Environmental Security Technology Certification Program (ESTCP)

Field Demonstration and Validation of a New Device for Measuring Water and Solute Fluxes at Naval Base Ventura County (NBVC), Port Hueneme, CA

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&
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Executive Summary

The use of contaminant flux and contaminant mass discharge as robust metrics for assessment of risks at contaminated sites and for evaluating the performance of site remediation efforts has gained increasing acceptance within the scientific, regulatory and user communities. The Passive Flux Meter (PFM) is a new technology that directly addresses the DoD need for cost-effective long-term monitoring, because flux measurements can be used for process control, for remedial action performance assessments, and for compliance purposes. However, the use of innovative technologies can be slow to gain acceptance in the environmental community; this is because an innovative technology requires a sound theoretical basis accepted widely in the technical circles and field-scale demonstration at diverse sites. Under ESTCP project No ER-0114, the PFM is demonstrated and validated at several locations including Hill AFB in Layton, Utah; NASA Launch Complex 34 in Cape Canaveral, Florida; a Canadian Forces Base in Ontario, Canada; Naval Base Ventura County (NBVC) at Port Hueneme, California; and the Naval Surface Warfare Center at Indian head, Maryland.

The projects at Hill and Borden included the objectives of evaluating the flux meter as an innovative technology for direct in situ measurement of cumulative water and contaminant flux for DNAPLs and compiling field data to transition the technology from the innovative testing phase to regulatory/end user acceptance and stimulate commercialization. The Indianhead project demonstrated the PFM could measure water and perchlorate contaminant flux. The focus of the NASA site was to demonstrate and validate the PFM, as a tool for measuring groundwater and contaminant fluxes at the Launch Complex 34 site (LC 34) where NASA was demonstrating bioaugmentation to enhance the removal of trichloroethylene (TCE) using an engineered microbial culture, KB-1™.

At NBVC groundwater and contaminant fluxes were measured using PFMs at the leading edge of a methyl-tertiary butyl ether (MTBE) plume. The objectives of PFM deployment at the NBVC site were to demonstrate the validity of the PFM and to compare flux measurements in wells reflecting different designs or construction techniques.

Site Study Objectives

- demonstrate and validate the PFM as an innovative technology for direct in situ measurement of cumulative water and contaminant [methyl tertiary butyl ether (MTBE)] fluxes in groundwater
- demonstrate and validate the methodology in wells constructed using different completion methods in the same region of an MTBE contaminated aquifer, and
- gather field data in support of an effort to transition of the technology from the innovative testing phase to a point where it will receive regulatory and end user acceptance and stimulate commercialization

Methods

To demonstrate the performance of the PFM, groundwater and contaminant flux was evaluated during four deployments using wells which were located in a close proximity (in a cluster), such that groundwater and MTBE fluxes could be assumed to be similar and the only observed differences were due to the well construction technique. Two different kinds of well construction techniques (direct-push installed monitoring wells and hollow stem auger drilled monitoring wells), two well sizes (3/4 inch wells and 2 inch wells), as well as different slot sizes and filter pack materials were tested. PFMs were constructed on site for each deployment.

Two types of samples were collected during this study, groundwater samples from wells, and sorbent samples from PFMs. During the construction process, field samples of PFM sorbent were collected to measure the initial concentrations of tracers present on the activated carbon. After exposure, each flux meter was extracted from the well and sub-sampled in 5 to 30-cm vertical intervals and transferred to containers for homogenization. Samples were homogenized and sub-sampled into 40-ml VOA vials containing an extraction fluid isobutanol. Approximately 20 g of sorbent were extracted with 20 ml of alcohol. These samples were cooled for shipping to Purdue University and analyzed within one month. These samples are more stable in the presence of the solvent. Laboratory extraction of the samples involved a two step process: the initial extraction with the isobutyl alcohol followed by a second extraction with an acetone and hexane mixture. From the extracts, all samples were analyzed for alcohols and contaminants by direct liquid injection on Gas Chromatographs. Headspace analysis (detection limit of 50 μg/L) was used in the event that low concentrations are encountered.

Groundwater samples were collected in EPA VOA vials with zero headspace. Samples were pumped (or bailed) from the wells. These samples were immediately placed in coolers and cooled during transport to Gainesville, FL. These samples were held for less than two weeks prior to analysis. Samples were analyzed for MTBE.

Groundwater fluxes measured from PFM quantification methods (Hatfield et al. 2004) were compared to independent flux calculations of 1) taking the product of the hydraulic gradient and independent measures of aquifer conductivity and 2) borehole dilution tests. MTBE fluxes measured from PFM quantification methods (Hatfield et al. 2004) were compared to independent calculations of taking the product of the above independent calculation of groundwater specific discharge and MTBE concentrations measured in open wells.

Groundwater Specific Discharge and Contaminant Mass Flux Results

The depth variation in groundwater fluxes corresponded closely with the stratigraphic information from the borehole logs. These fluxes were within a factor of 2 to 3 of estimates made from slug tests and laboratory conductivity measurements reported in previous studies. Differences in well size, slot size as well as filter pack material did not impact measured groundwater fluxes. However, the pushed wells recorded a lower groundwater and contaminant flux than did the drilled wells, confirming similar observations about pushed vs. drilled wells made in a previous study. It was possible that drilling increases hydraulic conductivity in the

vicinity of the wells and thus resulted in incorrect estimation of the flow convergence factor. The flux-averaged concentration, C_f, did not vary significantly between the pushed wells and the drilled wells, possibly because C_f is independent of the convergence factor. Kram et al. (2001) had also observed statistically insignificant variation in MTBE concentrations in pushed vs. drilled wells as compared to spatial and temporal variation of the concentrations

Cost Assessment and Comparison

Costs are calculated for the passive flux meter method (PFM) and the multilevel sample/ borehole dilution method (MLS/BDH) for contaminant flux characterization. Cost estimates indicate that the PFM method results in a lower unit cost per foot depending on cost variability; Site-specific conditions can lead to changes in the cost estimates for the alternate technology; however, a proper suite of resident tracers with a designed range in retardation factors and optimal deployment period permit a PFM to interrogate a wide range in groundwater fluxes at no additional costs. The principal cost drivers are mobilization/demobilization, labor, and sampling/analysis costs. Labor costs and analytical costs can easily vary by up to 50% and lead to total unit costs (per linear foot) varying by about 20-33%. Costs for both the PFM and the MLS/BDH appear to be similar in terms of mobilization, materials, and analytical costs.

The PFM generates cumulative measures of water and contaminant flux, while MLS/BDH method produces short-term evaluations that reflect current conditions and not long-term trends. 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 like the PFM 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. Finally on a per-well basis, the time required to execute field operations are less for the PFM, than typically required to collect MLS samples or to conduct borehole dilutions on site.

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Demonstration Conclusions

Groundwater and contaminant (MTBE) fluxes were measured in a cluster of wells constructed using five different techniques at an MTBE site in California. The purpose of the study was to measure spatially variable groundwater and contaminant fluxes and to investigate the effect of well construction type on flux measurements. The primary observations were:

i. The depth variation in groundwater fluxes corresponded well with the stratigraphic information from the borehole logs as well as previous estimates made from slug tests and laboratory conductivity measurements (Kram et al., 2001; Bartlett et al., 2004).
ii. Definite depth pattern in the groundwater and contaminant fluxes could be observed even though measurements across different depth sections were taken at different locations within the cluster.
iii. The depth-averaged groundwater fluxes matched with previous slug tests and laboratory tests except for the 2” drilled wells in which the PFM technique resulted in a much higher flux estimate.

iv. The pushed wells recorded a lower groundwater and contaminant flux than the drilled wells. A similar observation about pushed vs. drilled wells was made by Bartlett et al. (2004).
v. The flux-averaged concentration C_f did not vary significantly between the pushed wells and the drilled wells, possibly because C_f is independent of the convergence factor. Kram et al. (2001) had observed statistically insignificant variation in MTBE concentrations in pushed vs. drilled wells as compared to spatial and temporal variation of the concentrations.
vi. Similar depth pattern was observed in groundwater flux, contaminant flux and flux-averaged concentrations.

Recommendations

Based on these results, it appears that further investigation is warranted that will lead to improved methods for quantifying in situ flow convergence factors. These factors serve a critical role in the interpretation of PFM results, and they are expected to vary between well types and aquifer conditions as shown here. Thus, a facile independent method for determining flow convergence factors a priori would facilitate PFM implementation in the field and its ultimate adoption by the environmental community.

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List of Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
CAR	corrective action report
CM	chloromethane
CV	coefficient of variation
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FID	flame-ionization detector
FRTR	Federal Remediation Technology Roundtable
FTL	field team leader
GAC	Granular Activated Carbon
GC	gas chromatography
HASP	health and safety plan
IDL	instrument detection limit
IDLH	immediately dangerous to life or health
MDL	minimum detection level
MeCl	methylene chloride
MLS	multilevel samplers
MS	matrix spike
MSD	matrix spike duplicate
MSDS	materials safety data sheets
MTBE	methyl tertiary butyl ether
NBS	national bureau of standards
NIOSH	National Institute for Occupational Safety and Health
NITS	National Institute of Standards and Testing
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
PFM	passive flux meter
PPE	personal protective equipment
PSO	project safety officer
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
RRF	relative response factors
RRT	relative retention times
SD	standard deviation
SOP	Standard operating procedure
SRM	Standard Reference Materials
SSO	site safety officer

TCE	trichloroethylene
TLV	threshold limit value
TWA	time weighted averages
VOA	volatile organic acid

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1.0 Introduction

1.1. Background

The Department of Defense (DoD) has a critical need for technologies that provided for cost-effective long-term monitoring of volatile organic chemicals, petroleum and related compounds, trace metals, and explosives. Active remediation systems such as "pump and treat", passive remediation systems such as natural attenuation, and RCRA closure sites often require elaborate and expensive monitoring.

This project demonstrates and validate the 'passive flux meter' (PFM) which is a new technology for direct in situ measurement of both cumulative subsurface water and contaminant fluxes. The PFM is a technology that directly addresses the DoD need for cost-effective long-term monitoring, because flux measurements can be used for process control, for remedial action performance assessments, and for compliance purposes.

The PFM is a self-contained permeable unit that is inserted into a well or a boring such that it intercepts groundwater flow but does not retain it. The interior composition of the meter is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and 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'. These tracers are leached from the sorbent at rates proportional to the fluid flux.

The meter is inserted into a well or boring and exposed to groundwater flow for a period ranging from days to months. Next, the meter is removed and the sorbent carefully extracted to quantify the mass of all contaminants intercepted and the residual masses of all resident tracers. The contaminants masses are used to calculate time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative fluid flux. Existing, monitoring technologies cannot provide cumulative water and contaminant fluxes without continuous and therefore expensive sampling.

Use of innovative technologies such as the PFM can be slow to gain acceptance in the environmental community; this is because an innovative technology requires a sound theoretical basis accepted widely in the technical circles and field-scale demonstration at diverse sites. Under ESTCP project No ER-0114, the PFM is demonstrated and validated at several locations including Hill AFB in Layton, Utah; NASA Launch Complex 34 in Cape Canaveral, Florida; a Canadian Forces Base in Ontario, Canada; Naval Base Ventura County (NBVC) at Port Hueneme, California; and the Naval Surface Warfare Center at Indian head, Maryland.

The projects at Hill and Borden included the objectives of evaluating the flux meter as an innovative technology for direct in situ measurement of cumulative water and contaminant flux for DNAPLs and compiling field data to transition the technology from the innovative testing phase to regulatory/end user acceptance and stimulate commercialization. The Indianhead project demonstrated the PFM could measure water and perchlorate contaminant flux. The focus

of the NASA site was to demonstrate and validate the PFM, as a tool for measuring groundwater and contaminant fluxes at the Launch Complex 34 site (LC 34) where NASA was demonstrating bioaugmentation to enhance the removal of trichloroethylene (TCE) using an engineered microbial culture, KB-1™.

At NBVC groundwater and contaminant fluxes were measured using PFMs at the leading edge of a methyl-tertiary butyl ether (MTBE) plume. The objectives of PFM deployment at the NBVC site were to demonstrate the validity of the PFM and to compare flux measurements in wells reflecting different designs or construction techniques.

1.2. Objectives of the Demonstration

The specific objectives of this demonstration project are to:

1) demonstrate and validate the PFM as an innovative technology for direct in situ measurement of cumulative water and contaminant [methyl tertiary butyl ether (MTBE)] fluxes in groundwater,
2) demonstrate and validate the methodology in wells constructed using different completion methods in the same region of an MTBE contaminated aquifer, and
3) gather field data in support of an effort to transition of the technology from the innovative testing phase to a point where it will receive regulatory and end user acceptance and stimulate commercialization.

1.3. DoD Directives

The Department of Defense (DoD) has a critical need for technologies that provided for cost-effective long-term monitoring of volatile organic chemicals, petroleum and related compounds, trace metals, and explosives. Active remediation systems such as "pump and treat" of groundwater and passive remediation systems such as natural attenuation as well as RCRA closure sites often require elaborate and expensive monitoring.

This project demonstrates and validates the PFM which is a new technology for direct in situ measurement of both cumulative subsurface water and contaminant fluxes. Measurements of this nature can be used for process control and for both long- and short-term assessments of remedial action performance and compliance.

1.4. Stakeholder/End-User Issues

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

Issue 1: Will the PFM yield correct results?
Issue 2: How will measured fluxes differ between well types and completion methods?
Issue 3: Are monitoring costs of the PFM lower than the traditional or emerging technologies?

The demonstration focuses on the first two issues of concern. In situ flux measurements are compared between wells constructed using different completion methods in the same region of the aquifer. In addition, the PFMs are tested for MTBE, a contaminant with low sorption characteristics posing a challenge for deployment of PFMs.

2.0. Technology Description

2.1. Technology Development and Application

This demonstration plan describes the proposed strategy for testing and validating a new method for direct in situ measurement of both cumulative water and contaminant fluxes in groundwater. The new method uses a PFM, which is a self-contained permeable unit that is inserted into a well or boring such that it intercepts groundwater flow but does not retain it (See Figure 1-1).

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 groundwater intercepted by the unit. The sorbent matrix is also impregnated with known amounts of one or more fluid soluble 'resident tracers'. These tracers are leached from the sorbent at rates proportional to groundwater flux.

After a specified period of exposure to groundwater flow, the PFM is retrieved from the well or the boring. Next, the sorbent is carefully extracted to quantify the mass of all contaminants intercepted by the PFM and the residual masses of all resident tracers. The contaminants masses are used to calculate cumulative and time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative or time-average groundwater flux. Depth variations of both groundwater 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 mass of resident tracer remaining and the mass of contaminant intercepted. Note that multiple tracers with a range of partitioning coefficients are used to determine variability in groundwater flow with depth that could range over orders of magnitude. This data is used to estimate local, cumulative, groundwater and contaminant fluxes.

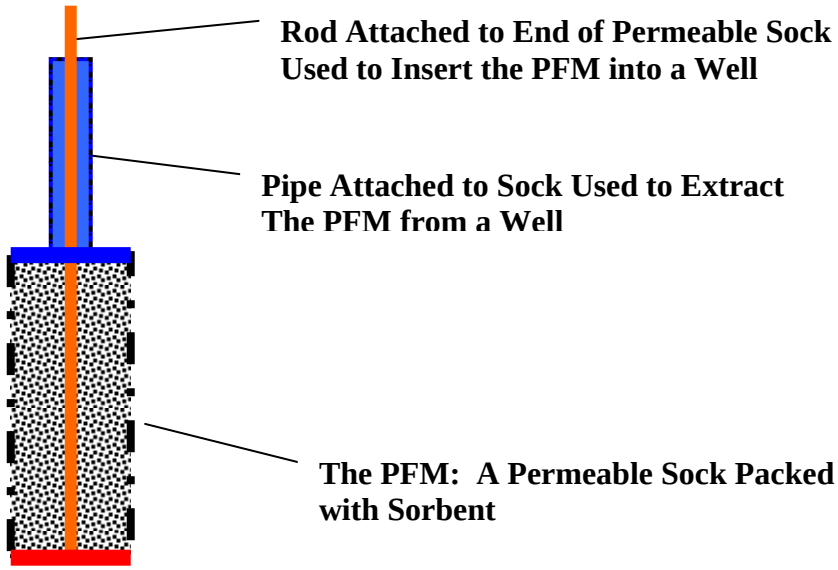


Figure 2-1 Schematic of a Passive Flux Meter comprised of a permeable sock filled with a selected sorbent.

As indicated above, resident tracers are used to estimate cumulative groundwater flux. As groundwater flows through the meter, soluble tracers are desorbed from the sorbing matrix and transported out of the PFM into the surrounding aquifer. Figure 2-2 displays two hypothetical cross-sections of a PFM configured as circular column (such as one installed in a monitoring well).

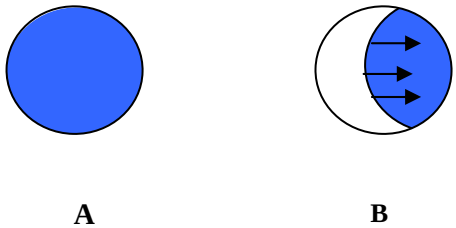


Figure 2-2 Passive flux meter cross-sections A: initial condition, B: displaced tracer distribution after exposure to a fluid flow field.

In Figure 2-2, cross-section-A reveals a single resident tracer uniformly distributed before any fluid has flowed through the PFM. 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 trasported from the section in a manner consistent with the assumption that the streamlines are parallel to the general direction of groundwater flow.

The mass of resident tracer remaining within the PFM (see section-B of Figure 2-2) can be used to estimate the cumulative groundwater volume intercepted by this section of the PFM. Assuming reversible, linear and instantaneous resident tracer partitioning between the sorbent and water, the dimensionless cumulative volume, ξ, of water intercepted by the PFM, at a specified well depth, is obtained iteratively using the following equation:

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

where M_R is the relative mass of tracer retained in the PFM sorbent at the particular well depth. The groundwater flux through the sorbent, q [L/T](e.g., m/day), is calculated using:

$$q = \frac{2r\theta R_d \xi}{t} \tag{2}$$

where, r is the radius of the PFM cylinder; θ is the volumetric 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, groundwater flux is unknown, multiple resident tracers should be used to represent a broad range of tracer retardation factors. Likewise, multiple tracers provide for PFMs designed for both long- and short-term deployment periods.

As indicated above, q, is the specific discharge (L/T) of groundwater 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:

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

where α' is a factor that can be calculated from the geometry of the well and the estimated permeabilities of the aquifer, the well screen, the well packing, and the sorbent (Hatfield et al., 2004; Annable et al., 2005; Klammler, et al., 2006).

The contaminant mass retained on the sorbing porous matrix can be used to estimate contaminant flux into the PFM. The measured flux, J_c, is valid over the dimensions of porous medium contributing flow to the device. For example, a meter designed to sample the entire vertical depth of an aquifer could be used to characterize horizontal groundwater and contaminant fluxes continuously over the vertical extent of an aquifer. Assuming reversible, linear and instantaneous contaminant partitioning between the sorbent and water, the contaminant mass flux (J_c)[M/L^2/T](e.g., kg/m^2/day) can be determined using Equation (3):

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

where M_c is the mass of contaminant sorbed, L is the length of the sorbent matrix or the vertical thickness of aquifer interval interrogated; R_{dc} is the retardation factor of the contaminant on the sorbent, 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 1 and 2 and the q determined from the resident tracers.

A listing of key criteria used to design a PFM is provided in Table 2.1.

Table 2-1 Key Design Criteria for the PFM

Key Design Criteria	
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 are 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 6 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	Of the aquifer zones being interrogated
Minimum Permeability of the Aquifer	Of the aquifer zones being interrogated

Primary consideration must be given to the desired sampling period (short- or long-term monitoring), the contaminant of interest, the nature of the sorbent to be used and the availability of non-toxic resident tracers with sufficiently large retardation factors. Assuming suitable sorbent and resident tracers exist, a PFM can be designed using estimated permeabilities for the aquifer, the well screen and the sorbent (Hatfield et al., 2004; Annable et al., 2005; Klammler et al., 2006).

Development of the PFM and pertinent design criteria evolved from theoretical work initially submitted as part of a patent application made in October 1999 (Hatfield et al., 2002). Since that time, multiple laboratory experiments have been performed to validate theory and design prototypes of devices that could be demonstrated in the field. Some of the initial investigations were bench scales studies of PFMs using hexadecane as a sorbent; this work was extended by Hatfield et al. (2001) to obtain consistent measurements of both water and contaminant fluxes in the laboratory. Annable et al (2005) presented field-scale validation of the PFM under controlled conditions at the Borden CFAB in Ontario, Canada, while Basu et al (2006) demonstrated the utility of the PFM at a TCE site to characterize the source strength and the TCE degradation rates though groundwater and contaminant fluxes measured within the dissolved plume. Campbell et al. (2006) devised a design to quantify both the magnitude and the direction chromium (VI) fluxes.

Several potential applications exist for the PFM. Simultaneous measurements of groundwater and contaminant fluxes have utility a tool for site assessment in long-term monitoring, aquifer restoration, natural attenuation, and contaminant source remediation. For example, in situ measurements of contaminant flux are needed to evaluate the strength of contaminant sources and to optimize the design and assess the performance groundwater remediation systems. Contaminant fluxes, when integrated over a source area, produce estimates of source strength and contaminant mass loads to groundwater and surface water.

$$\iint J_C dydz = Load[M/T]$$

Also, the flux-averaged concentration, C_f [M/L^3], can be determine $C_f = J_c/q$. Furthermore, from contaminant fluxes measured down-gradient from on-going remediation activities, it is feasible to verify the performance of existing technologies, assess cumulative benefits, and estimate prevailing environmental risks

2.2. Previous Testing of the Technology

Significant prior testing of the technology has been done in laboratory tests (Hatfield et al., 2001 and 2004; Campbell et al., 2006), and recent testing has been conducted at the University of Waterloo test site at Canadian Forces Base Borden (Annable et al., 2005) and at a TCE site in the Midwest (Basu et al., 2006). A number of other field tests are underway at the Hill AFB, Utah, Ft. Lewis, WA, Cape Canaveral AS, FL, Patrick AFB, FL, Vandenberg AFB, CA, and the Indian Head Division (IHDIV) of the Naval Surface Warfare Center (NSWC), MD.

2.3. Factors Affecting Cost and Performance

The types of expenses typically associated with groundwater sampling are anticipated to exist with the flux measurements; these would include both direct and indirect environmental activity costs associated with sampling and analysis, labor, and training. For example, it is anticipated that comparable analytical costs will be incurred for each tracer or contaminant analyzed per sample. One cost that is unique to this technology is the cost associated with the PFM sorbent (i.e., activated carbon or ion-exchange resin).

Another important factor that could affect costs is the frequency of sampling. A PFM provides time-integrated information in a single sample. The same type of information can be obtained through multiple water samples. It is expected that the long-term flux measurements will require less frequent sampling and fewer site visits. The final cost of concern is the number of analytes evaluated. With resident tracers the number of constituents analyzed will be greater than typical groundwater sampling.

As indicated above, the design and performance of the PFM will depend on several factors. For example, knowing the permeability of the sorbent and having a good estimate of the aquifer permeability is essential. For example, it is preferable the sorbent have a permeability that is at least 36 times a great as the aquifer (Hatfield et al., 2004). It is also important that the contaminant and some resident tracers have an affinity for the PFM sorbent that is considered high but reversible; thus, the sorptive characteristics of the contaminant and resident tracers must be known.

2.4. Advantages and Limitations of the Technology

The PFM is the only technology available that provides simultaneous measurements of both groundwater and contaminant fluxes. The prominent alternative technology is to quantify groundwater contaminant concentrations through multilevel samplers and then calculate contaminant fluxes using groundwater fluxes estimated from borehole dilution tests.

