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Field Demonstration and Validation of a New Device for Measuring Groundwater and Perchlorate Fluxes at IHDIV-NSWC, Indian Head, MD

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List of Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
AEC	anion exchange capacity
CAR	corrective action report
CV	coefficient of variation
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
HDTMA	hexadecyltrimethalammonium
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
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
SI-GAC	silver-impregnated GAC
SM-SI-GAC	surfactant-modified SI-GAC
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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Professor Robert Bowman, New Mexico Institute of Technology, generously provided research-grade SMZ samples from his collection, and provided contacts to the commercial supplier of zeolite (St. Cloud Mining Company), sent numerous reprints of his extensive work on modified zeolites, and emailed some of presentation materials. Such an open approach to scientific collaboration illustrates his trust in us as colleagues, his mentorship in helping a graduate student (Ms. Jimi Lee, Purdue University).

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 Indian Head Naval Surface Warfare Center (IHDIV-NSWC) in 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. At NBVC groundwater and contaminant fluxes were measured using PFMs at the leading edge of a methyl-tertiary butyl ether (MTBE) plume. 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^{TM}. Because all other field applications involved sites with organic contaminants that were constituents of DNAPLs and LNAPLs, the primary objective at IHDIV-NSWC was to demonstrate PFMs could measure water and perchlorate contaminant fluxes.

This report presents the results from field studies conducted at IHDIV-NSWC. In addition, this report presents results of laboratory efforts to extend the use of the PFM technology to assess contaminant fluxes at sites with inorganic anions (such as chromate, selenate, arsenate, phosphate, and nitrate, etc.) and organic acids that could serve as electron donors in bioremediation (such as lactate, citrate, benzoate, phenols, etc).

Site Study Objectives

- demonstrate and validate the PFM as an innovative technology for direct in situ measurement of cumulative groundwater and contaminant fluxes, with perchlorate serving as the specific inorganic contaminant of interest at this site,
- investigate vertical variability in perchlorate mass flux and groundwater flux between PFM deployed in different wells, 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

For this project new PFM sorbent matrices were evaluate for measuring anion fluxes, specifically perchlorate (used as solid rocket propellant). Silver-impregnated granular activated carbon (SI-GAC) was modified with hexadecyltrimethylammonium (HDTMA), a cationic surfactant with a quaternary amine functional group, to enhance the anion exchange capacity of the GAC. The surfactant-modified, silver-impregnated GAC (SM-SI-GAC) can retain substantial amounts of non-polar hydrophobic contaminants (such as DNAPL and LNAPL constituents or alcohol tracers) as well as oxyanions (such as perchlorate, ClO_4^-; chromate, CrO_4^{2-}; and selenate, SeO_4^{2-}) by anion exchange; the quaternary amine functional group is highly selective for perchlorate.

The use of SM-SI-GAC as a PFM sorbent was field-demonstrated for perchlorate flux measurements at a site located at IHDIV-NSWC. Five monitoring wells were selected within the perchlorate plume (concentration range approximately 2.5 mg/L to 190 mg/L), three wells with 10-ft screens and one each with 7-ft and 3-ft screens, respectively. Of the three wells selected for PMF tesing, MW1 was located in the suspected source zone, while MW3 and MW4 were located down gradient. PFMs packed with SM-SI-GAC were deployed for two events with different exposure times (three and six weeks) to 1) produce more reliable time-averaged flux measurements, 2) produce more accurate contaminant flux measurement in the low range concentration area by implementing a longer exposure period, and 3) confirm the robustness of the PFM construction materials under highly oxidizing conditions.

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 3 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. Because these samples were more stable in the presence of the solvent, they were analyzed within one month.

Novel laboratory extraction protocols were developed to extract: 1) the residual resident alcohol tracers using *iso*-butyl alcohol (IBA) as the solvent, and 2) the captured oxyanions with hot 1M KNO3 solution via a competitive ion exchange mechanism. In addition, an ion chromatography (Dionex DX600 Ion Chromatography system) analytical procedure was developed to compensate for the high nitrate background in sample extracts and to enable low detection limits (6 µg/L perchlorate, 10 µg/L chromate).

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 perchlorate.

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. Perchlorate 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 perchlorate concentrations measured in open wells.

Groundwater Specific Discharge and Contaminant Mass Flux Results

Groundwater fluxes – representative of the well-screen averages -- measured using the PFM approach favored comparably with those determined using conventional approaches. Depth variations in groundwater fluxes could be resolved at intermediate (~10 cm) and high (~3cm) depth resolution when using the PFM approach. Perchlorate mass flux was ~1.6 g/m^2/day near the perchlorate source zone, and ~1.0 g/m^2/day near the edge of the plume; the corresponding groundwater fluxes were ~1.8 cm/day and 6.3 cm/day. Groundwater and perchlorate flux distributions measured during the two deployments correlated well.

The depth distribution of perchlorate fluxes was used to formulate hypothesis about location of possible perchlorate sources. The groundwater concentration in MW-1, located near the suspected source zone, did not change over time from 2002 to 2005, indicating the presence of a persistent source since Hog-Out waste water containing perchlorate has not been discharged since 1996. The higher perchlorate fluxes near the water table and a relatively uniform flux distribution with depth in MW-1 indicates the possibility of a vadose zone source. The source in the vadose zone would be released to the aquifer by recharge induced by rainfall. With this scenario, higher perchlorate fluxes would be observed near the water table. A vadose zone source would also explain the high temporal variability of perchlorate concentrations observed in the down-gradient monitoring wells, MW-3 and MW-4.

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.

Demonstration Conclusions

The primary goal of the study was to demonstrate the applicability of a new PFM-sorbent SM-SI-GAC for field-scale measurement of groundwater and perchlorate fluxes. The measured fluxes showed good reproducibility between two deployments and also compared well with borehole dilution test and conventional groundwater monitoring data. Thus, SM-SI-GAC can be used as a PFM sorbent in sites with perchlorate concentrations ranging from 7 to 64 mg/L. The results also indicated the SM-SI-GAC was stable physically, chemically and biologically for a maximum of 44 days and the alcohol tracers and captured perchlorate on it were not biodegradable.

Another major goal of this study was to evaluate new sorbent matrices as packing material in Passive Flux Meters (PFMs) used for characterization of groundwater and contaminant fluxes at sites where anions are the contaminants of concern. We examined three types of sorbents: (1) anion exchange resins (AERs); (2) natural zeolites; and (3) granular activated carbon (GAC). All three sorbents can be purchased in bulk quantities.

Each sorbent type has a set of limitations and advantages for use in PFMs for investigating oxyanion fluxes. AERs do have large anion exchange capacity, but may not serve as good sorbents for nonpolar contaminants and alcohol tracers. However, organic acids (e.g., benzoate) can be used as the PFM resident racers. We modified zeolites and GAC with a quaternary ammonium surfactant (HDTMA) to enhance the anion exchange capacity (AEC) of these sorbents. While GAC can sorb large quantities of non-polar organic contaminants, it can sorb only small amounts of anions. Thus, surfactant modification imparts the dual sorption capacity we need for PFM applications. Natural zeolites have significant cation exchange capacity, but do not sorb nonpolar solutes. Cationic surfactant modification to produce an external bilayer yields a sorbent that can sorb anions, cations, and non-polar solutes.

The zeolite and GAC we used have similar external surface areas (~10-15 m^2/g), and the zeolite has an external CEC of about 100 meq/g. GAC modification requires only a monolayer coverage of HDTMA (~50 meq/g) to generate adequate AEC, where as for zeolite a bilayer formation is necessary requiring HDTMA loading ~200 meq/g. HDTMA modified GAC are cost effective when compared to ion exchange resins, but comparable in cost with SMZ. GAC costs about $500-1000/ton compared to about $500/ton for SMZ, and about $3000/tom for anionic resins (EPA, 1999; Mullin et al., 2002). SMZ might be suitable for large-volume applications, but because of low sorptive capacity it might have limitations in use at sites with high contaminant and ground water fluxes. Thus, surfactant-modified SI-GAC is recommended as the preferred sorbent for PFM applications to measure anion fluxes.

AEC of HDTMA-modified SI-GAC appear to be chemically and biologically stable. The positive charge on the quaternary amine functional group is not pH-dependent (in the pH range of environmental interest) and is less reactive than other primary, secondary and tertiary amines (Jungermann, 1970). HDTMA may also act as biocide, at least when in solution (Jacob and Heidelberger, 1915), and thus may preclude biodegradation of the resident tracers and captured contaminants.

Modification of GAC/SI-GAC with HDTMA surfactant reduces the alcohol tracer sorption coefficient, and thus the maximum deployment period is proportionately smaller, if the same suit of alcohol tracers is used. This could be a problem at sites with fast groundwater flux and low concentration of contaminants. But, this limitation could be overcome by using another suit of alcohol tracers with higher range of K_d values.

Recommendations

Thus, SM-SI-GAC can be used as a PFM sorbent in sites with perchlorate concentrations ranging from 7 to 64 mg/L. The applicable concentration ranges can be expanded using shorter exposure time and/or higher loadings of HDTMA on SM-SI-GAC to not exceed the sorption capacity of perchlorate.

The depth distribution of perchlorate fluxes was used to formulate hypothesis about location of possible perchlorate sources. A vadose zone source near MW1 would also explain the high temporal variability of perchlorate concentrations observed in the down-gradient monitoring wells, MW-3 and MW-4. Further investigations of soil concentrations near this area are required to confirm the hypothesis

HDTMA, a cationic surfactant with a long alkyl chain, was used to modify zeolites and GAC to produce a sorbent with anion exchange capacity. Long-chain surfactants are likely to be better candidates for modification than short-chain surfactants. The longer alkyl chain is correlated to larger enthalpies of sorption and larger K_ds (see Bowman et al.1995, 1998), thus, the surfactant will not be easily desorbed, and the introduced AEC will not diminish during the PFM deployment period. Further research to improve the performance of SM-SI-GAC using other surfactants is recommended.

GAC can also be modified with anionic surfactants and organic acids to impart cation exchange capacity (CEC). It is also possible to modify GAC with a mixture of anionic and cationic surfactants, to match the capabilities of SMZs. It is also possible to custom-select the surfactant head group so that it has high selectivity for the oxyanion of interest. Further research is recommended to explore these options.

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.

The focus of this project is to demonstrate and validate a Passive Flux Meter (PFM) which is a new technology for direct in situ measurement of both cumulative subsurface water and contaminant fluxes (Hatfield et al., 2002 and 2004). The PFM is a technology that directly addresses the DoD need for cost-effective long-term monitoring, because flux measurements can be used for (1) process control, (2) remedial action performance assessments, and (3) compliance purposes.

The PFM 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. 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 groundwater flux.

The PFM 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 groundwater 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 Indian Head Naval Surface Warfare Center (IHDIV-NSWC) in 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. At NBVC groundwater and contaminant fluxes were measured using PFMs at the leading edge of a methyl-tertiary butyl ether (MTBE) plume. 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^{TM}. Because all other field applications involved sites with organic contaminants that were constituents of DNAPLs and LNAPLs, the primary objective at IHDIV-NSWC was to demonstrate PFMs could measure water and perchlorate contaminant fluxes.

This report presents the results from field studies conducted at IHDIV-NSWC. In addition, this report presents results of laboratory efforts to extend the use of the PFM technology to assess contaminant fluxes at sites with inorganic anions (such as chromate, selenate, arsenate, phosphate, and nitrate, etc.) and organic acids that could serve as electron donors in bioremediation (such as lactate, citrate, benzoate, phenols, etc).

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 groundwater and contaminant fluxes, with perchlorate serving as the specific inorganic contaminant of interest at this site,
2. Investigate vertical variability in perchlorate mass flux and groundwater flux between PFM deployed in different wells, 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 borehole remediation systems such as natural attenuation as well as RCRA closure sites often require elaborate and expensive monitoring. The focus of this project is to demonstrate and validate the Passive Flux Meter, a new technology for direct in situ measurement of both cumulative groundwater and contaminant fluxes. Measurements of these fluxes at a contaminated site 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: Can the PFM assess pre- and post-remediation contaminant fluxes, such that remedial performance can be assessed?

Issue 3: Are monitoring costs of the PFM lower than the traditional or emerging technologies?

The demonstration focuses on the first issue of concern. In situ, passive measurements of groundwater and contaminant fluxes are compared for different deployment periods and to flux estimates made by traditional methods using groundwater flux and resident perchlorate concentrations.

2.0. Technology Description

2.1. Technology Development and Application

This demonstration plan describes the proposed strategy for extending the utility of a new method (Hatfield et al., 2002, 2004) for direct in situ, simultaneous measurement of cumulative fluxes for both groundwater and inorganic ions in groundwater. The new method involves a device, hereafter referred to as a 'PFM,' that 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 2-1).

The interior composition of the PFM is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and/or inorganic contaminants present in fluid intercepted by the unit. The sorbent matrix is also impregnated with known amounts of one or more fluid soluble 'resident tracers'. 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 removed 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 time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative 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. These data are used to estimate local values of cumulative groundwater and contaminant fluxes.

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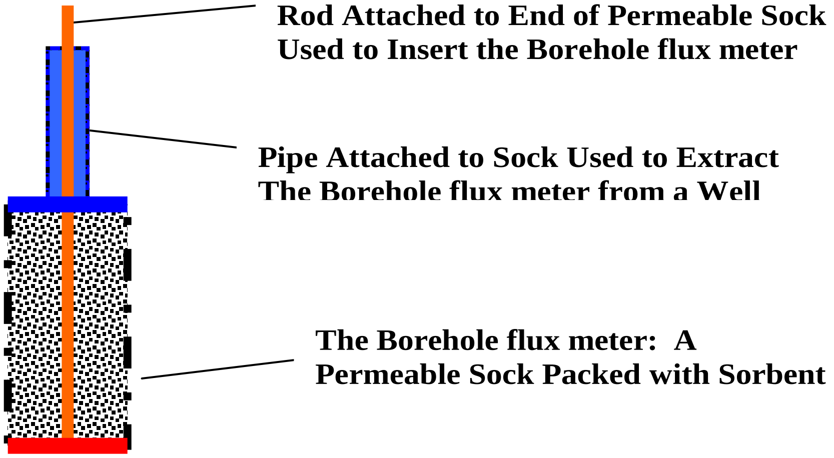

Figure 2-1. Schematic of a PFM comprised of a permeable sock filled with a selected sorbent

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

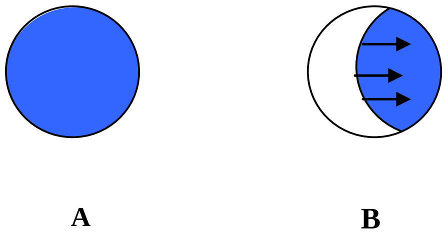

Figure 2-2. PMF cross-sections (A): initial condition, (B): displaced tracer distribution after exposure to a fluid flow field.

In Figure 2-2, cross-section-A reveals a single resident tracer uniformly distributed over the cross section before any fluid has flowed through the PFM, while cross-section-B reflects the subsequent spatial distribution of tracer after exposure to a groundwater flow field. Here, the tracer has been displaced to the right and displaced from the section in a manner consistent with the assumption that fluid streamlines are parallel to the general direction of groundwater flow.

The mass of resident tracer remaining within cross-section B (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 groundwater, the dimensionless cumulative volume, ξ, of groundwater intercepted by the PMF , at a specified well depth is obtained iteratively using the following equation:

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

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

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

where r is the radius of the PFM cylinder; θ, is the water content of the sorbent; R_d is the retardation factor of the resident tracer on the sorbent; and t is the sampling duration. Since in most field applications, 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 sampling durations.

As indicated above, q, is the specific discharge 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:

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

where α' is a factor, 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 is valid over the dimensions of porous medium contributing flow to the PFM. For example, a PFM 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 2-4:

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

where M_c is the mass of contaminant sorbed and L is the length of the sorbent matrix or the vertical thickness of the aquifer interrogated; R_{dc} is the retardation factor of the contaminant on the sorbent, 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. 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).

Table 2-1. Key Design Criteria for the PFM

Parameter	Comments
Sampling Period	The specified duration of continuous flux measurements
Sorbent	Must be resistant to microbial degradation
Retardation Factors of Resident Tracers	A suite of tracers 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

Several potential applications exist for the PFM. Simultaneous measurements of groundwater and contaminant flux have utility 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.

$$\iint J_C dydz = Load[M/T] \tag{2-5}$$

The flux average concentration C_f [M/L^3] can be determined $C_f = [J_c/q]$. Flux integration is performed across a "control plane" drawn perpendicular to the mean groundwater flow direction, located immediately down gradient of the source zone, such that it completely inscribes the dissolved plume extent. While flux across the source control plane helps in estimation of the 'source strength', flux across the plume control plane dictates the extent of reduction of source strength required to achieve regulatory compliance. These estimates help in risk characterization and assessment of the degree of remediation required at the site. Furthermore, contaminant fluxes measured down-gradient from on-going remediation activities, can be used to verify the performance of existing technologies, assess cumulative benefits, and estimate prevailing environmental risks.

2.2. Previous Testing of the Technology

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), and described more fully later (Hatfield et al., 2004). 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 PFM 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. Campbell et al. (2006) designed a devise to quantify both the magnitude and the direction chromium (VI) fluxes; Clark et al. (2005)used an activated alumina as the sorbent matrix. Annable et al. (2005) and Basu et al. (2006) demonstrated the use of PFM at two field sites.

Additional field testing is underway at a DNAPL site (OU-2) at the Hill AFB, Utah; an MTBE site at Port Hueneme, CA; a large DNAPL site at Ft Lewis, Washington; and DNAPL sites at Patrick Air Force Base and Cape Canaveral Air Station in Florida. All of these field tests have involved DNAPL sources (PCE or TCE), and to date no *field-scale* evaluation of the PFM technology for assessing fluxes of inorganic ions has been conducted. The proposed demonstration at the Indian Head site provides such an assessment, using perchlorate as the specific contaminant of DoD interest.

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 sorbent (i.e., activated carbon, ion-exchange resin or surfactant modified zeolite) packed in the sock.

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 therefore the performance of the PFM will depend on several factors. For example, knowing the permeability of the meter and having a good estimate of the aquifer permeability is essential. It is preferable the sorbent have a permeability that is at least 36 times as great as the aquifer. It is also important to note that sorption of the contaminants, and some resident tracers, by the sorbent used as packing in the flux meter may be large but reversible. Consequently, the sorptive characteristics of the contaminant and resident tracers must be known.

2.4. Advantages and Limitations of the Technology

The advantages and limitations of the PFM meter are listed Table 2-2:

Table 2-2. Advantages and Limitations of the PFM

Category	**Advantages**	**Limitations**
Resolution and reliability	▪ High resolution samples obtained ▪ Description of detailed local spatial distribution of contaminant flux ▪ More reliable since it provides time integrated estimate of flux; so transient fluctuations in fluxes are not an issue of concern ▪ Long term monitoring tool ▪ Simultaneous measurement of both water and contaminant flux possible	▪ Too many samples increase cost and time for analysis ▪ Convergence & divergence of flow lines leads to under- or over-estimates of actual flux ▪ Degradation of tracers and contaminants can lead to erroneous flux estimates
Ease of field application	▪ Simple to deploy and easy to retrieve ▪ Borehole technology ▪ Minimum training of personnel required ▪ Wells are not purged; disposal of contaminant purge water not an issue ▪ Does not require power; so can be used in remote locations	▪ Indirectly estimate contaminant discharge with integration of local values of contaminant and groundwater fluxes ▪ Implementation has to be long enough that the initial bore volume perturbation, both chemical and hydraulic, does not significantly affect measurement ▪ Need to cover a whole screen section
Cost	▪ Relatively cheaper than other flux monitoring technologies like IPT	
Data Analysis	▪ Simple to estimate integrated flux from local data obtained	▪ Integration of data obtained across a control plane requires interpolation techniques like Kriging that have their inherent limitations with sparse data sets ▪ Development of different extraction methods is needed depending on contaminants and sorbent
Regulatory or client acceptance	▪ Evolving acceptance of the flux meter	▪ New technology; wide scale application not yet achieved ▪ Tracers used need regulatory approval?

