344 to $516. Because both PFMs and the BHD/MLS method involve short-term (less than 1 year) field operations, costs have not been discounted.

5.3 COST COMPARISON

Cost estimates per linear foot for PFM deployments and BHD/MLS measurements indicate that the PFM method results in lower unit costs depending on cost variability and the number of wells monitored. Both approaches exhibit similar costs in terms of materials and analytical costs, costs that are scalable to larger and smaller deployments. Figure 5 shows costs per linear foot for PFMs and the BHD/MLS method as a function of number of wells monitored. For sites involving 5 or more wells, PFMs are less expensive. When monitoring involves as few as 3 to 4 wells, costs are comparable; however, contaminant flux values derived from the BHD/MLS method represent short-term evaluations and are not likely meet DoD's long-term monitoring needs. Therefore, in the absence of continuous monitoring, it may be more cost effective and in the best interests of stakeholders to deploy systems designed to gather cumulative measures of water flow and contaminant mass flow. Cumulative monitoring devices generate the same information derived from integrating continuous data. These systems should produce robust flux estimates that reflect long-term transport conditions and are less sensitive to day-to-day fluctuation in flow and contaminant concentration.

In general, the BHD/MLS method requires more time on site to collect samples from MLS and to conduct borehole dilutions than to deploy, recover, and sample PFMs. As a consequence, it may be impractical to conduct the BHD/MLS method when more than 7-10 wells are involved. Some cost savings may be realized by automating the BHD method such that one operator can conduct multiple tests simultaneously. Also, the estimation of 2 hours per BHD test may be appropriate for sites with average or high groundwater velocities but may be too small for lower velocity sites. Obviously, site specific conditions can lead to changes in the cost estimates.

To evaluate potential life-cycle costs of long-term monitoring, an analysis was performed to compare costs of quarterly sampling for projects lasting 5 to 25 years (see Table 11). Costs shown are per linear foot and expressed in present value assuming a constant 2.0% annual inflation rate and a 5% annual interest rate. As noted above, both methods generate the same number of samples and similar costs in materials/equipment (no large capital investments). Thus, calculated life-cycle costs were predicated on the same assumptions presented in Tables 9 and 10 concerning number of wells, number of samples, and current costs for PFMs and the BHD/MLS method.

Current methods of quarterly monitoring rely on instantaneous measures of concentration alone (i.e, no flux measurements). This quarterly sampling can be quite expensive for long-term monitoring. Because PFMs generate cumulative flux measures over extended deployment periods, it is conceivable that an annual 1-month PFM measurement of water and contaminant

fluxes could be substituted for quarterly concentration monitoring. The fourth column of Table 11 shows that considerable cost savings could be achieved with annual PFM deployments when compared to the BHD/MLS method.

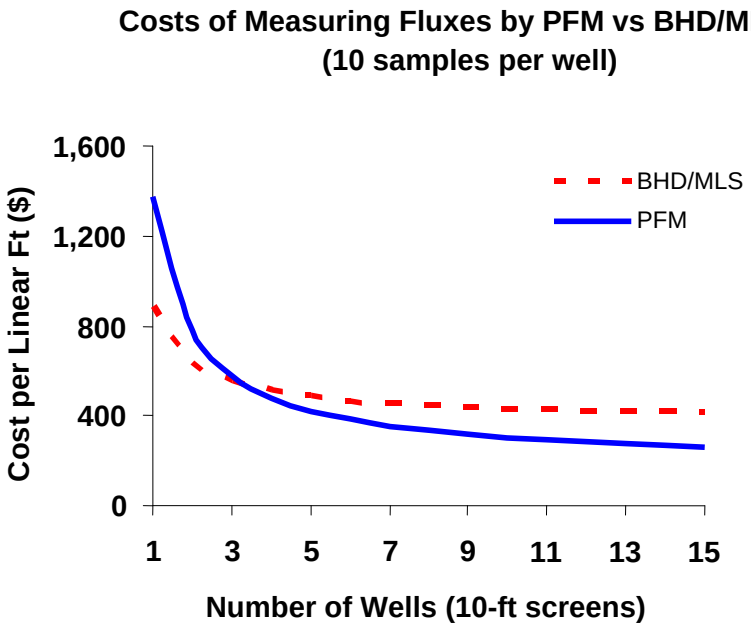

Figure 5. Cost of Measuring Water and Contaminant Fluxes by PFMs and the BHD/MLS Method as a Function of the Number of Wells Monitored.