The PFM possess the advantage of providing a long-term monitoring solution that generates time integrated estimates of both groundwater and contaminant fluxes. Hence, transient fluctuations in contaminant concentrations and groundwater flows are not an issue of concern, as they are with traditional monitoring methods, because such variations are directly integrated in flux estimates. Field measurements will 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 implementation will need to be long enough that the initial bore volume perturbation, both chemical and hydraulic, will not significantly influence the measurement. Finally, the PFM does not require power; thus, it can be used in remote locations, which is an advantage over other continuous monitoring technologies that require power (such as down-hole flow meter).

The primary limitation of the technology is that it could facilitate the collection of more samples at any single well because it is quite easy to collect acquire vertical samples (such as over the vertical extent of the well). Of particular concern is the vertical extent of sampling the PFM is designed to cover the entire screen length of a monitoring well. Proper design of the PFM should include aligning the vertical length of the sorbent material so as to cover just the screen length of the well, so that samples acquired are representative of the depth range over which the monitoring well is sampled. A second limitation is that the method quantifies groundwater fluxes by releasing resident tracer into the environment. Obtaining regulatory approval for the release of resident tracers could be time consuming. Selection of non-toxic, benign tracers could minimize permitting issues.

3.0. Demonstration Design

3.1. Performance Objectives

The performance objectives are a critical component of the demonstration plan. They provide the basis for evaluating the performance and costs of the technology. Performance objectives are the primary performance criteria (see sections 4.1 and 4.2) established for evaluating the innovative technology. Meeting these performance objectives is essential for successful demonstration and validation of the PFM.

Table 3-1 lists the performance objectives for the PFM testing at the Port Hueneme site. With regards to the quantitative performance objectives, the research team understands that future field application of this technology is contingent upon rigorous statistical comparison of contaminant and groundwater flux data between the PFM and conventional groundwater measuring devices, including multilevel samplers. For this demonstration, comparisons will be drawn between solute and water fluxes measured between wells of different construction; hence, the goal is to examine the effects of different wells type on measured fluxes. Given the limited number of wells in which the PFMs were deployed, a rigorous statistical analysis of the data is not feasible, however.

Table 3-1 Performance Objectives

Type of Performance Objective	**Primary Performance Criteria** *(examples)*	**Expected Performance (Metric)** *(examples)*	**Actual Performance Objective Met?** *(future)*
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

The site located on the Naval Base Ventura County (NBVC), Port Hueneme, CA has been selected for testing the PFM in a shallow, unconfined, sandy aquifer contaminated with MTBE and in wells constructed using different completion techniques.

3.3. Test Site History/Characteristics

The Naval Exchange (NEX) Service Station is located within the east-central portion of the base at the southeast corner of 23rd Avenue and Dodson Street (Figure 3-1). The site serves as a retail

outlet for gasoline and automotive service for military personnel working at the base. Gasoline is the only type of contamination reported to have been released from this site.

In December 1984, the CBC Public Works Department at the base discovered free product (gasoline) during the first investigation that was conducted on the area around the NEX Station. In March 1985, it was determined that two of the fuel delivery lines that ran from USTs to the gasoline dispensers were leaking. These leaking fuel lines were thought to be the single source of contamination. Inventory records indicated that an estimated combined total of 10,800 gallons of leaded regular and premium unleaded gasoline (containing methyl tertiary butyl ether (MTBE) and 1,2-dichloroethane additives) was released to the subsurface between September 1984 and March 1985. It is not known how much was released prior to that time interval. New tanks were installed shortly after the leak was detected. In December 1992, eight additional tanks were installed and contaminated soil around both the original and the new tank pits was removed to an *ex-situ* treatment facility.

A semi-perched aquifer has become contaminated as a result of this release. The saturated thickness of the semi-perched aquifer is estimated to be about 15 feet from the water table to the top of the underlying clay cap. The depth to ground water in the perched aquifer from ground surface is about 8 to 9 feet.

The land around the NEX Service Station is predominantly covered with asphalt or is occupied by buildings. There are a large number of utility lines (in service or abandoned in place) traversing the areas around the NEX Service Station, including an area containing USTs and product delivery lines. Utility lines that are present include electrical power, natural gas, water, sanitary sewer, and storm drains. In an effort to accurately locate utility lines, site investigators have reviewed the base facility plans and have performed general field surveys and a geophysical survey. Utility line depths are known or estimated to range in depth from 1 to 9.5 feet below ground surface.

In 1985, 1994, and 1996-97, seven major studies were performed to obtain a comprehensive understanding of the nature and extent of contamination (Table 3-2). The dissolved constituents have moved down-gradient (southwestwardly) in the ground water and have formed a long, narrow plume that was delineated and is currently being monitored (Figure 3-1).

The scope of the demonstration project includes testing the PFM within the NEX MTBE plume at Port Hueneme. The specific site selected is an area constructed for side-by-side testing of wells constructed using different completion methods. These wells are located in clusters so that the groundwater velocity and MTBE mass flux should be comparable. Two major cell areas exist (Cell A and Cell B) with each cell having four clusters of wells. The flux meter testing was conducted in well cluster B. The selection of the well cluster and specific wells was based on existing conditions of the wells and recommendations from on-site personnel.

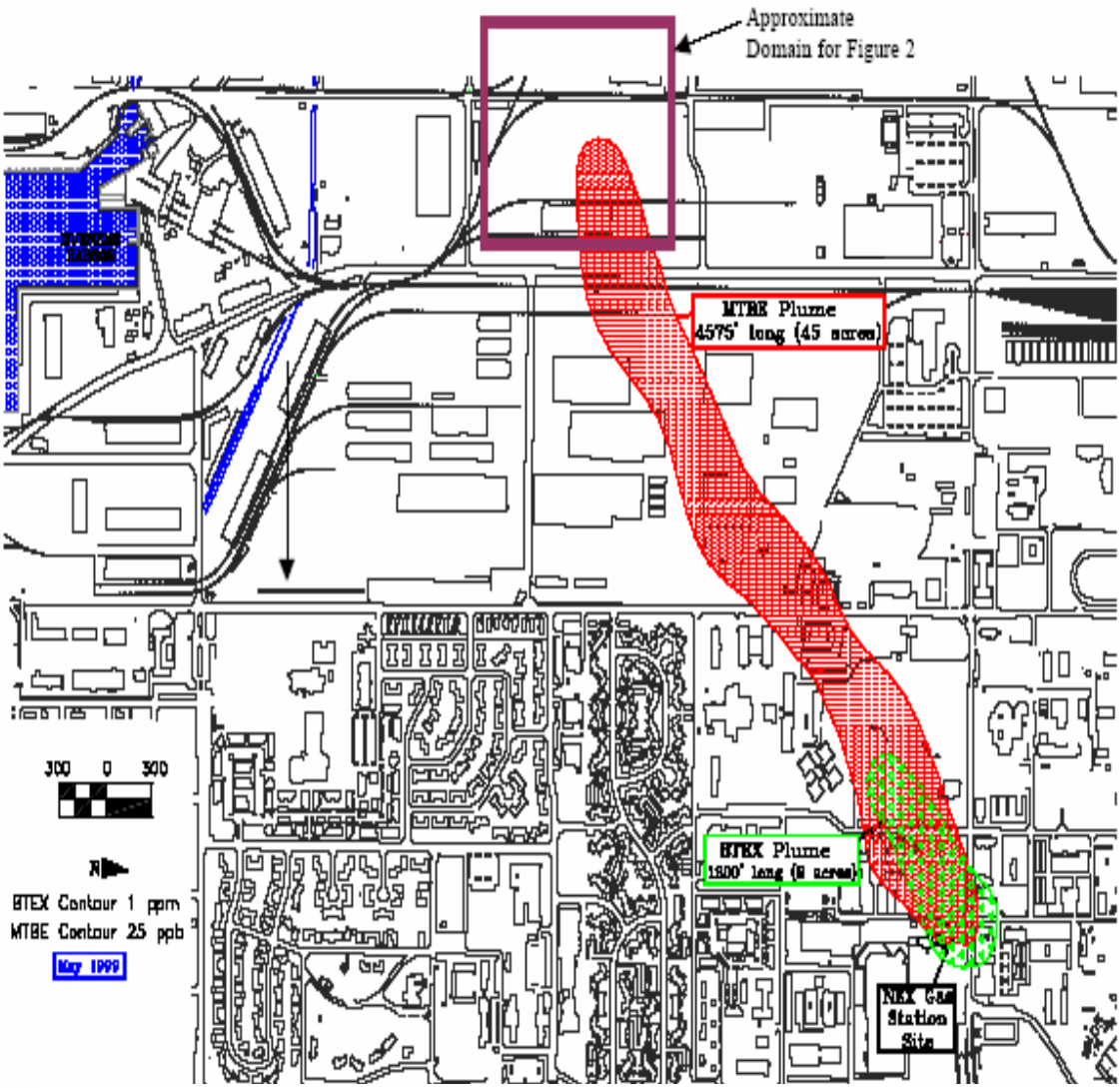


Figure 3-1. MTBE plume (May 1999) at the Naval Base Ventura County, Port Hueneme, California (NAVFAC 2001)

Figure 1. NBVC Port Hueneme MTBE plume map as of May 1999.

Figure 3-1. MTBE plume (May 1999) at the Naval Base Ventura County, Port Hueneme, California (NAVFAC, 2001)

Table 3-2 Hazardous Compounds to be Potentially Encountered at NTL Sites.

Substance	Environmental Media*	Exposure Pathways	Toxic Characteristics**
Diesel	Soil, surface water, air	Inhalation, dermal contact	Respiratory tract, headache, dizziness, nausea
Gasoline	Soil, surface water, air	Inhalation, dermal contact	Vomiting, burning of mucous membrane, throat and respiratory tract, dermatitus
Waste oil	Soil, surface water, air	Inhalation, dermal contact	Properties may vary depending on chemical
1-methylethylbenzene			Not available; see benzene
n-propylbenzene	Soil, surface water, air	Inhalation, dermal contact	Not available; see benzene
n-butylbenzene	Soil, surface water, air	Inhalation, dermal contact	Not available; see benzene
Naphthalene	Soil, surface water, air	Inhalation, dermal contact	Eye irritation, headache, confusion, excitement, nausea
Chloromethane	Soil, surface water, air	Inhalation, dermal contact	N/A
1,3,S-trimethylbenzene	Soil, surface water, air	Inhalation, dermal contact	Not available; see benzene
Methylene chloride	Soil, surface water, air	Inhalation, dermal contact	Inflammation of mucous membrane
Inorganic lead	Soil, surface water, air	Inhalation, dermal contact	Inflammation of mucous membrane, weakness
Benzene	Soil, surface water, air	Inhalation, dermal contact	Headaches, weakness, loss of appetite, cancer
Chlorinated compounds	Soil, surface water, air	Inhalation, dermal contact	Eye irritation, liver damage, reproduction effect
	Soil, surface water, air	Inhalation, dermal contact	
	Soil, surface water, air	Inhalation, dermal contact	
	Soil, surface water, air	Inhalation, dermal contact	

*Environmental media where hazardous materials are to be potentially encountered.
**Acute and chronic physiological symptoms of exposure to the hazardous materials to be potentially encountered.

3.4. Present Operations

With regard to the activities planned under this demonstration, the only relevant current activity is the pump-and-treat system located near the down-gradient portion of the MTBE plume. Approximately 15 wells extract water for plume capture and treatment. The hydraulic influence of this effort will have minimal influence on the well comparison study.

3.5. Testing and Evaluation Plan

3.5.1. Demonstration Set-Up and Start-Up

Laboratory batch experiments were conducted to select sorbents and tracers. In addition, flow-through-box aquifer experiments were conducted under known flow conditions to characterize the performance of the PFM in wells with and without sand packs (Hatfield et al., 2004; Annable et al., 2005).

Solid-aqueous phase batch partitioning tests were conducted to evaluate sorbents for intercepting contaminants (MTBE) and releasing tracers (Hatfield et al., 2004; Annable et al., 2005). Granular Activated Carbon (GAC) is the primary sorbent under consideration, because it was inexpensive, and it could be recycled. Batch tests followed well-established methods for determining the isotherms for the resident tracer sorption and desorption between GAC and aqueous phases. The measured isotherms were used to assess the applicability of each sorbent as a packing media for the PFM. Hysteretic and non-equilibrium partitioning behavior were considered in the sorbent and tracer selection process.

Flow-through-box aquifer experiments were conducted (Hatfield et al., 2001, 2004) under known flow conditions to characterize the performance of the PFM. A water-tight container (glass or stainless steel) was used to create an aquifer model. The two ends of the container was used for flow injection and extraction and packed with coarse gravel. This was done to provide a constant head across the width of the box, and a uniform gradient across the length of the box. The main section of the box was packed under water with sand.

The PFMs were packed with GAC packed in permeable cotton socks. The GAC was pre-equilibrated with several resident tracers. The PFMs were inserted into the well screens. After a known period of exposure, the PFMs were pulled from the box and the GAC extracted to assess the masses of surrogate contaminants intercepted and the masses of resident tracers lost. Results from the box experiments permit one to assess the accuracy of contaminant flux measurements under different volumes of intercepted cumulative flow. Hence, given an approximation of the ambient groundwater flow rate one can estimate the time needed to accurately measure MTBE fluxes. The box experiments were used to estimate the appropriate time for installation at the Port Hueneme site.

The PFMs were constructed on-site prior to installation in each well. The tracers used in some cases are volatile and therefore a minimum time between construction and installation is desired. The construction of each flux device involves packing the sorbent (with tracers) into the socks and including any impermeable dividers to minimize vertical flow. Following construction, the PFMs were installed into the two-inch monitoring well. Each PFM required about 15-30

minutes to construct and install (depending on personnel). Each flux monitoring event involved the deployment of 14 PFMs ranging in length from 2 to 5 feet.

The PFMs remained in the flow field for 5 to 10 days depending on the sorbent and tracers used. During PFM retrieval, the device is removed from the well and segmented vertically for sub-sampling. In each interval, the sorbent is homogenized and sub-sampled for analysis. The process of extraction and sub-sampling required about 30 minutes.

3.5.2. Period of Operation

The work at the Port Hueneme site was conducted over a one-year period. Groundwater and MTBE fluxes were measured in selected wells in cluster B.

3.5.3. Amount /Treatment Rate of Material to be Treated

Not applicable.

3.5.4. Residuals Handling

PFMs generate a minimal amount of waste. Deployment and retrieval of 14 PFMs generated approximately 52 liters of GAC, which contained tracers and contaminants. This solid waste was disposed by Port Hueneme personnel. All materials brought back to Purdue University for analysis were disposed according to the campus environmental and health protocols.

3.5.5. Operating Parameters for the Technology

Operationally, the PFM is very simple, and this is one of the primary advantages of the technique. A single individual can deploy the PFMs, especially if the PFMS are pre-packed in the lab and transported to the field site in sealed tubes; however, two operators is likely the best. About 50 PFMs can be installed in in a single day. The PFM retrieval and sampling is quite simple, and again could be conducted by a single operator. The method requires no electrical utilities and could be performed in remote locations. We do use an electronic balance; however, all measurements could be made prior to leaving the laboratory.

3.5.6. Experimental Design

The PFMs were deployed in selected wells in Cell cluster B, which had wells constructed using five different techniques (Figures 3-2, 3-3 and 3-4). These wells were previously installed to conduct a "Performance Comparison: Direct-Push versus Drilled Wells," study (NFESC Technical Report TR-2120-ENV (Kram et al., 2001)). The specific well screen design (filter pack and slot size) was determined using several criteria. To evaluate performance of wells adhering to the ASTM specifications (ASTM D5092), grain size distribution curves were used to determine filter pack grain size and corresponding slot size recommendations. To evaluate the performance of wells most commonly installed by drillers, a generic ("conventional") well design consisting of 20-40 mesh sand pack surrounding 0.010-inch (0.25-mm) slotted schedule 40 PVC pipe was used as one of the alternatives in each of the well clusters in Cell B. To evaluate performance of non-pack wells that are often installed by direct-push equipment operators, an additional set of wells consisting of 0.010-inch (0.25-mm) slotted schedule 40 PVC

pipe was installed without a filter pack in each of the clusters in Cell B. For Cell B, four clusters were installed, each consisting of the following five types of wells:

Type 1. 3/4-Inch Diameter Pushed Wells - No Filter Pack (#1 wells)
Type 2. 3/4-Inch Diameter Pushed Wells - ASTM Specifications (#2 wells)
Type 3. 3/4-Inch Diameter Pushed Wells - "Conventional" (0.010 slot; 20-40 sand) (#3 wells)
Type 4. 2-Inch Diameter Pushed Wells - ASTM Specifications (#4 wells)
Type 5. 2-Inch Diameter Drilled Wells - ASTM Specifications (#5 wells)

A nomenclature for each cluster was established to preserve relationships between wells, emplacement methods, and evaluation cells. The first two symbols in each well name refer to the cluster they belong to. For instance, each Bl well belongs to the Bl cluster. The "p" and "d" refer to emplacement method (pushed versus drilled, respectively), "pcv" refers to pushed conventional, and "pnp" refers to pushed, no-pack designs. Figures 3-2 a, b and c show well configuration and screen depths for cluster B. Additional information on well clusters can be found in Kram et al. (2001).

These wells clusters are located in a close proximity such that groundwater flow and MTBE flux will be comparable. PFMs were deployed in these wells at the same time and for the same duration. The results were compared for both groundwater flow and MTBE flux. Groundwater samples were collected from the wells prior to PFM deployment to assess variability in MTBE concentration between wells.

3.5.7. Sampling Plan

The PFMs was tested in selected cells in cluster B. Sub-samples were taken in vertical intervals of approximately 30 cm to provide spatially resolved flux distribution. Groundwater samples were collected from the wells prior to PFM installation. These samples were used to calculate flux based on estimated groundwater velocities from historical measures of hydraulic conductivity and gradients.

Sample Collection. Two types of samples were collected during this study, groundwater samples from wells, and sorbent samples from the PFMs. Both of these sampling methods and sample handling procedures are described here.

Grondwater samples were collected in EPA VOA vials with zero headspace. Samples were pumped (or bailed) from the wells. These samples were immediately placed in coolers and cooled during transport to Gainesville, FL. These samples were held for less than two weeks prior to analysis. Samples were analyzed for MTBE.

Sorbent samples were collected from the retrieved PFMs at about 30-cm vertical intervals and transferred to containers for homogenization. Samples were homogenized and sub-sampled into 40-ml VOA vials containing an extraction fluid such as isobutanol. Approximately 20 g of sorbent were extracted with 20 ml of alcohol. These samples were cooled for shipping to Purdue

University and analyzed within one month. These samples are more stable in the presence of the solvent.

Sample Analysis. All samples were analyzed at laboratories at the University of Florida or Purdue University. Volatile organics, including alcohol tracers, were analyzed by direct liquid injection on Gas Chromatographs. Details of analytical methods are provided in Appendix A. Detection limits are approximately 1 mg/L. Headspace analysis (detection limit of 50 μg/L) was used in the event that low concentrations are encountered.

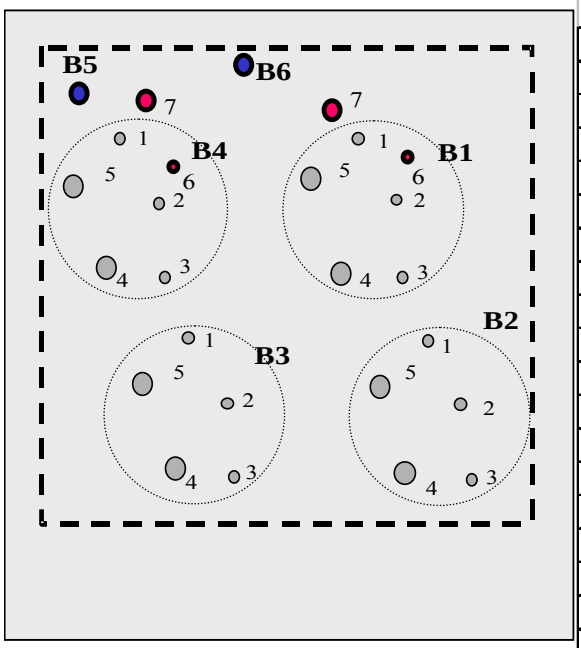
Experimental Controls. Port Hueneme personnel monitored natural groundwater flow conditions before and after PFM testing.

Data Quality Parameters. Data quality was maintained and checked throughout the project. Details on approaches for maintaining data quality are provided in the QA/QC plan in appendix C.

Calibration Procedures, Quality Control Checks, and Corrective Action. Initial and continuing calibration procedures for analytical instrumentation, quality control checks, and corrective actions are required to maintain reproducible experiments. These procedures are fully described in the QA/QC plan in appendix C.

Data Quality Indicators. Simple regression analysis was used to assess the quality of data collected at any single well. However, more sophisticated techniques of spatial analysis were performed with data collected to assess the spatial mean and variance of contaminant and water fluxes evaluated over transects or within a plume.