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.

Performance Objectives for the PFM testing at the Indian Head site are listed in Table 3-1.With regards to the quantitative performance objectives, future field application of this technology is contingent upon rigorous statistical comparison of solute and groundwater flux data between the PFM and conventional groundwater measuring devices. Thus, as part of this demonstration, statistics are developed and comparisons are drawn between contaminant and groundwater fluxes derived from the PFM deployments and flux data generated through the conventional methods.

Table 3-1. Performance Objectives

Type of Performance Objective	**Primary Performance Criteria** *(examples)*	**Expected Performance (Metric)** *(examples)*
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 Indian Head site at the Naval Surface Warfare Center (Maryland) was selected for testing the PFM in an aquifer contaminated with perchlorate. This site contained a well-defined dissolved plume in a shallow, permeable, unconfined aquifer (see Section 3.3). Furthermore, it was among few known perchlorate sites on DoD facilities on the Eastern Seaboard.

3.3. Test Site History/Characteristics

3.3.1. Site Description

The Indian Head Division, Naval Surface Warfare Center (IHDIV-NSWC) is located near Indian Head, Maryland (Figure 3-1). The study area (Figure 3-2) is located on the southeast side of IHDIV Building 1419 (Hog Out Facility), which was used to clean out ('hog out') solid propellant containing ammonium perchlorate from various devices, including spent rockets and ejection seat motors. The hog out process and former waste handling/disposal methods have resulted in a perchlorate plume in groundwater near Building 1419 (Figure 3-2).

3.3.2. Regional/Site Hydrogeology

The field demonstration area is located southeast of IHDIV Building 1419 and is approximately 300 feet from the Mattawoman Creek. This site has been characterized by hydrogeological investigations conducted by Envirogen (Envirogen Inc., 2003). The surficial geology of the test plot area was derived from soil samples collected from 17 Geoprobe borings and six test borings that ranged in depth from 16 to 20 feet below the ground surface (bgs). The top 2 to 4 feet consisted of fill material including organic material, gravel, and silty sand. The underlying 11 to 13 feet consisted of mottled light to olive brown clayey to sandy silts. The clay and sand fraction of the silts varied horizontally and vertically. Fine grained sand seams 1 to 2 inches in thickness were seen in many of the boring locations, but these seams were not continuous from boring to boring. At a depth of approximately 15 feet bgs, a 1 to 1 1/2 foot thick layer of sand and gravel was encountered. This layer was found to be continuous throughout the area near the Test Plot. The sand and gravel layer is underlain by a gray clay layer, which extends to a depth of at least 20 feet bgs, the deepest extent of the Geoprobe and test borings. This is likely the clays of the Potomac Group. Figure 3-2 and Figure 3-3 show the Geoprobe and well locations, cross-section plan view and geologic cross section A-A' for the demonstration area.

Groundwater elevations measured in the six monitoring wells in the demonstration area indicate a groundwater flow direction to the southeast toward the Mattawoman Creek. The flow direction essentially follows the surface topography. Depth to groundwater ranged from approximately 6.5 feet to 10.25 feet below the ground surface. The average hydraulic gradient, as measured between wells MW-1 and MW-3, was 0.023 ft/ft. The slug test results indicated an average hydraulic conductivity (K) of approximately 0.012 feet per minute (ft/min) within the aquifer. Based on these values, the estimated groundwater flux is 0.4 ft/day (~12 cm/day).

3.3.3. Perchlorate Plume Characterization

An initial investigation, conducted by Envirogen and IHDIV (Envirogen Inc., 2003), with 17 Geoprobe borings and 6 monitoring wells revealed a shallow, narrow plume of Perchlorate contamination behind IHDIV Building 1419 (Hog Out), with perchlorate levels ranging from 8 to 430 mg/L, and nitrate varying from 4 to approximately 50 mg/L (see Figures 3-2 and 3-6). The pH of site groundwater was generally below 5.0, and values as low as 4.2 were measured in several locations (Table 3-2).

3.4. Completed Operations

In 2002, Envirogen staff evaluated *in situ* perchlorate treatment using biostimulation and the following summary is based on their technical report (Envirogen Inc., 2003). Recirculation cells were used in two test plots (each 12ft x 20 ft); in each plot, two injection wells and two recovery wells were constructed (Figure 3-4) to recirculate buffered water enriched with an electron donor (lactate) to increase pH and promote reductive microbial dechlorination of perchlorate. The recirculation pattern induced within the test cells groundwater flow cross-gradient to the natural groundwater flow direction (Figure 3-4).

The injection wells were installed with approximately 8-feet of screen (0.010 slots) set at the gravel/clay interface. The recovery wells were installed with approximately 15-foot screens (0.010 slots) set four feet into the clay layer. Two sets of well nests were installed between each set of injection/recovery well pairs located at four-foot intervals. Each of the four well nests included one well screened within the saturated zone of the clayey silt layer and above the gravel layer, and one well with a screened interval intersecting the coarse sand and gravel layer located above the underlying clay soils found at the 13 to 16 foot depth interval. The nested and fully penetrating monitoring wells were constructed using 2-inch I.D. schedule 40 PVC well casing and screen materials. Screen lengths (0.010 slots) varied from approximately 7- to 8-feet long for the shallow nested wells, 2.5- to 3-feet long for the deep nested wells, and 10- to 11-feet long for the fully penetrating wells. The treatment and control cells (Test Plot and Control Plot) were located 20 feet apart to ensure that similar Perchlorate concentrations were present in both cells.

Rapid In situ perchlorate biodegradation, using lactate as an electron donor, was observed. Perchlorate levels were reduced by > 95 % in 8 of the 9 monitoring wells within the Test Plot during the demonstration. In two wells, with starting perchlorate concentrations in excess of 210 mg/L, final perchlorate levels after 20 weeks of treatment were < the PQL of 5 μg/L. Conversely, there was no significant reduction in perchlorate levels in the Control Plot.

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Figure 3-1A. IHDIV-NSWC, Indian Head, Maryland (photo source: Carey Yates, IHDIV-NSWC

Figure 3-1B. Hog Out facility in Bldg 1419 (photo source: Carey Yates, IHDIV-NSWC)

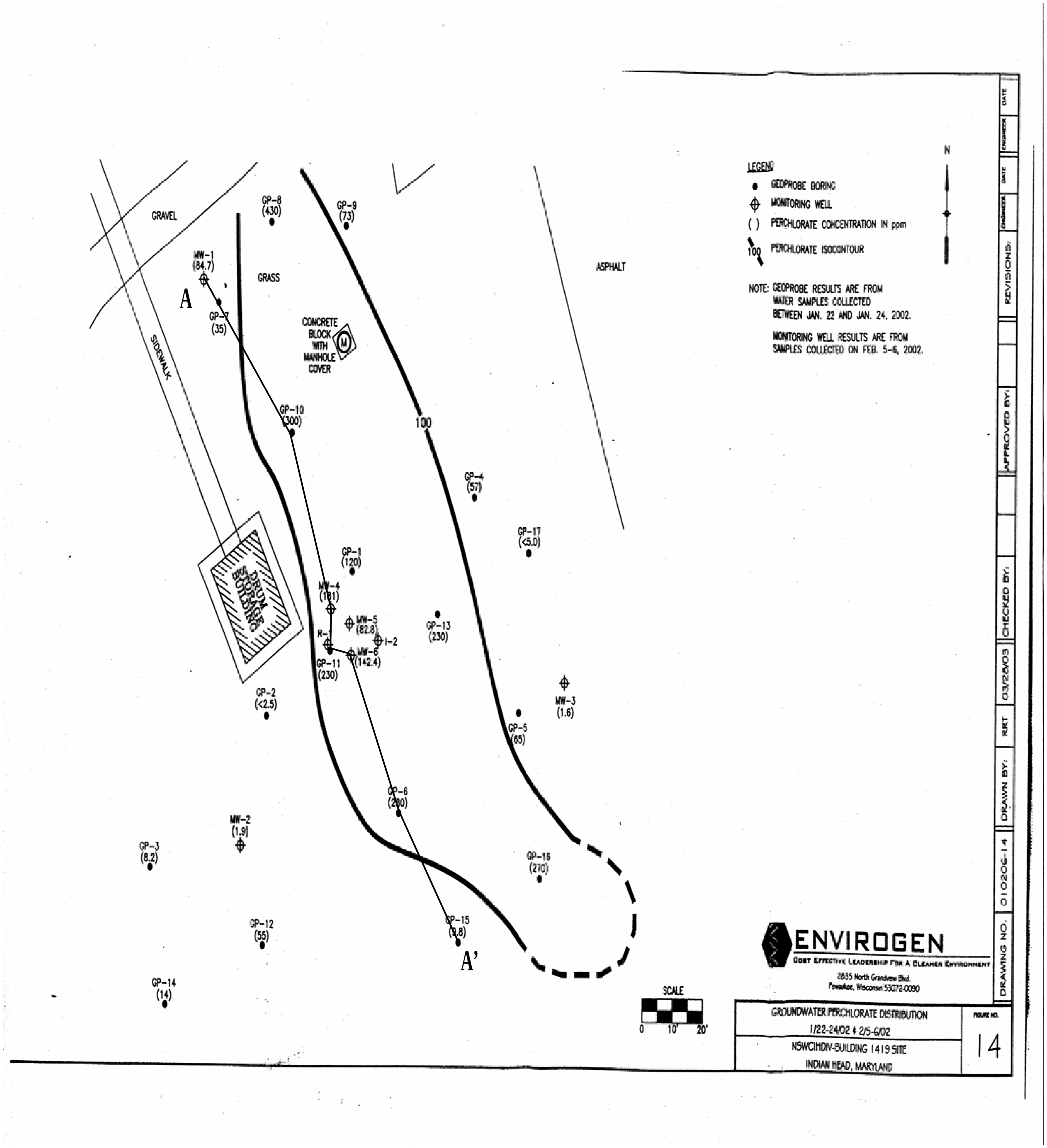


Figure 3-2. Site plan view at IHDIV-NSWC, Indian Head, Maryland (adapted from Envirogen Inc., 2003).

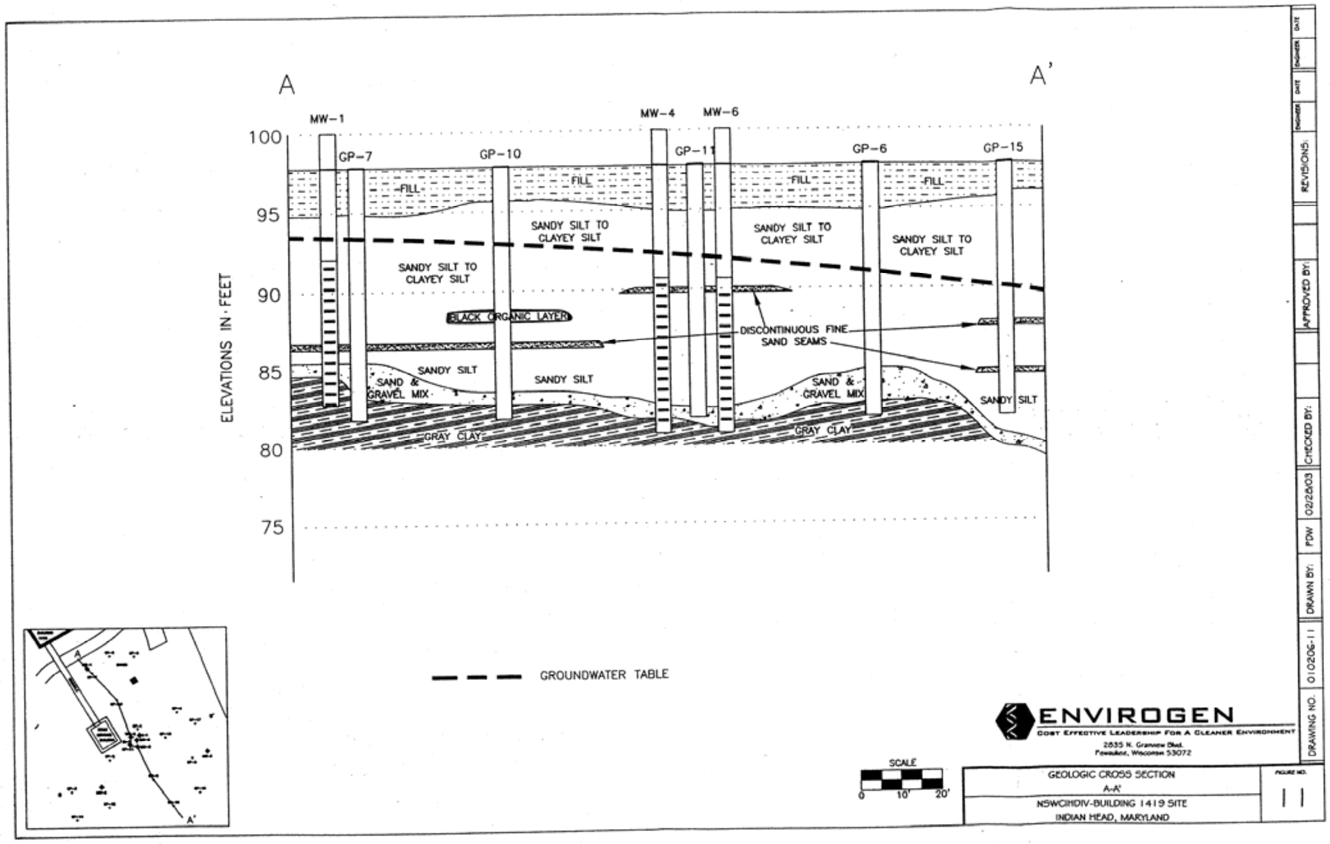


Figure 3-3. Geologic cross section A-A' (Adapted from Envirogen Inc., 2003)

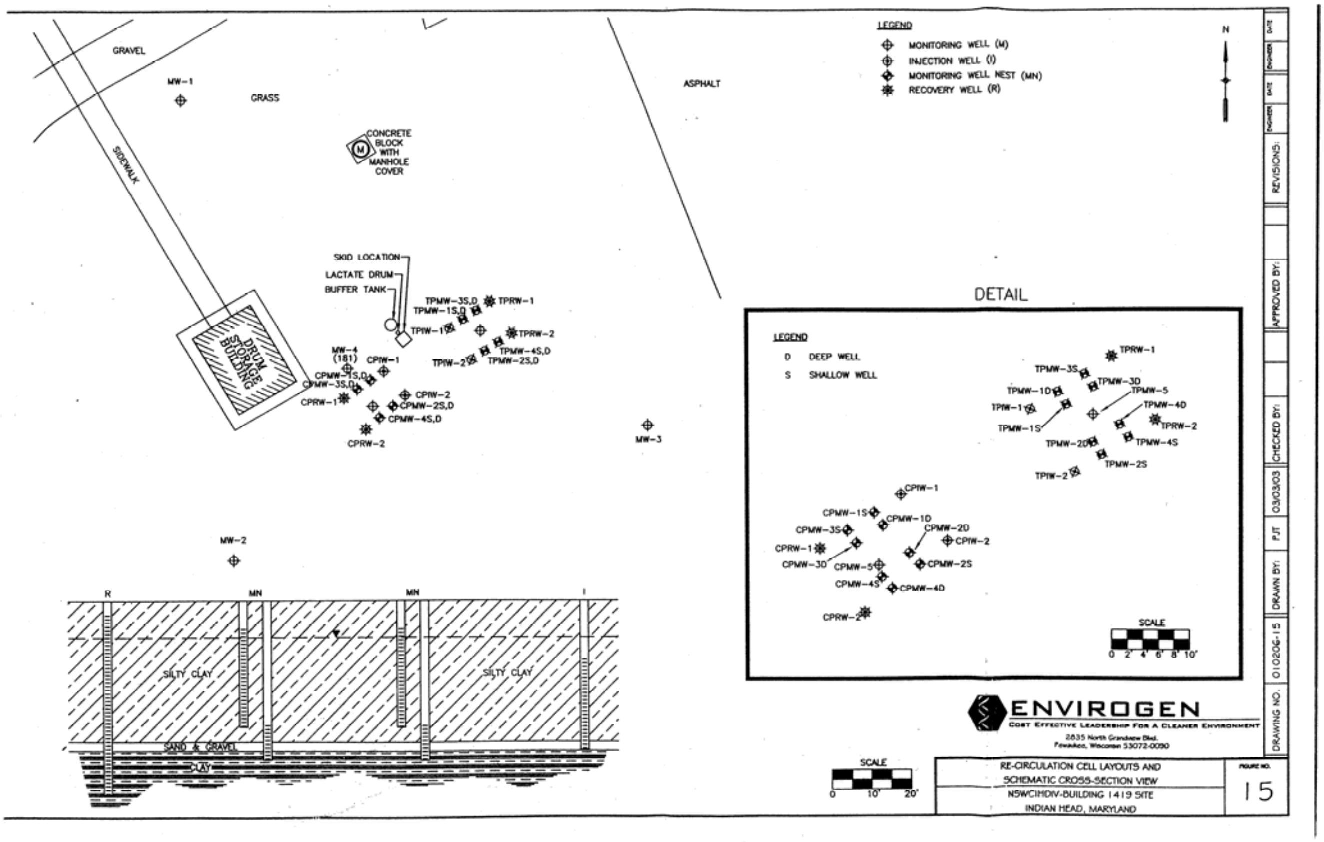
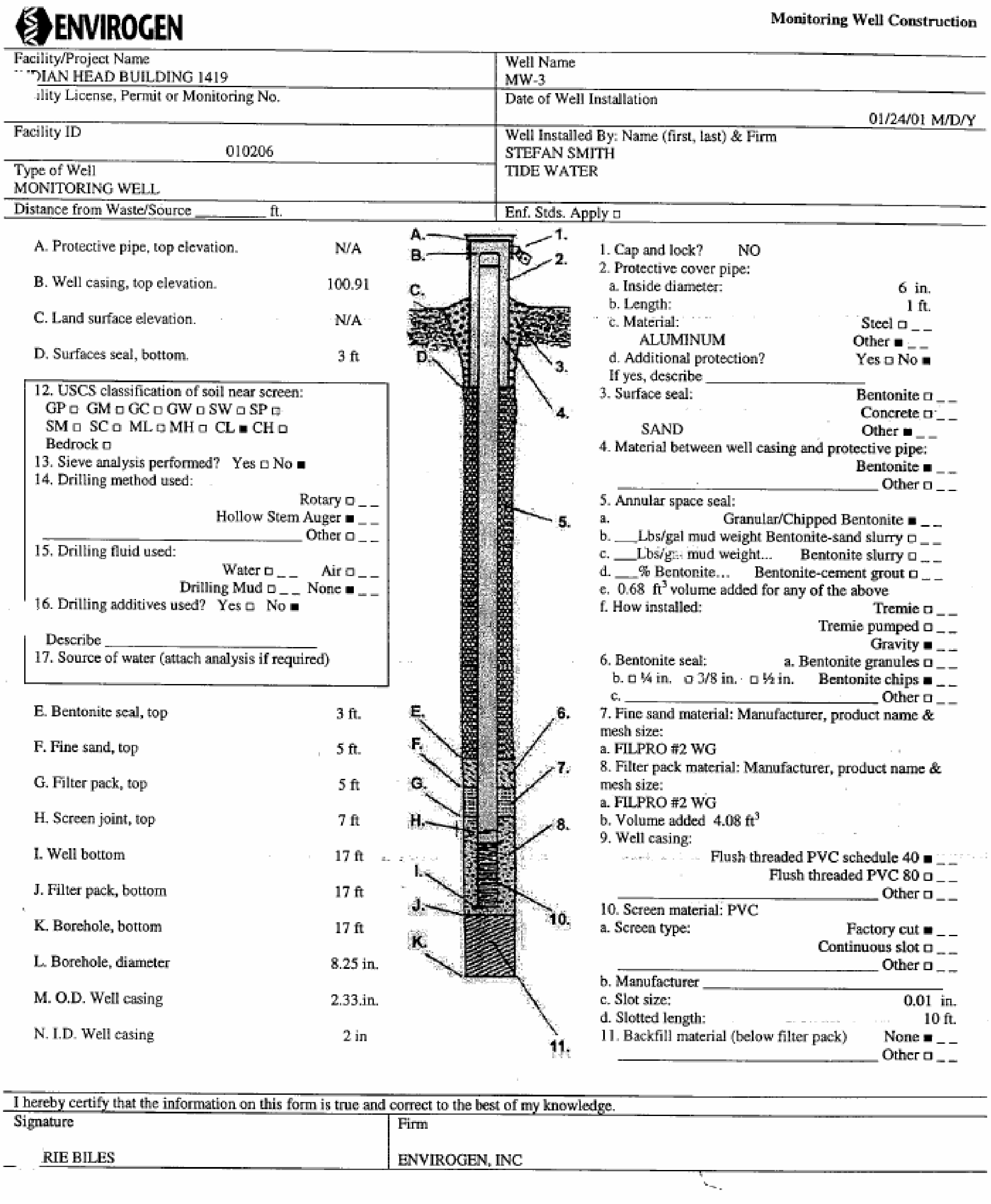


Figure 3-4. Previous *in situ* biotreatment study (Adapted from Envirogen Inc., 2003)



ENVIROGEN

Monitoring Well Construction

Facility/Project Name
DIAN HEAD BUILDING 1419

Well Name
MW-3

ility License, Permit or Monitoring No.