Table 11. Long-Term Monitoring Costs for Various Project Durations Using PFMs Versus the BHD/MLS Method at a Site with 10 Wells and 10 Samples per Well.

Project Life-Cycle Costs* (10 wells and 10 samples per well)			
Project Duration (years)	**BHD/MLS Costs Quarterly Sampling ($k/ft)**	**PFM Costs Quarterly Sampling ($k/ft)**	**PFM Costs Annual Sampling ($k/ft)**
5	8.1	5.8	1.4
10	15.2	10.7	2.7
15	21.2	15.0	3.7
20	26.5	18.7	4.7
25	31.1	21.9	5.5

* Costs expressed in present value assuming a constant 2.0% annual inflation rate and a 5% annual interest rate

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6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

For sites involving five or more wells, PFMs are less expensive than the most prominent alternative technology, which implies measuring groundwater contaminant concentrations through MLS, then calculating contaminant fluxes using groundwater fluxes estimated from BHD tests (the BHD/MLS method). Many costs associated with the alternative technology are the same as those identified for the PFM, and the cost for operating MLS systems is relatively well known. When monitoring involves as few as three to four wells, costs are comparable; however, contaminant flux values derived from the BHD/MLS method represent short-term evaluations and are not likely meet DoD's long-term monitoring needs.

Site-specific conditions can dramatically affect the cost of performing PFM assessment relative to conventional BHD/MLS technology. For example, if soils at a site are relatively heterogeneous, then the number of wells required to provide adequate flux assessments increases. In this regard, the cost per linear foot decreases faster for PFMs. The BHD/MLS method always demands significantly more time on site than required to deploy, recover, and sample PFMs. Thus, it may be impractical to conduct the BHD/MLS method when more than 7-10 wells are involved.

It is believed that the operational costs of PFM technology will decrease as it is implemented at additional sites. The operation of the systems will become more predictable, and labor costs should decrease as a result. Because PFMs generate cumulative flux measures over extended deployment periods, it is conceivable an annual one-month PFM measurement of water and contaminant fluxes could be substituted for the current quarterly program. The resultant 75% reduction in monitoring could generate considerable cost savings to DoD and generate the type of data pertinent to quantifying off-site risks.

6.2 PERFORMANCE OBSERVATIONS

Overall, the performance criteria set in the Demonstration Plan were successfully achieved in all four field demonstrations. The gate experiment provided the best conditions for validating the PFM. It was expected that that the PFM would measure water fluxes within 15% of the induced flow rate in the gate. Observed maximum absolute differences between the measured fluxes at any given well and the induced flux in the gate (8.23±0.66 cm/d) were less than 11.2%. Furthermore, integrated measures of water flux in the gate were even closer to the induced flow rate: -2.3% for screened wells and 0.7% for wells constructed with filter packs.

To evaluate the PFM as a device for measuring contaminant fluxes, it was again the case that the gate experiment provided the best testing conditions. PFM-measured MTBE fluxes were compared to fluxes calculated from the induced specific discharge in the gate and an average MTBE concentration estimated from measurements taken from wells and MLSs in the gate. It was expected PFMs would measure contaminant fluxes within 25% of calculated fluxes from MLS data and well concentrations. Actual PFM performance was better. Total MTBE fluxes, obtained from spatially integrating PFM measurements from FA wells (those without sand packs) compared within 16.63% of integrated calculations from MLSs. For the FB wells

containing sand packs, total MTBE fluxes were within 1.18% of integrated calculations using depth-average MTBE concentrations from six flux wells and three MLS wells determined.