Test Cell B



Cell "B" Description & Location					
		Screen	Screen		
Well ID	Well Type	Interval	Length		
B1-1	1pnp	10. - 12	2		
B1-2	1p1	10. - 12	2		
B1-3	1pcv	10. - 12	2		
B1-4	1p	10. - 12	2		
B1-5	1d	10. - 12	2		
B1-6	1p1	10. - 12	2		
B1-7	1d	10. - 12	2		
B2-1	2pnp	7.0 - 12.0	5		
B2-2	2p1	7.0 - 12.0	5		
B2-3	2pcv	7.0 - 12.0	5		
B2-4	2p	7.0 - 12.0	5		
B2-5	2d	7.0 - 12.0	5		
B3-1	3pnp	16. - 18	2		
B3-2	3p1	16. - 18	2		
B3-3	3pcv	16. - 18	2		
B3-4	3p	16. - 18	2		
B3-5	3d	16. - 18	2		
B4-1	4pnp	12.5 -17.5	5		
B4-2	4p1	12.5 -17.5	5		
B4-3	4pcv	12.5 -17.5	5		
B4-4	4p	12.5 -17.5	5		
B4-5	4d	12.5 -17.5	5		
B4-6	4p1	12.5 -17.5	5		
B4-7	4d	12.5 -17.5	5		

B5-1	7 Point multi-level monitoring well on North side of B4				
Sample	Depth	Depth	Center of		
Point #	cm	ft.	Screen		
1	250.0	8.20	8.0		
2	310.0	10.17	10.0		
3	372.5	12.22	12.0		
4	429.5	14.09	13.9		
5	495.5	16.26	16.0		
6	555.0	18.21	18.0		
7	596.0	19.55	19.3		

B6	Fully screened (12' screen interval) 0.75" well, no sand pac				
B6-1	6pnp	8. - 20	12		

Figure 3-2 Cell B well cluster configuration

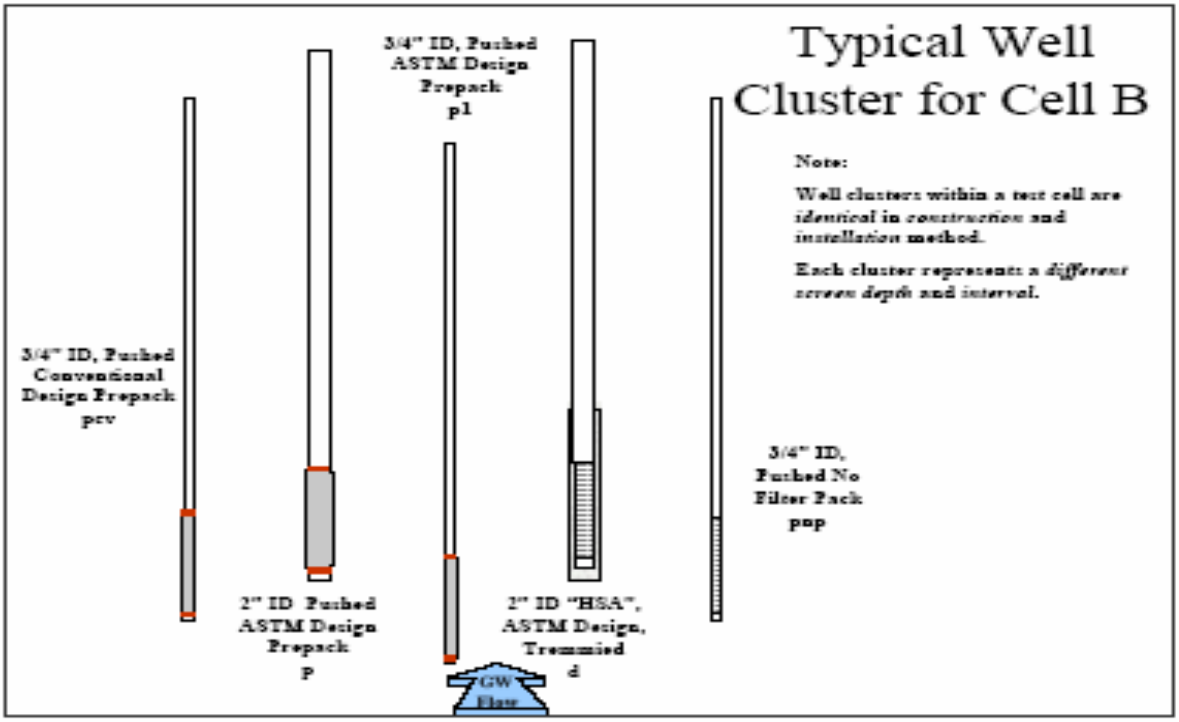
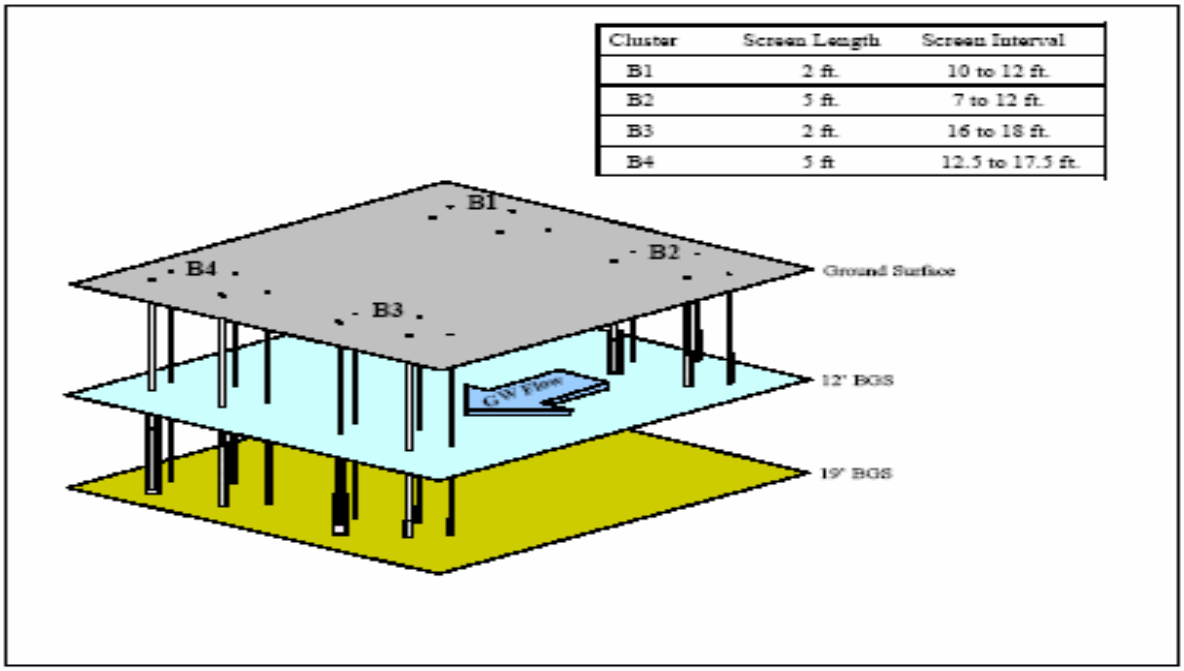


Figure 3-3 Typical Cell Cluster for Cell B



Cluster	Screen Length	Screen Interval
B1	2 ft.	10 to 12 ft.
B2	5 ft.	7 to 12 ft.
B3	2 ft.	16 to 18 ft.
B4	5 ft	12.5 to 17.5 ft.

Figure 3-4 Screen depths for Cell Cluster B

3.6. Demobilization

Minimal demobilization is required for the PFM testing. All equipment needed can be transported to and from the site for each event.

3.7. Health and Safety Plan (HASP)

The site health and safety plan is provided in Appendix D.

3.8. Selection of Analytical/Testing Methods

Analytical methods are provided in Appendix A.

3.9. Selection of Analytical/Testing Laboratory

No outside laboratories required.

3.10. Management and Staffing

Mike Annable and Suresh Rao were responsible for field activities at Port Hueneme. Graduate students assisted with field activities. Mike Annable oversaw laboratory analytical work at the University of Florida, and Suresh Rao and Irene Poyer oversaw analytical work at Purdue University.

3.11. Demonstration Schedule

Flux measurements were done using PFM in December 2004. Prior to this, some preliminary deployments of PFMs were done to overcome problems arising from unique construction of wells at this site (i.e., ¾ inch wells); all previous field tests of PFM were at sites with 2-inch wells. Data from these early trials are not included in this report. Groundwater and contaminant flux data presented here are from the last deployment, judged to be the most reliable.

4.0. Performance Assessment

4.1. Performance Criteria

Described in the tabular format below (Table 4-1) is the general performance criteria to be used to evaluate the performance of the PFM. Performance criteria may be qualitative or quantitative and are categorized as being primary (which are the project's performance objectives) or secondary criteria.

Table 4-1 Performance Criteria

Performance Criteria	**Description**	**Primary or Secondary** *(examples)*
Ground Water Flow Estimates	Compare ground water flow based on the PFMs between wells and borehole dilution	*Primary*
Contaminant Flux Estimates	Compare contaminant flux based on the PFMs between wells	*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 device in terms of site conditions (ground water velocity, media properties, temperature, salinity, etc.)	*Primary*
Reliability	Robustness of the approach. How much error is 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?	*Secondary*
Versatility	Potential for difficult environments and in MTBE plumes.	*Primary*

4.2. Performance Confirmation Methods

The quality of groundwater and contaminant flux estimates based on the PFM deployments were compared with alternative measures of these quantities (e.g. borehole dilution tests), slug tests, and between wells compared using different techniques. Table 4-2 lists an expected or a desired value for each performance criterion and the method that will be used to confirm performance. Qualitative metrics were selected for several performance criteria including: ease of use, reliability, safety, and versatility. Ease of use is an important performance criterion and it is expected that the results of the demonstration will document the level of training required to install/extract and interpret information from the PFM. Reliability was assessed from records of total device installations verses total numbers of device failures. The performance metrics for the versatility criterion was simply to demonstrate that the PFM can be successfully applied to generate both short- and long-term assessments, and help build a database to define the applicability of the PFM under different site conditions.

Table 4-2 Expected Performance and Performance Confirmation Methods

Performance Criteria	**Expected Performance Metric (pre demo)**	**Performance Confirmation Method***
PRIMARY CRITERIA (Performance Objectives) (Qualitative)		
Ease of Use	*Minimal training required*	*Experience from demonstration operations*
PRIMARY CRITERIA (Performance Objectives) (Quantitative)		
Comparison water flux between well.	*Estimate within 25%*	*Direct comparison*
Comparison water flux to Slug test results and borehole dilution.	*Estimate within 25%*	*Direct comparison to fluxes based on the gradient and slug test conductivity or BHD*
Comparison MTBE flux between wells	*Estimate within 25%*	*Direct comparison*
Comparison MTBE flux average concentration between wells	*Estimate within 25%*	*Direct comparison*
Process Waste - Generated	*25 gallons*	*Observation*

SECONDARY PERFORMANCE CRITERIA (Qualitative)		
Reliability (CU)	*No failures*	*Record keeping*
Safety (all) - Hazards - Protective clothing	*Contaminated sorbents* *Level D*	*Experience from demonstration operation*
Versatility (all) - Short/long term averaging - Other applications	*Yes* *In multiple well types*	*Experience from demonstration operation*

* Refer to Appendix A for further details

As indicated in Table 4.2, several quantitative performance metrics were identified to assess the performance of the new technology. Because the typical range for contaminant fluxes in the field can be 5 orders of magnitude (for groundwater fluxes the range is 2 orders of magnitude), it is believed that achieving the performance metrics identified would greatly reduce the

uncertainty of contaminant flux assessments. Clearly, a significant uncertainty reduction would be valuable to regulators and site managers. For the Port Hueneme experiments discussed above, a successful comparison would result if the and contaminant fluxes were estimated within 25% and the comparison between wells were within 25%. Errors for groundwater flux estimates are not provided since values can only be estimated using measured gradients and hydraulic conductivity measurements.

4.3 Data Analysis, Interpretation and Evaluation

4.3.1. Deployment of PFM and Data Treatment

PFMs was deployed in the selected wells (Table 4-3) in December 2004. A 9- day deployment period was selected based on available groundwater flux information and properties of resident tracers.

Table 4-3 Well Construction Details

Well ID	Well Diameter (in)	Emplacement Method	Screen Depth Range (feet)	Filter Pack Mesh	Slot Size (in)
B1-4	2	Pushed (ASTM)	10-12	10-20	0.020
B1-5	2	Drilled (ASTM)	10-12	10-20	0.020
B2-4	2	Pushed (ASTM)	7-12	10-20	0.020
B2-5	2	Drilled (ASTM)	7-12	10-20	0.020
B3-1	¾	Pushed no pack	16-18	No pack	0.010
B3-2	¾	Pushed (ASTM)	16-18	10-20	0.020
B3-3	¾	Pushed conventional	16-18	20-40	0.010
B3-4	2	Pushed (ASTM)	16-18	10-20	0.020
B3-5	2	Drilled (ASTM)	16-18	10-20	0.020
B4-1	¾	Pushed no pack	12.5-17.5	No pack	0.010
B4-2	¾	Pushed (ASTM)	12.5-17.5	10-20	0.020
B4-3	¾	Pushed conventional	12.5-17.5	20-40	0.010
B4-4	2	Pushed (ASTM)	12.5-17.5	10-20	0.020
B4-5	2	Drilled (ASTM)	12.5-17.5	10-20	0.020

Appendix D contains a detailed Standard Operating Procedure (SOP) on PFM preparation, deployment and retrieval protocols, GAC sampling and extraction protocols, and analytical protocols for detection of resident tracers and contaminant MTBE.

The cumulative, time-averaged groundwater flux, q ($L^3/L^2/T$), and contaminant fluxes, J ($M/L^2/T$), are given by equations (5) and (6) [see Hatfield et al, 2004 for details]:

$$q = \frac{1.67(1-\Omega_R)r\theta R_d}{\alpha t} \qquad (5)$$

$$J = \frac{1.67 m_c}{\pi r \alpha b t} \qquad (6)$$

where; r is the radius of the PFM cylinder, θ is the water content in the PFM, R_d is the retardation of the resident tracer on the sorbent, t is the sampling duration, Ω_R is the relative mass of the resident tracer remaining in the PFM sorbent at the particular well depth, m_c is the mass of contaminant sorbed by the PFM and b is the length of the sorbent matrix and α is a correction factor to account for flow convergence towards or divergence around the PFM; note that the permeability contrast between the well with the PFM and the surrounding aquifer determines flow convergence or divergence, the former being the preferred.

The convergence (divergence) factor, α, is a function of the *local* hydraulic conductivities of the aquifer (K), the PFM (k_d), the well screen (k_s) and the filter pack (k_f) (Klammler et al., 2006).

$$\alpha = \frac{8}{A+E+F+G} \qquad (7a)$$

$$A = \left(1+\frac{K_S}{K_D}\right)\left(1+\frac{K_F}{K_S}\right)\left(1+\frac{1}{K_F}\right) \qquad (7b)$$

$$E = \left(1-\frac{K_S}{K_D}\right)\left(1-\frac{K_F}{K_S}\right)\left(1+\frac{1}{K_F}\right)\left(\frac{1}{R_S}\right)^2 \qquad (7c)$$

$$F = \left(1-\frac{K_S}{K_D}\right)\left(1+\frac{K_F}{K_S}\right)\left(1-\frac{1}{K_F}\right)\left(\frac{1}{R_F}\right)^2 \qquad (7d)$$

$$G = \left(1+\frac{K_S}{K_D}\right)\left(1-\frac{K_F}{K_S}\right)\left(1-\frac{1}{K_F}\right)\left(\frac{R_S}{R_F}\right)^2 \qquad (7e)$$

where, $K_D = k_D/K$, $K_S = k_s/K$ and $K_F = k_f/K$ are the relative hydraulic conductivities of the PFM, the well screen and the filter pack with respect to the conductivity of the aquifer and $R_S = r_s/r_O$ and $R_F = r_f/r_O$ are the relative outer radii of the well screen r_s and filter pack r_f with respect to the PFM radius r_0.

For wells without any filter pack, equation 7 simplifies to

$$\alpha = \frac{4}{\left(1+\frac{1}{K_S}\right)\cdot\left(1+\frac{K_S}{K_D}\right)+\left(1-\frac{1}{K_S}\right)\cdot\left(1-\frac{K_S}{K_D}\right)\cdot\left(\frac{1}{R_S}\right)^2} \qquad (8)$$

Data analyses were performed using Equations 5 through 8 as per the protocols outlined in Hatfield et al. (2004). A GAC porosity of 0.55 (Annable et al., 2005) was used. The term α in these equations is subject to significant uncertainty because α is a function of the local-scale hydraulic conductivities of the media, the well screen and the filter pack.

For the present study, the following parameter values were assumed:

a) Hydraulic conductivity of the filter pack k_f (L/T) was estimated from Hagen-Poisseuille's equation: 0.93 cm/s (10 to 20 mesh) and 0.2 cm/s (20 to 40 mesh)
b) Hydraulic conductivity of the well screen was measured to be 0.09 m/s for 0.01 inch slot size screen and estimated to be 0.18 m/s for 0.02 inch slot size screen;
c) Hydraulic conductivity of the PFM was measured to be 0.518 cm/s (Annable et al., 2005);
d) Hydraulic conductivities of the media was estimated to be 0.000595 cm/s for wells B1- 4, B1-5, B2 - 4 and B2 - 5 (depth 7 to 12 feet bgs) and 0.0343 cm/s for the remaining wells (depth 12 to 18 feet bgs). This was based on grain size analysis (Kram et al., 2001) of cores taken from Cluster B.

For the five different well types used in this study, the estimated values of α ranged from 1.26 to 2. This is close to the values reported by Annable et al. (2005). The hydraulic conductivity used is an average value and thus its applicability for local estimation of α is a function of the heterogeneity of the site. The well screen and the filter pack hydraulic conductivity estimates are for new wells and would decrease with time due to clogging.

4.3.2. Robustness of the PFM Technique

Groundwater discharge through the PFM (Equation 5) can be estimated using multiple resident tracers and theoretically they should all yield the same flux value. However, each estimate is subject to its own set of analytical errors in addition to issues of non-linearity of the elution profile that occur when $\Omega_R < 0.32$. The robustness of the PFM technique can be thus tested by the correspondence of the flux values estimated using different tracers.

Hatfield et al. (2004) suggest that the optimum range of Ω_R values for the application of Equation 5 is within 0.32 to 0.7. However, due to variability in the groundwater flow with depth, it might not always be possible to obtain Ω_R values within that range. It is proposed that a wider range of Ω_R values can be used without significant loss in accuracy. In order to prove this hypothesis and also test the robustness of the PFM technique, flux estimates were made at each location in the flux meter using a pair of resident tracers with fractional mass remaining ranging between 0.08 and 0.95 and the results plotted in Figure 1.

If the two data points circled are neglected, a 1:1 trend line can be fitted through the data set thus proving that the estimate is independent of the analytical issues associated with the tracer selected. The close correspondence between the two fluxes also indicates that a wider range of Ω_R values can be used without significant loss in accuracy. The reason the two circled data points diverge from the 1:1 line is that at high fluxes, equation 5 underestimates the flux for tracers with low R due to excessive depletion of tracer mass (Hatfield et al., 2004).

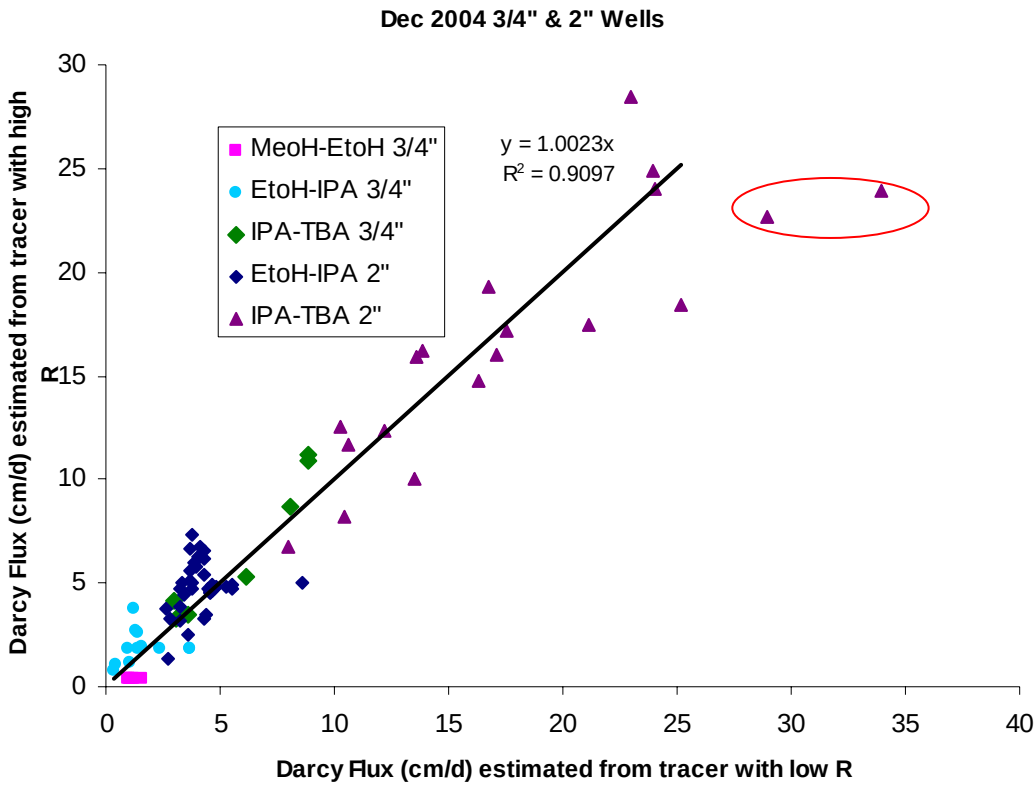


Figure 4-1 Comparison of Darcy Flux obtained using multiple tracers

4.3.3. Depth Variation of Groundwater and Contaminant Fluxes

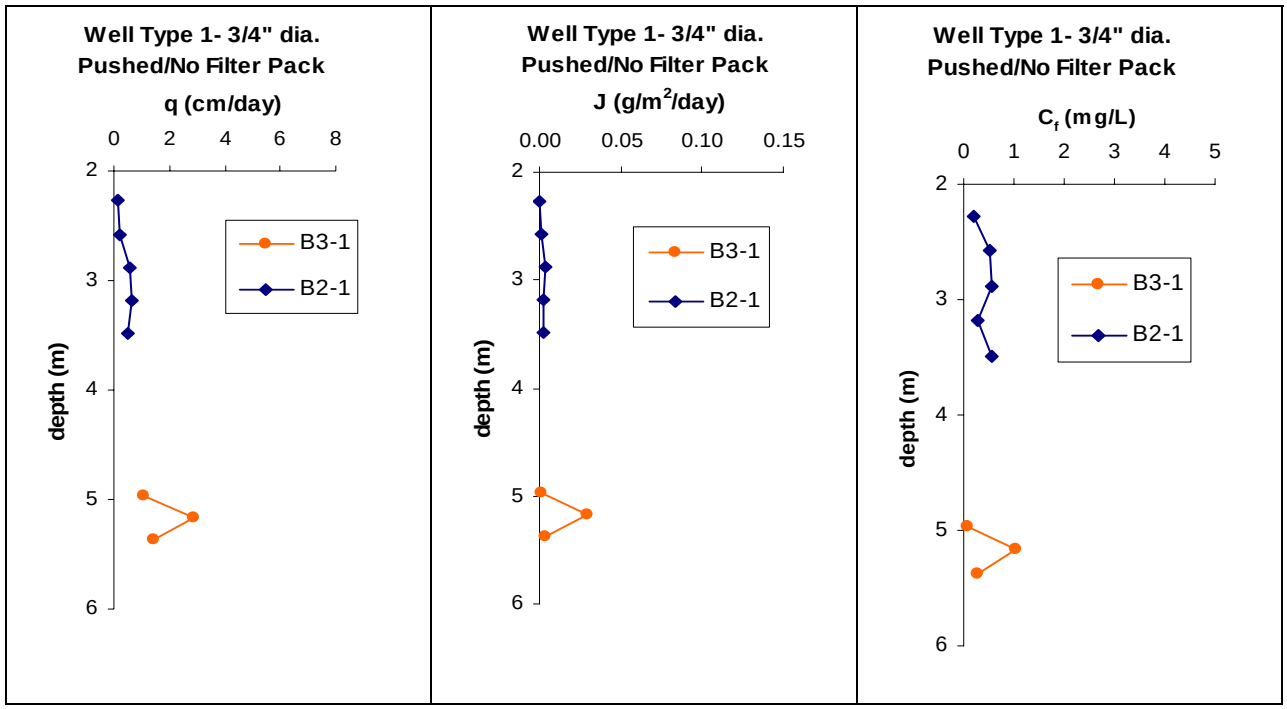
A consistent depth pattern was observed in the groundwater and contaminant fluxes across the five different well types (Figure 4-2). The depth variations in groundwater fluxes correspond with the borehole logs that indicate two orders of magnitude increase in the hydraulic conductivity, K, at 3.6 m (12 feet) bgs. Groundwater fluxes increase by a factor of 2 to 8 at about the same depth. Groundwater flux data also indicate that the zone of high K is narrow, between ~ 3.6 to 4.6 m bgs after which fluxes reduce to values of similar magnitude as those above 3.6 m.

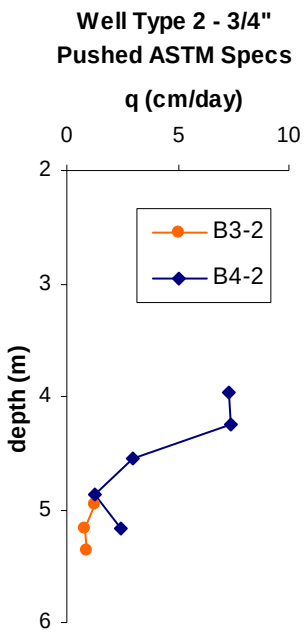
These trends are consistent with the observed change in stratigraphy with depth, which transitions from silt to gravel, then fines to clay. Slug tests and laboratory measurements of hydraulic conductivity made by Kram (2001) and Bartlett et al. (2004) showed similar trends.