Date of Well Installation
01/24/01 M/D/Y

Facility ID
010206

Well Installed By: Name (first, last) & Firm
STEFAN SMITH
TIDE WATER

Type of Well
MONITORING WELL

Distance from Waste/Source ________ ft.

Enf. Stds. Apply ☐

A. Protective pipe, top elevation.	N/A
B. Well casing, top elevation.	100.91
C. Land surface elevation.	N/A
D. Surfaces seal, bottom.	3 ft

12. USCS classification of soil near screen:
GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP ☐
SM ☐ SC ☐ ML ☐ MH ☐ CL ☒ CH ☐
Bedrock ☐
13. Sieve analysis performed? Yes ☐ No ☒
14. Drilling method used:
Rotary ☐ _ _
Hollow Stem Auger ☒ _ _
________________ Other ☐ _ _
15. Drilling fluid used:
Water ☐ _ _ Air ☐ _ _
Drilling Mud ☐ _ _ None ☒ _ _
16. Drilling additives used? Yes ☐ No ☒
Describe ________________
17. Source of water (attach analysis if required)

E. Bentonite seal, top	3 ft.
F. Fine sand, top	5 ft.
G. Filter pack, top	5 ft
H. Screen joint, top	7 ft
I. Well bottom	17 ft
J. Filter pack, bottom	17 ft
K. Borehole, bottom	17 ft
L. Borehole, diameter	8.25 in.
M. O.D. Well casing	2.33.in.
N. I.D. Well casing	2 in

1. Cap and lock? NO
2. Protective cover pipe:
a. Inside diameter: 6 in.
b. Length: 1 ft.
c. Material: Steel ☐ _ _
ALUMINUM Other ☒ _ _
d. Additional protection? Yes ☐ No ☒
If yes, describe ________________
3. Surface seal: Bentonite ☐ _ _
Concrete ☐ _ _
SAND Other ☒ _ _
4. Material between well casing and protective pipe:
Bentonite ☒ _ _
________________ Other ☐ _ _
5. Annular space seal:
a. Granular/Chipped Bentonite ☒ _ _
b. ___Lbs/gal mud weight Bentonite-sand slurry ☐ _ _
c. ___Lbs/gal mud weight... Bentonite slurry ☐ _ _
d. ___% Bentonite... Bentonite-cement grout ☐ _ _
e. 0.68 ft^3 volume added for any of the above
f. How installed: Tremie ☐ _ _
Tremie pumped ☐ _ _
Gravity ☒ _ _
6. Bentonite seal: a. Bentonite granules ☐ _ _
b. ☐ ¼ in. ☐ 3/8 in. ☐ ½ in. Bentonite chips ☒ _ _
c. ________________ Other ☐ _ _
7. Fine sand material: Manufacturer, product name & mesh size:
a. FILPRO #2 WG
8. Filter pack material: Manufacturer, product name & mesh size:
a. FILPRO #2 WG
b. Volume added 4.08 ft^3
9. Well casing:
Flush threaded PVC schedule 40 ☒ _ _
Flush threaded PVC 80 ☐ _ _
________________ Other ☐ _ _
10. Screen material: PVC
a. Screen type: Factory cut ☒ _ _
Continuous slot ☐ _ _
________________ Other ☐ _ _
b. Manufacturer ________________
c. Slot size: 0.01 in.
d. Slotted length: 10 ft.
11. Backfill material (below filter pack) None ☒ _ _
________________ Other ☐ _ _

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Signature
RIE BILES

Firm
ENVIROGEN, INC

Figure 3-5. Monitoring well construction (Adapted from Envirogen Inc., 2003)

Table 3-2. Groundwater Chemistry at the IHDIV-NSWC Demonstration Site (Envirogen Inc., 2003)

Geoprobe Boring	**Perchlorate (mg/L)**	**Nitrate as N (mg/L)**	**Sulfate (mg/L)**	**pH**	**DO (mg/L)**[1]
GP-1	120	0.6	66	4.67	NA[2]
GP-2	<2.5	3.0	220	8.08	NA
GP-3	8.2	1.9	280	5.23	NA
GP-4	57	0.3	110	4.54	NA
GP-5	65	0.1	130	4.21	1
GP-6	280	11	69	5.62	1
GP-7	35	1.5	66	4.21	0.1
GP-8	430	14	62	4.57	ND[3]
GP-9	73	0.4	56	4.44	0.8
GP-10	300	12	70	4.31	1
GP-11	230	14	72	4.71	0.8
GP-12	55	2.0	110	6.46	ND
GP-13	230	3.8	64	4.61	1.5
GP-14	14	1.5	250	4.97	ND
GP-15	9.8	<0.2	160	5.34	0.2
GP-16	270	2.8	74	4.16	1
GP-17	<5	<0.2	140	4.83	0.2

[1] Analysis performed by colorimetric field method (Chemets).

[2] NA: Not analyzed.

[3] ND: Not determined.

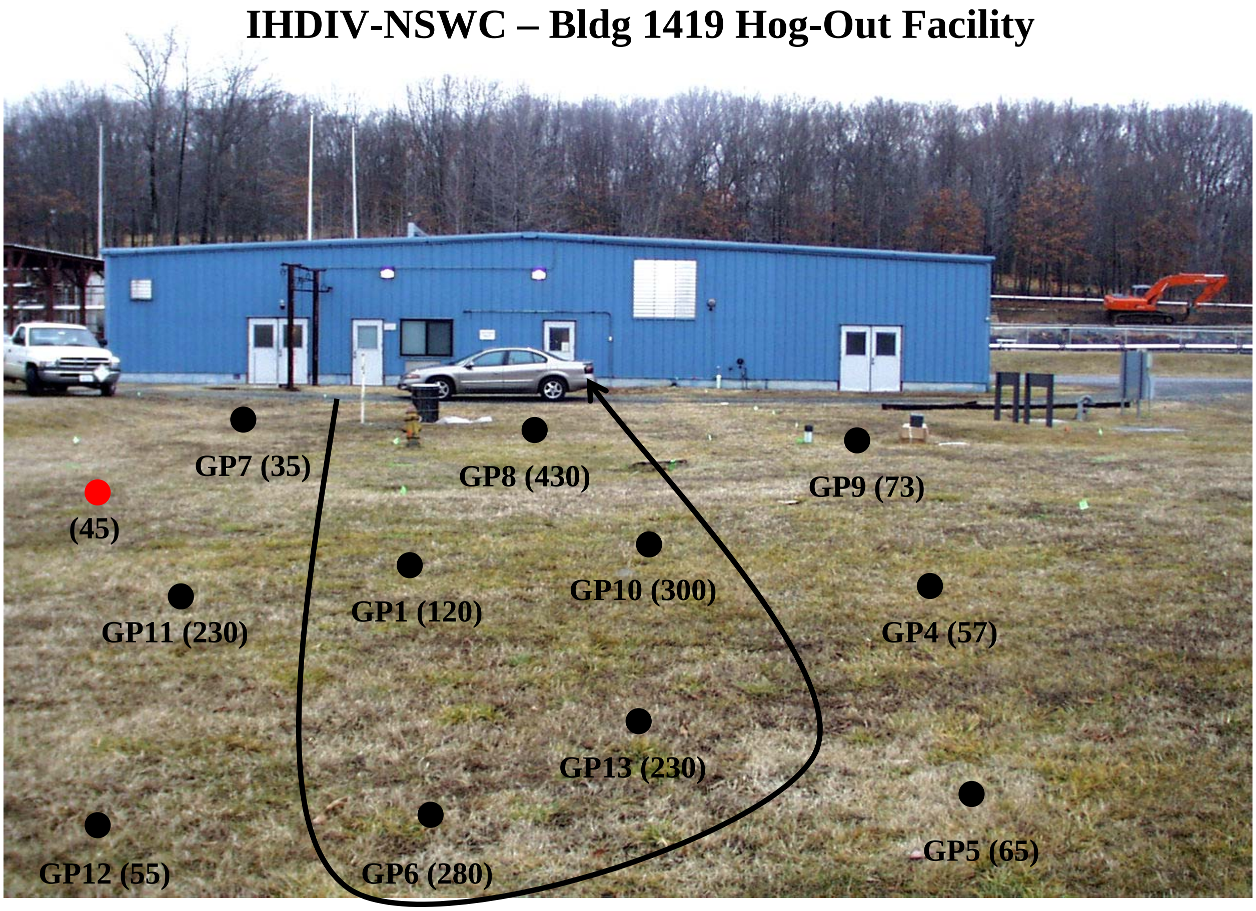


Figure 3-6. Perchlorate concentration distributions measured near Bldg 1419 using Geoprobe. Also see Table 3-2 for other geochemical data (photo source: Carey Yates, IHDIV-NSWC).

3.5. Pre-demonstration Testing and Analysis

Perchlorate concentrations measured by Envirogen were used in making initial assessment of the site. This site is suspected to have two sources, one around GP-8 and another around GP-6. This becomes evident if one studies the trend of groundwater concentrations down gradient from GP-8 (Figure 3-2). Concentrations decreased from 430 mg/L (GP-8) to 120mg/L (GP-1) and then abruptly increased to 230 mg/L (around GP-11 and 13) and to 280 mg/L at GP-6 (Figure 3-2, 3-6).

The importance of source remediation of DNAPL sites has been recognized widely over the last few years (Kavanaugh and Rao, 2003), but plume control is still one of the primary remedial objectives at perchlorate sites. A review of literature (Flowers and Hunt, 1999) revealed that perchlorate contamination in groundwater is similar to DNAPL contamination in quite a few aspects (Table 3-3) pointing to the fact that source zone treatment should also be considered at perchlorate sites. Perchlorate brine released in the vadose zone can “sink” through the saturated zone to confining layer (density contrast with groundwater is 0.11 g/ml) and can also penetrate the confining unit. The brine is then released back to the aquifer by both advective transport and molecular diffusion, and thus serves as a long-term source of perchlorate contamination for the permeable zone (Figure 3-7).

Table 3-3. Analogy of perchlorate contamination to TCE Contamination (Adapted from: Flowers and Hunt, 1999)

	TCE	Perchlorate
Solubility	1100 mg/L	200,000 mg/L
DW standard	0.005 mg/L	0.018 mg/L
Source	Pure Liquid	Brine
Emplacement	Lens/Pool	Confining Layer
Recovery	Mass transfer	Mass Transfer
Time scale	~100 Years	~100 Years

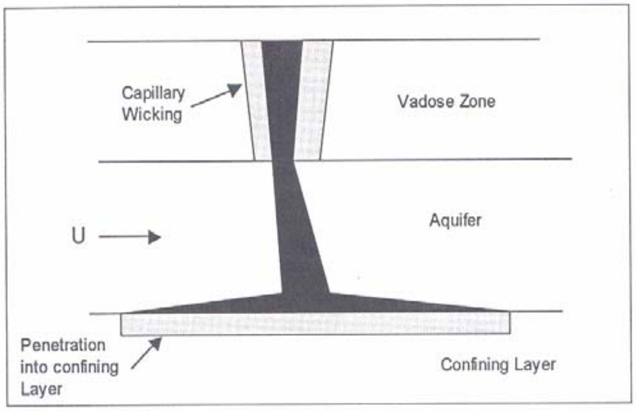


Figure 3-7. Conceptual model of subsurface brine transport (Adapted from: Flowers and Hunt, 1999).

To establish remedial goals for perchlorate source zone treatment, the source strength should be estimated. At the present site, this is accomplished by calculating the integrated mass discharge from the source zone using the concentration data provided by Envirogen. The maximum perchlorate concentration was observed at GP-8 (430 mg/L) and this is suspected to be the primary source zone (Figure 3-2). The strength of the source can be estimated by the integrated mass flux across a control plane passing through GP-8 and transverse to the flow direction. Visual examination (Figure 3-2) revealed that the plume width is about 30 feet around GP-8 and the saturated thickness of the aquifer is about 10 feet down to the confining unit. An average groundwater flux of 0.40 feet/day and a porosity of 0.46 are assumed over the entire control plane. As an upper bound, we assume the highest concentration actually observed (430 mg/L) to be uniform over the entire control plane. This would yield a mass flux of 0.64 kg/day. Similarly, for the second source around GP-6, the estimated mass discharge is 0.56 kg/day with 50-ft width and 8-ft depth of the control plane. But, 0.64 kg/day and 0.56 kg/day for the two (suspected) sources may still be a significant overestimation. A better estimation method will be to integrate flux contours across the control plane. To accomplish this, perchlorate flux contours needs to be generated using concentration contours and velocity profiles.

The flux averaged concentration C_f is given by:

$$C_f = \frac{J}{q} \tag{3-2}$$

Note that C_f can be calculated as an average over the entire well screen, and compared with perchlorate concentrations measured in samples collected using conventional methods. Also, depth distribution of *local* concentration values can be estimated such that variations along the well screen length can be examined. To compare these depth patterns delineated by PFM deployments, data from MLS samples need to be collected. The first type of comparison was attempted here since MLS were not installed at this site.

3.6. Testing and Evaluation Plan

3.6.1. Proposed Flux Meter Demonstration

The scope of the demonstration project included testing the performance of the PFM for anionic contaminants within the IHDIV perchlorate plume at Indian Head. This specific site was selected to provide an assessment of the SM-SI-GAC as a sorbent for PFM to measure perchlorate fluxes near the source zone and within the plume using existing wells. The SI-GAC was purchased from Barnaby & Sutcliffe Co. (Columbus, OH), preloaded with 0.026%. SI-GAC was a commercial product commonly used to treat water to potable drinking water standards, and therefore considered environmentally safe for use in PFM.

The groundwater velocity and perchlorate mass flux were compared for different deployment periods and with those from conventional methods (i.e., estimation using Darcy flux and perchlorate concentration). The final selection of the wells used was be made on-site and based on existing conditions of the wells and recommendations from on-site personnel.

3.6.2. Demonstration Set-Up and Start-Up

Laboratory batch experiments were conducted at Purdue University to select sorbents and tracers. In addition, flow-through-box aquifer experiments were conducted under known flow conditions to assess the reliability of the sorbents and tracers to be used at the Indian Head test site for evaluating the field-scale performance of the PFM.

Solid-aqueous phase batch partitioning tests were conducted to evaluate two types of sorbents for intercepting contaminants (perchlorate) and releasing tracers. Silver Impregnated Granular Activated Carbon (SI-GAC) and Surfactant Modified Zeolite (SMZ) were the primary sorbents tested in lab studies because they were inexpensive compared to anionic resin. SMZ and GAC cost \$450/ton and \$500/ton to \$1000/ton, respectively while anionic resin was priced at \$3000/ton to \$4000/ton; furthermore, they could be recycled. In batch tests, sorption of alcohol tracers and perchlorate were measured, and the isotherms were used to assess the applicability of each sorbent as a packing media for the PFM.

Flow experiments in 3-D aquifer analogs were conducted under known flow conditions to characterize the performance of the PFM. Water-tight containers (glass or stainless steel) with dimensions of 70 cm by 30 cm and 11 cm deep (perchlorate) were packed homogeneously with sand, and used as the aquifer analog. The two ends of the box were packed with coarse gravel, and used for flow injection and extraction. A constant head gradient was maintained across the width of the box to generate steady, saturated, confined flow conditions. An aqueous solution of oxyanions (~100 mg/L of perchlorate) was allowed to flow through the aquifer analog, until the influent and effluent solution concentration were nearly identical.

The PFMs were packed with SM-SI-GAC, pre-loaded with tracers, were packed in permeable cotton socks and including any impermeable dividers to minimize vertical flow. Before packing, the sorbent was pre-equilibrated with a suite of resident alcohol tracers. The socks were prepared in the laboratory and transported to the field site in the sealed PVC pipes which were kept cold with blue ice. The PFMs were installed into the two-inch monitoring wells. It was estimated that the construction and installation time of each PFM was around 30 minutes (depending on personnel).
The PFMs were to remain in the flow field ranging from 2 to 8 weeks for the purpose of assessing short and long term performance. During PFM retrieval, the device was removed from the well and segmented vertically into one-foot sections for sub-sampling. The GAC in each segment was homogenized and sub-sampled for analysis. Analysis involves extraction of GAC to assess the contaminant intercepted and the mass of resident tracer lost. The analysis was done as per the procedure developed at the University of Florida (Annable et al., 2005). The process of extraction and GAC sub-sampling required about 30 minutes.

3.6.3. Period of Operation

The work plan at the Indian Head site was conducted over 10 weeks (two events) measuring groundwater and perchlorate fluxes in existing wells.

3.6.4. Amount /Treatment Rate of Material to be Treated

Not applicable.

3.6.5. Residuals Handling

PFM generate a minimal amount of waste. An event of deploying PFMs in 5 wells generated approximately 25 liters of sorbent, which contains tracers and contaminants. This waste was stored on-site in drums for later disposal. All materials brought back to West Lafayette for analysis were disposed of using proper laboratory protocol.

3.6.6. Operating Parameters for the Technology

Operationally, the PFM is very simple to install which is among the major advantages of this technique. Although one operator can deploy the PFMs, it is operationally more convenient to have two or more operators, and it is feasible for a three-person team to install 40 to 60 PFMs in a day at a site. In addition, the GAC sample extraction method is also a simple procedure, which can be completed by a single analyst. Sample extraction vials are pre-weighed prior to transport to the site.

3.6.7. Experimental Design

Flux Measurements

It was estimated the field-scale demonstration of the PFM technology at the Indian Head site would require a ten-week period. The PFMs were installed in several of the existing 2-inch monitoring wells, constructed by ASTM: D1586. From the perchlorate concentration contours shown in Figure 3-2, the site was divided into two zones: near-source zone and plume. Perchlorate fluxes were measured in wells representing a broad range of ambient concentrations. Water samples were taken in advance of PFM installation to ensure meter performance was evaluated over a broad range of perchlorate fluxes.