With regard to measures that can be taken to address potential failures, it must be remembered that the PFM provides point measures of cumulative water and contaminant fluxes. Thus, the efficacy of a PFM transect depends on the number of wells and the vertical sampling resolution. The spatial resolution of flux measurements is important because spatial integration of point measures is necessary to quantify the total water and contaminant mass discharge in the aquifer or downgradient from the contaminant source. Thus, reported water and contaminant discharge estimates should be stated with appurtenant uncertainties.

Kubert and Finkel (2006) found that the error in field-estimated contaminant mass discharges decreased with more wells included in the monitoring transect and when more samples were taken in the vertical at any given well. However, they demonstrated that these errors decreased in asymptotic manner with respect to the number of wells (i.e., the rate of error reduction decreased with each additional well). Furthermore, they achieved good results with fewer wells as long as good depth-average fluxes were obtained at these wells.

6.3 SCALE-UP

The cost of the PFM and the BHD/MLS approach were provided on linear-foot sampling basis and for short- and long-term monitoring horizons. Scale-up did not vary linearly between larger and smaller deployments, as shown in Figure 5. The major factor inducing cost differences between PFMs and the BHD/MLS method is the time required on site. The PFM has a significant advantage in this regard (time on site is kept to a minimum). Hence, it may be impractical to conduct the BHD/MLS method when more than 7-10 wells are involved. Some cost saving may be realized by automating the bore hole dilution method such that one operator can conduct multiple tests simultaneously. The estimation of 2 hours per BHD test may be appropriate for sites with average or high groundwater velocities; but it may be too small for lower velocity sites. Again, in this case it may be impractical to conduct the BHD/MLS method.

6.4 OTHER SIGNIFICANT OBSERVATIONS

Measuring the groundwater gradient can be of great value to PFM monitoring. This information coupled with an independent estimate of the well screen permeability can be used with raw PFM measurements of water flux to estimate groundwater flow convergence to the well and local aquifer permeabilities. Because direct measures of water and contaminant data represent a recent development, combined measures of aquifer permeability, water flux, and contaminant mass flux have not been used in a conjunctive manner to characterize flow and transport at a site.

6.5 LESSONS LEARNED

One of the major factors that can effect PFM implementation is the depth to the sampling interval. For measurements taken in excess of 60 m, the current PFM design can be difficult to implement. It may be of value to consider an inflatable PFM design that could be installed at great depths.

6.6 END-USER ISSUES

There are three primary issues of concern to stakeholders and end users:

1) Will the flux meter yield correct results?
2) Can the flux meter yield reliable results from long-term monitoring?
3) Are the costs of PFM monitoring competitive?

In regard to the first issue, this study demonstrated that PFMs can produce accurate measures of both contaminant and water fluxes. The technology is very simple to construct and implement. We anticipate minimal issues for transfer to end users. Installations used in the demonstration will be similar to the anticipated final product.

The maximum duration of flux measurements was 7.3 weeks, which addressed the second issue of concern. Minimal resident tracer degradation was detected in these long-term deployments.

In regard to the third issue, the cost of PFM monitoring was shown to be at least 30% less expensive than monitoring conducted with a combination of BHD and MLS when 10 or more wells are involved. It is conceivable an annual 1-month PFM measurement of water and contaminant fluxes could be substituted for the current quarterly program. The resultant 75% reduction in monitoring could generate considerable cost savings to DoD and generate the type of data pertinent to quantifying off-site risks.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

One of the primary objectives of this demonstration was to gather field data in support of transitioning the technology from the innovative testing phase to a point where it would receive regulatory and end-user acceptance and stimulate commercialization. To use this technology at some locations (e.g., California), the user may be required to obtain a permit to release tracers. Thus far, obtaining a permit has not been a significant issue except in California; as a result, subsequent PFM deployments have been carried out at more than 25 sites throughout the United States, Australia, Canada, and Wales. Thus, the utility of contaminant flux and contaminant mass discharge as robust metrics for assessing site risks and site remediation performance has gained increasing acceptance within scientific, regulatory, and end-user communities.

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APPENDIX A
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