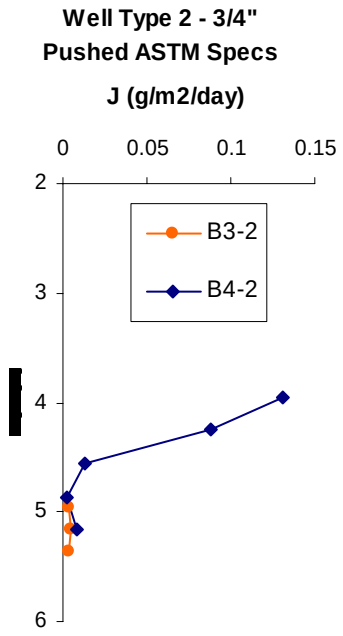
The contaminant flux, J (g/m^2/day) and the flux-averaged concentrations, C_f (mg/L) show similar depth pattern as the groundwater flux (Figure 4-2). Our original hypothesis was that the flux-averaged concentration would be more or less uniform with depth since we are at the down-gradient edge of the plume. Similar depth patterns of q and C_f can be explained by an LNAPL (MTBE) plume that migrated vertically with the infiltrating groundwater to the high conductivity layer, whereupon its flow vector became primarily horizontal. The fact that the groundwater

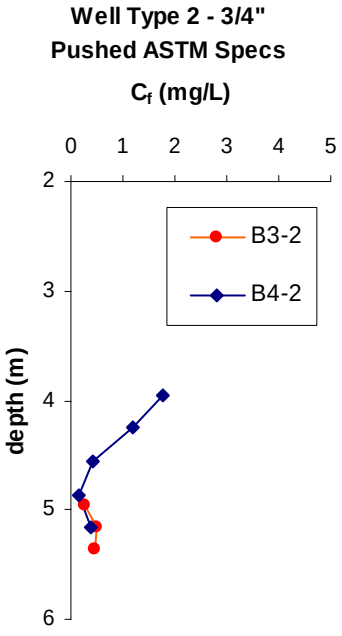
table at this site varies from 1.5 to 3.7 m bgs and the high conductivity layer is at 3.6 m bgs lends credence to this hypothesis. It is also proposed that since MTBE degrades via oxidative pathways, greater degradation and lower concentrations are expected near the water table which is consistent with the observed depth variations in the flux-averaged concentration. Note that the variance (with depth) of the contaminant flux J is higher than the variance of C_f and q.

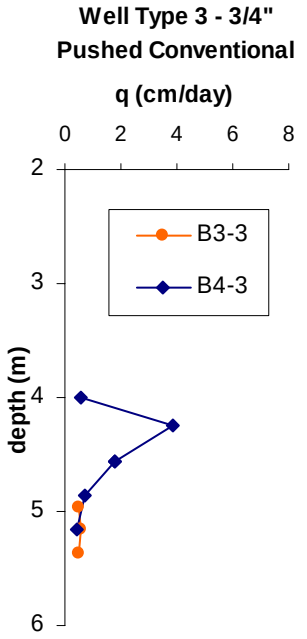
Thus, the narrow high conductivity zone between 3.6 m to 4.6 m bgs will contribute to a significant portion of the cumulative mass discharge across any control plane. This is an important observation since remedial activities targeted at this zone will cause greater reduction in mass discharge with less effort. The absolute magnitudes of the groundwater fluxes, contaminant fluxes and how they compare with other methods of flux estimation and also across wells constructed using different techniques are discussed in the following sections.

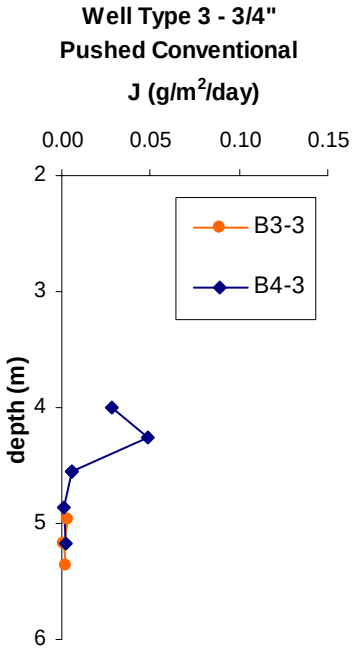


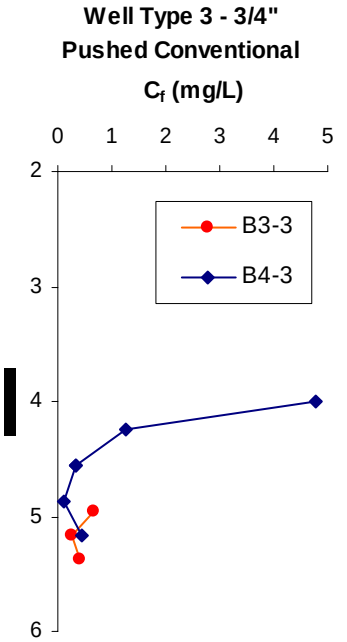

Well Type 2 - 3/4"
Pushed ASTM Specs
q (cm/day)
0
5
10
2
3
4
5
6
depth (m)
B3-2
B4-2


Well Type 2 - 3/4"
Pushed ASTM Specs
J (g/m2/day)
0
0.05
0.1
0.15
2
3
4
5
6
B3-2
B4-2


Well Type 2 - 3/4"
Pushed ASTM Specs
Cf (mg/L)
0
1
2
3
4
5
2
3
4
5
6
depth (m)
B3-2
B4-2


Well Type 3 - 3/4"
Pushed Conventional
q (cm/day)
0
2
4
6
8
2
3
4
5
6
depth (m)
B3-3
B4-3


Well Type 3 - 3/4"
Pushed Conventional
J (g/m2/day)
0.00
0.05
0.10
0.15
2
3
4
5
6
depth (m)
B3-3
B4-3


Well Type 3 - 3/4"
Pushed Conventional
Cf (mg/L)
0
1
2
3
4
5
2
3
4
5
6
B3-3
B4-3

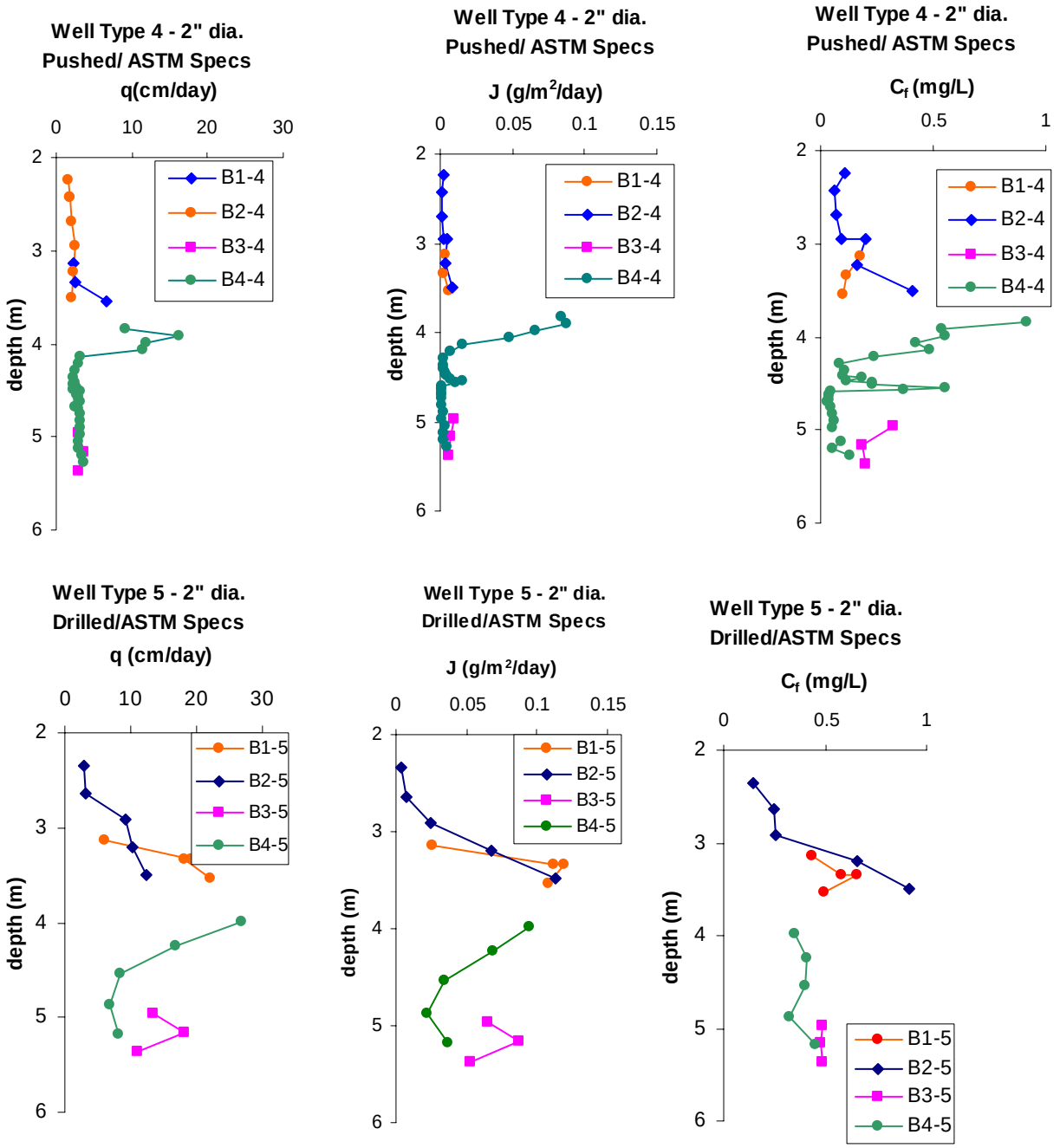


Figure 4-2 Groundwater fluxes, contaminant fluxes and flux-averaged concentrations for the five different well types.

4.3.4. Flux Comparison in Wells constructed using different techniques

Spatial patterns (Figure 4-2) of groundwater and contaminant fluxes are similar in wells constructed using different techniques. However, the absolute magnitudes of the fluxes are lower in the ¾ inch wells than the 2 inch wells with maximum flux being recorded by the 2 inch drilled wells (Table 4-4 and Figure 4-3). Bartlett et al. (2004) also observed that the drilled well measured higher conductivity than the pushed pre-packed wells (Figure 4-3). The drilling process may cause loosening of the soil, thus increasing hydraulic conductivity of the soil in the vicinity. Direct pushed wells on the other hand are installed in holes made by hammering and pushing rods into the ground, a process that can cause soil compaction and lower hydraulic conductivities in the vicinity. The relative disturbances caused by both these processes and thus the representativeness of the flux measurements made in pushed vs. drilled wells have to be investigated in greater detail.

Bartlett et. al (2004) also observed that the hydraulic conductivity for the naturally developed pushed well without pre-pack (Well Type 1) was higher than the other pushed wells and of similar magnitude with the conventional drilled wells. We, however, did not observe any significant difference in groundwater fluxes across the four pushed wells.

Table 4-4 Groundwater Fluxes estimated using PFM, slug test and borehole dilution test.

Well Type	q_{avg} (cm/day)	Location			
		1 (10'-12')	2 (7' - 12')	3 (16' - 18')	4 (12.5' - 17.5')
1 (3/4" dia. Pushed Wells - No Filter Pack)	PFM[1]		0.4	2.5	Lost
	Slug Test	4.0	3.8		
	BDT[2]		3.6	1.6	
2 (3/4" dia. Pushed Wells - ASTM Specifications)	PFM			1.2	4.8
	Slug Test	2.1		0.4	2.6
	BDT				12.21/46.63
3 (3/4" dia. Pushed Wells - "Conventional" 0.010 slot;20-40 sand)	PFM			0.6	2.0
	Slug Test				
	BDT				4.0
4 (2" dia. Pushed Wells - ASTM Specifications)	PFM	4.3	2.4	4.5	4.8
	Slug Test	1.2	0.4		
	BDT		1.1		3.2
5 (2" dia. Drilled Wells - ASTM Specifications)	PFM	25.6	8.9	13.5	14.7
	Slug Test	3.8	3.1		
	BDT	43.19/54.99	21.06/20.16	31.9	25.39/20.2

[1] Average flux was calculated from depth-varying PFM data using $q_{avg} = \frac{\int q dz}{\int dz}$ over the screen interval

[2] Borehole Dilution Test results calculated using a convergence factor of 2.

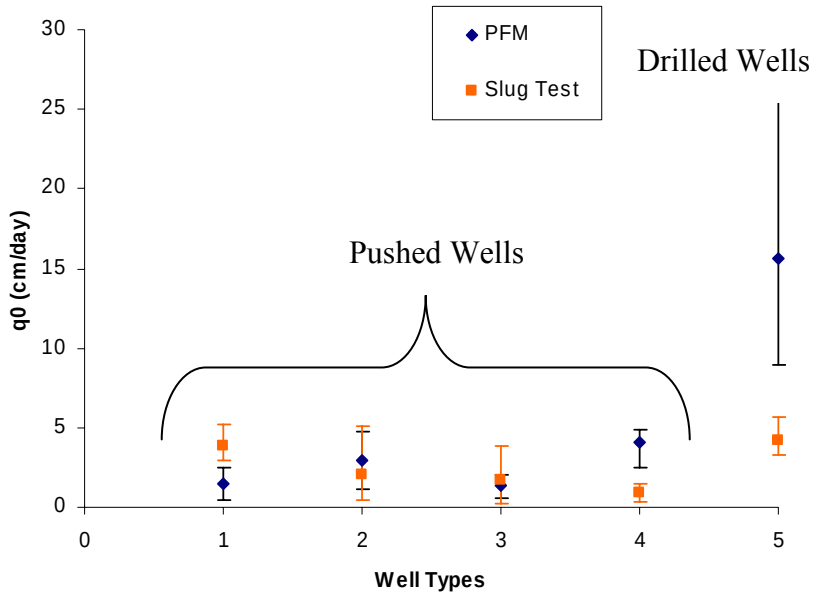


Figure 4-3 Depth Averaged Groundwater Flux (Error Bars represent the mean, minimum and maximum fluxes over all depths).

Table 4-5 Flux-averaged concentrations estimated from PFM compared with groundwater monitoring data

Well Type	C_f (ug/L)	Location			
		1 (10'-12')	**2 (7' - 12')**	**3 (16' - 18')**	**4 (12.5' - 7.5')**
1 (3/4" dia. Pushed Wells - No Filter Pack)	PFM		**438**	**638**	**lost**
	GW monitoring				
2 (3/4" dia. Pushed Wells - ASTM Specifications)	PFM			**389**	**1116**
	GW monitoring				
3 (3/4" dia. Pushed Wells - "Conventional" 0.010 slot; 20-40 sand)	PFM			**440**	**913**
	GW monitoring			**300**	
4 (2" dia. Pushed Wells - ASTM Specifications)	PFM	**118**	**191**	**233**	**364**
	GW monitoring		**520 (Apr 2004)/ 370 (July 2004)**	**580**	**550 (Apr 2004)/ 470 (July 2004)**
5 (2" dia. Drilled Wells - ASTM Specifications)	PFM	**560**	**581**	**483**	**385**
	GW monitoring		**230**		

Flux-averaged concentrations estimated from PFM were not significantly different for the five well construction types (Table 4-5). This confirms a previous study (NAVFAC, 2001) that concluded: (1) there was no significant difference in MTBE concentrations across the different well types, and (2) the chemical variability among well types was less than the variability associated with spatial heterogeneities due to wells screened at different depths or due to temporal variability.

4.3.5. Validation with Site Monitoring and Borehole Dilution Data

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. The groundwater fluxes estimated by PFM (Table 4-4) were compared with (1) borehole dilution test results (2) flux estimates made using pneumatic slug test conductivity values (Bartlett et al., 2004) and an average hydraulic gradient of 0.002. For most cases, the fluxes vary within a factor of 2 to 3.

Any measurement technique is subject to its own set of errors and assumptions like convergence factor, support volume, averaging time, etc. and thus these issues should be investigated in greater detail before any definite conclusion can be made. In the average, we can say that the groundwater fluxes compared well for the ¾ inch wells (Figure 4-3), but for the 2-inch wells, fluxes estimated from slug test results were significantly lower than the flux meter results, especially for the drilled 2" well. As mentioned before the drilling process causes loosening of the soil in the vicinity and it is possible that the PFM is more sensitive to local conductivity changes than the pneumatic slug test.

The groundwater and contaminant fluxes estimated are a function of the convergence factor α which as mentioned in the previous section is subject to uncertainty. However, the flux-averaged concentration C_f is independent of α (Equation 9) and is thus inherently a more robust estimate. The flux-averaged concentrations estimated from PFM results were within a factor of 3 of the groundwater monitoring data (Table 4-5).

The groundwater monitoring data were collected in April and July 2004. For wells B2-4 and B4-4 in which samples were collected in both these months, temporal fluctuations of concentrations were observed (Table 4-5). Thus, factor of 3 differences among the groundwater data and the PFM measurements which were done in December 2004 appear reasonable. Furthermore, C_f estimated using equation 9 represents a time-averaged concentration, while traditional groundwater samples represent 'instantaneous' measurements. Over the 9-day deployment period of PFM, approximately 24 liters of groundwater would have passed through the PFM (over the screen depth), and C_f is an average over that volume. In contrast, 2-3 well volumes (~6 to 9 liters) are bailed out before traditional groundwater sampling is done.

$$C_f = \frac{\int_A J dA}{\int_A q dA} = \frac{\int_A m_C dA}{\pi r^2 b \int_A \left(1 - \Omega_R\right) R_d dA} \tag{9}$$

4.3.6 Performance Assessment

The performance of the PFM was assessed based on criteria developed in section 4.2 and presented in Table 4-6.

Table 4-6 Expected and Actual Performance

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.
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Comparison water flux between well.	*Estimate within 25%*	*Direct comparison*	Usually within a factor of 2 for all Pushed wells
Comparison water flux to Slug test results and borehole dilution.	*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 MTBE flux between wells	*Estimate within 25%*	*Direct comparison*	Pushed well measured significantly lower fluxes than 2" wells
Comparison MTBE flux average concentration between wells	*Estimate within 25%*	*Direct comparison*	No significant differences between wells
Process Waste - Generated	*25 gallons*	*Observation*	15.3 gallons

* Refer to Appendix A for further details

Table 4-6 continued

SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	*No failures*	*Record keeping*	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.

4.3.7Conclusions

Groundwater and contaminant (MTBE) fluxes were measured in a cluster of wells constructed using five different techniques at an MTBE site in California. The purpose of the study was to measure spatially variable groundwater and contaminant fluxes and to investigate the effect of well construction type on flux measurements. The primary observations were:

vii. The depth variation in groundwater fluxes corresponded well with the stratigraphic information from the borehole logs as well as previous estimates made from slug tests and laboratory conductivity measurements (Kram et al., 2001; Bartlett et al., 2004).

viii. Definite depth pattern in the groundwater and contaminant fluxes could be observed even though measurements across different depth sections were taken at different locations within the cluster.

ix. The depth-averaged groundwater fluxes matched with previous slug tests and laboratory tests except for the 2” drilled wells in which the PFM technique resulted in a much higher flux estimate.

x. The pushed wells recorded a lower groundwater and contaminant flux than the drilled wells. A similar observation about pushed vs. drilled wells was made by Bartlett et al. (2004).

xi. The flux-averaged concentration C_f did not vary significantly between the pushed wells and the drilled wells, possibly because C_f is independent of the convergence factor. Kram et al. (2001) had observed statistically insignificant variation in MTBE concentrations in pushed vs. drilled wells as compared to spatial and temporal variation of the concentrations.

xii. Similar depth pattern was observed in groundwater flux, contaminant flux and flux-averaged concentrations.

5.0. Cost Assessment

5.1 Cost Reporting

For evaluating costs of site characterization methods we follow the guidelines of the EPA document "Innovation in Site Characterization: Interim Guide to Preparing Case Studies" (EPA-542-B-98-009). We report costs associated with the passive flux meter and the alternative using multilevel samplers and borehole dilution methods. This alternative approach is the only available method that most closely measured groundwater and contaminant mass flux. Reported fixed costs include general categories of capital costs needed for PFM deployment in regard to planning and preparation. In addition we report operational and variable costs including costs associated with mobilization/demobilization, labor, training, consumables, residual waste handling, sampling, and analysis. Finally, both total costs and unit cost per sample are provided.

The major categories of costs that have been tracked are provided in Tables 5-1 and 5-2 for the two approaches. In the analysis provided, we assume a deployment of PFMs in 3 wells each well having a screen interval of 10 feet. This produces a deployment of 30 linear feet. PFMs are constructed in five-foot long units therefore 6 PFMs are deployed. In the analysis, the vertical sampling interval selected is one foot thus a total of 30 data points providing both Darcy and contaminant flux results. This assessment is compared to a network of 25 multilevel sampling points, 3 extraction well points and modeled Darcy flux at the well locations. (For cost comparison, 30 points were assumed.)

The passive flux meter is the only technology that provides simultaneous measurements of both water and contaminant fluxes. The most prominent alternative technology is to measure groundwater contaminant concentrations through multilevel samplers and then calculate contaminant fluxes using groundwater fluxes estimated from borehole dilution tests. Many of the costs associated with the alternative technology are the same as those identified for the passive flux meter and are included in cost comparisons. The alternative technology has some capital and training expenses associated with purchasing and using equipment to perform borehole dilution tests and with acquiring equipment to collect multilevel samples. Both methods require fully screened wells and therefore the cost of installation for these is the same and not considered in this analysis. Also, the additional cost of installing multilevel samplers has not been considered here.

By varying the principal cost drivers of tables 5.1 and 5.2 which include 1) mobilization - demobilization, 2) labor and 3) analytical costs, the cost impacts can be determined. A 50% percent 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 MLS/BDH costs would alter the total cost by ~20%. Therefore, the unit cost per linear foot for the PFM method could range from $325 to $650; the unit cost per linear foot for the MLS/BDH method could range from $372 to $560.

Table 5-1. Cost tracking for PFM deployment. The costs considered here are for site characterization assuming 3 wells are sampled with 10 feet of screen in each well.

COST CATEGORY	Sub Category (3 wells - 30 linear feet)	Costs ($)
	FIXED COSTS	
1. CAPITAL COSTS	Operator Training For passive flux meter installation and sampling. Cost of $2500 per person. Amortize over 10 deployments.	$500
	Planning/Preperation (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 capitol) amortize over 10 major deployments	$1,000
	Environmental Safety Training ($1000/yr/person). Amortize over 10 deployments for two people	$200
	Sub-Total	$2340
	VARIABLE COSTS	
2. OPERATING COSTS	Operator Labor - 2 people are require 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 * 2 people *2 days *$80/hr)	$2560*
	Mobilization/demobilization Assumes 2 trips to and from the site, each requires 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 * 4hrs/trip * 2 people * $80/hr +2 *~$800)	$4200*
	Raw Materials Sorbent and resident tracers	$500
	Consumables, Supplies Sorbent, Socks, ancillary components of the Passive flux meter, and sample vials	$550
	Residual Waste Handling Consumed sorbent and socks	$1000
	Sampling and Analysis for contaminants and resident tracers retained on passive flux meter sorbent $100/sample	$3000*
	Sub-Total	$11,810
3. OTHER TECHNOLOGY-SPECIFIC COSTS	Data analysis. Six hours required.	$480
	Sub-Total	$14,630
TOTAL TECHNOLOGY COST	$14,630	
Unit Cost per linear foot (ft)	$488/ft	

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

5.2. Cost Analysis

The cost of measuring fluxes is compared with the baseline alternative technology (MLS and BHD). Table 5-2 provides estimates for the alternative technology.