The location of the near-source zone was estimated to exist near Geoprobe 8 (GP-8) where the highest perchlorate concentration was previously reported to be 430 mg/L. The plume zone was further subdivided into mid-plume zone around Monitoring well 4 (MW-4), and the toe of plume, around Monitoring Wells 2 and 3 (MW-2 and -3). Since MW-1 was the nearest available monitoring well to the GP-8, it was used to estimate local perchlorate flux in the near-source zone. For the mid-plume zone, MW-4 and nested wells, installed by Envirogen Inc. for the previous *in situ* biotreatment study, were used. Monitoring Well MW-3 was used to estimate perchlorate flux for the toe of the plume. Two other wells – CPMW3S (shallow) and CPM3D (deep) were also selected for PFM deployment. However, it was discovered that significant amount (~1 foot) of sand and silt had accumulated at the bottom of these wells, indicating collapse of the well casing. Thus, PFM data are not reliable for these wells. Attention here is therefore focused on the three wells: MW-1, MW3, and MW-4. All three monitoring wells have 10-ft screen, and two 5-ft socks were installed in each well to cover the whole screened interval. After retrieval, the socks were sampled in one-foot intervals, and the lab data on perchlorate capture and resident tracer loss were used to estimate local groundwater fluxes and contaminant fluxes with a depth-resolution of one foot. These data were compared with estimated contaminant fluxes based on measured perchlorate concentrations and estimated groundwater flux. The PFMs were deployed twice, once for a period of 2 weeks and the second for a period of 8 weeks.

Advantages & Limitations

The PFM allows for an estimation of the time-averaged fluxes, thus reducing the errors from under- or over-estimation by discretely measured data that are easily affected by seasonal fluctuations. Therefore, perchlorate fluxes in the near-source zone and the plume zone, using the PFMs, produce more reliable local estimates. However, because existing wells are used, both the locations and the numbers of wells are sub-optimal for estimation of the total contaminant mass discharge (i.e., local fluxes integrated over a control plane normal to the mean plume transport direction). Thus, the data are not appropriate for evaluating the “source strength” and the likely natural attenuation in the plume.

The other primary concern is that the locations of most of the existing wells (MW-1, and MW-3) are outside of the concentration contours shown in Figure 3-2. Thus, perchlorate flux estimates using these wells are likely to underestimate the perchlorate fluxes within the dissolved plume (volume inscribed within the contour) at this site.

Another concern is that MW-4 is located in the mid-plume area that had high perchlorate concentrations. but one well is not enough to characterize entire site. Additionally, MW-4 was in the control area of previous *in situ* biotreatment study; thus, this well might be influences by the geochemical and hydrological changes from the previous study and therefore may not produce the representative estimation of perchlorate fluxes for mid-plume area.

3.6.8. Sampling Plan

The PFM testing experiments used screened wells. Sub-samples were taken in vertical intervals of approximately 30 cm to provide depth-resolved flux distributions. Groundwater samples were collected from the wells prior to PFM installation. These samples were used to calculate perchlorate fluxes based on estimated groundwater fluxes from prior measures of hydraulic conductivity and current measures of hydraulic gradients.

Sample Collection. Two types of samples were collected during this study: groundwater samples from wells, and sorbent samples from PFMs. Sampling methods and sample handling procedures were as follows.

Water Samples - Wells were pumped or bailed prior to sampling. Ground water samples were collected in 40-mL VOA vials, placed immediately in coolers containing dry ice and transported to Purdue University, West Lafayette, Indiana. Sample analysis for alcohol tracers was less than a 14-day holding time.

Sorbent Samples – Sorbent samples were collected from the extracted PFMs. The 5-foot PFM were segmented into 1 foot sub-sections and transferred to containers for homogenization. Samples were thoroughly mixed and sub-sampled into 250mL wide-mouth jars, placed in a cooler and transported to Purdue University, West Lafayette, Indiana. Sample analysis was completed within a 28-day holding time.

Sample Analysis. All samples were analyzed at laboratories at Purdue University. Alcohol tracers were analyzed by direct liquid injection on a Gas Chromatograph. Perchlorate was analyzed according to EPA Method 314.1, utilizing Ion Chromatography. Details of analytical methods provided in Appendix A. Detection limits were approximately 1 mg/L for alcohol tracers and 1μg/L for perchlorate.

Experimental Controls. Project personnel measured water levels in each well before and after PFM deployment. Small socks were used to calibrate the loss of pre-loaded alcohol tracers during transport; subsequent data analyses suggested that volatilization and other losses were negligibly small.

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 were required to maintain reproducible experiments. These procedures were fully described in the QA/QC plan in appendix C.

Data Quality Indicators. Average groundwater flux for the site was estimated based on the PFM data, and compared to previously reported data. Depth profiles of groundwater flux, as measured by the PFMs, were compared with the borehole logs for each well. Perchlorate flux-average concentrations were calculated for each well, and compared to concentration in groundwater samples of previously reported concentration data (Envirogen Inc., 2003).

3.7. Demobilization

Minimal demobilization is required for the PFM testing. All equipment required to conduct the field work was transported to and from the site for each event.

3.8. Health and Safety Plan (HASP)

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

3.9. Selection of Analytical/Testing Methods

Analytical methods are provided in Appendix A.

3.10. Selection of Analytical/Testing Laboratory

No outside laboratories required.

3.11. Management and Staffing

Dr. Suresh Rao and Ms. Irene Poyer (both at Purdue University) were responsible for planning and managing the field activities at the Indian Head site. Drs. Annable and Hatfield (University of Florida) were involved in design of the demonstration, deployment and retrieval of the flux meters, and interpretation of the collected flux data. Several doctoral students at Purdue University assisted with field activities, laboratory sample analysis, and data analysis. Ms. Irene Poyer oversaw all analytical work at Purdue University.

3.12. Demonstration Schedule

The actual schedule of demonstration events is provided below. The first event required 21 days while the second 44 days.

Experiment	Deployment Period
First round flux assessment (21 days)	Nov. 22 to Dec. 13, 2004
Second round flux assessment (44 days)	Dec. 23, 2004 to Jan. 26, 2005.

4.0. Performance Assessment

4.1. Performance Criteria

Described in the tabular format below (Table 4-1) is the general performance criteria 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**
Ground Water Flux Estimates	Compare ground water flow based on the PFMs between wells and sampling events	*Primary*
Contaminant Flux Estimates	Compare contaminant fluxes based on the PFMs between wells and sampling events	*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 Perchlorate plumes.	*Primary*

4.2. Performance Confirmation Methods

The quality of groundwater and contaminant flux estimates based on the PFM installations is compared to alternative measures of these quantities. Future field application of this technology is contingent upon rigorous statistical comparison of solute and groundwater flux data between the PFM and conventional groundwater measuring devices.

The installation and interpretation of the PFM data are generally the same in all experiments designed to conduct this comparison. Contaminant fluxes from PFM deployments are compared with estimates based on perchlorate concentrations in groundwater samples collected from the fully screened wells.

Table 4-2 lists for each performance criterion and expected or a desired value and the method that used to confirm performance such that the performance of the PFM is assessed as acceptable or not.

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)		
Water flux estimates	*Estimate within 25%*	*Compare PFM measured water fluxes between wells and sampling events*
Contaminant flux estimates	*Estimate within 25%*	*Compare PFM measured contaminant fluxes between wells and sampling events*
Vertical variations in water and contaminant flux between wells	*Estimate within 40% (for water fluxes alone)*	*Compare flux statistics between wells*
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* *Fractured rock, radionuclides*	*Experience from demonstration operation*

Qualitative metrics were considered for several performance criteria including: ease of use, reliability, safety, and versatility. Ease of use was considered an important performance criterion and it was expected that the results of the demonstration would document the level of training required to install/extract and interpret information from the PFM. Deploying and recovering pre-packed PFMs was a simple task, and does not require specialized training to perform these tasks. Special precautions were, however, necessary to use stainless steel cables, etc that would not be corroded by strongly oxidizing conditions in groundwater, especially near the source. Reliability was assessed from records of total device installations verses total numbers of device failures. For this demonstration, no failures of PFM deployments or recoveries were recorded. However, PFMs could not be deployed in two wells that had collapsed. A positive assessment the versatility criterion was simply an objective assessment that the PFM was successfully applied to generate both short- and long-term flux assessments, and that it help build a database to define the applicability of the PFM under different site conditions.

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 several orders of magnitude (for groundwater fluxes the range is expected to be within two orders of magnitude), 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 Indian Head experiments discussed above, a successful comparison would results if depth-averaged contaminant fluxes were estimated within 25% of fluxes calculated using measured depth-averaged perchlorate concentrations in the flux wells and groundwater fluxes estimated from measured gradients and historical measures of hydraulic conductivity. Depth variations in perchlorate and groundwater fluxes were compared between PFMs deployed in different wells. A well-to-well comparison of groundwater fluxes that are within 40% will be viewed as measurements taken from within the same geological formation. No quantitative comparison criterion was specified for vertical variations in perchlorate fluxes; however, values and trends were assessed. Errors for groundwater flux estimates were not provided since values could only be estimated using measured hydraulic gradients and hydraulic conductivity measurements.

4.3. Data Analysis, Interpretation and Evaluation

4.3.1. Extending PFM Applications to Oxyanions

In field-scale testing of PFM, the contaminants of concern to date have been DNAPL (PCE, TCE, DCE, VC, etc.) and fuel hydrocarbon (BTEX, MTBE, TBA, etc) constituents. Here, we report the extension of the PFM application to measuring fluxes of inorganic contaminants. Specifically, we examined applications for sites contaminated with *oxyanions* such as perchlorate, chromate, selenate, and arsenate. It is also possible to extend the PFM application to monitoring fluxes of e-receptors and e-donors and their byproducts (nitrate, sulfate, lactate, etc) as well as nutrients (nitrate, phosphate, etc). While commercially available anion exchange resins can be used as PFM sorbents, our goal was to develop alternate sorbents as less expensive options. Research focused on surfactant modification of natural zeolite and granular activated carbon (GAC); however, emphasis in this report is on the work completed on surfactant-modified GAC.

Development and assessment of these new sorbents for PFMs comprised three groups of activities: (1) laboratory batch and column studies on surfactant modification of GAC and SI-GAC (SM-GAC; SM-SI-GAC) and zeolites (SMZ), and evaluating their anion exchange capacity (AEC) and selectivity; (2) development and implementation of oxyanion extraction and ion-chromatography protocols; and (3) laboratory and field studies to examine the utility of the SM-GAC for measuring groundwater and oxyanion fluxes. Each of these phases is discussed in the following sections.

4.3.2. Surfactant Modified Sorbents for PFMs

Design Criteria and Constraints

Selection of the sorbent matrix to be used in the PFM is based on two groups of attributes: (1) hydrologic properties, and (2) sorptive properties. The particle-size distribution of the solid matrix needs to be sufficiently large compared to the saturated conductivity of the aquifer in which the PFM is deployed, so that flow convergence (rather than divergence) is to be expected. The solid matrix needs to have a large Hardness Number in order to retain its physical integrity during surfactant modification, packing, field deployment and retrieval. Furthermore, the sorbent should have sufficiently large sorption capacity for both resident tracers (here, branched alcohols) and the contaminants of interest at the site (here, oxyanions).

The sorption isotherms for the resident tracers should preferably be linear to simplify data analysis, and non-competitive allowing multiple tracers to be used for measuring groundwater fluxes. The modification of the sorbent should not significantly interfere with tracer sorption capacity and should generate sufficient AEC. The modifier (in our case, a cationic surfactant HDTMA) should have high affinity for the sorbent, and the functional group providing the AEC should have high selectivity for the oxyanions (here, perchlorate) of interest. Ion exchange processes are controlled by the geochemistry of the solution phase (e.g., ion composition; ionic strength; pH) and the solid matrix (e.g., mineralogy; ZPC, pH), and the ion-exchange isotherms are nonlinear. But, two characteristics of the sorbent are important for our applications here: (1) the maximum capacity for sorption of the anions as defined by the AEC; and (2) Competitive ion exchange among the ions present, as defined by their selectivity, given the functional groups on the sorbent responsible for the anion exchange capacity, physical and chemical accessibility of these charge sites (e.g., pore-size distribution of the sorbent; edge or exterior vs internal or inter-lamellar sites; steric hindrance, etc.), and the anionic contaminant properties (charge density, ionic radius, etc). However, large AEC and highly selective functional group (here, a quaternary amine) ensures that all of the perchlorate passing through the PFM is ‘captured’ even in the presence of other competitive anions (e.g., sulfates, carbonates, nitrate, etc) typical in groundwater at contaminated sites. Also, in the low-coverage region, a liner sorption isotherm approximation is valid.

Stable AEC of the modified sorbent is ensured by strong sorption of the modifier (here, the HDTMA surfactant) to the sorbent (i.e., losses by desorption during the deployment period are minimal), and recalcitrance to microbial or chemical degradation. Finally, bulk quantities of the modified sorbent are needed at a reasonable cost for deployment of multiple PFMs at one or more field sites. Thus, one commercial resin (AG1-X8) and two alternatives (zeolites and GAC) were compared and examined in this study.

Anion Exchange Resins

AG1-X8 is a porous, adsorbent material having a high sorption capacity for the groundwater contaminant of interest here, chromate. The AG1-X8 is a 20-50 mesh resin with a 1.2 meq/ml capacity which was shipped in the hydroxide form from Bio-Rad Laboratories (Hercules, CA). For laboratory use, it was converted to the bicarbonate form by washing slowly with 12 bed volumes of 1M $NaHCO_3$, followed by 12 bed volumes of deionized water. The wet, drained AG1-X8 (HCO_3^-) resin has a bed density of 0.75 g cm^{-3}, a porosity measured to be 0.50, and a saturated hydraulic conductivity of 0.84 cm s^{-1} (Diniz et al., 2000). Although the sorbent properties of this commercially available resin has advantages for use in controlled laboratory scale experiments, the overall preparation for a field-scale implementation is time consuming and cost prohibitive.

Natural Zeolites

Zeolites are naturally occurring minerals with a rigid, 3-dimensional crystalline structure. A variety of synthetic zeolites are also used for a broad range of applications. Unlike clays, the rigid structure of zeolites prevents it from shrinking and swelling upon hydration. A defining feature of zeolites is their cage-like structure, and the "hole" dimensions range from 3 to 10 A (Figure 4-1). Zeolites also have a large surface area (external BET surface area: 14 m^2/g), a large cation exchange capacity (Total CEC: 900 meq/kg; external CEC: 100 meq/kg), resulting from a permanent, negatively charged surface created by isomorphic substitution of the trivalent aluminum cation for tetravalent silica. Because of these intrinsic physical and chemical properties, zeolites are excellent candidates as a PFM packing material.

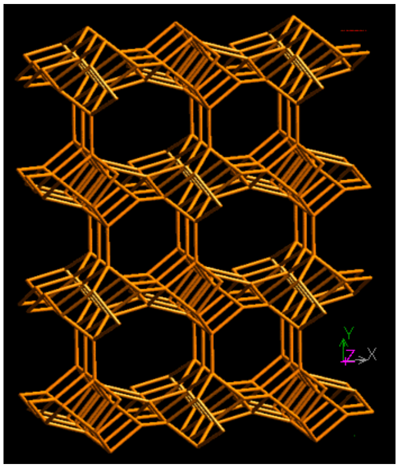


Figure 4-1. Molecular Structure of Zeolite (Adapted from: Li and Bowman, 1997).

Research groups at the New Mexico Institute of Mining and Technology have investigated surfactant-modified zeolite (SMZ) for the removal of various types of contaminants such as perchloroethylene, phenol, chromate, and lead (Bowman et al., 1997, Li et al., 2000, Li and Bowman, 1998). The zeolite material they used was clinoptilolite [(Ca, Na_2, K_2) ($Al_6Si_{30}O_{72}$).24H_2O] mined from the St Cloud deposit in southeastern New Mexico.

The ion exchange of the cationic surfactants -- such as hexadecyltrimethyammonium (HDTMA) -- on zeolites occurs directly on the external mineral surface (Figure 4-2). The "cage" dimensions (3-10 A) are too small for the HDTMA cation (TMA head diameter: 0.69 nm; HD-chain diameter: 0.4 nm; HD-chain length: 3.5 nm) can not access the interior sites. The positively charged head attaches itself to the negatively charged *external* surfaces of the mineral. Surfactants can be loaded on to the zeolite at rates exceeding the external CEC because of the tail-to-tail interactions. For example, at loading nominally twice the external CEC (see Figure 4-2), a surfactant "bilayer" is formed (Figure 4-3). As a result, the surfactant-modified zeolite (SMZ) now provides; 1) a hydrophobic sorption domain within the brush-like, bilayer comprising of the long alkyl chains (see Figure 4-3); 2) 'external' anion exchange sites from the inverted quaternary amine heads; and 3) cation exchange sites for small cations that can access the interior of the zeolite 'cage'.

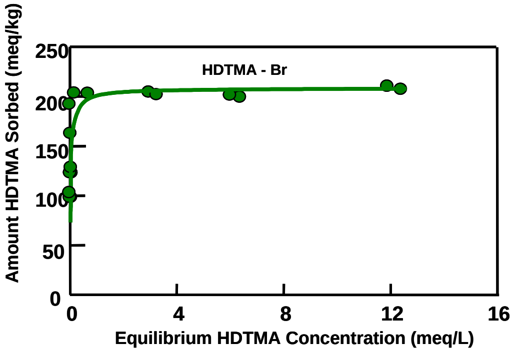


Figure 4-2. Isotherm of HDTMA Sorption onto Natural Zeolite.

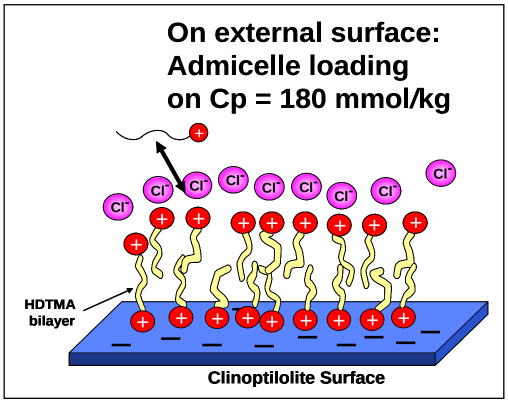


Figure 4-3. Schematic of "Bilayer" Coverage of HDTMA on Zeolite.

In addition to structure stability, zeolites are available in various grain (mesh) sizes to accommodate the range of hydraulic characteristics required for use a sorbent in PFMs for site characterization or as the sorbent placed in reactive permeable barriers (PRBs) for plume treatment at contaminated sites (Haggerty and Bowman, 1994; Sullivan et al., 1997). Here, we have assessed SMZ qualities as a sorbent used in PFMs to measure groundwater and perchlorate fluxes in laboratory experiments.

<u>Granular Activated Carbon (GAC)</u>

Properties of silver-impregnated granular activated carbon (SI-GAC) and granular activated carbon (GAC) and their use in water and wastewater treatment are well known (Bayati, 1997; Etris, 1991). GAC and SI-GAC have been used in previous lab and field studies as the sorbent matrix for PFMs (Hatfield et al., 2004; Annable et al., 2005; Basu et al., 2006). The GAC and SI-GAC we used was ASTM 12-30 mesh material supplied by Barnebey & Sutcliffe Corp., Columbus, OH. High sorption capacity for a broad range of organic contaminants is the result of large surface area, and physical integrity is ensured by its hardness (Figures 4-4 and 4-5; Table 4-3). The saturated hydraulic conductivity of GAC is about 3 m/hr (Hatfield et al., 2004; Annable et al., 2005).