5.3 Cost Comparison

The cost estimates for the PFM deployments and the MLS/BDH measurements indicate that the PFM method results in a lower unit cost per foot depending on cost variability. The cost of each approach is fairly scalable to larger and smaller deployments. Both approaches do have similar costs in terms of mobilization, materials, and analytical costs. However, contaminant flux values derived from MLS/BDH methods represent short-term evaluations that reflect current conditions and not long-term trends. 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. Another major advantage over the MLS/BHD method results from the lengthy time required to collect samples from MLS and to conduct borehole dilutions on site. Some cost savings may be realized by automating the borehole dilution method such that one operator can conduct multiple tests simultaneously. Also, the estimation of 2 hours per BDH test may be appropriate for sites with average or high groundwater velocities, but may be too small for lower velocity sites. In this case, BDH tests may be impractical to conduct. Obviously, site specific conditions can lead to changes in the cost estimates. In general, it is likely that for most conditions, costs for the two approaches would be comparable with future PFM method costs perhaps significantly lower depending on method refinements and cost driver variations.

Table 5-2. Cost Tracking for MLS and BHD deployment. The costs considered here are for site characterization assuming 3 MLS with one foot vertical sampling interval.

COST CATEGORY	Sub Category (3 MLS - 30 samples)	Costs ($)
	FIXED COSTS	
1. CAPITAL COSTS	Operator Training for BHD ($5000). Amortize over 10 sampling events	$500
	Planning/Perperation (assume 8 hours, $80/hr) Organizing supplies, site access, deployment duration, sorbent/tracers selection and approval	$640
	Equipment: Borehole dilution and MLS sampling equipment PFM packing equipment ($5,000). Amortize over 10 sampling events.	$500
	Environmental Safety Training ($1000/yr/person) Amortize over 10 sampling events.	$200
	Sub-Total	$1840
	VARIABLE COSTS	
2. OPERATING COSTS	Operator Labor 2 people are require to sample the MLS network 15 min per sample per person. (30 samples * 1/4 hr * $80/hr)	$560*
	Mobilization/demobilization Assume 1 trips to the site each 0.5 days of travel plus travel costs for 2 people. $80/hour labor, air fare, travel costs up to ~$800 per person. (2 trips * 4 hrs * 2 people *$80 +2*~$800)	$2100*
	Conduct BHD tests at 30 locations. Each test requires approximately 2 hours. (30 locations *2 hrs *$80/hr)	$4800
	Consumables, Supplies Sample vials gloves, tracers	$200
	Residual Waste Handling Purge water for MLS sampling	$1000
	Sampling and Analysis for contaminants in water samples $100/sample	$3000*
	Sub-Total	$11,660
3. OTHER TECHNOLOGY-SPECIFIC COSTS	Data analysis.	$480
	Sub-Total	$13,980
TOTAL TECHNOLOGY COST		$13,980
Unit Cost per linear foot (ft)		$466//ft

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

Note that because both PFM and MLS sampling involve short-term (less than 1 year) field operations, costs have not been discounted.

6.0. Implementation Issues

6.1. Environmental Checklist

Permission to introduce small quantities of tracers was obtained through California State agencies.

University of Florida is currently working on the development of a flux meter with a sorbent annulus to retain all tracer mass within meter. Furthermore, Campbell et al. (2006) present a new flux meter design that retains resident tracers.

6.2. Other Regulatory Issues

Contact with regulators was initiated after the site selected. Contact with consultants and the users of the technology continued throughout the project in order to avoid any problems in regulation.

6.3. End-User Issues

The technology was very simple to construct and implement. We experienced only minimal issues for transfer to end-users. Installations used in the demonstration were similar to the anticipated final product.

As we continue technology deployments, refinements are made and applied to future installations of the flux meter. These refinements may be site specific.

The PFM technology is now commercialized and the services are offered through EnviroFlux LLC, located in Gainesville, FL. First commercial deployment of PFM is underway at Cape Canaveral AS, FL.

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8.0. Points of Contact

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone/Fax/email	Role in Project
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P.S.C. Rao	School of Civil Engineering Purdue University West Lafayette, IN 47907-1284	Ph: (765)-496-6554 Fax: (765)-496-1107 pscr@purdue.edu	Co-PI

Dated Signature of Project Lead

Appendix A: Analytical Methods Supporting the Experimental Design

Details of, or references to, the analytical methods employed in sampling and analysis to determine the results of application (i.e. performance) of the technology.

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF ALCOHOL TRACERS (November 15, 1995)

SCOPE AND APPLICATION

1. This SOP describes the analytical procedures utilized by the Soil and Water Science Department, University of Florida, IFAS, for analysis of alcohols used as partitioning tracers in both lab and field studies in order to quantify the amount and distribution of residual non-aqueous phase liquids (NAPLs) present in the saturated zone.

2. This SOP was written by R.D. Rhue, Soil and Water Science Department, University of Florida, Gainesville, Fl. It is a modification of SOP-UF-Hill-95-07-0010-v.2, prepared by D.P. Dai, H.K. Kim, and P.S.C. Rao, Soil and Water Science Department, University of Florida. The SOP of Dai, Kim, and Rao was modified from a protocol provided to them by Professor Gary Pope at the University of Texas-Austin.

3. The alcohol tracers used in the UF lab and field studies are ethanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, 2,2-dimethyl-3-pentanol, and 6-methyl-2-heptanol.

4. The method involves gas chromatography (GC) analysis for alcohol concentrations in aqueous samples. A flame-ionization detector (FID) is used to quantify the analyte concentrations in the sample. The method has been found to provide reliable and reproducible quantitation of alcohols for concentrations > 1 ug/mL. This value may be considered the minimum detection level (MDL). The standard calibration curve for FID response has been found to be linear up to 3,000 ug/mL for ethanol.

5. Samples selected for GC-FID analysis may be chosen on the basis of preliminary screening which will provide approximate concentration ranges and appropriate sample injection volumes, standard concentrations, etc.

PURPOSE

The purpose of this SOP is to insure reliable and reproducible analytical results for alcohols in aqueous samples for laboratory-based or on-site (field-based) GC-FID analyses, and to permit tracing sources of error in analytical results.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 5-mL glass sample vials (Fisher Catalog # 06-406-19F) with teflon-faced septa caps. Glass vials and caps are not reused.

Sample Collection: Each field sample vial will be completely filled with liquid, such that no gas headspace exists, and capped. The vials will not be opened until the time for analysis.

Transportation and Storage: Field samples will be stored in coolers containing "blue ice", and later stored in refrigerators in a trailer located on the site. Samples may be subjected to on-site GC analysis, and/or shipped back to UF labs; samples will be packed in coolers and shipped via overnight air express (e.g., FedEx). The samples will be stored in the cold storage room or refrigerator at 4C, until GC analysis. After sub-sampling, the samples are returned to cold storage.

For lab studies, samples will be collected directly in 2 mL GC vials whenever possible and stored in a refrigerator if analysis is expected to take more than a day.

2. Sub-sampling and Dilution

Field samples will be sub-sampled into 2-ml vials for automated GC analysis. Disposable, Pasture glass pipets (Fisher Catalog # 13-678-20B) will be used to transfer samples from 5-mL sample vials to the 2-mL GC vials.

For samples needing dilution prior to GC analysis, a dilution of 1:10 should be sufficient. Dilutions will be made using double-distilled, deionized water.

3. Apparatus and Materials

Glassware: Disposable micro-pipets (100 uL; Fisher Catalog # 21-175B; 21-175F) and Class A volumetric pipets (1 or 2 mL) are required for sample dilution.

Disposable Pasteur glass pipets (Fisher Catalog # 13-678-20B) are required for sub-sampling.

GC vials (2-mL) with Teflon-faced caps (Fisher Catalog # 03-375-16A) are required for GC analysis.

Volumetric class A pipets and volumetric class A flasks are required for preparations of the calibration standards.

Gas Chromatograph System: An analytical GC system with a temperature-programmable oven, auto-injector capable of on-column injection, and either an integrator or a PC-based data acquisition/analysis software system are required. Also required are other accessories, including analytical columns and the gases required for GC-FID operation.

A Perkin Elmer Autosystem with an FID and an integrated autosampler will be used for analysis of field and laboratory samples. The Perkin Elmer system will be linked to an IBM-compatible PC loaded with Turbochrom (version 4.01) software.

A J&W Scientific DB-624 capillary column (30m X 0.53mm, 3 m film thickness) will be used. Zero-grade air and ultra-high purity hydrogen will be used for the FID. Ultra-high purity nitrogen or helium will be used for carrier gas.

4. Reagents

Deionized, Double-Distilled Water: Deionized, double distilled water is prepared by double distillation of deionized water in a quartz still. This water will be referred to as reagent water.

Alcohols: Certified ACS grade alcohols will be purchased from Fisher Scientific and used as received.

5. Standard Solutions

Stock Standard Solution: Analytical standards will be prepared from reagent chemicals by the laboratory. Stock standards each contain a single alcohol dissolved in reagent water and stored in 20 mL glass vials (Fisher Catalog # 03-393-D) with teflon-lined caps. These stock solutions will be kept in a refrigerator at 4 C. Fresh stock standards will be prepared every six months. The procedure for making stock standard solutions is essentially that given in the Federal Register, Rules and Regulations, Thursday, November 29, 1979, Part III, Appendix C, Section 5.10, "Standard Stock Solutions". The only modification of the procedure for the current study is that reagent water is used as the solvent in place of methanol.

Calibration Standards: Calibration standards will be prepared by diluting the stock standards in reagent water. Each calibration standard will contain each of the alcohols listed above. Five concentrations will be prepared that cover the approximate concentration range utilized in the partitioning tracer experiments.

6. QC blank Spike/Matrix Spike

Two 1 mL aliquots of the sample to be spiked will be transferred to clean vials. To one vial, 1 mL of reagent water will be added. To the second vial, 1 mL of a calibration standard will be added. The spike recovery will be calculated using the difference between the two measured concentrations and the known spike concentration.

7. Quality Control

GC injector septa will be changed every 80 to 100 injections, or sooner if any related problems occur.

Injector liner will be cleaned or changed every 80 to 100 injections or sooner if any related problems occur.

A method blank will be included in every 50 samples

A complete set of calibration standards (5) will be run at the beginning of each day and after every fiftieth sample.

One standard and a blank will be included in every 25 samples.

A sample spike and a blank spike will be included in every 50 samples.

8. Instrumental Procedures

Gas Chromatography: For J&W DB-624 Column:

Injection port temperature 200C
FID detector temperature 225C

Temp Program: Isothermal at 60C for 0 min; Ramp to 120C at 5 C/min.

9. Sample Preparation

Sub-sampling: Field samples will be transferred from the 5 mL sample vials to the 2 mL GC vials and capped with open-top, teflon-lined septa caps.

Dilution: Samples will be diluted if chromatographic peak areas for any of the alcohols exceed those of the highest calibration standard. One mL of sample will be added to an appropriate amount of reagent water to make the dilution.

10. Sample Analysis

Analysis: The samples will be allowed to reach ambient temperature prior to GC analysis.

Sample vials (2 mL) will be loaded onto the Perking Elmer GC auto-injector. A one uL injection volume will be used for both samples and standards.

Analyte Identification: Analyte identification will be based on absolute retention times. The analytes of interest should elute at their characteristic retention times within 0.1 minute for the automated GC system.

Analyte Quantitation: When an analyte has been identified, the concentration will be based on the peak area, which is converted to concentration using a standard calibration curve.

11. Interferences

Contamination by carry-over can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carry over, the injector syringe should rinsed with reagent water between samples.

Potential carry-over will be checked by running a highly concentrated sample, but one still within the standard concentration range, followed by a blank. A negligible reading for the blank will insure that carry-over has been minimized.

12. Safety

The main safety issue concerning the use of the GC at a field site relates to the compressed gases. The FID gases (hydrogen and air) form explosive mixtures. It is important to keep this in mind at all times, and be aware of the hazard potential in the event of an undetected hydrogen leak. All gas connections will be properly leak tested at installation.

High-pressure compressed-gas cylinders will be secured to a firm mounting point, whether they are located internally or externally.

Gas cylinders should preferably be located outside the trailer on a flat, level base, and the gas lines run inside through a duct or window opening. If the gases are located outside, then some form of weatherproofing for the gauges will be necessary. As a temporary measure, heavy-duty polyethylene bags, secured with tie-wraps, have been used successfully; this may not be very elegant but it is very effective for short-term use of the GC. A more permanent protective housing must be built if the GC is located at the trailer for an extended time period.

The main operating drawback to locating the gas cylinders externally is that it is not easy to monitor the cylinder contents from inside. The gas which could be used up most quickly is air for the FID, particularly if two instruments are hooked up to the same supply and they are running continuously. A reserve cylinder of air should be available at all times to prevent down time.

If it is not possible to arrange external citing easily, the gas cylinders should be secured to a wall inside the trailer.

It is a good laboratory operating practice to make sure the flame is attended at all times.

When it is necessary to change the injection liner on the GC, the detector gases should be shut off.

The column must be connected to the detector before igniting the flame.

The trailer should be kept well ventilated when using the GC.

Reference to the Materials Safety Data Sheets (MSDS) will be made for information on toxicity, flammability, and other hazard data.

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF TARGET ANALYTES IN GROUNDWATER SAMPLES (February 20, 1996)

SCOPE AND APPLICATION

1. This SOP describes the analytical procedures utilized by the Department of Environmental Engineering Sciences, University of Florida, for analysis of target analytes in groundwater samples from both lab and field studies. This analysis provides characterization of existing site and lab column aqueous contamination both before and following flushing technology applications.

2. This SOP was written by M.D. Annable, Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL. It is a modification of SOP-UF-Hill-95-07-0012-v.2, prepared by D.P. Dai and P.S.C. Rao, Soil and Water Science Department, University of Florida.

3. The selected constituents are benzene, toluene, o-xylene, 1,1,1-trichloroethane, 1,3,5,-trimethylbenzene, 1,2-dichlorobenzene, decane, and naphthalene.

4. The method involves gas chromatography (GC) analysis for target analyte concentrations in aqueous samples. Headspace analysis with a flame-ionization detector (FID) is used to quantify the analyte concentrations in the sample. The method has been found to provide reliable and reproducible quantitation of the above constituents for concentrations > 5 ug/L. This value may be considered the method detection level (MDL).

5. Samples selected for GC-FID analysis may be chosen on the basis of preliminary screening which will provide approximate concentration ranges and appropriate sample injection times, and standard concentrations, etc.

PURPOSE

The purpose of this SOP is to insure reliable and reproducible analytical results for soluble NAPL constituents in aqueous samples for laboratory-based GC-FID analyses, and to permit tracing sources of error in analytical results.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 20-mL glass sample vials (Fisher Catalog # 03-340-121) with teflon-faced rubber backed caps. Glass vials and caps are not reused.

Sample Collection: Each field sample vial will be completely filled with liquid, such that no gas headspace exists, and capped. The vials will not be opened until the time for analysis.

Transportation and Storage: Field samples will be stored in coolers containing "blue ice", and later stored in refrigerators in a trailer located on the site. Samples will be sent to UF labs packed in coolers and shipped via overnight air express (e.g., FedEx). The samples will be stored in the cold storage room or refrigerator at 4C, until GC analysis. After sub-sampling, the samples are returned to cold storage.

For lab studies, samples will be collected directly in 20 mL Headspace vials whenever possible and stored in a refrigerator if analysis is expected to take more than a day.

2. Sub-sampling and Dilution

Field samples will be sub-sampled placing 10-ml into 20-ml headspace vials containing 2 g of sodium chloride for automated GC analysis. Pipets will be used to transfer samples from 20-mL sample vials to the 20-mL GC headspace vials.

3. Apparatus and Materials

Glassware: Glass pipettes are required for sub-sampling.

GC headspace vials (20-mL) with Teflon-faced caps are required for GC analysis.

Volumetric class A pipettes and volumetric class A flasks are required for preparations of the calibration standards.

Gas Chromatograph System: An analytical GC system with a temperature-programmable oven, headspace sample injection system, and either an integrator or a PC-based data acquisition/analysis software system are required. Also required are other accessories, including analytical columns and the gases required for GC-FID operation.

A Perkin Elmer Autosystems with an HS40 Auto-headspace sampler and a FID will be used for analysis of field and laboratory samples. The Perkin Elmer system will be linked to an IBM-compatible PC loaded with Turbochrom (version 4.01) software.

A J&W Scientific DB-624 capillary column (50m X 0.53mm, 3 m film thickness) will be used. Zero-grade air and high purity hydrogen will be used for the FID. Ultra-high purity nitrogen or helium will be used for carrier gas.

4. Reagents

Deionized, Double-Distilled Water: Deionized, double distilled water is prepared by double distillation of deionized water in a quartz still. This water will be referred to as reagent water.

5. Standard Solutions

Stock Standard Solution: Analytical standards will be prepared from reagent chemicals by the laboratory. Stock standards will each contain a single analyte dissolved in methanol and stored in 20 mL glass vials (Fisher Catalog # 03-393-D) with teflon-lined caps. These stock solutions will be kept in a refrigerator at 4 C. Fresh stock standards will be prepared every six months. The procedure for making stock standard solutions is essentially that given in the Federal Register, Rules and Regulations, Thursday, November 29, 1979, Part III, Appendix C, Section 5.10, "Standard Stock Solutions".

Calibration Standards: Calibration standards will be prepared by diluting the stock standards in water. Each calibration standard will contain each of the eight analytes listed above. Five concentrations will be prepared that cover the approximate concentration range from 0 to 20 mg/L.

6. QC blank Spike/Matrix Spike

Two 1 mL aliquots of the sample to be spiked will be transferred to clean vials. To one vial, 1 mL of reagent water will be added. To the second vial, 1 mL of a calibration standard will be added. The spike recovery will be calculated using the difference between the two measured concentrations and the known spike concentration.

7. Quality Control

A method blank will be included in every 50 samples

A complete set of calibration standards (5) will be run at the beginning of each day and after every fiftieth sample.

One standard and a blank will be included in every 25 samples.

A sample spike and a blank spike will be included in every 50 samples.

8. Instrumental Procedures

Gas Chromatography: For J&W DB-624 Column:

Headspace sample temperature	90C
Injection needle temperature	100C
Transfer line Temperature	110C
FID detector temperature	225C
Carrier gas pressure	8psi

Temp Program: Isothermal at 50C for 0 min; Ramp to 200C at 5 C/min; hold for 10 min.

9. Sample Preparation

Sub-sampling: Field samples will be transferred from the 20 mL sample vials to the 20 mL GC headspace vials and capped with open-top, teflon-lined septa caps.

Dilution: Samples will be diluted if chromatographic peak areas for any of the analytes exceed those of the highest calibration standard. One mL of sample will be added to an appropriate amount of reagent water to make the dilution.

10. Sample Analysis

Analysis: Sample headspace vials (20 mL) will be loaded onto the Perking Elmer HS40 auto-sampler. Samples will be pressurized for 1 min followed by a 0.1 minute injection time and a withdrawal time of 0.5 minute.

Analyte Identification: Analyte identification will be based on absolute retention times. The analytes of interest should elute at their characteristic retention times within ±0.1 minute for the automated GC system.

Analyte Quantitation: When an analyte has been identified, the concentration will be based on the peak area, which is converted to concentration using a standard calibration curve.

11. Interferences

Contamination by carry-over can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carry over, the injector needle should purged with carrier gas between samples.

Potential carry-over will be checked by running a highly concentrated sample, but one still within the standard concentration range, followed by a blank. A negligible reading for the blank will insure that carry-over has been minimized.

12. Safety

The main safety issue concerning the use of the GC relates to the compressed gases. The FID gases (hydrogen and air) form explosive mixtures. It is important to keep this in mind at all times, and be aware of the hazard potential in the event of an undetected hydrogen leak. All gas connections will be properly leak tested at installation.

High-pressure compressed-gas cylinders will be secured to a firm mounting point, whether they are located internally or externally.

When it is necessary to change the injection liner on the GC, the detector gases should be shut off.

The column must be connected to the detector before igniting the flame.

Reference to the Materials Safety Data Sheets (MSDS) will be made for information on toxicity, flammability, and other hazard data.

STANDARD OPERATING PROCEDURE FOR EXTRACTION OF ANALYTES FROM FLUX DEVICE SORBENTS (October 10, 2001)

SCOPE AND APPLICATION

1. This SOP describes the procedures used by the Department of Environmental Engineering Sciences, University of Florida, for extraction of target analytes (including tracers) from sorbents used in flux devices inserted in monitoring wells.

2. This SOP was written by M.D. Annable, Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL.

3. The selected constituents are MTBE, PCE, and alcohol tracers:

Methanol
Ethanol
2-propanol (IPA)
2-methyl-1-propanol (IBA)
2-methyl-2-propanol (TBA)
n-propanol
n-butanol
n-pentanol
n-hexanol
n-heptanol
3-heptanol
n-octanol
2-octanol
2,4-dimethyl-3-pentanol
2-ethyl-1-hexanol
3,5,5-trimethyl-1-hexanol
6-methyl-2-heptanol
2,6-dimethyl-2-heptanol
n-decane

Potential Sorbents include:

Liquid (mixed in a sand matrix at a pore volume saturation of 10%)
Tetradecane
Heptadecane
Hexadecane

Solid
Activated Carbon
Surfactant modified zeolytes

4. The method involves liquid extraction in 20 or 40 ml VOA vials using organic solvents.

PURPOSE

The purpose of this SOP is to insure reliable and reproducible analytical results. Extracted constituents will be quantified suing analytical methods described in other SOPs.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 20-mL or 40-ml glass sample vials (Fisher Catalog # 03-340-121) with Teflon-faced rubber backed caps.

Sample Collection: Each field sample vial will be partially filled with the extraction solvent (alcohol IPA, IBA, etc. or Methylenechloride) using a pipet or repeating volume dispenser. Typically 10 or 20-ml of solvent will be used.

Transportation and Storage: Field samples will be stored in coolers containing "blue ice", and later stored in refrigerators in a trailer located on the site. Samples will be sent to UF labs packed in coolers and shipped via overnight air express (e.g., FedEx). The samples will be stored in the cold storage room or refrigerator at 4C, until GC analysis. After sub-sampling, the samples are returned to cold storage.

For lab studies, samples will be collected directly in 20 mL Headspace vials whenever possible and stored in a refrigerator if analysis is expected to take more than a day.

2. In the laboratory, samples will be rotated for a minimum of 8 hours on a rotator (Glass-Col model RD 4512).

3. Sub-sampling and Dilution

Field samples will be sub-sampled into 2 ml GC vials. Pipets will be used to transfer samples from 20-mL sample vials to the 2-mL GC vials.

3. Apparatus and Materials

Glassware: Glass pipets are required for sub-sampling.

Safety

Gloves and eye protection will be worn during all extraction activities.

Reference to the Materials Safety Data Sheets (MSDS) will be made for information on toxicity, flammability, and other hazard data.

Appendix C: Quality Assurance Project Plan (QAPP)

C.1. Purpose and Scope of the Plan
This Quality Assurance plan is written to cover activities associated with testing the PFM at the Port Hueneme site. The plan focuses on field installation, sampling and processing of data from the PFMs.

C.2. Quality Assurance Responsibilities
The responsibility for QA will be shared by Kirk Hatfield and Mike Annable at the University of Florida. During field activities one of the PI's will be present to oversee QA procedures. Other personnel present during field sampling activities will include graduate students or post-doctoral researchers from the University of Florida, Purdue University, and the University of Waterloo.

C.3. Data Quality Parameters
This section discusses measures to be taken to ensure the representativeness, completeness, comparability, accuracy, and precision of the data.

<u>Accuracy</u>

Accuracy is defined as the closeness of the results to the true value.

The percent recoveries of surrogates, QC check standards, and matrix-spiked analytes are used to evaluate the accuracy of an analysis. The percent recovery represented by X can be calculated using the following equations:

For surrogates and QC check standards:

$$X = \frac{SSR}{SA} x\ 100$$

For matrix spikes:

$$X = \frac{SSR - SS}{SA} \times 100$$

where:

SSR = Spiked sample result
SS = Sample result
SA = Spike added from spiking mix

The mean percent recovery (X) is defined by:

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i}{N}$$

where:

X_i = The percent recovery value of a spike replicate
N = Number of spikes

Precision

Precision is a measure of the mutual agreement among individual measurements of the same parameters under prescribed similar conditions.

The analytical precision is determined using results from duplicate or replicate analyses of samples and from matrix spike results for a given matrix. The Relative Percent Difference (RPD) is used to evaluate the precision of duplicate analyses. Relative Percent Difference is defined in the following equation:

$$\%RPD = \frac{2(X1 - X2)}{\overline{x}} \; x\ 100$$

X1 = First duplicate value
X2 = Second duplicate value

When replicate analyses are performed, precision is measured in terms of the Standard Deviation (SD) which is defined in the following equation:

$$S = \sum_{i=1}^{N} \left[\frac{(X_i - \overline{X})^2}{N - 1} \right]^{‰}$$

where:

X_i = The recovery value of a spike replicate
X = Arithmetic average of the replicate values
N = Number of spikes

Completeness

Completeness is defined as the percent of parameters falling within acceptance criteria and the results subsequently reported. A goal of 95 percent completeness has been set for all samples.

The general requirement of this quality assurance program is to analyze a sufficient number of standards, replicates, blanks, and spike samples to evaluate results adequately against numerical QA objectives.

C.4 Calibration Procedures, Quality Control Checks, and Corrective Action

The focus of the following section is to describe initial and continuing calibration procedures for analytical instrumentation, duplicate and control testing and data reduction, validation, and reporting.

Supplies and Quality Control Materials

All supplies (i.e., glassware, chemicals, reagents) used will be of the best possible quality to ensure proper instrument calibration and avoid contamination. All reagents used are prepared from Analytical Reagent Grade (AR) chemicals or higher purity grades, unless such purity is not available. The preparation of all reagents will be documented, including source, mass, and dilutions. Each reagent will be clearly labeled with the composition, concentration, date prepared, initials of preparer, expiration date, and special storage requirements, if any.

Reagents

Reagent solutions are stored in appropriate glass, plastic, or metal containers. Reagents are stored under conditions designed to maintain their integrity (refrigerated, dark, etc.). Shelf life is listed on the label and the reagent is discarded after it has expired. Dry reagents such as sodium sulfate, silica gel, alumina, and glass wool are either muffled at 400°C or extracted with solvent before use for organic chemical analyses. Water used in the laboratory is glass distilled or deionized, and periodically checked for purity. In addition, water used in the organics area is carbon-filtered or purchased as HPLC grade. All organic solvents used are either glass-distilled or pesticide grade. Solvents and reagent solutions are checked for contamination by employing reagent blanks, before use in any analysis.

Quality Control Reference Materials

All Quality Control Reference Materials are acquired only from authorized vendors or sources commonly used by U.S. EPA Regional Laboratories.

Standards Traceability

When standard reference materials arrive at the laboratory, they are registered in a bound log book, "Standards Notebook for Neat Materials and Primary Solutions." An example of a logging sequence is used to illustrate this process.

(1-S-XXX-12-4) (label and log sequence)

Where:

1 = Notebook log number
S = Standard Notebook--"Neat and Primary Standards"
XXX = Receiving analyst's initials
12 = Notebook page
4 = Entry number on notebook page

All working standards prepared at the site lab are logged in the "Standards Notebook for Intermediate and Working Standards." A similar labeling convention has been adopted for classifying these working standard materials. An example is given below.

1-W-XXX-6-5 (label and log)
Where:
1 = Number of notebook
W = Standards notebook - "Intermediate and Working" Standard
XXX = Analyst's initial
6 = Page Number
5 = Page entry number in sequence

Instrument Calibration

Every instrument used to analyze samples must pass the calibration criteria established in the appropriate SOP. Initial calibration criteria for instrument linearity, sensitivity, resolution, and deactivation must be met before samples can be analyzed. Sustained performance is monitored periodically during sample analyses by the use of continuing calibration check standards.

GC Section

Initial Calibration

The linear calibration range of the instrument must be determined before the analysis of any samples. Gas chromatographic conditions used for sample analyses are used during calibration.

The calibration is performed in accordance with the SOP derived from the methods used. For most GC analyses, a 5-level calibration is run. The concentrations of the standards must bracket the linear range of the instrument. Calibration using fewer than 5-levels is done only when specifically allowed by the method.

Relative Retention Times and Relative Response Factors

Instrument calibration and sample analysis must be performed using appropriate internal standards to establish relative retention times (RRT) and relative response factors (RRF) where required. Internal standards appearing in a chromatogram will establish primary search windows for those target compounds nearby in the chromatogram. RRT are calculated using this equation:

$$RRT = \frac{RT^{target}}{RT^{is}}$$

The RRF may be calculated as follows:

$$\text{Absolute Response Factor} = RF = \frac{\text{Area}}{\text{Amount}}$$

Note: Amount in this equation refers to the mass (e.g. ug) of compound mixed into the solution injected.

Each calibration standard is analyzed and the RRF is calculated for each analyte according to the following equation:

$$RRF = \frac{A_s \, x \, C_{is}}{A_{is} \, x \, C_s}$$

A_s = Area of analyte
A_{is} = Area of internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of analyte

Note: Certain data processors may calculate the RRF differently.

The standard deviation (SD) and the % coefficient of variation (CV) of RRFs for the compounds are calculated using the following equations:

$$S = \sum_{i=1}^{N} \left[\frac{(RRF_i - RRF_m)^2}{N - 1} \right]^{‰}$$

Where:

RRF_i	=	Individual RRF
RRF_m	=	Mean RRF
N	=	Number of RRFs

and

$$\%CV = \frac{S \ x \ 100}{RRF_m}$$

Coefficient of Variation

The %CV of each compound must be less than 30 percent. This criterion must be achieved for the calibration to be valid.

If the %CV is less than 20 percent, the RRF of the compound can be assumed to be invariant, and the average RRF can be used for calculations.

If the %CV is between 20 percent and 30 percent, calculations must be made from the calibration curve. Both the slope and the intercept of the curve must be used to perform calculations.

Initial Calibration Verification

The calibration curve must be validated further by analyzing a QC check sample. The QC check sample must be obtained from EPA, another vendor, or it must be from another lot number. The QC check sample verifies the validity of the concentrations of the standards used to obtain the initial calibration.

All analytes in the QC check standard must be recovered within 80 to 100 percent. If any analyte exceeds this criterion, then a new calibration curve must be established. All sample results for a target analyte can be reported only from valid initial calibrations.

Continuing Calibration

The working calibration curve or RRF for each analyte must be verified daily by the analysis of a continuing calibration standard. The ongoing daily continuing calibration must be compared to the initial calibration curve to verify that the operation of the measurement system is in control.

The continuing calibration check must be performed during each day of analysis to verify the continuing calibration of the instrument. A day is defined as 24 hours from the start run time of the last valid continuing calibration. Generally, a continuing calibration check sample is injected every 10 samples.

Verification of continuing calibration is performed by the analysis of a midpoint standard containing all of the analytes of interest. Verification of continuing calibration of the measurement system is done by calculating the percent difference (%D) of the continuing calibration RRF from the mean RRF from the initial calibration curve using the following equation:

$$\%D = \frac{(RRF_m - RRF) \times 100}{RRF_m}$$

Where:

RRF_m = The mean relative response factor from the initial calibration curve

RRF = The relative response factor from the continuing calibration standard

The %D must meet the acceptance criteria established in the appropriate SOP. If these criteria are exceeded, a new calibration curve must be established.

Other Calibrations

Weekly calibrations are performed for equipment such as balances, thermometers, ovens, incubators, and dissolved oxygen (D.O.) meters that are required in analytical methods, but which are not recorded in a dedicated QA instrument log.

Balances

Balances are checked with Class S weights on a daily basis. Before a weighing session, the analyst is required to perform at least one calibration check in the range of the material to be weighed. This value is also recorded on the specific balance control chart and must be within the control limit. The criteria for calibration checks are given in Table E.1.

Table C.1. **CRITERIA FOR BALANCE CALIBRATION CHECKS**

Analytical Balances		
Class S Weight (grams)	Warning Level (grams)	Control Level (grams)
0.0100	0.0098-0.0102	0.0097-0.0103
0.1000	0.098-0.102	0.097-0.103
1.000	0.995-1.005	0.990-1.010
10.000	9.995-10.005	9.990-10.010
50.00	49.98-50.02	49.95-50.05

Top Loading Balances		
1.00	0.95-1.05	0.90-1.10
10.0	9.9-10.1	9.8-10.2
50.0	49.7-50.3	49.5-50.5

Incubators, ovens, and waterbaths

Temperatures are checked daily with an NBS grade thermometer and necessary adjustments made as required. All temperature readings are recorded and posted on the appropriate equipment.

DO meters

DO meter is calculated daily using a modified Winkler technique. The Winkler solution is titrated against 0.025N sodium thiosulfate.

Conductivity bridges

Conductivity meter is standardized daily against a solution of KCl to obtain a new cell constant.

pH meters

The pH meter is standardized daily using buffers at pH of 4, 7, and 10.

Refrigerators

Refrigerators are maintained at 4°C, with control levels ranging from 1°C to 10°C. A temperature reading is taken each workday morning immediately after unlocking the refrigerator. The temperature reading is recorded and entered on the control chart posted on the door of the refrigerator. If a trend is apparent or if the temperature is outside the acceptable range, the Lab Manager is notified so that corrective action can be initiated if required.

Freezers

Freezers are maintained at -10°C, with control levels ranging from 0°C to -35°C. A temperature reading is taken each workday morning immediately after unlocking the freezer. The temperature reading is recorded and entered on the control chart posted on the door of the freezer. If a trend is apparent, or if the temperature is outside the acceptable range, the Lab Manager is notified so that corrective action can be initiated if required.

Calibration Standards

All calibration standards, including internal standards used in LMG, are obtained from chemical suppliers with certificates of high purity and concentration.

Traceability

All standards are traceable to the National Institue of Standards and Testing (NITS) Standard Reference Materials (SRM) or to the U.S. EPA Reference Standards.

Working Standards

The commercial standards are used as stock standards. Working standards are made from the stock standards at appropriate concentrations to cover the linear range of the calibration curve. The working standards are used for initial calibration curves, continuing calibration checks, and preparation of analyte spiking solutions as appropriate for a particular analysis. All stock and working solutions are uniquely identified, dated, labeled, and initialed.

Standards Logbook

All stock solutions are given a unique code number and are entered into a bound "Primary Standards" logbook. The name of the compound and other pertinent information, including concentration, date of receipt, and analyst's name, are also entered.

Working standards are given a unique code number that allows them to be traced to a specific stock solution. The working standard is entered in a "Working Standards" logbook with analyst's name, date and method of preparation, and other pertinent information.

CORRECTIVE ACTIONS

Laboratory Imposed

Corrective actions will be initiated if the quality control criteria indicate an analysis is out of control.

- Check calculations for accuracy
- Check instrumentation to ensure it is operating properly. Recalibrate if necessary.
- Remake standards and reagents and reanalyze samples.
- Re-prep and re-analyze samples.

The analyst is responsible for initiating corrective actions for analytical problems encountered during analysis of samples. Most problems which occur and are corrected during the analytical run will be explained in the run log or analytical bench sheet for that run. A corrective action

report (CAR) may be necessary for some problems encountered, such as complete system failure, chronic calibration failure, or severe matrix interferences.

During data review, the reviewer may initiate corrective actions based on problems or questions arising from the review. A CAR will be initiated.

The Laboratory Manager may initiate corrective actions if a problem is noticed during a QC review of data, a system audit, or a performance audit. A CAR will be initiated.

CARs are signed and dated by Project Manager, and by the Laboratory Manager. CARs will be filed in appropriate department files and in the Lab Manger's files.

Agency Imposed

Any actions deemed necessary by regulatory agencies, such as EPA, will be taken. These actions are most likely to arise from a systems or performance audit, or from data review conducted by the agency.

Corrective Action Reports

Corrective Action Reports

The field laboratory will have a Corrective Action System that ensures the proper documentation and dispositions of conditions requiring corrective action. The system will also ensure that the proper corrective action is implemented to prevent recurrence of the condition. Figure 13.1 shows a corrective action report form.

Situations Requiring Corrective Action Reports

The Corrective Action System applies to all situations that affect data quality. These situations include, but are not limited to, quality control criteria being exceeded, statistically out-of-control events, deviations from normally expected results, suspect data, deviations from the standard operating procedure, and special sample handling requirements. Corrective actions may also be initiated as a result of other QA activities, such as performance audits, systems audits, laboratory/interfield comparison studies, and QA project-related requirements of certifying agencies such as EPA.

Corrective Action Procedures

The procedure requires documenting the condition requiring corrective action on a Corrective Action Report and implementing corrective action based on the results of the investigation performed to determine the cause of the condition (Table E.2).

When a condition requiring corrective action arises, the Corrective Action Report is initiated. The initiator describes the condition requiring corrective action. An investigation, if necessary,

is conducted to determine the cause of the condition. A corrective action is recommended based on the results of the investigation. The Corrective Action Report is reviewed by the Project Manager and the Field Site Manager who either approve the recommended corrective action or indicate a different corrective action. The originator has the responsibility of following up to be sure that the corrective action is implemented. Implementation of the corrective action is documented by the Corrective Action Report being signed and dated by the person who implemented the corrective action.

Table C.2
Corrective Actions

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial instrument blank	Instrument response <MDL response	Prepare another blank, if same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc.
Initial calibration standards	Coefficient of variation >0.99995 or standard concentration value ± 10% of expected value	Reanalyze standards. If still unacceptable, then remake standards
QC Check Standard	± 10% of expected value	Reanalyze standard. if still unacceptable, then remake standards, or use new primary standards if necessary
Continuing calibration Standards	± of expected value	Reanalyze standard. If still unacceptable, then recalibrate and rerun samples from the last cc stnd. Check
Method blank	<MDL	Reanalyze blank. If still positive, determine source of contamination. If necessary, reprocess (i.e., digest or extract) sample set
Initial calibration Standards (GC/MS)	RRF <30%	Reanalyze standards. If still unacceptable, prepare new standards.
Surrogate recovery (GC/MS Semivolatiles)	0 or 1 outside CLP criteria	Re-extract and/or re-analyze
Surrogate recovery (GC/MS volatiles)	0 outside criteria	Re-analyze

Table C.3
Corrective Action Report Criteria for Control Charts

Criteria	Corrective Action
A point outside ±3 standard deviations	Attempt to determine the source of the problem. Verbally report the deviation and results of preliminary investigation to the Field Site Manager, who will decide jointly what action to take. After implementing corrective action, complete the Corrective Action Report and submit it to the Project Manager and the Field Site Manager for approval.
Three consecutive points accuracy outside ± standard deviation	Conduct investigation. Check accuracy of data input, calculations, instrument, standards, etc., to locate the source of the problem. Document results in a Corrective Action Report. Have the report approved by the supervisor. No results can be reported until the Corrective Action Report has been approved. Send a copy of the Corrective Action Report and a copy of the QC chart to the Field Site Manager.
Obvious outlier.	Conduct investigation. Check accuracy of data input, calculations, dilutions, instrument, standard, etc.. present initial findings to the Field Site Manager. They will jointly decide what actions need to be taken. Document the results in a Corrective Action Report and have it approved by the Field Site Manager. No results can be reported until the Corrective Action Report is approved. Send a copy of the Corrective Action report and a copy of the control chart to the Field Site Manager.
Obvious shift in the mean.	Conduct investigation. Check calculations, data entry, standards, instrument, calibrations, etc. Document results in a Corrective Action Report. Have the Corrective Action Report approved by the Field Site Manager. No results can be reported until the report is approved. Send a copy of the Corrective Action Report and a copy of the QC chart to the Field Site Manager.

C.5 Demonstration Procedures

Initiating the PFM experiments will involve limited field effort. All of the components of the device can be prepared prior to field activities. In the field, the primary activity will be assembly of the PFMs which can be completed with two people in a mater of minutes. Extraction and sub-sampling also required fairly minimal time and personnel. Only the controlled flow flume experiments will require establishing steady flow from one end of the flume using peristaltic pumps. These pumps will be calibrated in the field using simple time and volume measurements. Periodic flow measurements will be made to determine total average flow.

Samples collected at the OU2 site will be sent to the University of Florida for analysis. In the laboratory, instrument maintenance will include the following.

Maintenance Schedule

Preventive maintenance, such as lubrication, source cleaning, and detector cleaning, is performed according to the procedures delineated in the manufacturer's instrument manuals.

The frequency of preventive maintenance varies with different instruments. Routine maintenance performed includes cleaning and/or replacement of various instrument components. In general, the frequency recommended by the manufacturer is followed. In addition to the regular schedule, maintenance is performed as needed. Precision and accuracy data are examined for trends and excursions beyond control limits to determine evidence of instrument malfunction. Maintenance is performed when an instrument begins to degrade as evidenced by the degradation of peak resolution, shift in calibration curves, decreased ion sensitivity, or failure to meet one or another of the quality control criteria. Table E.4 lists routine equipment maintenance procedures and frequency.

Instrument maintenance logbooks are maintained in the laboratory at all times. The logbook contains a complete history of past maintenance, both routine and non-routine. The nature of work performed, the date, and the signature of the person who performed the work are recorded in the logbook. Preventive maintenance is scheduled according to each manufacturer's recommendation. Instrument downtime is minimized by keeping adequate supplies of all expendable items on hand. Expendable items are those with an expected lifetime of less than one year. Routine instrument preventive maintenance is handled by the instrument operator. Repair maintenance is performed by a full-time electronics technician, or by the manufacturer's service personnel.

Table C.4
PREVENTIVE MAINTENANCE

Instrument	Activity	Frequency
Gas Chromatograph	Change septum Check carrier gas Change carrier gas Change in-line filters Perform ECD wipe test Clean ECO Check system for leaks Clean/replace injection point liner Clean/replace jet tip Service flame photomeric detector	As needed Daily As needed As needed As license requires Return to vendor as needed As needed As needed As needed As needed
IR	Change desiccant Electronics maintenance	Every six months Every six months
UV	Clean and align optics Replace lamp Calibrate	Annually As needed Weekly
pH Meter	Calibrate Check fluid in probe	Daily Daily
D.O. Meter	Clean and replace membrane and HCl solution Calibrate	Daily Daily
Balance	Calibrate Maintenance	Daily Annually
Ovens	Temperature checks	Daily
Refrigerators and Freezers	Temperature checks	Daily
COD Heating Block	Check temperature with NBS thermometer	As needed
Conductivity Meter	Standardize with KCl Check probe visually	Daily Daily

C.6 Calculation of Data Quality Indicators

The focus of this section is to present methods of calculating data quality that will be used for this project.

Control Samples

The laboratory will employ control samples to assess the validity of the analytical results of the field samples. Determination of the validity of field sample results is based on the acceptance criteria being met by the control sample. The acceptance criteria for each type of control sample

are delineated in the appropriate SOP. These acceptance criteria are based on the laboratory's statistical process capabilities determined from historical data, and meet the EPA CLP acceptance criteria as a minimum. Often, in-house criteria are more stringent than required by CLP. The control samples are analyzed in the same manner as the field samples. They are interspersed with the field samples at frequencies that are specified by the appropriate SOP.

Method Blank Analyses

A method blank is a "clean" sample (i.e., containing no analyte of concern), most often deionized water, to which all reagents are added and analytical procedures are performed. Method blanks are analyzed at a rate of one per sample lot or at least every 20 samples. The blank is analyzed in order to assess possible contamination from the laboratory or the procedure. If the analyte of interest is found in the blank at above reporting levels, inorganic analysis is suspended until the source of contamination is found and corrective action is taken. The Laboratory Manager is notified when blank results are unacceptably high, and may assist in the investigation.

Surrogate Spike Analyses

For certain an analysis, such as those performed by GC/MS, each sample and blank is spiked with one or more surrogate compounds before preparatory operations (e.g., purging or extraction). These surrogate standards are chosen for properties similar to sample analytes of interest, but are usually absent from the natural sample.

Surrogate spikes evaluate the efficiency of the analytical procedure in recovering the true amount of a known compound.

The results of surrogate standard determinations are compared with the true values spiked into the sample matrix prior to extraction and analysis, and the percent recoveries of the surrogate standards are determined. Recoveries should meet the upper and lower control limits as specified for each compound. If control limits are exceeded for surrogate standards, the following sequence of actions is taken:

a. The sample is re-injected.

b. Raw data and calculations are checked for errors.

c. Internal standards and surrogate spiking solutions are checked for degradation, contamination, or solvent evaporation.

d. Instrument performance is checked.

e. If a, b, and c fail to reveal the cause of the noncompliance surrogate recoveries, the sample is re-purged or re-extracted.

f. If all the measures listed above fail to correct the problem for laboratory blank surrogate analyses, the analytical system is considered out of control, and the instrument must be recalibrated and examined for mechanical faults.

g. If all the measures listed above fail to correct the problem for field sample surrogate analyses, the deficiency probably is due to sample interferences, and not due to any procedural or mechanical problems in the laboratory. The surrogate spike recovery data and the sample data from both extractions are reported and are flagged. The Laboratory Manager is notified with an exceptions report and the corrective actions taken.

Matrix Spike/Matrix Spike Duplicate Analyses

To evaluate the effect of the sample matrix on the analytical methodology, two separate aliquot samples may be spiked with a standard mix of compounds appropriate to a given analysis. The matrix spike and the matrix spike duplicate (MS/MSD) are analyzed at a frequency of one per lot or one per 20 samples, whichever is more frequent. The percent recovery for each of the spiking compounds is calculated. The relative percent difference (RPD) between the MS/MSD is also calculated.

The observed percent recoveries (%R) and relative percent differences (RPD) between the MS/MSD are used to determine the accuracy and the precision of the analytical method for the sample matrix. If the percent recovery and RPD results exceed the control limits as specified for each spiking compound, the sample is not reanalyzed. Poor recovery in matrix spiked samples does not necessarily represent an analytical system out of control. It is possible that unavoidable interferences and matrix effects from the sample itself preclude efficient recoveries. The poor recovery is documented for the Project Manager.

Internal Standards Analysis

Once an instrument has been calibrated, it is necessary to confirm periodically that the analytical system remains in calibration. The continuing calibration and precision of the organics analytical system are checked for each sample analysis by monitoring the instrument response to internal standards. When internal standard addition is not appropriate to a particular method, other means of accuracy checks, such as standard addition, are used. Results from internal standard analyses are compared to the mean calibrated value. Deviation from this mean beyond a predetermined magnitude, depending on the type of analysis, defines an out-of-control condition. The system must then be brought back into control by:

- Checking the quality of the internal standards and reanalyzing the sample
- Recalibrating the system
- Correcting the malfunctions causing the instrument to fall out of calibration

Duplicate Sample Analyses

Duplicate analyses are performed for cations analyses and upon special request for selected other parameters to evaluate the reproducibility of the method. Results of the duplicate analyses are used to determine the RPD between replicate samples. For each parameter analyzed, at least one duplicate sample is run per group of 20 samples.

The precision value, RPD, is reviewed by the section supervisor and the division manager. If the precision value exceeds the control limit or the established protocol criteria for the given parameter, the sample set is reanalyzed for the parameter in question unless it is determined that heterogeneity of the sample has caused the high RPD.