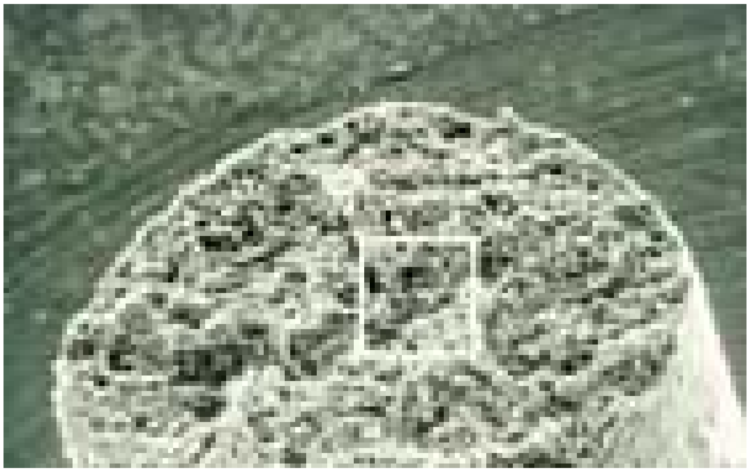


Figure 4-4. Picture of GAC Surface

Figure 4-5. Magnification of GAC Surface of ASTM 12-30 mesh

Table 4-3. GAC Properties

Pore-size Distribution	
Micropores (0-20 A)	62
Mesopores (20-500 A)	22
Macropores (>500 A)	16
Total Surface Area (m^2/g)	1100-1200
Ash Content (%)	2-3
Iodine Number (mg/g)	1050
Hardness Number (%)	98
Bulk Density (g/cm^3)	0.48

Surfactant Modification of GAC

We modified GAC and SI-GAC with a cationic surfactant, hexadecyltrimethylammonium (HDTMA), to enhance the anion exchange capacity from the quaternary amine functional groups of HDTMA. The modified GAC can sorb non-polar hydrophobic contaminants (such as DNAPL and LNAPL constituents or alcohol tracers) on the carbon matrix, as well as oxyanions such as perchlorate (ClO_4^-), chromate (CrO_4^{2-}) and selenate (SeO_4^{2-}) at the quaternary ammonium functional group. In addition, the HDTMA monomers in aqueous solutions are known to have inhibitory or toxic effects to Gram-negative bacteria, but sorbed surfactant may not exhibit similar properties (Lee et al., 1998). Thus, the silver ions and the surfactant monomers should help prevent biodegradation losses of resident alcohol tracers and the captured contaminants during the PFM deployment period.

The use of SM-SI-GAC as a sorbent for the PFM is preferred for field-scale applications because the impregnated silver limits microbial activity and thus loss of resident tracers and captured organic contaminants is minimized. For PFM applications at sites with oxyanions, this requirement of microbial recalcitrance, of course, applies only to the resident tracers. The mechanisms responsible for silver acting as a biocide are complex, but the following mode of action has been suggested. The Ag^{+2} released from the impregnated silver (Ag^0) on the SI-GAC combine with the sulphur-hydryl groups within the bacterial cell producing an Ag-S complex. This complex prevents the transfer of hydrogen and oxidative reactions, thus causing the death of the bacterial cells by inhibiting their respiratory activity and preventing their reproduction. (Jennings, 2005; Etirs, 1991).

4.3.3. Batch Sorption Experiments

Sorption of Oxyanions on Modified GAC

Batch equilibration experiments were conducted to measure the sorption of three oxyanions (perchlorate, chromate, and selenate) on two modified sorbents (SM-SI-GAC and SM-SI-GAC) and data fitted well to the Langmuir model. Oxyanion sorption capacity on the SM-GAC was in the following order: perchlorate (183 meq/kg) > chromate (104 meq/kg) >> selenate (40 meq/kg). While nearly all of the AEC was satisfied by perchlorate, less than 50% and 20% of the AEC is occupied by chromate and selenate, respectively. The anion selectivity, based on the Langmuir isotherm parameter, K_L, on the quaternary ammonium group is also in the order expected: perchlorate (70 L/meq) > chromate (14.5 L/meq) >> selenate (1.9 L/meq). These results are also comparable to the elution order of these oxyanions (selenate < chromate < perchlorate) from the anion exchange analytical column (AS16), which has quaternary amine functional groups as a sorbent. Other researchers have also shown perchlorate to be highly selective towards quaternary amines due to its low hydration energy and large hydrated size (Magnuson et al., 2000a,b; Gu et al., 2000). The equilibrium solution concentration range covered in these isotherm plots (<1.2 meq/L or ~62.6 mg/L) from above detection limit of IC to the sorption plateau.

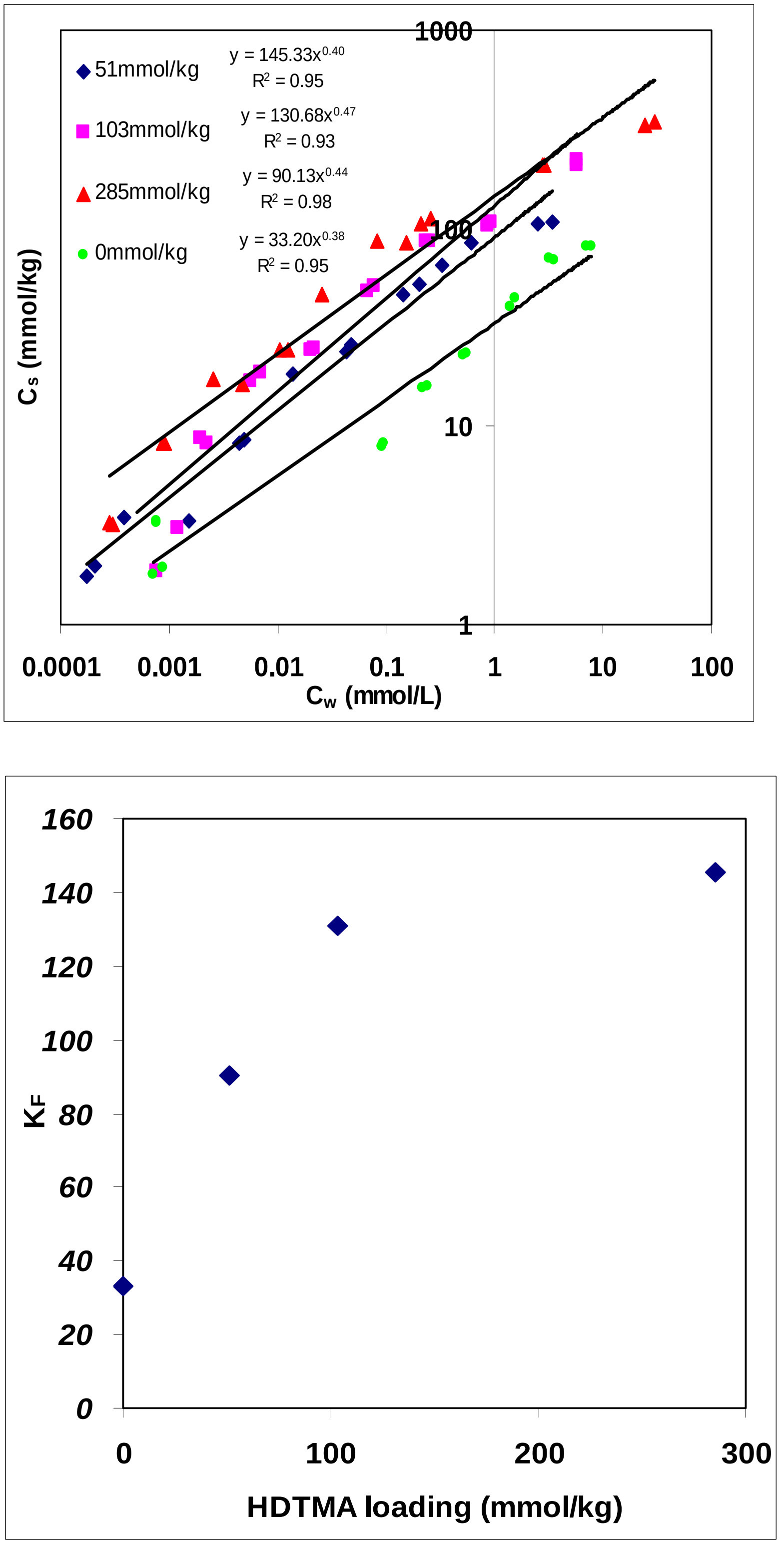


Figure 4-6. (A)Perchlorate Sorption Isotherms on SM-SI-GAC at different HDTMA loadings; (B) Freundlich isotherm K_F dependence on HDTMA loading on SI-GAC.

For field applications, silver-impregnated granular activated carbon (SI-GAC) modified with HDTMA was used. To optimize the loading capacity of HDTMA-Br on SI-GAC for creating a high selectivity and large sorption capacity for oxyanions, the following loading capacities were assessed: 51, 103, and 285 mmol/kg of HDTMA. Aqueous solubility for HDTMA-Br was determined to be 8.2 mmol in water at 20°C. Perchlorate sorption isotherms with SM-SI-GAC as the sorbent are plotted (Figure 4-6). The isotherm data fitted well to the Freundlich model; over a larger perchlorate concentration range the isotherm would conform to the Langmuir model, with a distinct plateau whose magnitude will be proportional to the AEC. The increase in Freundlich K_F was linearly proportional to the nominal surfactant loading at the two lower loading rates (51 and 103 mmol/kg), but became distinctly nonlinear at the higher loading (285 mmol/kg), appearing to reach a plateau. These data (Figure 4-6) suggest that high selectivity for perchlorate results in essentially 100% coverage of the anion exchange sites created by HDTMA loading rates of 51 and 103 mmol/kg. At higher surfactant loading rates (~285 mmol HDTMA/kg SI-GAC), however, only 75% of the quaternary amine sites were accessible to perchlorate. Thus, surfactant configuration on SI-GAC at the highest loading capacity is deemed sub-optimal in terms of generating additional AEC. For field-scale application at the Indian Head site, the lower HDTMA loading of 200 mmol/kg was determined to provide sufficient AEC, and thereby allow capture of approximately 50-70 mmol of perchlorate per kg of SM-SI-GAC.

Sorption of Anions and Nonpolar Contaminants on SMZ

Bowman et al (1995) and Haggerty and Bowman (1994) studied the sorption of several inorganic anions on both untreated and surfactant-modified clinoptilolite. Their data (Figure 4-7) demonstrate dramatic increases in anion sorption resulting from AEC gained from the cationic surfactant (HDTMA) modification of the zeolite. Note the non-linear shape of the isotherms (for the modified zeolite), which conform to the Freundlich isotherm model and likely better to the Langmuir isotherm model. Also, note the order of selectivity for the three ions: perchlorate > chromate > selenate; note that the same selectivity sequence was found for SM-SI-GAC.

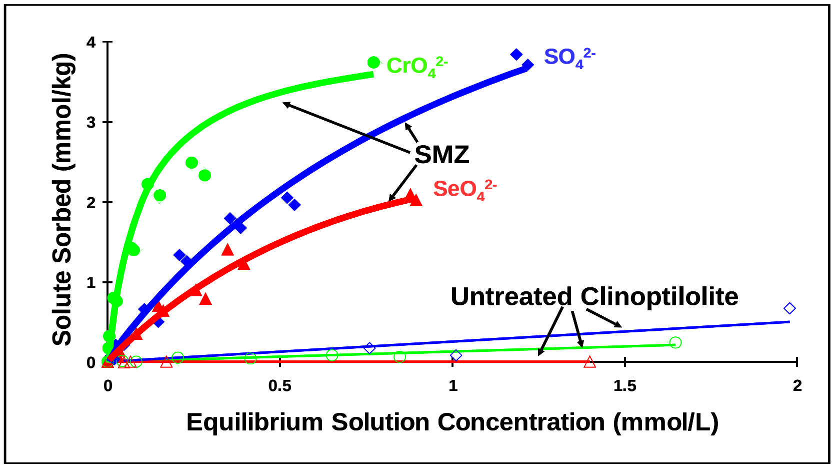


Figure 4-7. Oxyanion Isotherms on Treated and Untreated Zeolite (Adapted from: Bowman et al., 1995; Haggerty and Bowman, 1994).

Bowman et al (1995) and Neel and Bowman (1992) also examined the sorption of several nonpolar organic contaminants on surfactant modified zeolite. Their sorption data (Figure 4-8) show that 1) significant capacity for hydrophobic sorption can be generated by surfactant modification of the zeolite; and 2) the carbon-normalized sorption isotherm coefficients (K_{oc}) are proportional to the octanol-water partition coefficient (K_{ow}) values. This suggests that the mechanism responsible for nonpolar contaminant sorption by the SMZ is dominantly within the hydrophobic (partitioning) domains created by the surfactant bilayer on the modified zeolite.

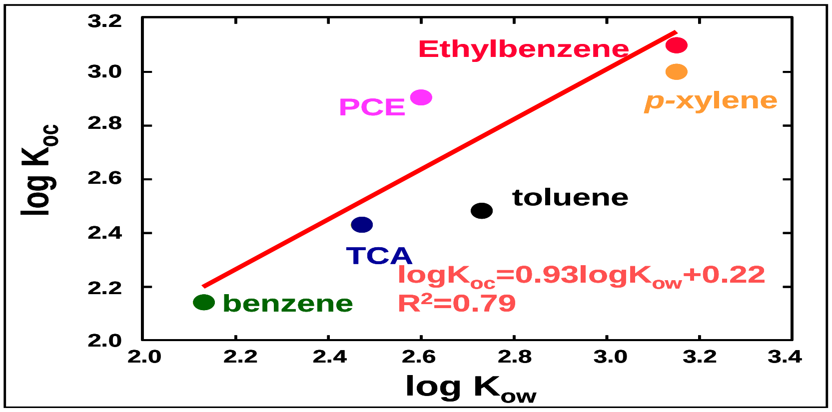


Figure 4-8. Comparison of Sorption Coefficients to Octanol-Water Partitioning Coefficients for Several Contaminants (Adapted from: Bowman et al., 1995; Neel and Bowman, 1992).

In addition to our data for oxyanion sorption on modified GACs, excessive loading of HDTMA on to zeolites has been shown to be not as effective in generating sorption capacity for nonpolar solutes as well. Li and Bowman (1998) examined the sorption of PCE on HDTMA-modified zeolite at various surfactant loadings. Their results (Figure 4 - 9) show that at rates lower than 100 mmol/kg, PCE sorption increased in proportion to surfactant mass added, but at loadings > 100 mmol/kg (equivalent to an organic carbon content of ~2%), the gain in PCE sorption was less than that expected from a 1:1 than that based on a linear in relationship.

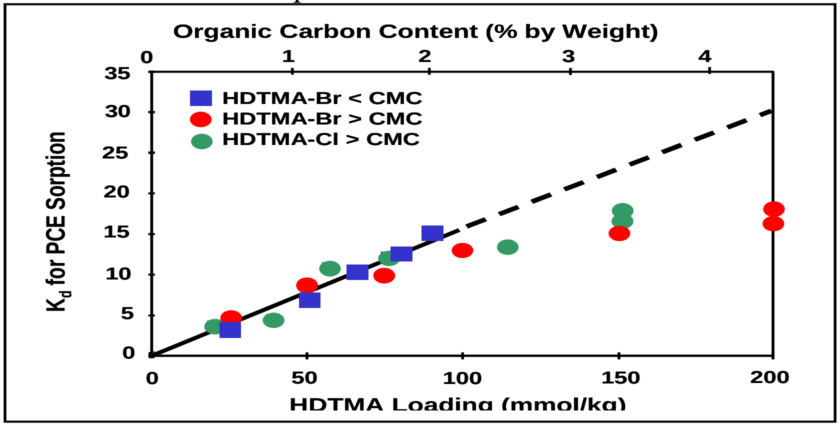


Figure 4-9. Sorption of PCE at varied HDTMA Loadings (Li and Bowman, 1998)

Recall that for the specific zeolite studied by Bowman et al. (2000), the external CEC is ~100 meq/kg, and at loading rates smaller than this, the adsorbed layer conformation is roughly similar to a brush-like structure (Sullivan et al., 1998), with, on the average, all surfactant molecules are sorbed via cation exchange (tails projected out; cation head attached to mineral surface). In this case, no AEC is generated. At loadings twice the external CEC of the zeolite (~200 mmol/kg), a brush-like bilayer results, with half the surfactant molecules are in an "inverted" formation, with their cation head groups stick out into the solution phase (Li and Bowman, 1997 and 1998). In this case, the new AEC gained is ~100 mmol/kg. For our applications, the surfactant loading rate must be about twice the external CEC for the zeolites.

The actual distribution of the surfactants is likely to be some intermediate structure, probably patchy, heterogeneous distribution of surfactant molecules depending on the surface-charge and physical heterogeneity of the zeolite external surfaces (Sullivan et al., 1998). The changes in the conformation and packing density of the adsorbed layer(s) of the surfactant on the zeolite, and the resulting changes in the hydrophobic properties of the surfactant alkyl chains are the reasons for the observed loss in "efficiency" of generating either exchange capacity for anions or hydrophobic domains for nonpolar contaminants.

Sorption of Alcohol Tracers on GAC

Methylated alcohols -- such as methanol, ethanol, *iso*-propanol and *tert*-butyl alcohol -- are used as resident tracers to cover a wide range of groundwater fluxes, while 2,4-dimethyl-3-pentanol with a $K_d \sim 2000$ ml/g is used as an internal standard. Equilibrium sorption isotherms for all alcohol tracers on the modified and unmodified GAC and SI-GAC were linear, and the sorption coefficient (K_d, ml/g) estimated from these isotherms are summarized in Table 4-4.

Table 4-4. Comparison of Alcohol Tracer Sorption Coefficients on Unmodified and Modified GAC

PFM Sorbent	Linear sorption coefficient K_d (L/kg)		Linear sorption coefficient K_d (L/kg)	
	MEOH	ETOH	IPA	TBA
GAC	2.6	18.1	109.1	228.2
SI-GAC	2.7	25.6	197.7	508.8
SM-GAC	0.9	7.0	34.4	69.8
SM-SI-GAC	1.6	14.4	92.7	221.0

K_d values of alcohols for sorbents with and without surfactant modification are compared with K_{ow} values of alcohols in Figure 4-10. Linear correlation between K_d and K_{ow} confirms that alcohol tracers sorb by a hydrophobic sorption mechanism regardless of HDTMA modification. However, and of interest, the silver-impregnation of SI-GAC appears to influence alcohol K_d values even though SI-GAC and GAC supposedly have the same basic physical and chemical properties. Further research into the effects of the silver impregnation on alcohol sorption mechanisms is underway.

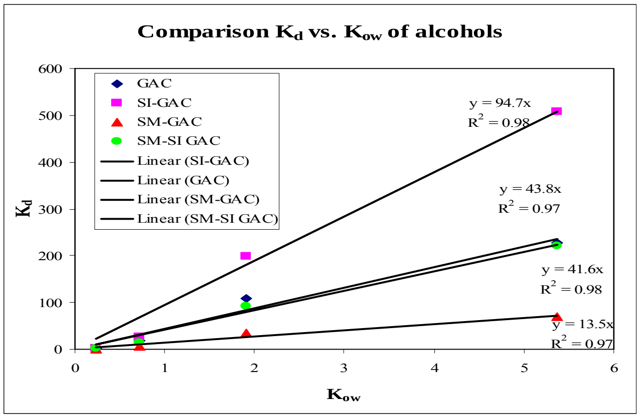


Figure 4-10. Comparisons of K_{ow} and K_d for Alcohol Tracers

For all the alcohol tracers we investigated, HDTMA modification reduces their K_d values by about 44% for SM-SI-GAC and by about 31% for SM-GAC. The reduction of K_d values in HDTMA modified sorbents might result from the decreased interaction between alcohols and modified sorbents due to: (1) attached HDTMA in the macro- and meso-pores blocking access to the surface area in micro-pores; (2) sorbed HTMA reducing the sorptive surface area available (Bartelt-Hunt et al., 2003); and (3) electrostatic hindrance to the hydrophobic interior of the GAC from the negatively charged head groups of the surfactants covering the external surfaces.