QC Check Standard Analyses

Analysis of QC check standards is used to verify the preparation process or the standard curve, and is performed with each group of samples. Results of these data are summarized, evaluated, and presented to the section supervisor and the division manager for review.

The results of the QC check standard analysis are compared with the true values, and the percent recovery of the check standard is calculated. If correction of a procedure or instrument repair is done, the check standard is reanalyzed to demonstrate that the corrective action has been successful.

At least twice a year, a QC check standard for each parameter group is analyzed as a double-blind sample. Samples are prepared, submitted, and evaluated by the Laboratory Manager.

Other Quality Control Samples

Under some sampling analysis, additional quality control samples may be required. These may include:

a. **Blank/Spike--**Analyte of interest or surrogate is spiked into blank water rather than into a sample. The blank/spike goes through the entire analytical procedure, and percent recovery is calculated with no likelihood of matrix effect. For many contracts, an externally provided LCS sample (EPA) serves as a blank/spike sample.

b. **Trip Blank--**A sample bottle filled with laboratory blank water travels with the sample kit to the sampling site, and is sent back to the laboratory packed in the same container as any volatile samples collected. Trip blank analyses check for possible volatile contamination during shipping or sampling.

c. **Field Blank--**A field blank can be a sample container filled with laboratory blank water and sent to the sampling site, or it may be filled at the site with purchased distilled water or decontamination water. The field blank analysis checks for possible contamination by the sampling team.

d. **Equipment Rinsates--**After equipment has been cleaned in the field, many contracts require that the equipment be rinsed and the rinsate analyzed for the same parameters requested on the samples. The rinsate analysis proves the equipment has been cleaned properly and will not contaminate the next samples taken.

Control Charts

The laboratory will use control charts to monitor for out-of-control conditions.

Control Charting Process

The control chart program uses a series of Lotus (or equivalent) macros to perform data processing and control charting. These macros also perform statistical decisions on the acceptability of the data.

The control chart used is a variation of the Shewart control chart of averages. The chart plots individual quantitative results against the order of time measurement. The plotted values are compared with control limits determined by the variability about the mean of the standard "in control" process. The control chart estimates the process mean and the variability from a moving window of 50 to 200 samples, depending upon the analytical parameters involved. The mean is estimated from the arithmetic average of the samples in the current window. The variability is estimated as the sample SD of the sample values in the current window. The program calculates the 2 SD and the 3 SD limits and displays them on the chart. The t-statistic is used to estimate the 99.7 percent tolerance limits for the degrees of freedom in the current window. Values outside the t-statistic limits are unconditionally rejected from inclusion in the sample window and automatically documented in a Corrective Action Report (CAR). The CAR prompts the analyst to initiate investigation and corrective action.

When the maximum number of samples has accumulated in the current window, the summary statistics of the mean and SD are written to the long-term data base. The last 20 samples in the old window are then transferred to a new window for continued use in the charting process.

The long-term data base charts the mean ±1 SD error bars.

Instrument Detection Limits, Method Detection Limits, and Reporting Limits

Instrument Detection Limits (IDL)

Instrument Detection Limit (IDL) studies are performed for inorganic parameters when an instrument is installed, when major maintenance or repair work has been done, and routinely once per calendar quarter.

To determine IDL, seven consecutive measurements per day are made on a prepared standard solution (in reagent water) of an analyte at a concentration 3 to 5 times the instrument manufacturer's suggested IDL. Each measurement is performed as though it were a separate analytical sample. This procedure is repeated on three nonconsecutive days. The standard deviation is calculated for each set of seven replicates and the average of the standard deviations is obtained. This average is multiplied by 3 to give the instrument detection limit (IDL).

Method Detection Limits (MDL)

The Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The sample must be carried through the entire method under ideal conditions. MDL is determined according to the method outlined in 40 CFR 136, Appendix B. MDLs are determined at least annually for all parameters. MDL studies are also conducted for new methods introduced in the lab, after major maintenance or modification to an instrument, and as part of the training of new analysts.

To determine MDL, seven replicate analyses are made of analytes spiked into blank water at 1 to 5 times the estimated method detection limit. The spiked samples must be carried through the entire analytical procedure, including any extraction, digestion, or distillation process, for MDL calculation. The SD of these replicates is calculated. Where: t = The student t value for a 99% confidence interval

$$MDL = t \ x \ S$$

S = Standard deviation of the replicate analyses

Reporting Limits

In most cases, final report forms list reporting limits rather than either IDL or MDL. Reporting limits are taken from EPA SW846 published limits or from historical data. Matrixes or analyte concentrations which require dilution will change the detection limits for that sample.

E.7 Performance and System Audits

In this section information is provided on performance audits and onsite system audits.

Performance Evaluation Samples

Performance evaluation samples are analyzed throughout the project for all parameters, as a constant check on accuracy and precision for all analyses.

Audits

Internal audits of the laboratory are conducted in two phases. The first phase is conducted by the Laboratory Quality Assurance Coordinator during the fourth quarter of the year. This is usually a 2-day systems audit which covers all sections of the laboratory. An audit report is issued within 2 weeks of completion. The Field Site Manager has the responsibility for coordinating all responses to the audit finding and for following up on the required corrective action. A follow up audit is made when deemed necessary by the by the Field Site Manager or the Laboratory Manager. A quality assurance review questionnaire is provided in the Appendix.

The second phase consists of quarterly audits performed by the Field Site Manager. These are half-day or day-long audits, and are concentrated on specific areas that are deemed problem areas by the Field Site Manager. An audit report is issued at the completion of the audit. Responses and followup corrective action to the audit findings are required, and are monitored by the Field Site Manager.

All audit reports are issued to management and circulated to all staff. Copies are filed with the Field Site Manager and the Laboratory Manager.

C.8 Quality Assurance Reports

The performance of the field laboratory as assessed by the quality monitoring systems in place is reported by the Field Site Manager to management quarterly and as needed. Copies of all quality reports are maintained in the Field Site Manager and Laboratory Manager files.

Quality assurance reports to management include, but are not limited to, the following:

- Results of performance and systems audits
- Status of corrective actions
- Periodic assessment of data accuracy, precision, and completeness
- Significant QA problems and recommended solutions

In addition to the quarterly reports, a final report summarizing items covered in the quarterly reports is provided by the Field Site Manager to the Project Manager.

C.9 Data Format

Introduction

In order to provide analytical data which is technically sound and defensible, a system of data management will be implemented in the laboratory. All activities which pertain to a sample are documented.

All data generated during the demonstration, except those that are generated by automated data collection systems, will be recorded directly, promptly, and legibly in ink. All data entries will be dated on the day of entry and signed or initialed by the person entering the data. Any change in entries will not obscure the original entry, will indicate the reason for such change, and will be dated and signed or identified at the time of the change.

In automated data collection systems, the individual responsible for direct data input will be identified at the time of data input. Any change in automated data entries will not obscure the original entry. Updated entries will indicate the reason for the change, the date, and the person responsible for making the change.

Data Tracking in the Laboratory

The Field Site Manager is responsible for developing a system for tracking and maintaining sample identity between the collection point, analysis and reporting. This process will be periodically reviewed by the Project Manager.

Analyses and Data Reduction

The Field Site Manager is responsible for the reduction of raw data when such steps are required to produce the correct data format for reporting. Data reduction may be done manually or through one of a number of computer programs used in the laboratory.

Chromatogram Identification

In the GC section computer software is used to identify chromatograms. A system-supplied file name (a hexadecimal date-time) and a user-supplied file name (related to an entry in the injection log) identify each acquisition.

Data Reduction Formulas

Linear regression formulas are used in a computer software system to calculate samples values for many general inorganic parameters and metals analyses. These programs use the general formula for linear regression:

$$Y' = a + bx$$

where:

Y'	=	The predicted value of y for a selected value of x
a	=	The value of y when x = 0
b	=	The slope of the straight line
x	=	Any value of x selected

Sample values for GC/MS parameters are calculated by systems software using the general formula:

$$\frac{Area_{Target} \ x \ Amount_{IS}}{Area_{IS} \ x \ Response \ Factor}$$

GC data is calculated using either an internal or an external standard. For internal standards:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}}\right)\left(\frac{A_{IS}^{standard}}{A_{IS}^{sample}}\right)\left(amt_x^{standard}\right)\left(\frac{P}{T}\right)\left(\frac{amt_{IS}^{Sample}}{Amt_{IS}^{standard}}\right)$$

where: P = 1/fraction of extract to which IS is added

For calculations using an external standard:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}}\right)\left(C_x^{standard}\right)\left(\frac{V}{T}\right)$$

where: C	=	concentration of x in standard
V	=	volume of final extract
T	=	total sample extracted

C.10 Data Storage and Archiving Procedures

Data from GC's will be saved and archived in P&E Turbochrom format. All data will be backed-up on ZIP disks. This data will be batch processed into an Excel .csv file that can be easily converted to an Excel Worksheet. These files will be backed-up and transferred to individuals responsible for calculating flux results. All data related to the project will be organized for rapid retrieval and transfer to other interested parties.

Appendix D: Health and Safety Plan

Field Evaluation of the Florida Passive flux meter at the Port Hueneme NEX Site

Health and Safety Plan

February 5, 2007

University of Florida, Gainesville, FL

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INTRODUCTION

This Health and Safety Plan (HASP) has been developed for conducting field tests of the Florida PFM at the Port Hueneme site. The HASP describes hazards that may be encountered at the site, decontamination procedures, and an emergency contingency and response plan. The HASP also indicates the type of protective equipment site personnel will wear in order to minimize the potential for exposure to hazardous materials. This plan is consistent with current, applicable state and federal laws, regulations, and guidelines, including:

- Occupational Safety and Health Administration (OSHA) standards 29 CFR 1910 and 1926, including the final rule for hazardous waste operations 29 CFR 1910.120
- U.S. Environmental Protection Agency (EPA) "Standard Operating Safety Guide" November, 1984
- NIOSH/OSHA/USCG/EPA "Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities" October, 1985.

1.0 SITE DESCRIPTION, INVESTIGATION ACTIVITIES, AND HAZARD SUMMARIES

1.1. Site Background

The NEX Port Heuneme is a gasoline station where an extensive MTBE plume exists as a result of a gasoline spill.

1.2. Field Activities

This Health and Safety Plan (HASP) is written to provide an analysis of the site hazards that need to be considered for this study and to present the proper procedures to follow while performing the field activities associated with this study. The field activities that are covered in this HASP are as follows:

- Ground water sampling
- PFM installation, extraction and sampling

1.3. Site Hazard Evaluation

1.3.1. Groundwater. The shallow ground water downgradient within and down gradient of the NEX source zone is contaminated with MTBE and some degradation by-products. MTBE concentrations range up to about 10 mg/L.

1.3.3. Exposure Potential. The chemical contaminants present at OU2 may be a health hazard to site personnel via ingestion, skin absorption, or inhalation. Accidental ingestion of contaminants may occur via hand-to-mouth actions. Inhalation of vapors may occur when collecting ground-water samples or when sub-sampling PFM sorbents. Skin absorption is possible if skin is in direct contact with contaminated soil, water, or NAPL, particularly when collecting ground-water samples.

1.3.4. The potential toxic exposure hazard to site personnel associated with chemical contaminants possibly present at the site can be expressed in Permissible Exposure Limit (PEL) values established by the Occupational Safety and Health Administration (OSHA), the Threshold Limit Values-Time Weighted Averages (TLV-TWA) as established by the American Conference of Governmental Industrial Hygienists (ACGIH) and by Immediately Dangerous to Life or Health (IDLH) values established by the National Institute for Occupational Safety and Health (NIOSH).

- TLV-TWA: The time-weighted average airborne concentration of a substance, for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. Certain substances will have a skin notation in the exposure route column. This indicates that the overall exposure to that substance is enhanced by skin, mucous membrane, or eye contact.
- PEL: PELs are similar in concept to TLV-TWAs, except that PELs are promulgated by OSHA and are legally enforceable. The numerical values for the PEL and TLV-TWA for a given compound may be different. In the absence of a PEL for a given substance, OSHA will enforce the lowest published "safe" exposure level.
- IDLH (NIOSH): The maximum airborne concentration of a substance which one could escape within 30 minutes without escape-impairing symptoms or any irreversible health effects.

1.3.5. Table 1 identifies the PEL, TLV-TWA and IDLH values for the contaminants of concern while conducting the field work associated with the PFM assessment. Ionization potentials (IP) are listed to determine which compounds can be detected by a photoionization detector with a 10.2 electron volt (eV) probe. Additionally, routes of exposure, symptoms of acute exposure and carcinogenicity are summarized.
1.3.6. All site activities will comply with the exposure standards mandated by OSHA; personnel will adhere to TLV-TWA recommendations when these are more protective of employee health.

1.3.7. Levels of Protection. Based on the concentrations of contaminants anticipated at the site, **Level D protection** will be used for all sampling operations performed as part of this study. If conditions indicate the need for a higher level of protection, work will be discontinued.

1.3.9. All site activity locations will be clearly delineated; the site exit/entry point will be established upwind of the site operations when feasible.

TABLE 1
SITE CHEMICAL HAZARD SUMMARY

Contaminant	PEL (ppm)	TLV-TWA (ppm)	IDLH (ppm)	IP (eV)	Route of Exposure	Symptoms
Chloromethane	1,000	1,000	20,000	10.5	Inhalation, skin,	Mucous membrane irritation, headache, ingestion, eyes, dizziness, nervousness, fatigue, nausea
Trichloroethelene	50	50	1,000	9.5	Inhalation,	Headache, vertigo, nausea, tremors, ingestion, eye and skin irritation
Tetrachloroethelene	1	5	NA	10.0	Inhalation	Weakness, abdominal pain

1.4. Activity Hazard Analysis

1.4.1. Each field activity listed in Section 1.2 is subject to the hazards of slip, trip, and fall. The FTL/SSO will mitigate as many of these hazards as possible, and warn field team members of remaining hazards. **Confined spaces will not be entered during the work performed under the safety plan.** The potential hazards specific to each site activity and the control measures to be implemented to minimize or eliminate them are discussed below.

1.4.2. Ground-Water Sampling. The major potential hazard associated with this activity is exposure to contaminants (principally VOCs) present in the ground water through inhalation or skin contact. Waterproof, chemical resistant gloves shall be worn by site personnel when collecting ground-water samples.
1.4.3 Flux Meter Tests. Hazard associated with this activity is exposure to contaminants (MTBE, TBA) present in the sorbent material used in the PFMs through inhalation or skin contact. Waterproof, chemical resistant gloves shall be worn by site personnel when sub-sampling the PFMs and transferring to sample vials.
1.4.4 Site Housekeeping. Good housekeeping practices will be used to minimize slip, trip, and fall hazards. This includes promptly returning tools to their proper storage locations, and keeping materials off the ground to the extent practical.

2.0 ASSIGNMENT OF RESPONSIBILITIES

Assignment of responsibilities for development, coordination and implementation of the HASP is essential for proper administration of the Plan's requirements. Implementation of the HASP will be accomplished under the

supervision of field personnel. Figure 1 shows the site safety responsibility chart. Responsibility assignments are described below.

2.1. Project Manager (PM). The PM maintains overall responsibility for the performance of the project in a safe manner and is the central point of contact with Port Heuneme. Should a health and safety issue develop in the performance of the contract requiring consultation, the PM will immediately contact the Port Heuneme representative.

2.2. Project Safety Officer (PSO). The PSO is responsible for the preparation of the site-specific HASP. The PSO will ensure that the safety plan complies with all federal, state and local health and safety requirements. If necessary, the PSO can modify the site-specific HASP to adjust for on site changes that affect safety. The Field Team Leader/Site Safety Officer cannot modify the HASP without the approval of the PSO in order to avoid conflicts between meeting program deadlines and safety issues. The PSO will prepare the materials to be used in the training program and insure that the Site Safety Officer is knowledgeable of all components of the HASP.

2.3. Field Team Leader/Site Safety Officer (FTL/SSO). The FTL/SSO is responsible for the implementation of the HASP and has the responsibility and authority to halt or modify any working condition, or remove personnel from the site if he considers conditions to be unsafe. The FTL/SSO will be the main contact in any on-site emergency situation, and will direct all field activities involved with safety. The FTL/SSO is responsible for assuring that all on-site personnel understand and comply with all safety requirements. Except in an emergency, the FTL/SSO can modify the HASP requirements only after consultation with and agreement of the PSO. The FTL/SSO will conduct an initial safety meeting with all on site personnel prior to beginning the field experiments. Additional safety meetings will be conducted when new personnel arrive and when site health and safety conditions change. In the meetings, the potential hazards that the workers may encounter while performing the field work will be discussed.

2.4. Field Staff. All field staff, including subcontractor personnel, are responsible for understanding and complying with all requirements of the HASP. Field staff will be instructed to bring all perceived unsafe site conditions to the attention of the FTL/SSO.

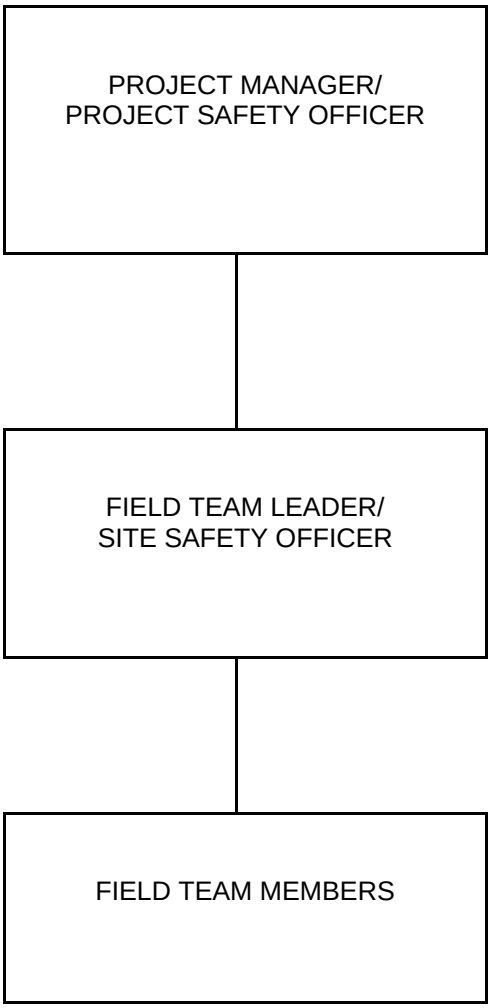


FIGURE 1. SITE SAFETY RESPONSIBILITY CHART

3.0 PERSONNEL TRAINING

3.0.1. The FTL/SSO shall ensure that all personnel have received the required training for those tasks they are assigned to perform, prior to working on-site.
3.0.2. The FTL/SSO shall maintain a file of completed personal acknowledgments (Figure 2). Each site worker must sign and date this document acknowledging that he or she has read, understood, and intends to comply with the HASP. Copies of completed personal acknowledgments will be submitted to the client or the authorized representative on request.
3.0.3. As discussed in section 2.3, the FTL/SSO must conduct a site safety meeting before the experiment begins, whenever new personnel arrive at the site, and as site conditions change. A brief daily safety meeting will be conducted to address such issues as the types of accidents most likely to occur and areas where improvements need to be made with respect to health and safety. Potential topics of discussion at all sessions include:

- Protective Clothing/Equipment
- Chemical Hazards
- Physical Hazards
- Emergency Procedures
- Hospital/Ambulance Route
- Standard Operating Procedures
- Other safety topics which are relevant to the site

A site safety meeting form will be completed and signed at the end of the kickoff safety meeting. A sample site safety meeting form is presented in Figure 3.

As a component of the Health and Safety Plan (HASP) designed to provide personnel safety during the Field Evaluation of PFMs at Port Heuneme, California, you are required to read and understand the HASP. When you have fulfilled this requirement, please sign and date this personal acknowledgment.

Signature	Date	Name (Printed)

FIGURE 2. PERSONAL ACKNOWLEDGMENT

Date: _____ Time:
Client: Port Heuneme
Site Location: NEX Port Heuneme, California
Scope of Work:

SAFETY TOPICS PRESENTED
Protective Clothing/Equipment:
Chemical Hazards:
Physical Hazards:
Special Equipment:
Other:
Emergency Procedures:
Hospital: _____ Phone: _____ Ambulance Phone:
Hospital Address and Route:
ATTENDEES
NAME PRINTEDSIGNATURE

Meeting Conducted By:

Project Manager/Project Safety Officer:

_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

FIGURE 3. SITE SAFETY MEETING FORM

3.0.4. Part of personnel training is to know standard and emergency procedures. These procedures are specified in Sections 9 and 10. A hospital route map is shown in Figure 4. All personnel should be familiar with the route to the hospital.

4.0 PERSONAL PROTECTIVE EQUIPMENT

4.0.1. Personal protective equipment (PPE) will be required during the course of the field work at Port Heuneme. PPE selection will be based primarily on hazard assessment data and work task requirements.
4.0.2. Based on the known contaminant release, the level of protection for all field activities is Level D. The personal protective equipment associated with Level D is described below.

4.1. Level D Personal Protective Equipment

4.1.1. Personnel working in an exclusion zone, which is defined in Section 8.1, shall wear as a minimum:

- Work uniform - during ground-water sampling, if there is limited potential for contaminated ground water to splash onto site personnel.
- Gloves, chemical-resistant (nitrile) - Chemical resistant gloves required for ground-water sampling.
- Safety glasses - Eye protection required if there is a potential for injection fluids or contaminated ground water to splash onto site personnel.

5.0 HAZARD ASSESSMENT

5.0.1. Hazard assessment is essential for determination of hazard control measures that must be implemented during site activities; it involves characterization of the chemical, physical and other safety hazards at the site. Hazard assessment is an on-going process.

5.1. Site Area Survey

5.1.1. The FTL/SSO shall conduct a site survey at each work area to locate hazards and to determine appropriate control measures prior to initiation of work activities. Hazards may include obstacles to ground traffic and slip/trip and fall hazards.

5.2. Cold Stress Monitoring

5.2.1. Because the field work will probably be conducted in summer and fall, there is a potential for either frostbite or hypothermia to occur. The following paragraphs describe these phenomena and measures that should be taken to prevent them from occurring.
5.2.2. Hypothermia. Hypothermia is defined as a decrease of the body core temperature below 96□F. Symptoms of hypothermia include shivering, apathy, listlessness, sleepiness, and unconsciousness. Hypothermia can occur at temperatures as high as 40°F, especially if it is raining.
5.2.3. Frostbite. Frostbite refers to areas of local cold injury. Symptoms of frostbite include whitening of the skin, skin that has a waxy or white appearance and is firm to the touch, and tissues that are cold, pale, and solid. Unlike hypothermia, frostbite rarely occurs unless the temperature is below freezing, and normally temperatures must be less than 20°F.
5.2.4. Prevention of Cold Related Illnesses. When there is a significant potential for cold stress, the following measures should be taken:

- Educate workers to recognize the symptoms of frostbite and hypothermia.
- Ensure that workers wear clothing that will keep them warm and dry.

- Take breaks in a heated area as necessary to allow workers to warm up. Hot liquids should be available in this area.

6.0 SITE CONTROL

6.0.1. Site control requires the establishment of a regulated area, designated work zones, an evacuation protocol, and site security.

6.1. Regulated Area(s)

6.1.1. To minimize the potential transfer of and exposure to potentially hazardous substances, contamination control procedures are necessary. Two general methods will be used: establishing site work zones (Exclusion, Contamination Reduction, Support) and personnel/equipment decontamination. The site must be controlled to reduce the possibility of: 1) exposure to any contaminants present, and 2) their transport by personnel or equipment from the site. The possibility of exposure or translocation of substances will be reduced or eliminated in a number of ways, including:

- Setting up physical barriers to exclude unnecessary personnel from the work areas
- Minimizing the number of personnel on site consistent with efficient operations
- Establishing work zones around the ground-water sampling area and storage tank area
- Establishing control points to regulate access to work zones
- Implementing appropriate decontamination procedures.