4.3.4. Bench-Scale Flow Experiments

<u>Chromate Flux Studies</u>

Campbell et al. (2006) proposed a variation of the PFM method for simultaneous measurement of local groundwater specific discharge (q) and Cr(VI) mass flux (J^{Cr}) as two-dimensional vectors, with each vector composed of an angular (q_θ, J_θ^{Cr}) and a radial (q_r, J_r^{Cr}) components. The interior of the PFM is divided into a center well and three outer sectors, each packed with a granular anion exchange resin (AG1-X8) having high adsorption capacity for the Cr(VI) oxyanions CrO_4^{2-} and $HCrO_4^-$. The adsorbent in the center well of the device is loaded with benzoate as resident tracer.

Laboratory flow experiments were conducted in which these devices were placed in porous packed bed columns through which was passed a measured quantity of simulated groundwater containing Cr(VI). Benzoate served as the resident tracer, while the oxyanion contaminant of interest is chromate. The AG1-X8 anion exchange resin was then removed from the four sectors separately and extracted to determine the masses of Cr(VI) and resident tracer bound in each. A linear solute transport model was used to relate the observed rate of resident tracer displacement to q_θ and q_r, and a simple mass balance equation was used to calculate J_r^{Cr}. The obtained results are shown in Figures 4-11 and 4-12.

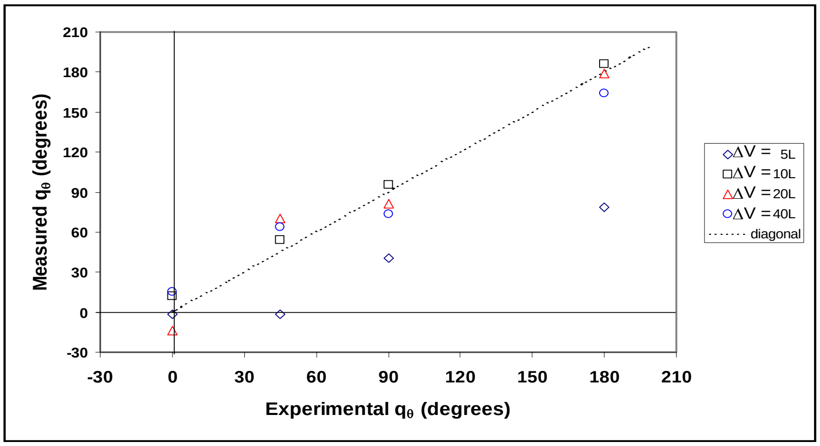


Figure 4-11. Comparison of Measured and Experimental q_{θ}. (Adapted from: Campbell et al., 2006)

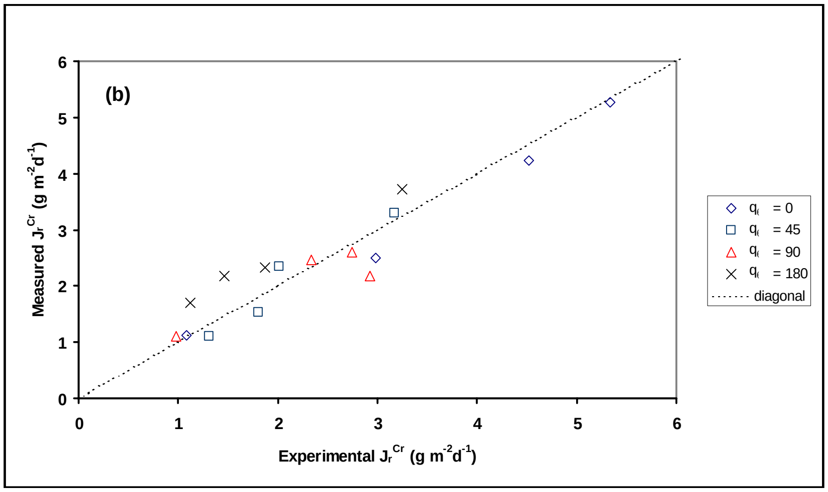


Figure 4-12. Comparison of Measured and Experimental J_r (Adapted from: Campbell et al., 2006).

Experimental results showed q_{θ} was measured to an accuracy of ± 15° (see Figure 4-11). Accuracy of the radial specific discharge vector component depended on the degree of displacement of the resident tracer. The mass flux vector radial component (J_r^{Cr}) was measured to an accuracy of ± 17% (see Figure 4-12). These results demonstrate that the new PFM method proposed by Hatfield et al. (2004) represents a promising technique for determination of specific discharge and contaminant mass flux for oxyanions in contaminated aquifers. Additional laboratory studies to improve this approach for field-scale applications are needed.

<u>Chromate Experiments</u>

Laboratory experiments were conducted in a rectangular tank (20 cm length, 19 cm width, and 15 cm height) packed with medium sand (grain size 0.42 to 0.83 mm) to validate the use of SM-GAC as a packing material for PFMs. Experiments were conducted at three water fluxes (23.2, 9.1, and 2.0 cm/day) with a chromate input concentration of 25 mg/L.

The imposed and PFM-estimated water and contaminant fluxes are listed in Table 4-5. Note that the higher of the two imposed fluxes produced an underestimate of both the water flux (53% error) and contaminant flux (71% error), most likely because of insufficient residence time to allow the alcohol tracers to desorb and to allow the chromate to adsorb.

Table 4-5. Comparison of Imposed and Observed Fluxes in Chromate 3D Box Studies

Flux	Imposed Flux	Observed Flux
Water Flux (cm/day)	23.2	11.0
	9.1	9.1
	2.0	2.0
Chromate Flux (mg/cm^2/day)	0.58	0.17
	0.23	0.23
	0.05	0.04

4.3.5. Field-Scale Assessments at a Perchlorate Site

PFM Deployments at the Indian Head Site

Field-scale assessment of the use of SI-SM-GAC as sorbent material for PFMs was evaluated at a perchlorate site located at Indian Head, MD. PFMs packed with SM-SI-GAC were deployed in selected wells reported to have perchlorate concentrations ranging from 1.6 to 181 mg/L.

One set of PFMs were deployed on November 22, 2004 and retrieved 21 days later on December 13th in 2004 [Event 1]. A second set of PFMs were deployed for 44 days, from December 13, 2004 to January 26, 2005 [Event 2], to assess the performance of PMF for longer exposure periods to obtain more reliable time-averaged data without exceeding the sorbent sorption capacity of perchlorate. In addition, for Event 2, high-resolution sampling of the socks (~5-cm sections vs the standard 25-30 cm sections) was accomplished to produce a more detailed characterization of the vertical distribution of groundwater and contaminant flux distributions within the screen interval of the wells.

PFM Performance

Table 4-7 summarizes the PFM performance assessment at the demonstration site. In general, when comparing measurements between the two sampling events at a given well, water and contaminant fluxes were both similar (i.e., little change in flux between events). The major exception was for contaminant flux measures at MW3 (see Table 4-6). Further discussion of results was provided in the sections that follow. The 12 PFM installation/extractions were 100% successful. Only 3.2 gallons of process waste (mostly spent activated carbon) was produced which was considerably lower than expected.

Table 4-6. Expected and Actual Performance and Performance Confirmation Methods.

Performance Criteria	**Expected Performance Metric (pre demo)**	**Performance Confirmation Method**	**Actual (post demo)**
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Ease of Use	*Minimal training required*	*Experience from demonstration operations*	*Level of Training similar to water sampling*
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Water flux estimates	*Estimate within 25%*	*Compare PFM measured water fluxes between wells and sampling events*	*Between events, measures at a given well agreed within 21 to 35%*
Contaminant flux estimates	*Estimate within 25%*	*Compare PFM measured contaminant fluxes between wells and sampling events*	*Between events, measures at MW1 and MW4 agreed within 22 and 0%, and 193% for MW3*
Vertical variations in water and contaminant flux between wells	*Estimate within 40% (for water fluxes alone)*	*Compare flux statistics between wells*	*See Figures 4-3-15 to 4-3-19*
Process Waste - Generated	*25 gallons*	*Observation*	*3.2 gallons*

SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	*No failures*	*Record keeping*	*100% (no failures)*
Safety (all) - Hazards - Protective clothing	*Contaminated sorbents* *Level D*	*Experience from demonstration operation*	*On the same order as water sampling*
Versatility (all) - Short/long term averaging - Other applications	*Yes* *Fractured rock, radionuclides*	*Experience from demonstration operation*	*Consistent perchlorate fluxes were quantified over short and long term*

Groundwater Flux Characterization
The average groundwater fluxes (q_d) for the two PFM deployments were ~1.8 cm/day in MW- 1, 7.6 cm/day and 4.9 cm/day in MW-3, and 2.8 and 2.1 cm/day in MW-4. These values compared well with the Darcy flux of 7 cm/day as q_d , measured using the borehole dilution method at CPMW 3S (Figure 4-13).

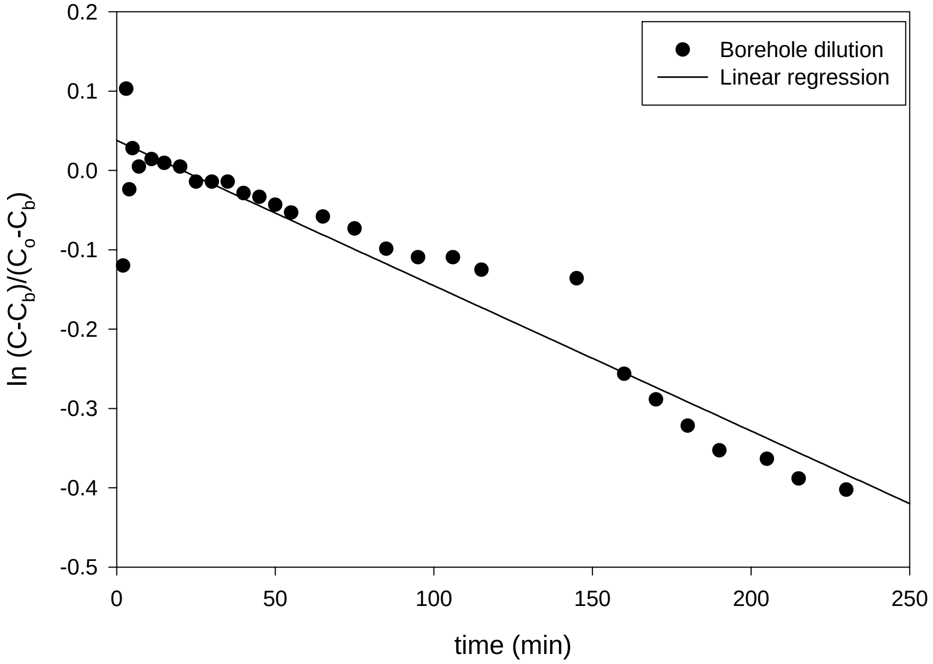


Figure 4.13 Borehole dilution test result in CPSM3S: Linear regression provide fitting parameter -0.0019 as a slope and 0.04 as an intercept on Y axis. R^2 value was 0.92

The groundwater flux calculated from reported hydraulic conductivity (483 cm/day to 1931 cm/day) and hydraulic gradient (0.012 cm/cm) [Envirogen Inc., 2003], was however, higher, and ranged from 11 cm/day to 44 cm/day. The wells used for the conventional estimates were in a different section of the aquifer that was composed of gravelly sand as opposed to sandy silt near CPMW 3S and the wells in which PFMs were deployed.

There was reasonable reproducibility between the two deployments. The lower groundwater flux in MW-3 and MW-4 in the second deployment could be a function of recharge induced by rainfall since the aquifer is unconfined.

Depth patterns of groundwater fluxes showed reasonable agreement between the two deployments (Figure 4.14), confirming the reproducibility of PFM measurements. For the second deployment in monitoring wells MW-1 and MW-4, sampling was done at a higher resolution (5 cm intervals vs. 25-30 cm intervals) than the first deployment. Thus, to compare these two data sets, fluxes measured using high resolution sampling were averaged over 25-30 intervals. The flux distribution pattern at MW-1 corresponded well

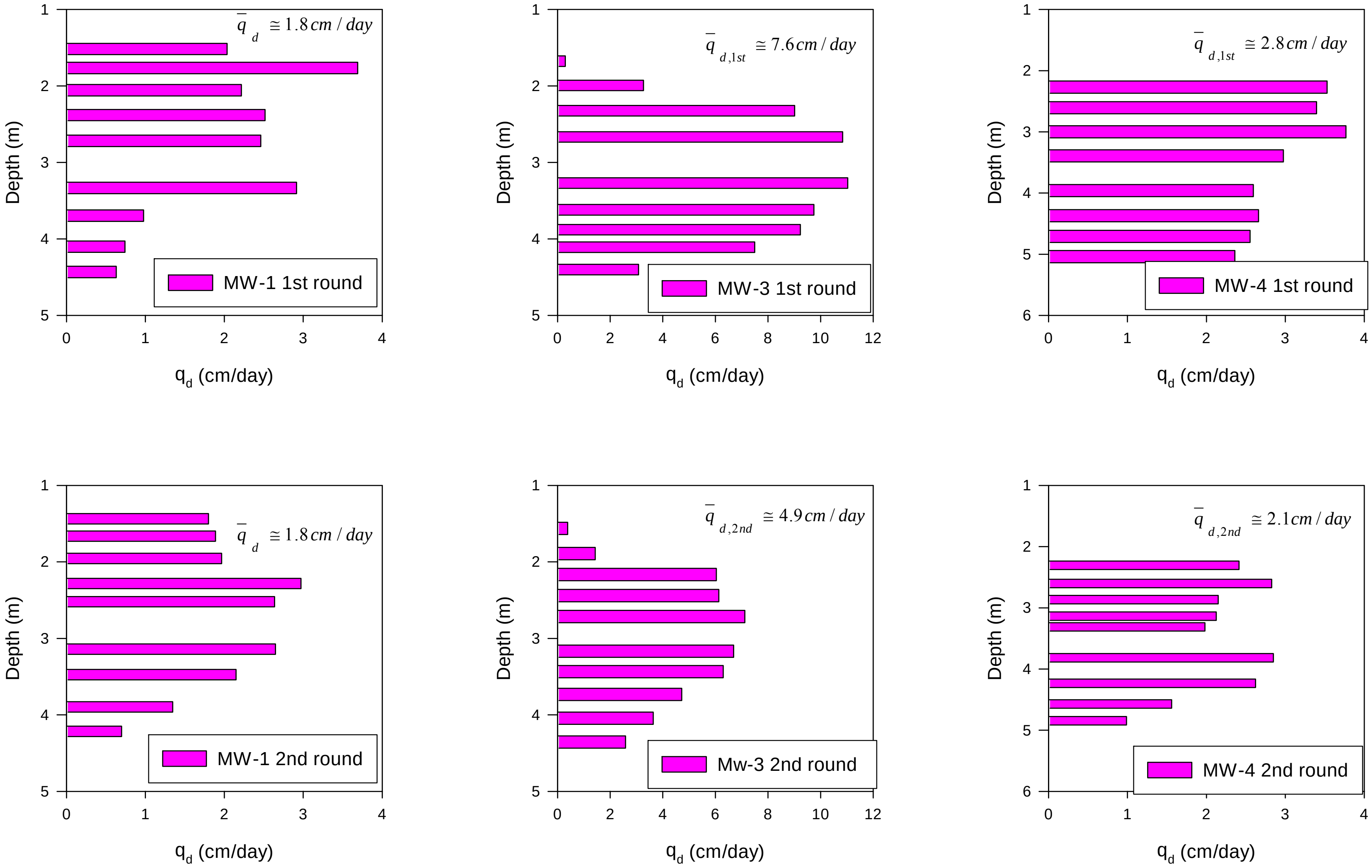


Figure 4.14 Groundwater flux (q_d) distribution in MW-1, MW-3 and MW-4 for two deployments

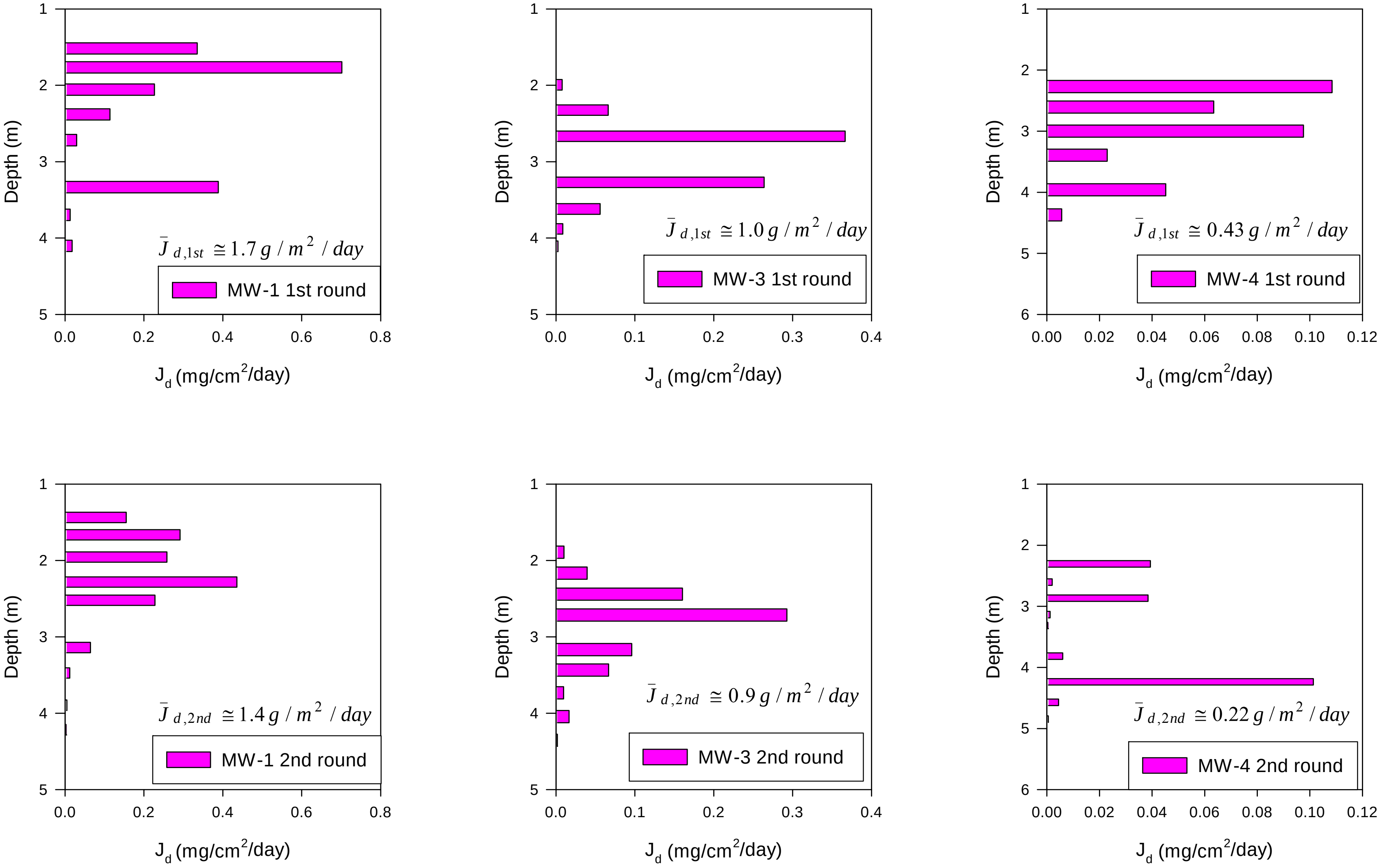


Figure 4.15 Perchlorate flux (J_d) distribution in MW-1, MW-3 and MW-4 for two deployments

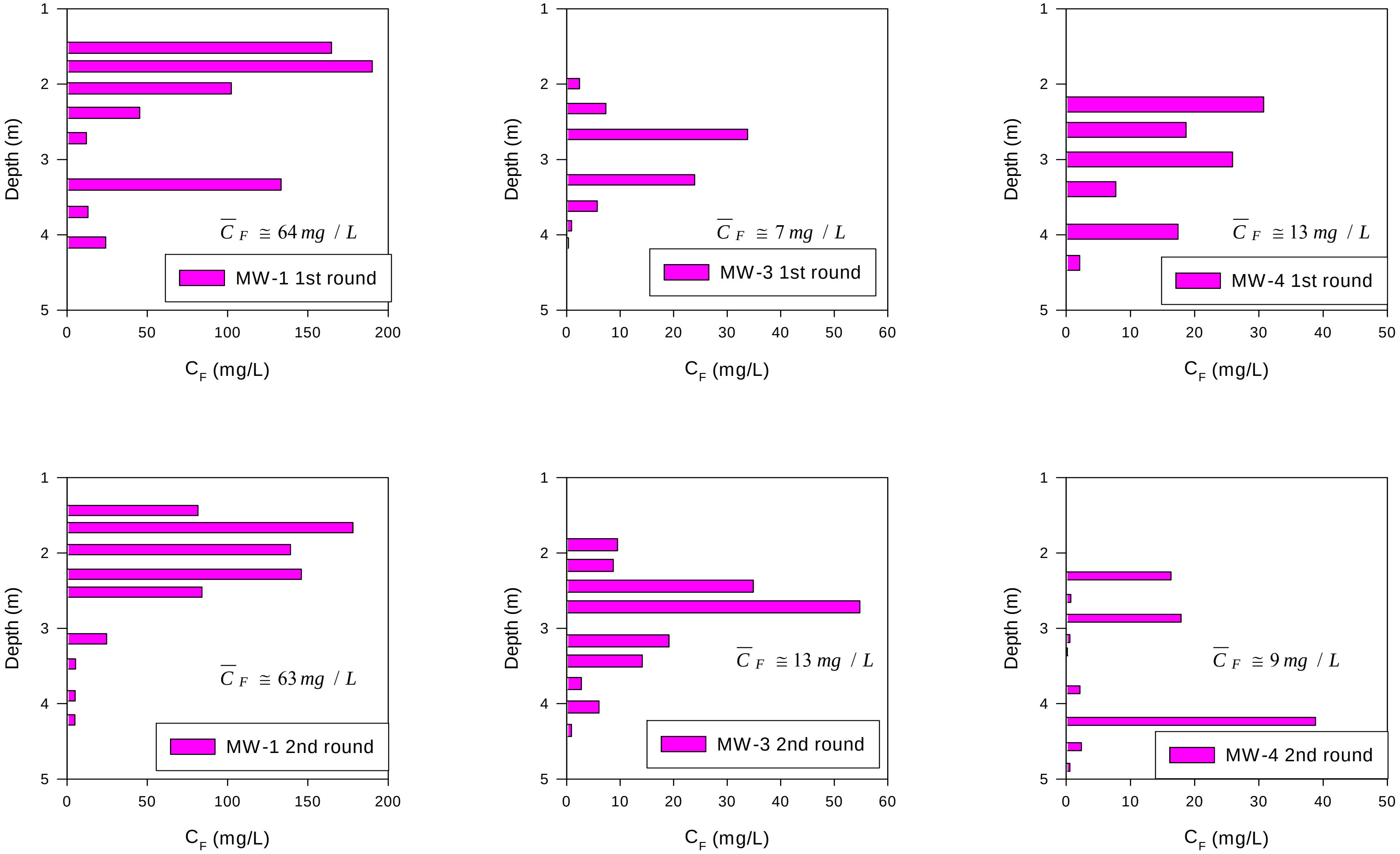


Figure 4.16 Flux-average perchlorate concentration (C_F) distributions in MW-1, MW-3 and MW-4 for two deployments

with the borehole log (Figure 4.15). No significant depth pattern in groundwater fluxes was observed indicating that the aquifer was relatively homogeneous. The slightly lower fluxes at the bottom of aquifer indicated the possible presence of a fine sand seam or clay layer.

Perchlorate Flux Distribution & Flux-Averaged Concentrations

The average perchlorate fluxes for the first and second deployments were 1.7 and 1.4 g/m^2/day in MW-1, 1.0 and 0.9 g/m^2/day in MW-3, and 0.43 and 0.22 g/m^2/day in MW-4, respectively. Depth patterns of perchlorate fluxes (Figure 4.15) were less uniform than the groundwater fluxes. Similar to groundwater fluxes, the high resolution data from the second deployment were averaged to compare with the first deployment. At MW-1, the well closest to the suspected source zone, higher perchlorate fluxes were observed near the water table indicating the possible presence of a vadose zone source. At MW-3, depth pattern of Darcy and perchlorate fluxes were similar.

Depth patterns of perchlorate fluxes were similar between two deployments in MW-1 and MW-3 (Figure 4.15), but different in MW-4. In MW-4, higher perchlorate fluxes existed in the upper layer for the firstdeployment, while fluxes were higher in the lower layer for the 2nd deployment. This discrepancy is attributed to the transient state of perchlorate fluxes that will be discussed in greater detail later.

Flux-averaged concentrations were estimated from the measured perchlorate and Darcy fluxes using equations 3-2. The flux-averaged concentrations for first and second deployment were 63.9 and 62.7 mg/L in MW-1, 7.2 and 13.2 mg/L in the MW-3, and 13.1 and 9.1 mg/L in the MW-4, indicating once again a reasonable reproducibility of PFM measurements.

Flux averaged concentrations estimated using PFM were compared with perchlorate concentrations in the groundwater samples to assess the reliability of PFM-measured perchlorate fluxes. Perchlorate concentrations in the groundwater sampled on November 22, 2004 and February 5, 2002 were 74.7 mg/L and 84.7 mg/L in MW-1, 2.5 mg/L and 1.6 mg/L in MW-3, and 95.2 mg/L and 181 mg/L in the MW-4, respectively. The PFM measurements were made in November 22, 2004 through December 13, 2004 and December 13, 2004 through January, 26 2005 (Table 4.7). Thus, PFM estimates and conventional groundwater monitoring data matched reasonably well except for monitoring well MW-4.

Table 4.7. Comparison of flux-averaged concentrations (CF, mg/L) from a PFM and a conventional method for groundwater sampling.

Measurements	Period	C_F (mg/L)		
		MW-1	MW-3	MW-4
PFM	1st event	63.9	7.2	13.1
	2nd event	62.7	13.2	9.1
Conventional method	Nov.22, 2004 (bailing)	74.7	2.5	95.2
	Feb.5, 2002 (Pumping)	84.7	1.6	181

Perchlorate concentration of ~95 mg/L was reported in a sample taken just before the PFM deployment. The flux-averaged concentration measured using the PFM was, however, an order of magnitude lower (~10 mg/L). A number of factors may be responsible for this discrepancy in MW-4. These are as follows, but further research is required at this location to arrive at definite conclusions.

:

- MW4 is located within the zone influenced by the recirculation wells used in the previous bioremediation study. Perchlorate concentrations and fluxes in these wells may be significantly impacted by the induced changes in hydrologic and geochemical conditions.
- Even prior to bioremediation activities, perchlorate concentrations were observed to vary between 3 and 205 % between May 2, 2002 and July 18, 2002 (Table 4.8). This highly dynamic nature of perchlorate maybe due to a shallow water table and a vadose zone source that cause high groundwater and contaminant fluxes following infiltration events.

The depth patterns of the flux-averaged perchlorate concentrations (Figure 4.16), C_F (mg/L), are similar to the perchlorate flux distribution. The patterns were reproducible for the two PFM deployments in MW-1 and MW-3, but different in MW-4. The higher flux-averaged perchlorate concentration, C_F, near the water table in MW-1 strongly supports the vadose zone source scenario.

Table 4.8. Seasonal fluctuations in perchlorate concentrations measured in wells.

Date	Perchlorate concentration (mg/L)								
	Test plot monitoring wells (TPMW)								
	1S	**1D**	**2S**	**2D**	**3S**	**3D**	**4S**	**4D**	**5**
5/10/02	250	158	215	207	72	153	124	211	151
7/18/02	260	150	241	276	115	161	109	97	155
Control plot monitoring wells (CPMW)									
	1S	**1D**	**2S**	**2D**	**3S**	**3D**	**4S**	**4D**	**5**
5/10/02	103	148	46	176	53	160	119	162	172
7/18/02	255	54.5	101	209	182	174	177	152	203

Source: Cramer *et al.*, (2004)

High Resolution Sampling

High resolution sampling (~5 cm intervals) was done in MW-1 and MW-4 for the second deployment to investigate the effect of averaging (over the 25-30 cm vertical interval) on the estimation of depth varying groundwater and contaminant fluxes (Figure 4.17). Significant differences were not observed in the Darcy flux profile indicating that the spatial scale of variability (correlation lengths) was greater than scale of averaging. It was anticipated since MW-1 is located near the source zone significant depth pattern in the perchlorate flux distribution would be observed with high resolution sampling. Lack of such pattern, once again, points towards the presence of a vadose zone source. The perchlorate flux distribution patterns in MW-4 are different in the two deployments. Possible causes of the difference have already been discussed in the previous sections.

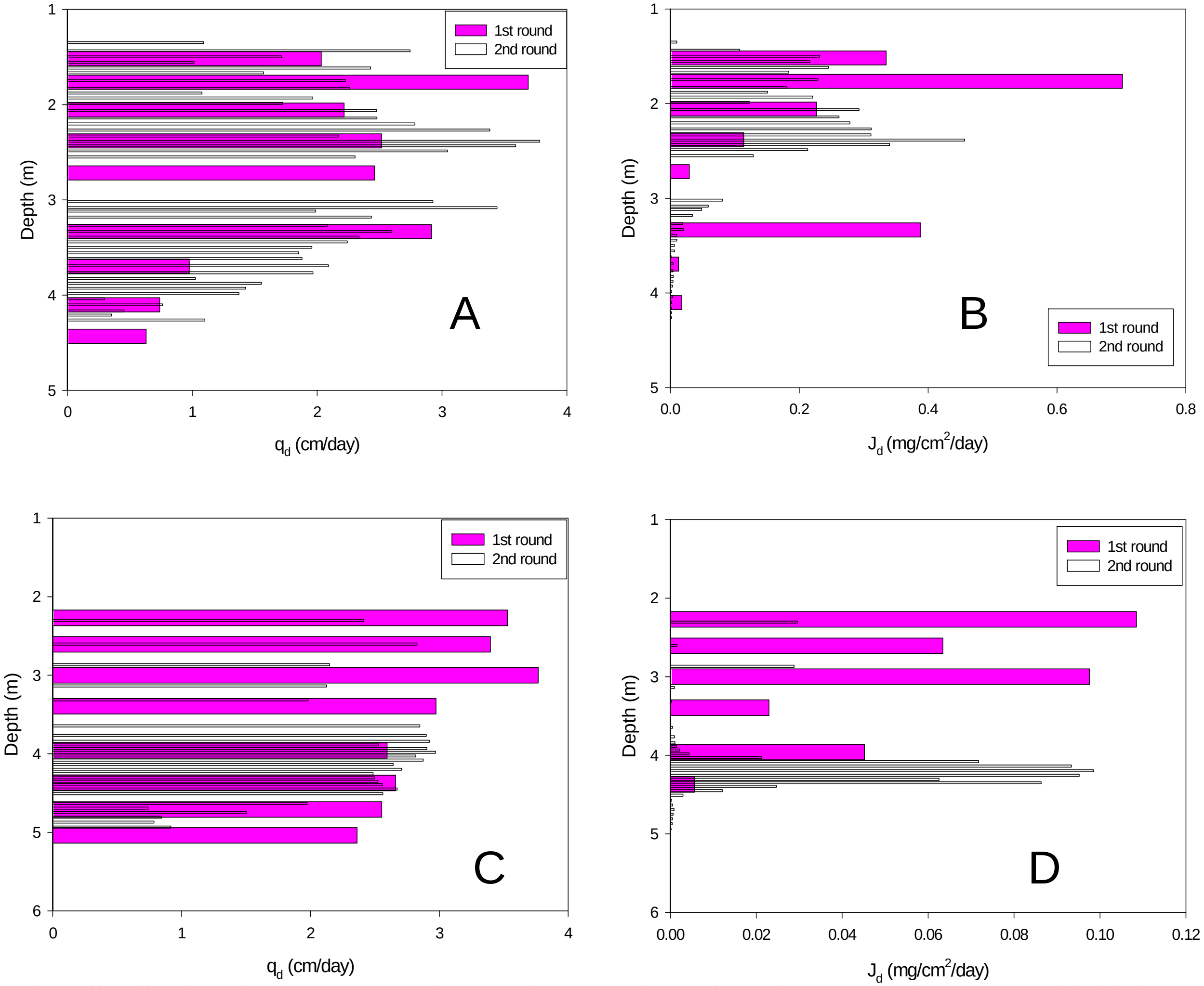


Figure 4.17 Flux distributions in MW-1(A and B), and MW-4 (C and D) for two deployments with high resolution

Conclusions from field study

Groundwater and contaminant (perchlorate) fluxes were measured in a perchlorate plume at the IHDIV-NSWC site, Indian Head, WA. The primary purpose of the study was to demonstrate the applicability of a new PFM-sorbent SM-SI-GAC for field-scale measurement of groundwater and perchlorate fluxes. The measured fluxes showed good reproducibility between two deployments and also compared well with borehole dilution test and conventional groundwater monitoring data. Thus, SM-SI-GAC can be used as a PFM sorbent in sites with perchlorate concentrations ranging from 7 to 64 mg/L. The applicable concentration ranges can be expanded using shorter exposure time and/or higher loadings of HDTMA on SM-SI-GAC to not exceed the sorption capacity of perchlorate. The results also indicated the SM-SI-GAC was stable physically, chemically and biologically for a maximum of 44 days and the alcohol tracers and captured perchlorate on it were not biodegradable.

The depth distribution of perchlorate fluxes was used to formulate hypothesis about location of possible perchlorate sources. The groundwater concentration in MW-1, located near the suspected source zone, did not change over time from 2002 to 2005, indicating the presence of a persistent source since Hog-Out waste water containing perchlorate has not been discharged since 1996. The higher perchlorate fluxes near the water table and a relatively uniform flux distribution with depth in MW-1 indicates the possibility of a vadose zone source. The source in the vadose zone would be released to the aquifer by recharge induced by rainfall. With this scenario, higher perchlorate fluxes would be observed near the water table. A vadose zone source would also explain the high temporal variability of perchlorate concentrations observed in the down-gradient monitoring wells, MW-3 and MW-4. Further investigations of soil concentrations near this area are required to confirm the hypothesis.

PFMs deployed in the CPMW 3S and 3D wells were not processed for data analysis. This is because CPMW3S collapsed partially before the 2nd deployment of PFMs. This would affect the hydrology and geochemistry of CPMW3S and the nested well CPMW3D and thus the flux measurements may not be reliable.

4.3.6. Summary and Discussion

The primary goal of this study was to evaluate new sorbent matrices as packing material in Passive Flux Meters (PFMs) used for characterization of groundwater and contaminant fluxes at sites where anions are the contaminants of concern. We examined three types of sorbents: (1) anion exchange resins (AERs); (2) natural zeolites; and (3) granular activated carbon (GAC). All three sorbents can be purchased in bulk quantities.

Each sorbent type has a set of limitations and advantages for use in PFMs for investigating oxyanion fluxes. AERs do have large anion exchange capacity, but may not serve as good sorbents for nonpolar contaminants and alcohol tracers. However, organic acids (e.g., benzoate) can be used as the PFM resident racers. We modified zeolites and

GAC with a quaternary ammonium surfactant (HDTMA) to enhance the anion exchange capacity (AEC) of these sorbents. While GAC can sorb large quantities of non-polar organic contaminants, it can sorb only small amounts of anions. Thus, surfactant modification imparts the dual sorption capacity we need for PFM applications. Natural zeolites have significant cation exchange capacity, but do not sorb nonpolar solutes. Cationic surfactant modification to produce an external bilayer yields a sorbent that can sorb anions, cations, and non-polar solutes.

A list of possible surfactants and organic acids that can be used to modify zeolites and GAC is included in Table 4-9 below. We used HDTMA, a cationic surfactant with a long alkyl chain, to modify zeolites and GAC to produce a sorbent with anion exchange capacity. Long-chain surfactants are likely to be better candidates for modification than short-chain surfactants. The longer alkyl chain is correlated to larger enthalpies of sorption and larger K_ds (see Bowman et al.1995, 1998), thus, the surfactant will not be easily desorbed, and the introduced AEC will not diminish during the PFM deployment period. GAC can also be modified with anionic surfactants and organic acids to impart cation exchange capacity (CEC). It is also possible to modify GAC with a mixture of anionic and cationic surfactants, to match the capabilities of SMZs. It is also possible to custom-select the surfactant head group so that it has high selectivity for the oxyanion of interest.

The zeolite and GAC we used have similar external surface areas (~10-15 m^2/g), and the zeolite has an external CEC of about 100 meq/g. GAC modification requires only a monolayer coverage of HDTMA (~50 meq/g) to generate adequate AEC, where as for zeolite a bilayer formation is necessary requiring HDTMA loading ~200 meq/g. HDTMA modified GAC are cost effective when compared to ion exchange resins, but comparable in cost with SMZ. GAC costs about $500-1000/ton compared to about $500/ton for SMZ, and about $3000/tom for anionic resins (EPA, 1999; Mullin et al., 2002). SMZ might be suitable for large-volume applications, but because of low sorptive capacity it might have limitations in use at sites with high contaminant and ground water fluxes. Thus, surfactant-modified SI-GAC is recommended as the preferred sorbent for PFM applications to measure anion fluxes.

AEC of HDTMA-modified SI-GAC appear to be chemically and biologically stable. The positive charge on the quaternary amine functional group is not pH-dependent (in the pH range of environmental interest) and is less reactive than other primary, secondary and tertiary amines (Jungermann, 1970). HDTMA may also act as biocide, at least when in solution (Jacob and Heidelberger, 1915), and thus may preclude biodegradation of the resident tracers and captured contaminants.

Modification of GAC/SI-GAC with HDTMA surfactant reduces the alcohol tracer sorption coefficient, and thus the maximum deployment period is proportionately smaller, if the same suit of alcohol tracers is used. This could be a problem at sites with fast groundwater flux and low concentration of contaminants. But, this limitation could be overcome by using another suit of alcohol tracers with higher range of K_d values.

Table 4-9. Alternative Surfactants and Resident Tracers

Short-Chain Cationic Surfactants	Tetramethylammonium(TMA) Tetrabutylammonium(TBuA) Butylamine (BuA) Tetraethylammonium (TEA) Tetrapropylammonium (TPA)
Long-Chain Cationic Surfactants	Hexadecyltrimethylammonium (HDTMA) Chain diameter: 0.4 nm Chain length: 3.5 nm Head group diameter: 0.694 nm
Anionic Surfactants	Sodium dodecylsulfate (SDS) Sodium dodecylbenzenesulfonate (SDBS)
Organic Acids	Carboxylic acid salts Sulfonic acid salts: Sufuric acid ester salts Posphoric & polyposphoric acid esters

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 the “resident” alcohol tracers was obtained site managers and when necessary from the 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 had 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 will be 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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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 the application (i.e. performance) of the technology.

The following described Standard Operating Procedures (SOP) are currently utilized by the Environmental Engineering area of the School of Civil Engineering at Purdue University, West Lafayette, Indiana.

This SOP was updated March 3, 2004 by I.C. Poyer, School of Civil Engineering, Purdue University, West Lafayette, Indiana. 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.