6.1.2. Safety procedures for preventing or reducing the migration of contamination require the delineation of zones in the work areas on the site where prescribed operations occur. Movement of personnel and equipment between zones and onto the site itself will be limited by access control points. The site will be outlined with survey tape or other appropriate means to define the work areas and to identify the entry and exit points.
6.1.3. Personnel on site will use the "buddy system" and will maintain communication or visual contact between team members at all times in the designated work zones where ground-water sampling and storage tank operations occur.

6.2. Work Zones

6.2.1. All work areas requiring PPE will have the following zones established:

Zone 1: Exclusion Zone (work zone in which prescribed PPE will be maintained)
Zone 2: Contamination Reduction Zone/Corridor
Zone 3: Support Zone (no PPE required)

6.2.2. Zone 1: Exclusion Zone (work zone). The exclusion zone, the innermost of the three designated areas, will be the area where activities require personnel protective equipment (PPE). All personnel entering the exclusion zone must wear the prescribed PPE. An entry and exit check point must be established at the periphery of the exclusion zone to regulate the flow of personnel and equipment into and out of the zone. The outer boundary of the exclusion zone, the "hotline", will be established by visually surveying the site and determining the area where significant amounts of organic vapors and/or a potential for explosive vapor conditions might exist. Physical hazards associated with the work task will be identified in the exclusion zones. Once the "hotline" has been determined, it will be defined by the use of stakes, cones, or surveyor tape. During subsequent site operations, the boundary may be modified and adjusted by the FTL/SSO as more information becomes available. Potential exclusion zones at the OU2 site have been identified as the ground water sampling sites.
6.2.3. Personnel will be decontaminated as they move through the contamination reduction corridor. Detailed decontamination procedures are provided in Section 7.

6.2.4. Zone 3: Support Zone. The support zone, the outermost part of the site, will be considered a noncontaminated or clean area. Support equipment (command post/trailer, safety vehicle, etc.) is located in this area.

6.2.6. The location of the command post and other support facilities in the support zone at each site depends on a number of factors, including:

- Accessibility: topography; open space available; locations of roads; or other limitations
- Wind direction: preferably the support facilities should be located upwind of the exclusion zone. Shifts in wind direction and other conditions may be such that an ideal location based on wind direction alone does not exist
- Resources: water, electrical power.

6.2.7. Access to the contamination reduction corridor from the support zone is through a controlled access point. Personnel entering the contamination reduction corridor to assist in decontamination must wear the prescribed personal protective equipment. Reentry into the support zone requires removal of any protective equipment worn in the contamination reduction corridor.

7.0 DECONTAMINATION PROCEDURES

7.0.1. Establishment of decontamination procedures for personnel and equipment are necessary to control contamination and to protect field personnel.

7.1. Decontamination of Personnel

7.1.1. Personnel will be decontaminated upon leaving the exclusion zone to the appropriate extent as directed by the FTL/SSO based upon organic vapors generated or gross visual contamination of protective clothing. When complete decontamination is required, it will consist of the following:

- At the "hotline" of the contamination reduction corridor, personnel will deposit equipment used on site, such as tools, sampling devices and containers, monitoring instruments, and clipboards.
- If being worn, chemical resistant gloves and coveralls or apron will be disposed of at the “hotline”.
- Ground-water sampling equipment will be cleaned in a solution of detergent and water, followed by multiple rinsings with water.
- PPE will be removed in the following order: disposable coveralls or apron, respirator, and gloves.

7.1.2. Personnel shall be instructed in the proper decontamination technique, which entails removal of protective clothing in an "inside-out" manner. Removal of contaminants from clothing or equipment by blowing, shaking or any other means that may disperse material into the air is prohibited.

7.1.3. All disposable personal protective clothing that has been removed will be containerized at the decontamination station pending disposal. At the conclusion of work in a site exclusion zone, all protective equipment must be placed in plastic bags prior to disposal or transfer off-site. Non-disposable equipment will be decontaminated and properly stored outside the exclusion zone when not in use.

7.1.4. All employees will wash their hands and face with soap and water or disinfectant moist towelettes before eating, drinking, smoking, or applying cosmetics. These activities will be restricted to the designated rest area(s) in the support zone. This restriction also applies to work activities that do not require an exclusion zone, such as ground-water sampling.

7.2. Equipment Decontamination and Disposal of Contaminated Materials

7.2.1. Equipment that may require decontamination includes water sampling devices and certain protective equipment.

7.2.2. All materials and equipment used for decontamination must be disposed of properly. Disposable clothing, tools, buckets, brushes, and all other equipment that is contaminated will be secured in appropriate Department of

Transportation (DOT) specification 55-gallon drums or other containers and marked. Clothing that will be reused, but which is not completely decontaminated on site, will be secured in plastic bags before being removed from the site. Contaminated wash water solutions shall be transferred to the effluent storage tank, pending transfer to a specified location for subsequent treatment.

8.0 GENERAL SITE SAFETY REQUIREMENTS

8.0.1. The following practices are expressly forbidden during on-site investigations:

- Smoking, eating, drinking, or chewing gum or tobacco while in the work zone or any potentially contaminated area.
- Ignition of flammable materials in the work zone; equipment shall be bonded and grounded, spark-proof and explosion resistant, as appropriate.
- Contact with potentially contaminated substances. Walking through puddles or pools of liquid, kneeling on the ground or leaning, sitting or placing equipment on contaminated soil should be avoided.
- Performance of tasks in the exclusion zone individually, except for those tasks explicitly permitted by the HASP.

8.0.2. Equipment to be maintained on site is listed in Table 2. Posted at the site will be the hospital route map (Figure 4). Personnel should keep the following rules in mind when conducting an on-site investigation:

- Hazard assessment is a continual process; personnel must be aware of their surroundings and constantly be aware of the chemical/physical hazards that are present.
- Personnel in the exclusion zone shall be the minimum number necessary to perform work tasks in a safe and efficient manner.
- Team members will be familiar with the physical characteristics of each investigation site, including wind direction, site access, location of communication devices, and safety equipment.

9.0 EMERGENCY PROCEDURES

9.1. Accident Prevention and Hazard Analysis

9.1.1. The prevention of injuries and the minimization of risks are the responsibility of all site workers. Specific procedures to both prevent accidents and to handle them should they occur are presented in this section.

TABLE 2. SAFETY AND EMERGENCY EQUIPMENT

- Cellular Phone
- Emergency Evacuation Routes (map)
- Emergency Assistance Information
- A vehicle which can be used to evacuate injured personnel
- First Aid Kit
- Eyewash Station or Kit
- Disinfectant Moist Towelettes
- Fire Extinguisher (A.B.C.)
- Surveyor Tape and Stakes
- Gatorade or drinking water
- Health and Safety Plan (copy)

9.1.2. The Field Team Leader/Site Safety Officer will be responsible for implementation of this accident prevention plan and all on-site personnel will be accountable for reading, understanding and following the guidelines contained herein.

- An initial indoctrination of all site personnel, and site-specific safety training, will be accomplished during the training session described in Section 3.
- The Field Team Leader/Site Safety Officer will be responsible for maintaining a clean job site, free from hazards, and providing safe access and egress from the site. Cones and high visibility surveyor tape will be utilized for traffic control, and limiting access to hazardous and restricted areas.
- Emergency phone numbers will be posted for the Fire Department and the nearest emergency medical clinic/hospital. The fastest route to the clinic/hospital, along with emergency telephone numbers, are found in Table 3. The FTL/SSO will be the lead person in all emergency situations.
- A site safety meeting will be conducted to discuss pertinent site safety topics at the beginning of the study, whenever new personnel arrive at the job site and as site conditions change. These meetings shall be conducted by the FTL/SSO and, after each meeting, a completed Site Safety Meeting Form shall be posted at the job site. A sample Site Safety Meeting Form is found in Figure 3.

9.2. Emergency Medical Assistance and First Aid Equipment

9.2.1. Emergency phone numbers are given in Table 3. Included in this plan is a map and directions to Royal Victoria Hospital or Stevenson Memorial Hospital (Figure 4). A vehicle shall be available on site during all work activities to transport injured personnel to the identified emergency medical facilities.
9.2.2. Two first-aid kits will be available at the site for use by trained personnel. An adequate supply of fresh water is available in the support zone. Portable emergency eye wash stations will be available at each work site.

9.3. Emergency Protocol

9.3.1. It is the objective of this HASP to minimize chemical/physical hazards and operational mishaps. The following items will assist personnel in responding to emergency situations in a calm, reasonable manner.

- An evacuation route from the site will be established by the FTL/SSO and communicated to all personnel during the site safety meeting prior to work start-up in any area.
- The FTL/SSO is responsible to assure the availability of communication devices at each investigation site for general and emergency use.

9.3.2. In the event of an emergency, the first step will be to survey the scene. If there are unconscious or otherwise immobile personnel, move them only if their life or serious injury would be threatened by not moving them. Then summon assistance, administer first aid, and make sure that all personnel are accounted for. Then secure the area and transport injured people to the hospital. If the injured person's condition needs to be stabilized before moving, transportation to the hospital should be by ambulance; otherwise, uninjured personnel or an ambulance can provide transportation.
9.3.3. Team members will be familiar with emergency hand signals:

Hand gripping throat: Respiratory problems, can't breathe
Grip team member's wrists or place both
hands around waist: Leave site immediately, no debate!
Thumbs up: OK. I'm all right, I understand

Thumbs down: No, negative

9.4. Decontamination During Medical Emergencies

9.4.1. If prompt life-saving first aid and/or medical treatment is required, decontamination procedures should be omitted.
9.4.2. Life-saving care shall be instituted immediately without considering decontamination. The outer garments can be removed if they do not cause delays, interfere with treatment or aggravate the problem. Respiratory equipment must always be removed. Chemical-resistant clothing can be cut away. If the outer contaminated garments cannot be safely removed, the individual shall be wrapped in plastic, rubber or blankets to help prevent contaminating the inside of ambulances and/or medical personnel. Outer garments are then removed at the medical facility. No attempt will be made to wash or rinse the victim, unless it is known that the individual has been contaminated with an extremely toxic or corrosive material which could also cause severe injury or loss of life. For minor medical problems or injuries, the normal decontamination procedure will be followed.
9.4.3. Exposure to chemicals can be divided into two categories:

- Injuries from direct contact, such as acid burns or inhalation of toxic chemicals.
- Potential injury due to gross contamination on clothing or equipment.

9.4.4. For inhalation exposure cases, treatment can only be performed by a qualified physician. If the contaminant is on the skin or the eyes, immediate measures can be taken on site to counteract the substance's effect. First aid

treatment consists of flooding the affected area with copious amounts of water. The FTL/SSO must assure that an adequate supply of running water or a potable emergency eyewash is available on site.

9.4.5. When protective clothing is grossly contaminated, contaminants can possibly be transferred to treatment personnel and cause an exposure. Unless severe medical problems have occurred simultaneously with personnel contamination, the protective clothing should be carefully removed.

9.5 Emergency Contacts and Phone Numbers

The key person at the work location to respond to accidents and unusual conditions is the Site Manager. The Site Manager or SSO shall ensure that the emergency phone numbers (Table A.1.9.1-1) and the location of the nearest medical facility to be used in emergencies (Figure A.1.9.1-1) are posted in a visible place at the work site, and that the site workers know where they are posted.

The succession of authority at the site until relieved by the on-scene Base Emergency Director is as follows:

Port Heuneme Emergency Response Personnel
Site Manager

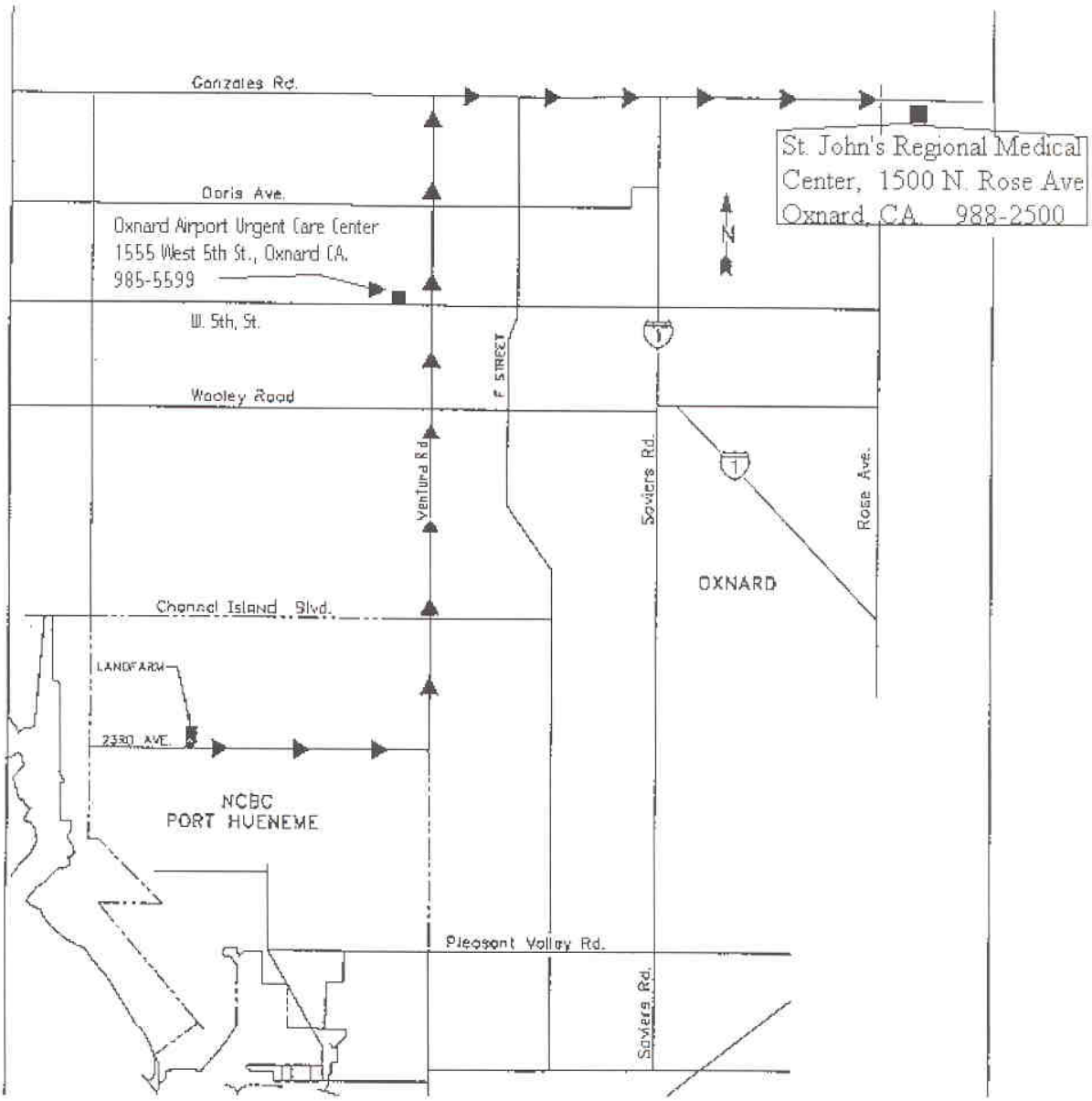
In the event of a site emergency or condition that is immediately dangerous to life and health, the following personnel have the authority to stop work and evacuate the site:

Port Heuneme Project Manager
Health and Safety Officers
Site Safety Officers

The Port Heuneme Project Manager and the Project Manager have the additional authority to stop work at any time for any reason.

Table 9.5-1. Emergency Telephone List

HOSPITALS	Off Base — St. John's Regional Medical Center	805-988-2500
	On Base — Urgent Care Clinic	805-985-5599
FIRE	On Base	911
	Off Base	911
AMBULANCE	On Base	911
	Off Base	911
POLICE	On Base	911
	Off Base	911



Emergency clinic and hospital routes.

9.5.2 Emergency Signals

During the execution of a specific task, the task supervisor may stop work and evacuate personnel from the exclusion zone if an emergency condition exists. In the absence of a supervisor, individual project workers may stop work and leave their work area if an emergency condition exists. If the situation warrants, personnel may exit the exclusion zone without performing decontamination procedures.

In the event of a site condition or emergency requiring site evacuation, any of the personnel with site evacuation authority listed in Section A.1.9.1 may obtain an air horn kept in the following locations:

ground-water treatment plant;
process building control room; and
on-site at the field trailer or the SSO's vehicle.

Three short bursts will indicate that all personnel shall discontinue work, shut down equipment (as needed), and immediately assemble in the front of the treatment facility building. The assembly point in the parking area will provide a safe distance from the process building and the test area. On-site supervisors will be responsible for assembling and accounting for their personnel.

Should an emergency site evacuation become necessary for any reason, the On-Site Manager will alert all personnel to leave the site. Personnel will not return to the site until an ALL CLEAR has been received from the On-Site Manager.

9.5.3 Medical Emergency Procedures

Illnesses, injuries, and accidents occurring on site must be attended to immediately in the following manner:
Survey the scene to determine if it is safe to render first aid. Remove the injured or exposed person(s) from immediate danger.
Conduct a primary survey (check the victim for unresponsiveness).

C - CHECK C - CALL C - CARE

Phone the emergency medical services listed on the emergency contacts posting. This procedure should be followed even if there is no apparent serious injury.
Perform a secondary survey (interview, vital signs, and head-to-toe examination). Decontaminate affected personnel, if necessary and appropriate.
Follow with the appropriate American Red Cross First Aid procedure for any follow-up care required until medical help arrives.
Report the on-site illness or injury immediately to the Project Manager.
Develop procedures, in conjunction with the Project Manager and the Corporate Health and Safety Officer, to prevent a recurrence.

9.5.4 Fire Response Procedure

The following steps shall be taken when a fire occurs at the project work site:

Using the available communications equipment (telephone) contact the Port Heuneme Fire Department and notify them of the situation
Small, localized fires may be handled using the appropriate fire extinguisher to bring the situation under control.
The Port Heuneme Fire Department shall handle large uncontrolled fires. Evacuate and isolate the area, and deny entry to unauthorized personnel.
Under no circumstances shall field personnel take any actions to save equipment or property which could put them at personal risk.

10.0 CHEMICAL HAZARDS AND CONTROLS

10.1. Tracers. Small quantities of alcohol and inorganic tracers will be used in the PFMs. The health hazard data associated with these two substances are minimal.

10.2. Fire Protection Plan

10.2.1. Fire or Explosion Response Action. The actions listed below are in a general chronological sequence. Conditions and common sense may dictate changes in the sequence of actions and the addition, elimination, or modification of specific steps.

10.2.2. Immediate Action. Upon detecting a fire/explosion, employees will notify the fire department and determine whether or not the fire is small enough to readily extinguish with immediately available portable extinguishers or water, or if other fire-fighting methods are necessary. Non-essential personnel will be directed away from the area of the fire. If it is judged that a fire is small enough to fight with available extinguishing media, employees will attempt to extinguish the fire provided that:

- They are able to approach the fire from the upwind side, or opposite to the direction of the fire's progress.
- The correct extinguisher is readily available. Type ABC fire extinguishers will be
- provided in work areas.
- No known complicating factors are present, such as likelihood of rapid spread,
- imminent risk of explosion, or gross contamination.

Personnel leaving a fire/explosion area will notify the fire department and will account for all employees in that work area as soon as possible. The Site Safety Officer or designee will perform a head count for that work area.

10.2.3. Notification. The Site Safety Officer will be notified as soon as possible of the location, size, and nature of the fire/explosion. As conditions dictate, the Site Safety Officer will declare an emergency, initiate the remedial procedures, request assistance from the fire department, and make the necessary on-site and off-site notifications. If assistance from the fire department is required, an escort appointed by the Site Safety Officer will direct responder's vehicles over clean roads to the extent possible to limit contamination. Note: National Fire Protection Association (NFPA) guidelines call for notifying the fire department, even for small fires to ensure proper extinguishment.

10.2.4. Rescue. If employees are unable to evacuate themselves from a fire/explosion area for any reason, their rescue will be the first priority of responders. The Project Manager and/or Site Safety Officer will determine whether on-site resources are sufficient to proceed, or if rescue must be delayed until outside responders arrive.

10.2.5. Fire-Fighting Procedures. Planned fire-fighting procedures are described below. These apply to small fires that the project team members are able to control.

10.2.6. Fire During Working Hours. In the event a fire occurs during working hours, the following measures will be taken to put out the fire. These measures are sequential, that is, if the first measure does not succeed in containing the fire, the next measure will be initiated.

- Utilize fire extinguishers.
- Confirm that request for assistance from the fire department has been made.
- Utilize earth moving equipment, foam unit, and water resources as appropriate. Brush

fires will be extinguished with water.

10.2.7. Fire During Non-Working Hours. In the event of a fire during non-working hours, existing alarms, site security (if applicable), or whomever from the project team is notified, will notify the Site Safety Officer. Additional actions will be consistent with procedures established for a fire during working hours.

10.2.8. Response Coordination. Upon arrival of outside responders from the fire department, the Site Safety Officer will coordinate with the leader of the outside responders to direct fire-fighting activities. Once a municipal fire department responds to the scene, the control of the scene is under the leader of the responding fire department.

10.2.9. Protection of Personnel. The primary methods of protecting personnel from fire conditions will be by distance and remaining upwind. Based on the conditions, the Site Safety Officer will determine appropriate

distances and the selection of personal protective equipment. For approach in close proximity to fire areas, Level B or greater protective equipment suitable for fire fighting will work. Field team members will not participate in activities requiring Level B protection.

10.2.10. Decontamination. At the conclusion of fire fighting activities, the Site Safety Officer will:

- Determine to the extent practicable the nature of the contaminants encountered during the incident.
- Arrange for all outside responders' fire response equipment, and on-site equipment as necessary, to be processed through the site decontamination zone, using methods appropriate for the contaminants involved.
- Equipment not easily decontaminated shall be labeled and isolated for further action, such as determining specific contaminants by wipe sampling or awaiting the delivery of specific decontamination media and supplies.

10.2.11. Fire Extinguisher Information. The four classes of fire, along with their constituents, are as follows:

Class A - Wood, cloth, paper, rubber, many plastics, ordinary combustible materials
Class B - Flammable liquids, gases and greases
Class C - Energized electrical equipment
Class D - Combustible metals such as magnesium, titanium, sodium, potassium.

10.2.12. Examples of proper extinguishing agents are as follows:

Class A - Water
Water with one percent AFFF Foam (wet water)
Water with five percent AFFF or Fluoroprotein Foam
ABC Dry Chemical
Halon 1211
Class B - ABC Dry Chemical
Purple K
Halon 1211
Carbon Dioxide
Water with six percent AFFF Foam
Class C - ABC Dry Chemical
Halon 1211
Carbon Dioxide
Class D - Metal-X Dry Chemical

10.2.13. No attempt should be made to extinguish large fires. These should be handled by the fire department. The complete area of the fire should be determined. If human life appears to be in danger, or the spread of the fire appears to be rapidly progressing, move personnel further upwind away from the fire.

10.2.14. Use of Fire Extinguishers. Inspect the fire extinguisher on a monthly basis to ensure that the unit is adequately charged with extinguishing media. Do not store a fire extinguisher on its side. To use the extinguisher, follow the acronym PASS for below listed instructions:

1. **P**ull the pin on the top of the unit.

2. **A**im at the base of the fire.

3. **S**queeze the handle on the top of the unit.

4. **S**weep the extinguishing media along the base of the fire until the fire is out.
   Ensure that the fire is fully cooled before assuming it is completely extinguished.