STANDARD OPERATING PROCEDURE FOR THE SAMPLING, COLLECTION, EXTRACTION AND ANALYSIS OF ALCOHOL TRACERS FROM SORBENTS PACKED IN PFMS

SCOPE AND APPLICATION

1. This Standard Operating Procedure (SOP) describes the extraction and analytical procedures of alcohol tracers from a sorbent (Silver-impregnated Activated Carbon) packed into PFMs. Some of the alcohols have been used as partitioning tracers in both laboratory and field studies to quantify the amount and distribution of DNAPLs in source zones. Here, these alcohols are used as “resident” tracers that are pre-loaded on to the sorbent packed into the flux meter sock; loss of tracers via desorption and advective/diffusive/dispersive transport resulting from groundwater flow under natural hydraulic gradients is measured to estimate cumulative groundwater and contaminant fluxes.

2. The alcohol tracers used in the Purdue University field studies are methanol, ethanol, iso-propanol, t-butanol, and 2,4-dimethyl-3-pentanol.

3. The established analytical method to determine and quantify alcohol concentrations in extracted samples is direct injection of 1 μL of sample into a Shimadzu GC17A gas chromatograph (GC) equipped with a flame-ionization detector (FID). This method provides reliable and reproducible quantitation of alcohols at concentrations greater than or equal to 1 μg/mL, which is the reportable minimum detection limit (MDL). The linear standard calibration range for the FID response is from the reported MDL up to a concentration of approximately 1500 μg/mL per analyte of interest.

PURPOSE

The purpose of this SOP is to: (1) insure reliable and reproducible results, and (2) track possible sources of error in the extraction of alcohols from a sorbent and the subsequent analysis by GC-FID analytical methodology.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Sorbent samples will be collected in 40mL VOA vials (Fisher Scientific Catalog # 05-719-106) sealed with Teflon-lined septa caps. Vials will contain 20mL of extraction solvent (*iso*-butanol), prepared previously in the laboratory. All vials and caps are non-reusable.

Sample Collection: Sorbent aliquots collected over 1-foot increments from an exfiltrated Flux meter will be transferred to a mixing bowl and homogenized with a metal spatula. Approximately 10 to 20 grams of mixed sorbent will be placed into the 40 mL VOA vials containing extracting solvent.

Transportation and Storage: Field samples will be stored, on site, in coolers containing "blue ice" then shipped via overnight air express (e.g., FedEx) to the Purdue University laboratory. Samples will be stored in a cold storage room or refrigerator at 4^{o} C until extraction and GC analysis.

2. Laboratory Supplies and Materials

Volumetric class 'A' pipettes and volumetric class 'A' flasks for preparation of calibration standards and sample dilutions.

Disposable Pasteur glass pipettes (Fisher Catalog # 13-678-6A) for sub-sampling.

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

3. Reagents

Deionized water prepared by filtration of potable water through a Barnstead Ultrapure Deionization Unit. This water will be referred to as 'reagent water'.

Certified ACS grade pure alcohols purchased from one or more of the following vendors; Fisher Scientific, VWR and/or Sigma-Aldrich and used as received.

4. Calibration and Stock Standard Solutions

Individual alcohol stock standard solutions will be prepared in reagent water using volumetric glassware and stored in 20 mL glass vials with Teflon-lined caps. Stock solutions will be kept in a refrigerator at 4° C. Fresh stock standards will be prepared every six months and follows protocols outlined in the Federal Register, Rules and Regulations, Thursday, November 29, 1979, Part III, Appendix C, Section 5.10, "Standard Stock Solutions". The single modification from the cited procedure is the use of reagent water instead of methanol as the solvent.

Mixed calibration standards will be prepared by diluting stock standards in reagent water using volumetric glassware. A minimum of five standards will be prepared and will bracket the expected concentration range.

5. Quality Control (QC) Blank Spike/Matrix Spike

A blank spike will be prepared by the addition of 1 mL of calibration standard to 1mL of extraction solvent. A matrix spike will be prepared by the addition of 1mL of calibration standard to 1 mL of extracted sample. Spike recoveries will be calculated using the difference between the two measured concentrations and the known spike concentration.

6. Analytical Instrumentation

A Shimadzu GC17A Gas Chromatograph equipped with an AOC17 Autosampler, a temperature-programmable oven, heated auto-injector and detector zones, a 30 meter or greater capillary separations column, nitrogen carrier gas, standard compressed air and hydrogen flame gases and controlled by a PC-based data acquisition/analysis software system.

7. GC Procedure

Column dimensions	J&W DB-624 Column, 75m X 0.53um X 3um
Injection port temperature	180C
FID detector temperature	220C
Column Temperature Program	Isothermal at 60C for 3 min; ramp to 120C at 5 C/min, hold 1min; ramp at 20C/min to 200C, hold 1 min.
Carrier gas	Nitrogen 99.995% purity
Flame gases	Air, 99.995% purity; Hydrogen, 99.995% purity

8. Quality Control of GC System

GC injector septa will be changed every 100 to 150 injections, or sooner if instrument performance deteriorates.

Injection port glass liner will be cleaned or changed after 100 to 150 injections or sooner if instrument performance deteriorates.

A method blank will be analyzed at the beginning of each sample set and after every 25 samples to monitor instrument background.

A complete set of calibration standards (minimum 5) will be analyzed at the beginning of each day with a mid-range continuing calibration standard analyzed after every 25 samples.

A matrix spike and a blank spike, and up to 5 sample duplicates will be analyzed with each daily sample set.

10. Extraction of Alcohol Tracers from Sorbent Matrix

The collected sorbent samples will be rotated for a period not to exceed 24 hours on a Glas-Col Rotator, centrifuged for 5 minutes at 2000 rpm (Jouan, Inc., centrifuge), and sub-sampled into a 2 mL vial for GC analysis. Extraction vials will be stored at 4° C.

10. Sample Analysis

Individual alcohol identification will be based on absolute retention times compared to calibration standards.

Alcohol concentrations will be calculated on chromatographic peak area response converted to units of concentration in mg/L based on standard calibration curves.

11. Interferences

Contamination by carry-over may occur when high-level and low-level samples are sequentially analyzed. Subsequent dilution and reanalysis will be completed on samples identified as outside the standard concentration bracket. Samples analyzed immediately following a ‘high-concentration sample’ will be reanalyzed.

In an attempt to minimize carryover, samples suspected of being in a higher concentration range will be isolated and bracketed by the analysis of reagent water samples.

12. Safety

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

STANDARD OPERATING PROCEDURE FOR THE SAMPLING, COLLECTION, EXTRACTION AND ANALYSIS OF PERCHLORATE FROM SORBENTS PACKED IN PFMS

SCOPE AND APPLICATION

1. This Standard Operating Procedure (SOP) describes the extraction and analytical procedures of perchlorate from sorbent (Silver-impregnated Activated Carbon) packed into the PFMs. The mass of perchlorate accumulated by sorption on the sorbent from the groundwater passing through the flux meter is used to estimate the cumulative contaminant flux.

3. The established analytical method to determine and quantify perchlorate concentrations in extracted samples is direct injection of 1 μL of sample into a Dionex DX600 Ion Chromatograph equipped with an Electrochemical Detector (ED). This method provides reliable and reproducible quantitation of perchlorate at concentrations greater than or equal to 2 μg/L, which is the reportable minimum detection limit (MDL). The linear standard calibration range for the ED response is from the reported MDL up to a concentration of approximately 100 mg/L for the analyte of interest.

PURPOSE

The purpose of this SOP is to: (1) insure reliable and reproducible results, and (2) track possible sources of error in the extraction of perchlorate from a sorbent and the subsequent analysis by IC-ED analytical methodology.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 250mL wide-mouth jars, sealed with Teflon-lined septa caps.

Sample Collection: Sorbent aliquots collected over 1 foot increments from an exfiltrated Flux meter, will be transferred to a mixing bowl and homogenized with a metal spatula. Approximately 100 grams of mixed sorbent will be placed into the wide-mouth jar. Excess sorbent will be collected in a plastic-lined container for proper hazardous waste disposal.

Transportation and Storage: Sorbent samples will be stored, on site, in coolers containing "blue ice" then shipped via overnight air express (e.g., FedEx) to the Purdue University laboratory. Samples will be stored in a cold storage room or refrigerator at 4°C until extraction and IC-ED analysis.

2. Laboratory Supplies and Materials

Volumetric class ‘A’ pipets and volumetric class ‘A’ flasks for preparations of calibration standards and sample dilutions.

Disposable Pasteur glass pipets (Fisher Catalog # 13-678-6A) for sub-sampling.

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

3. Reagents

Deionized water prepared by filtration of potable water through a Barnstead Ultrapure Deionization Unit. This water will be referred to as reagent water.

Certified ACS grade granular ammonium perchlorate purchased from Sigma-Aldrich.

4. Calibration and Stock Standard Solutions

A stock standard solution will be prepared in reagent water using volumetric glassware and stored in 20mL glass vials with Teflon-lined caps. The stock solution will be refrigerated at 4^oC. Two concentration ranges will be prepared. The higher concentration range will be 100mg/L to 1mg/L. The low concentration range will be 2ug/L to 100ug/L. A minimum of five standards per range will be prepared.

5. Quality Control (QC) Blank Spike/Matrix Spike

A blank spike will be prepared by the addition of 1 mL of calibration standard to 1mL of reagent water. A matrix spike will be prepared by the addition of 1mL of calibration standard to 1 mL of sample. Spike recoveries will be calculated using the difference between the two measured concentrations and the known spike concentration.

6. Analytical Instrumentation

A Dionex DX600 Ion Chromatograph (IC) Autosystem equipped with an ED50 Electrochemical Detector, a GP50 Gradient Pump, a GD40 Eluent Generator, an AS50 Thermal Compartment, and an AS50 Autosampler will be used for analysis of all perchlorate samples. The Dionex IC system is linked to an IBM-compatible PC loaded with Peaknet (version 6.00) software for acquisition, analysis interpretation and quantitation.

A Dionex IonPac AS11 column and guard column will be used and the analyte perchlorate eluted with 35mM potassium hydroxide solution.

7. IC Parameters and Analytical Conditions

Analytical & Guard Column	Dionex IonPac AS11, 4mm
Column temperature	30C
Suppressor Current	104 mV
Eluent Concentration	35mM potassium hydroxide
Column flow rate	1.2 mL/min
Injection loop volume	50ul (high concentration range); 950ul (low concentration range)

8. Quality Control of IC System

Nanopure water is used to provide ion-free solvent for the Eluent Generator and eliminate high background signal

A method blank will be analyzed at the beginning of each sample set and after every 25 samples to monitor instrument background.

A complete set of calibration standards (minimum 5) will be analyzed at the beginning of each day with a mid-range continuing calibration standard analyzed after every 25 samples.

A matrix spike and a blank spike, and up to 5 sample duplicates will be analyzed with each daily sample set.

9. Extraction of Perchlorate from Sorbent Matrix

Perchlorate extraction from the sorbent will be completed utilizing a Dionex ASE300 Accelerated Solvent Extractor, with hot reagent water as the solvent. Glass fiber filters and Ottowa 40 mesh sand will be used to filter and as a filler respectively, in the extraction cell.

10. Sample Analysis

Perchlorate identification will be based on the absolute retention time compared to calibration standards.

Perchlorate concentrations will be calculated on a chromatographic peak area response converted to units of concentration in ug/L or mg/L based on the standard calibration range of analysis.

11. Interferences

Contamination by carry-over may occur when high-level and low-level samples are sequentially analyzed. Subsequent dilution and reanalysis will be completed on samples identified as outside the standard concentration bracket. Samples analyzed immediately following a ‘high-concentration sample’ will be reanalyzed.

In an attempt to minimize carryover, samples suspected of being in a higher concentration range will be isolated and bracketed by the analysis of reagent water samples.

12. Safety

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 Indian Head 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.

Accuracy

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:

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

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:

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

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 and IC 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:

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:

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

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 C.1.

Table C.1

CRITERIA FOR BALANCE CALIBRATION CHECKS

Class S Weight (grams)	Warning Level (grams)	Control Level (grams)
Analytical Balances		
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 Indian Head site will be sent to Purdue University 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 C.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 nonroutine. 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 analyses such as those performed by GC/MS, each sample and blank is spiked with one or more surrogate compounds before preparatory operations such as purging or extraction are completed. 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

$$MDL = t \times S$$

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 followup 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 Passive Flux Meter at the Indian Head Site

Health and Safety Plan

February 7, 2007

Purdue University, West Lafayette, IN

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INTRODUCTION

This Health and Safety Plan (HASP) has been developed for conducting field tests of the Florida PFM at the IHDIV Indian Head 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 Indian Head Division, Naval Surface Warfare Center (IHDIV) is located near Indian Head, Maryland. Geographically, the site (Figure 3-1) is located at 38 35’05” N latitude, 77 09’50” W longitude, Charles County, Maryland (United States Geological Survey [USGS] Indian Head, MD-VA 15’ Quadrangle, 1982). The study area (Figure 3-2) is located on the southeast side of IHDIV Building 1419 (Hog Out Facility), which was used to clean out (‘hog out’) solid propellant containing ammonium perchlorate from various devices, including spent rockets and ejection seat motors. The hog out process and former waste handling methods have impacted the groundwater near Building 1419.

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 IHDIV source zone is contaminated with Perchlorate. Perchlorate concentrations range from 5 mg/L to 430 mg/L.

1.3.2. Exposure Potential. The chemical contaminants present at Indian Head 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 or water, particularly when collecting ground-water samples.

1.3.3. Exposure Guidelines. 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.

1.3.4. 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. Additionally, routes of exposure, symptoms of acute exposure and carcinogenicity are summarized.

1.3.5. 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.

1.3.6. 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.

1.3.7. 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	PELTLV- (ppm)	IDLH TWA (ppm)	Route of Exposure	Symptoms
Ammonium Perchlorate	n/a	n/a	Inhalation, skin, ingestion	Mucous membrane irritation, headache
Isobutanol	50	1600	Inhalation, skin, ingestion and/or eye contact	Irritation eyes, skin, throat, headache drowsiness: skin cracking

n/a = not available from either NIOSH, TSCA,MSDS

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 perchlorate present in the ground water through 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 (Perchlorate, Isobutanol) 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 Indian Head. Should a health and safety issue develop in the performance of the contract requiring consultation, the PM will immediately contact the Indian Head 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.

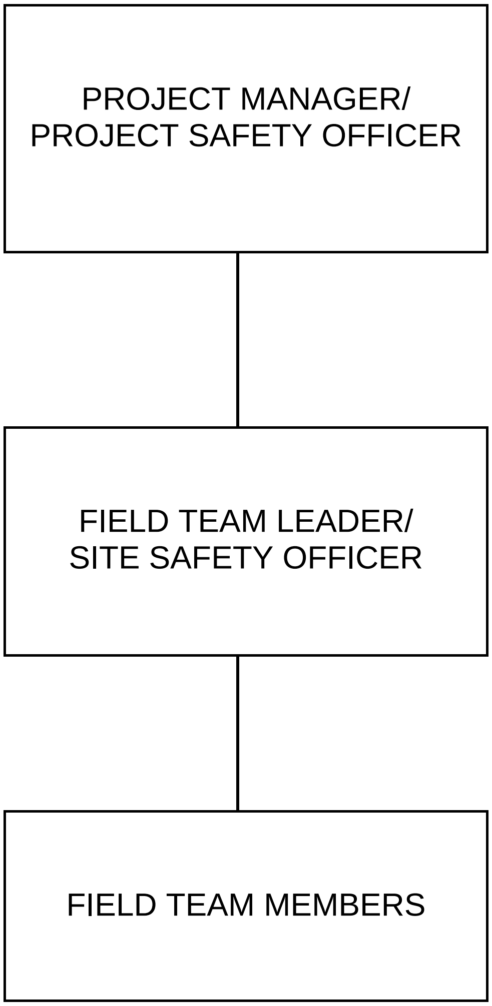

FIGURE 1. SITE SAFETY RESPONSIBILITY CHART

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 Indian Head, Maryland, 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

FIGURE 3. SITE SAFETY MEETING FORM

Date: ____________ Time:
Client: Indian Head
Site Location: IHDIV Indian Head, Maryland
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:

From:

Indian Head Hwy & Pye St (This is the location for one of the gates for the base)
Indian Head, MD 20640

To:

Civista Medical Ctr
701 Charles St, La Plata, MD 20646

Total Est. Distance: 13.87 miles

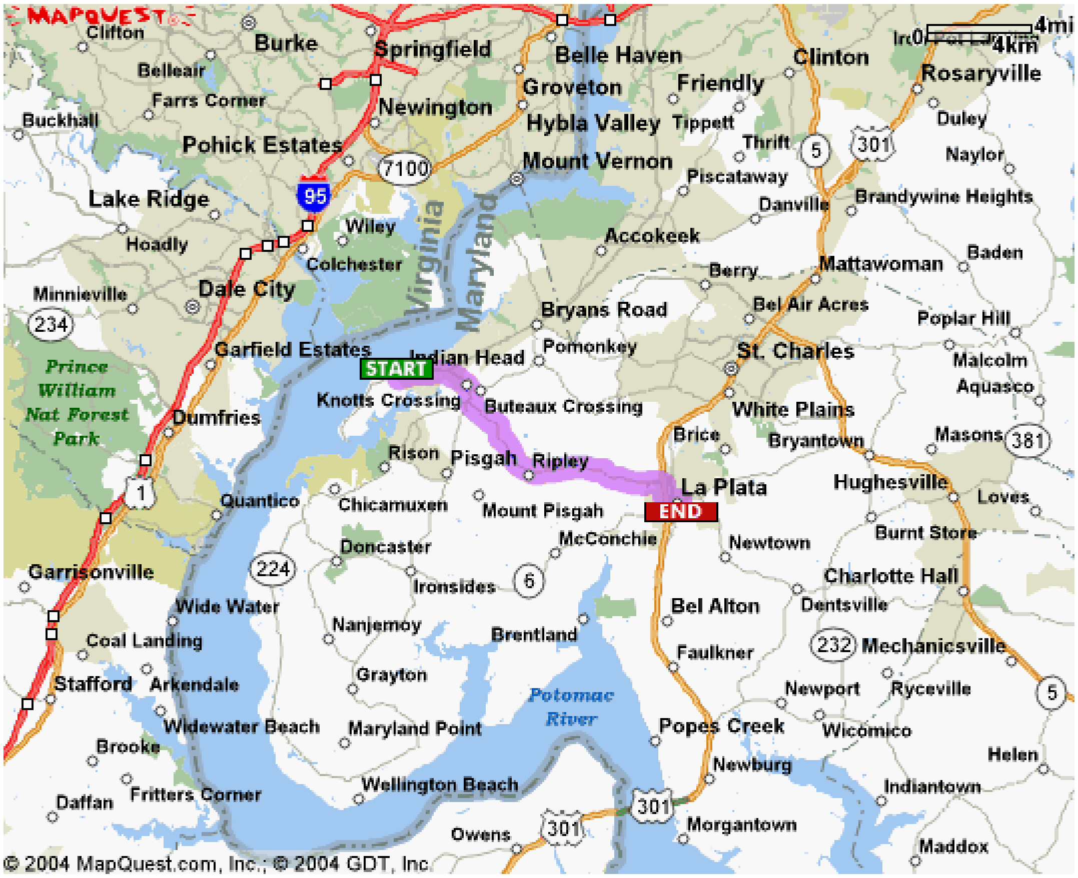

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FIGURE 4. Map and Directions to Civista Medical Center

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 Indian Head. 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 may be conducted during the winter months, 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 Indian Head site have been identified as the ground water and PFM 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 Civista Medical Center (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:

Indian Head 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:

Indian Head Project Manager
Health and Safety Officers
Site Safety Officers

The Indian Head 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 On Base — Urgent Care Clinic	805-988-2500 805-985-5599
FIRE	On Base Off Base	911 911
AMBULANCE	On Base Off Base	911 911
POLICE	On Base Off Base	911 911

Emergency clinic and hospital routes.

See Figure 4.

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 Indian Head 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 Indian Head 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 <u>correct</u> 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.